

SYMPOSIUM MM

MM: Amorphous and Nanocrystalline Metals

December 1 - 4, 2003

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* Invited paper

8:30 AM *MM1.1

The Scale of Devitrification in Bulk Glasses. A. Lindsay Greer, Materials Science & Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Partial or complete devitrification of metallic glasses is of interest for improving properties ranging from mechanical to magnetic. In optimizing properties the microstructural scale is important. The crystals formed on devitrification of bulk metallic glasses can be nanometric or visible with the naked eye. This great range of behaviour can be useful for tailoring properties, but is a challenge to explain. Various approaches to the problem are reviewed, the special features of metallic systems being appreciated by comparison with other systems, notably oxide and chalcogenide glasses. A particular comparison is made with current work on nanoscale glass ceramics. While fragility is often used as a basis for comparing different glass-forming systems, it is found to have limited utility in interpreting the scale of devitrification. Factors influencing the scale of crystallization in metallic glasses include amorphous phase separation and inoculation with nucleating agents, but this review focuses on intrinsic nucleation kinetics. The range of atomic sizes in the alloy, can determine the relative mobilities of the species below and above the glass-transition temperature. In turn, these mobilities influence the nature of crystal nucleation and growth, and importantly their relative rates. Prospects for alloy design will be considered.

9:00 AM *MM1.2

Microstructural Design by Controlled Crystallization of Metallic Glasses. Uwe Koster and Rainer Janlewing, Dept. Biochem. & Chem. Eng., University of Dortmund, Dortmund, Germany.

Nanocrystalline materials can be produced e.g. by high energy ball milling or vacuum condensation; these methods require powder compaction as a final step. In another route - the nano-crystallization - metallic glasses are used as precursors for nanocrystalline materials without any porosity. The conditions for achieving an ultra-fine grained material by crystallization are small growth, but large nucleation rates. Whereas in fragile glasses (e.g., Fe-Ni-B) the finest microstructure is produced at annealing temperatures above the glass transition close to the maximum of the nucleation rate, in Zr-based metallic glasses, i.e. strong glasses, nanocrystallization was found to proceed only at relatively low temperatures below the glass transition. The aim of this contribution is to study systematically the micromechanisms involved in the microstructural design. Crystallization was studied in detail in Fe-Ni-B and Zr-based metallic glasses by means of TEM, X-ray diffraction and DSC. Nucleation and growth rates were estimated from crystallization statistics. By modeling the obtained time-dependent nucleation rates in the framework of diffusion controlled classical nucleation all relevant crystallization parameter could be derived. Using these data TTT-diagrams could be drawn and annealing conditions deduced, e.g. for the formation of a nanocrystalline alloy; a bimodal grain size distribution can be achieved by combination of heterogeneous and homogeneous nucleation. In addition, a computer simulation of the time-dependent microstructural development will be presented. Isothermal DSC plots even for polymorphic crystallization can only be explained with a very significant decrease in the growth rate at later stages. Such a decrease is assumed to result from stresses building up during crystallization beyond the percolation limit for the crystalline phase; under this condition stresses resulting from the volume change during crystallization cannot be compensated by viscous flow as in the case of isolated crystals in an amorphous matrix.

9:30 AM MM1.3

Effects of Positive Feedback on Crystallization Kinetics and Recalescence. Sven Bossuyt² and A. Lindsay Greer¹; ¹Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; ²VUB-TW-MEMC, Vrije Universiteit Brussel, Brussel, Belgium.

In bulk metallic glasses cooled at nearly the critical cooling rate for glass formation, nucleation is observed to be spatially localized; nanocrystals are clustered together in spherical regions. This implies that a positive feedback mechanism locally increases the nucleation rate in the vicinity of other nucleation events. Linear stability analysis and computer simulation of differential equations describing crystal nucleation and growth are used to theoretically examine the plausibility of different potential feedback mechanisms. It is shown that interactions between different crystallizing phases can lead to counter-intuitive composition dependence of the crystallization kinetics in the case of non-polymorphic crystallization.

9:45 AM MM1.4

Icosahedral Ordering in Liquid Metals and Glasses - Link to the Nucleation Barrier. K F Kelton¹, G W Lee¹, A K Gangopadhyay¹, R W Hyers², T J Rathz³, J R Rogers³, M B Robinson³ and D S Robinson⁴; ¹Department of Physics, Washington University, St. Louis, Missouri; ²University of Massachusetts, Amherst, Massachusetts; ³NASA Marshall Space Flight Center, Huntsville, Alabama; ⁴Ames Laboratory, U.S. DOE, Ames, Iowa.

Icosahedral short-range order (ISRO) is often presumed to dominate the atomic structures of liquid and amorphous metals. ISRO is often used to explain micro-alloying effects on glass formation and stability, and to account for nanostructure formation in the growing number of glasses that crystallize to quasicrystals. Frank first proposed the existence of ISRO over fifty years ago for liquid metals, to explain the surprisingly high nucleation barrier to crystallization that had been reported by Turnbull. Recently, we presented the first direct experimental demonstration of Frank's hypothesis, clearly demonstrating the link between the nucleation barrier and a growing icosahedral short-range order with decreasing temperature in a $\text{Ti}_{39.5}\text{Zr}_{139.5}\text{Ni}_{21}$ liquid.¹ The short-range order data were obtained using BESL, a new facility that allows synchrotron x-ray measurements on deeply undercooled electrostatically levitated liquids. Those results and their implications for nucleation for phases with similar short range order to that in the liquid and glass (such as quasicrystals) are presented and discussed.¹ K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Rathz, J. R. Rogers, M. B. Robinson and D. S. Robinson, Phys. Rev. Lett., 90, 195504 (2003).

10:30 AM *MM1.5

Amorphisation and devitrification of Al-rare earth-transition metal alloys. L. Battezzati, M. Baricco, M. Kusy, M. Palumbo, V. Ronto and P. Rizzi; Dipartimento di Chimica IFM, Universiti Torino, Torino, Italy.

Al-based amorphous alloys contain at least a transition metal (TM) and a rare earth element (RE). Their peculiarity is that they can be obtained in composition ranges where no deep eutectic exists. Most of these off-eutectic compositions correspond to the field of the phase diagram where Al coexists with intermetallic compounds and there are steep liquidus curves. So, it may even be surprising that these melts can undercool to the extent of forming glasses. The issue of amorphisation is reviewed here considering transport and thermodynamic properties of the melt. Calculation of a ternary Al-Ni-Ce phase diagram is progressing with the inclusion of metastable phase equilibria involving the glass and intermetallic compounds. Some experimental data for metastable phases (glass transition temperatures, transformation enthalpy) have been produced to improve the optimisation procedure. Transport properties are considered in the melt and in the glass and further insight is derived from analyses of devitrification paths of various alloys Al87Ni7RE6 where RE = La, Ce, Nd and Sm. Additions of Ti or Zr to the ternary alloys are also performed with the aim of revealing possible phase separation in the melt.

11:00 AM *MM1.6

Nanocrystallization of Bulk-forming Metallic Glasses. Kazuhiro Hono, Tadakatsu Ohkubo and Masato Ohnuma; Materials Engineering Lab., National Institute for Materials Science, Tsukuba, Japan.

Recent studies have shown that a variety of crystallization reactions occurs from bulk-forming metallic glasses. Although the nucleation barrier for crystallization is expected to be high in bulk-forming metallic glasses, nanocrystalline microstructures are commonly reported in many bulk metallic glasses. In some cases, nano-sized quasicrystalline particles precipitate in the early stage of crystallization as a transient stage from glass to crystal. Also, in several bulk-forming metallic glasses, phase separation in a glassy phase is reported to occur prior to nanocrystallization. To obtain a better understanding of the crystallization mechanisms of bulk-forming metallic glasses, we have investigated the early crystallization stages of $\text{Pd}_{74}\text{Si}_{18}\text{Au}_8$, $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$, $\text{Zr}_{36}\text{Ti}_{24}\text{Be}_{40}$, $\text{Zr}_{41.8}\text{Ti}_{14.1}\text{Cu}_{12.5}\text{Ni}_{10.4}\text{Be}_{21.2}$ alloys, all of which were reported to decompose into two glass phases prior to crystallization. The major experimental challenge was to distinguish the glass phase decomposition from nanocrystallization. Melt-spun amorphous ribbon of the above alloys were annealed right above the glass transition temperatures, and the microstructure evolution was studied by transmission electron microscopy (TEM), three-dimensional atom probe (3DAP) and small angle x-ray scattering (SAXS). Utmost attention has been paid to separate chemical decomposition and structural transformation by the complementary use of TEM, energy-filtered TEM, energy-filtered electron diffraction (EFED), 3DAP, and SAXS. So far, we have not obtained any convincing evidence for the phase decomposition in the glassy state. All crystallization processes observed in the above alloys appear to be

explained either by a primary or a eutectic crystallization mechanism. However, there remains an unanswered question for the $Zr_{36}Ti_{24}Be_{40}$ metallic glass. The differential scanning calorimetry (DSC) trace clearly shows an inflection between the glass transition temperature (T_g) and the crystallization temperature (T_x), which used to be interpreted as T_g for one of the two decomposed glassy phases. However, no evidence for the presence of two phase glassy phases was confirmed by TEM and 3DAP observations.

11:30 AM MM1.7

Early Stages Of Al-Nanocrystal Formation in $Al_{92}Sm_8$.

Gerhard Wilde¹, Harald Roesner¹, Nancy Boucharat¹, Joe Hamann², William S. Tong² and John H. Perepezko²; ¹Institute of Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Nanoscale dispersions of high number densities of nanocrystals that are embedded in a residual amorphous matrix have attracted considerable interest owing to the unusual properties and property combinations and due to the as yet controversially discussed crystallization mechanism. Several proposals involving solute effects, phase separation or quenched-in nuclei and heterogeneous nucleation have been advanced to account for the high nanocrystal density, but recent crystallization measurements and kinetics analyses provide new evidence for the role of the as-quenched structure on nanocrystal synthesis. In this respect, the $Al_{92}Sm_8$ alloy is regarded as a model system since the phase evolution sequence is typical for these so-called marginally glass-forming alloys, but only binary interactions need to be taken into account. Here, isothermal microcalorimetry investigations and quantitative electron microscopy measurements including high-resolution imaging and electron spectroscopy analyses were performed at different temperatures below the glass transition to analyze the nanocrystallization kinetics isothermally as a function of time and temperature. From the combined measurements, the size distributions and the transformed fractions were determined with a high accuracy for extended ranges of temperatures and times. As one result, the nanocrystal size distribution functions for melt-quenched Al-Sm samples following different annealing treatments at temperatures below T_g demonstrate a partial nanocrystallization reaction resulting from a decaying nucleation rate and a limited supply of heterogeneous nucleation sites. The results are analysed regarding the kinetics of the early stages of nanocrystallization and are additionally evaluated with respect to the origin of the nanocrystal dispersion. The support by the DFG within the Emmy Noether program (WI 1899/1-3) and by the ARO (DAAD19-01-1-0486) is gratefully acknowledged.

11:45 AM MM1.8

Modification of the Phase Selection during the Nanocrystallization of Amorphous Al-Y-Fe.

Nancy Boucharat¹, Harald Roesner¹, Rainer J. Hebert², John H. Perepezko² and Gerhard Wilde¹; ¹Institute of Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Al-rich metallic glasses that are obtained by rapid melt quenching often undergo a primary crystallisation reaction upon heating that yield dispersions of extremely high number densities of nanometer-scaled Al crystallites embedded in a residual amorphous matrix. The high nanocrystal number density seems to originate from quenched-in nuclei that can grow during subsequent heat treatment processes at temperatures near the glass transition. In this respect, the large disparity of the component diffusivities that involves the soft impingement of the solute diffusion fields between neighbouring nanocrystals limits the crystal growth and stabilizes the nanoscale microstructure. Calorimetric and structural analyses have been performed on samples after different thermal treatments at temperatures well below the glass transition and after following different processing pathways to the vitreous state including mechanical alloying by cold-rolling or the incorporation of different immiscible elements into the melt prior to quenching. The phase formation sequences and their modification in the presence of concentration gradients have been determined on samples that have been heat treated isothermally at low temperatures or alternatively have been severely strained by mechanical alloying. Moreover, the precipitation of a transient phase is discussed on the basis of the presence of a changing concentration gradient at the nanocrystal/amorphous interface and with respect to different nucleation kinetics models. The results indicate that the possibility for controlling the concentration gradient allow for new opportunities for an active phase selection. The support by the DFG (Emmy Noether program and center for functional nanostructures, CFN) and the ARO is gratefully acknowledged.

SESSION MM2: Processing, Glass Forming Ability, and Novel Alloys

Chairs: A. Lindsay Greer and Uwe Koster

Monday Afternoon, December 1, 2003

Republic B (Sheraton)

1:30 PM *MM2.1

Bulk Amorphous Foam. Jan Schroers,¹ Materials Science,

California Institute of Technology, Pasadena, California; ²Liquidmetal Technologies, Lake Forest, California.

Foams are chosen in nature when high stiffness to weight ratio is required as can be found in wood or bones. Metallic foam is increasingly regarded in the automotive and aerospace industry as a solution for problems such as high stiffness to weight ratio and passenger safety due to their energy absorption ability. Making metallic foams is a challenging task since they are highly unstable structures. Its properties strongly depend on the structures homogeneity. The kinetics of the foaming process, of the sedimentation of the bubbles, and the collapsing of the structure scales with the viscosity. The viscosity of a bulk glass forming liquid at its melting temperature is about 1 Pa s compared to the viscosity of a pure metal of about 10-3 Pa s. Therefore, the foaming kinetics of BMGs can be expected to be more sluggish. Thus better control over the foaming process can be gained and thereby a more homogeneous structure obtained. The challenge of making amorphous foam by cooling from the melt is to crystallization during avoid solidification. This will restrict the original dimensions of the foam to below the critical casting thickness. However, a method is going to be presented which allows a substantial control over the bubble size and volume fraction, and in addition enables production of amorphous foam with final dimensions which is much larger than the critical casting thickness. With this technique, amorphous metallic foam with up to 90 % of bubbles and bubble sizes between 10^{-4} m and 10^{-3} m can be prepared.

2:00 PM MM2.2

Thermal Tempering of Bulk Metallic Glasses. Cahit C.

Aydiner¹, Ersan Ustundag¹, Bjoern Clausen², Michael B. Prime³ and Robert A. Winholtz⁴; ¹Materials Science, California Institute of Technology, Pasadena, California; ²Lujan Neutron Science Center, Los Alamos National Laboratory, Los Alamos, New Mexico; ³Engineering Sciences and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico; ⁴Department of Mechanical Engineering, University of Missouri, Columbia, Missouri.

Multi-component metallic alloys with superb glass formation ability have recently been developed allowing, for the first time, the processing of large specimens with amorphous structure. Called bulk metallic glasses (BMGs), these materials possess impressive properties such as very high elastic strain limit (2%) and yield strength (~2 GPa), good fracture toughness (up to 140 MPa.m^{1/2}), excellent corrosion resistance, etc. An important question that arises with bulk production is the nature and magnitude of processing-induced residual stresses. The BMG processing typically involves casting an alloy into a mold followed by severe quenching. This procedure can lead to large thermal gradients due to the low thermal conductivity of BMG. In addition, during glass transition the alloy exhibits large changes in its viscosity within a small temperature range. All of these parameters lead to "thermal tempering" which generates compressive surface residual stresses (up to several hundred MPa in BMGs) balanced with mid-plane tension. We have recently studied the thermal tempering phenomenon in BMGs using analytical [1] and finite element modeling [2,3]. The residual stresses were measured in BMG plates [2] and cylinders [3] via the crack compliance (or slitting) method. We also developed a viscoelastic model [2,3] that can predict the final residual stresses within 15-30% of the experimental values. In addition, neutron diffraction measurements were performed in a BMG/stainless steel composite [4] and the results were compared to the estimates of the viscoelastic model. This presentation will review these studies and will relate the residual stresses due to thermal tempering to the processing conditions of BMGs. References 1. C. C. Aydiner, E. Ustundag and J. C. Hanan, "Thermal Tempering Analysis of Bulk Metallic Glass Plates Using an Instant Freezing Model," *Mater. Trans.*, 32A, 2709-2715 (2001). 2. C. C. Aydiner, E. Ustundag, M. B. Prime and A. Peker, "Modeling and Measurement of Residual Stresses in a Bulk Metallic Glass Plate," *J. Non-Cryst. Solids*, 316 [1], 82-95 (2003). 3. C. C. Aydiner and E. Ustundag, "Residual Stresses in a Bulk Metallic Glass Cylinder Induced by Thermal Tempering," submitted to *Mechanics of Materials* (2003). 4. C. C. Aydiner, B. Clausen, E. Ustundag, J. C. Hanan, M. A. M. Bourke and R. A. Winholtz, "Residual Stresses in a Bulk Metallic Glass / Stainless Steel Composite," submitted to *Mater. Sci. and Eng.* (2003).

2:15 PM MM2.3

Reactive Joining of Bulk Metallic Glass.

Albert Joseph Swiston¹, A. Duckham¹, J. C. Trenkle¹, E. Besnoin²,

O. M. Knio², T. C. Hufnagel¹ and T. P. Weihs¹; ¹Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ²Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

This presentation describes the welding of metallic glass components using reactive foils as local heat sources. Reactive foils are freestanding, nanostructured multilayers that contain at least two materials with a large, negative heat of mixing. With a small pulse of energy, the alternating layers begin to mix, creating a self-propagating exothermic reaction. By sandwiching a foil between two metallic glass components and igniting the reaction, the interfaces are heated rapidly and uniformly above their glass transition temperature, the softened glass begins to flow, and welding of the components occurs. Because the total energy evolved is small, the components cool quickly with limited risk of crystallization. During reaction propagation, the foils contract and often crack due to constraints from the surrounding glass components. Once cracking occurs, the viscous supercooled liquid region at each glass interface flows into and through these cracks to form continuous metal-metal veins. The strength of the joint is largely due to these veins or welded regions. We observe a monotonic increase in the failure strength of the joints with the fraction of the joint composed of such veins. For the strongest joint tested (shear strength of 480 MPa), nearly 60% of the fracture surface is comprised of metal-metal veins. We believe that flow of the glass, induced by pressure applied during joining, exerts shear stresses on the foil, dragging the reacted foil out of the joint and increasing the proportion of the metal veins. This process is affected by the total heat evolved during joining (which scales with the foil thickness) as well as the pressure during joining. In this presentation, we describe the joining mechanism, focusing on the viscous flow of the glass and its role in determining the joint microstructure and strength. Infrared measurements of the joining process, showing cooling rates in excess of the critical cooling rate for the alloy, will be discussed and compared with numerical predictions of the cooling rates, maximum temperatures, and glass flow.

2:30 PM MM2.4

Formation of High-Strength ZrNbCuNiAl Alloys by Warm Extrusion of Gas Atomized Powders. E. A. Rozhkova¹, X. Y. Yang¹, P. B. Wheelock¹, J. Eckert², U. Kuehn² and D. J. Sordelet¹; ¹Metal and Ceramic Program, Ames Laboratory, Iowa State University, Ames, Iowa; ²IFW Dresden, PO Box 270016, D-01171 Dresden, Germany.

Recently developed Zr-based metallic glass composites containing a ductile phase demonstrate improved mechanical properties such as high strength combined with good ductility compared to the glass monoliths. These advantages are of great interest and potentially allow using these materials for many structural applications. Zr-Nb-Cu-Ni-Al amorphous powders with bcc phase precipitates were obtained by high pressure He gas atomization. Formation of the bcc phase in amorphous matrix strongly depends on the material composition and cooling rates during solidification. Melt spinning using various wheel speeds, which provides cooling rates comparable to those during the gas atomization, was used to select compositions for gas atomization. Phase formation and microstructure as a function of the atomized powder fraction size were characterized using X-ray diffraction, differential scanning calorimetry, optical, scanning and transmission electron microscopy. Gas atomized powders were consolidated by warm extrusion. Temperatures for the extrusion were obtained from the time-temperature-transformation curve for the onset of crystallization of the amorphous phase in the powder. Various processing conditions such as size of the starting powder, temperature and extrusion ratio were manipulated to obtain materials having various microstructural features. Size and distribution of the precipitated ductile second phase were investigated. Structure and thermal stability of consolidated bulk metallic glass composites as well as some mechanical and physical properties will be discussed.

2:45 PM MM2.5

Solidification Modeling of Bulk Amorphous Alloys. Sang Bok Lee and Nack J Kim; Center for Advanced Aerospace Materials, Pohang University of Science and Technology, Pohang, South Korea.

Solidification behavior of several bulk amorphous alloys has been studied. In amorphous alloys, crystallization is the only event which terminates the transformation of undercooled liquid to amorphous solid. Therefore, studying the crystallization behavior of undercooled amorphous alloys is important for understanding the formation mechanism of amorphous structure. The effect of undercooling on the crystallization behavior of the undercooled amorphous alloys has been studied using the classical heterogeneous nucleation theory. Coupled with classical heterogeneous nucleation theory, thermal analysis data have been shown to give an accurate estimation of the degree of undercooling for various cooling rates as well as prediction of

solidification behavior. Time-temperature-transformation (TTT) diagrams of several amorphous alloys have been constructed by simulation and it has been shown that the simulated TTT diagrams match well with the experimentally constructed TTT diagrams. The critical cooling rates for the formation of amorphous phase for several amorphous alloys have also been simulated, which agree well with the experimental values of critical cooling rates. Based on analyses of several amorphous alloys, a new parameter for glass forming ability (GFA) is being suggested.

3:30 PM MM2.6

Optimum Glass Forming Ability and Type of Eutectic-coupled Zone in Eutectic Alloys. H. Tan, Y. Zhang, D. Ma and Yi Li; Department of Materials Science, National University of Singapore, Singapore, Singapore.

Bulk metallic glasses have been found in many alloy systems over the last ten years. Despite the fact that many parameters have been used to find the best glass forming alloys and some of them are very successful, the way to find the alloy composition with the optimum glass forming ability within one alloy system is still not clear. We have analyzed the glass forming ability around eutectic composition in terms of the competitive growth/formation of primary dendrites, eutectic and glass. It is concluded that the glass forming ability of a eutectic alloy system depends on the type of the eutectics, i.e. symmetric or asymmetric eutectic coupled zone. For the alloy systems with symmetric eutectic coupled zone, the best glass forming alloys should be at or very close to the eutectic composition. For the alloys with asymmetric eutectic coupled zone, the best glass forming alloys should be at off-eutectic compositions, probably towards the side of the faceted phase with a high entropy in the phase diagram. We will show our latest results on the glass formation in Zr, Pd, La and Ni based alloy discovered using the above analysis method.

3:45 PM MM2.7

Glass formation by a first order transition: Growth of an isotropic phase in Al-Fe-Si. Leonid A. Bendersky and John W. Cahn; Materials Science and Engineering Laboratory, NIST, Gaithersburg, Maryland.

Most glassy solids are thought to be kinetically frozen liquids, but the possibility of forming some glasses by growth along a moving interface, as in a first order transition, has been advocated. We present evidence of the growth of a metallic glass phase in the Al-Fe-Si system from a melt. Microstructures of a number of rapidly solidified alloys provide evidence that the glassy phase is the first to form from the melt, and that there is compositional partitioning between particles of the growing glass phase and the melt at the interface. We suggest a metastable Al-Fe-Si phase diagram, consistent with the microstructural and constitutional observations, in which a glassy phase forms by a first order transition. Since many Al-Tm-Si systems (Tm-transition metals) form quasicrystals, we discuss a possible structural concept for the observed glass using aperiodic tilings, such as pinwheel tilings, that lead to isotropic structures.

4:00 PM MM2.8

New Ca-based Bulk Metallic Glasses. Oleg N Senkov, J. Mike Scott and Joe Tatalovich; Materials and Processes Division, UES Inc., Dayton, Ohio.

New Ca-based bulk metallic glasses have recently been discovered based on Senkov-Miracle topological/thermodynamic model for metallic glass formation. In addition to already known empirical criteria for bulk metallic glass forming systems such as requirements of three or more elements, significant difference in atomic size ratios above about 12% and negative heats of mixing among the three main constituent elements, the Senkov-Miracle model provides an additional incite to narrow the compositional range for searching new metallic glasses. In particular, according to this model, the atomic radii and concentrations of the alloying elements should provide a characteristic atomic size distribution plot (ASDP), atomic size ratios of the solvent and solute atoms should have particular discrete numbers and the atom size of the solvent element must be as large as possible to provide better conditions for amorphization. Calcium was selected as the solvent element because it has a large atomic size and forms deep eutectics with many other elements. The compositional ranges of the new metallic glasses follow to the formula: $CaA(Y,L)B(Mg,Sn)C(Ga,Zn,Al,Ag)D(Cu,Ni,Si)E$, where A ranges from 0.45 to 0.70, B = 0 to 0.15, C = 0 to 0.15, D = 0 to 0.35, E = 0 to 0.35, A+B+C+D+E=1, and L represents the La group elements. Experimental results on stability and kinetics of crystallization of these metallic glasses will be shown and discussed.

4:15 PM MM2.9

Formation of Ca-Al-based bulk amorphous alloys with high thermal stability. Paqiang Guo¹, Joseph Poon¹ and Gary Shiflet²; ¹physics, university of Virginia, Charlottesville, Virginia; ²materials

science and engineering, university of virginia, charlottesville, Virginia.

It was found that binary Ca-Al alloys can be readily cast into amorphous rods of 1 mm in diameter. Upon further alloying to depress the liquidus temperature, the amorphous rod diameter is increased to 3 mm. The high glass transition temperature of 210 °C and crystallization onset temperature of 240 °C or higher observed are attributed to the covalent bonding trend noted in Ca-Al alloys that exhibit complex network structures. Along with high fracture strengths of 700 MPa and low mass density of 2 g/cc, these thermally stable light-metal alloys are recognized as potential structural amorphous metals.

4:30 PM MM2.10

Development of Amorphous Metals Using High Throughput Experiments. C. Eric Ramberg, Youqi Wang, Qun Fan, Eriko McDermott, Jason Wang, Kirk Kenyon and Sum Nguyen; Symyx Technologies, Santa Clara, California.

Physical vapor deposition (PVD) has been used to make libraries of different metallic compositions under high purity conditions. These samples have been screened using a variety of methods, such as isothermal annealing experiments combined with post-situ X-ray diffraction, to examine phase stability. These data have been complemented by in-situ, high throughput measurements of properties vs. temperature, also in library format. Thin film measurements have been compared to measured values of T_g , T_x , and T_m from differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The advantages and challenges of using high throughput methods will be discussed, using examples from different classes of amorphous metals.

4:45 PM MM2.11

Devitrification Of Aluminum-Rare Earth-Transition Metal Alloys. Alexandre L Vasiliev¹, Mark Aindow¹, Martin J. Blackburn¹ and Thomas J. Watson²; ¹IMS, University of Connecticut, Storrs, Connecticut; ²Pratt & Whitney, East Hartford, Connecticut.

Metallic glasses can be produced from certain aluminum alloys containing rare earths (RE) and transition metals (TM), if they are cooled rapidly enough from the melt. In most cases, the glasses are metastable and crystallization will occur during subsequent processing that involves thermal exposure. The devitrification products can result in extremely fine and homogeneous microstructures and these are coupled with attractive properties. In our work, the crystallization has been studied ex-situ using high resolution lattice imaging, diffraction and energy-dispersive X-ray spectrometry experiments in the transmission electron microscope. It has been shown that the first stage of crystallization depends critically on the alloy composition, and two main types of decomposition products appeared: spherical nanoscale a-Al particles embedded in an amorphous matrix, or mixtures of crystalline phases with a fractal morphology. Within these latter regions, complicated ordered structures were observed. Sheets or metastable rod-like precipitates of Al-TM or Al-TM-RE were formed with habit planes parallel to {100} of a-Al and consisting of ordered Al₂TM₂ or Al₂TM-RE rhombs. In the second and third stages of crystallization these ordered structures transformed into the more well-established binary and ternary compounds. A summary of these data will be presented and the structure of these metastable ordered structures and the nature of the phase transformations will be discussed.

SESSION MM3: Physical Properties
Chairs: Akihisa Inoue and Yi Li
Tuesday Morning, December 2, 2003
Republic B (Sheraton)

8:30 AM *MM3.1

From Hard to Soft Magnetic Properties in the Nd₆₀Fe₃₀Al₁₀ Composite: A Study on Microstructure in Bulk, Splat-Cooled and Thin Film. Alberto Bracchi¹, Susanne Schneider², Pappannan Thiyagarajan³ and Konrad Samwer¹; ¹I. Physikalisches Institut, University of Goettingen, Goettingen, Germany; ²IV. Physikalisches Institut, University of Goettingen, Goettingen, Germany; ³Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois.

Amorphous ferromagnetic alloys have progressively attracted the interest of physicists and material scientists during the last years because of their outstanding features, their forward-looking possible applications and due to the opportunity of tailoring their physical properties by controlling the preparation parameters (i.e. cooling rates). Among the growing family of metallic glasses a number of ferromagnetic systems is known and the Nd₆₀Fe₃₀Al₁₀ is probably one

of the most investigated. Previous results have shown that soft or hard magnetic samples can be prepared just by changing the cooling rate which is used to solidify them. In this work, thin films, foils and bulk samples of nominal composition Nd₆₀Fe₃₀Al₁₀ have been prepared by different solidification methods achieving cooling rates between 10¹⁰ K/s and 10 K/s. Structure and magnetic properties have been studied by high-energy wide angle x-ray diffractometry, small angle neutron scattering (SANS), high resolution electron microscopy (HRTEM) and with the use of a SQUID magnetometer. The SANS investigations have been performed with and without magnetic field in order to separate nuclear from magnetic scattering contributions. The microstructure which might be related to phase separation in the supercooled liquid during the cooling process shows fractal behavior with mass-fractal dimension ranging between 2.3 and 2.5 depending on the cooling rate. The interplay of domain wall pinning processes and magnetic coupling between two different magnetic phases will be discussed and the dependence of the Curie temperature from the cooling rate will be taken into account to understand the distinct magnetic behavior of bulk samples and Nd₆₀Fe₃₀Al₁₀ thin films. Support by Deutsche Forschungsgemeinschaft via SFB 602 (TP A5) is acknowledged. This work benefited by the use of Intense Pulsed Neutron Source and Advanced Photon Source at Argonne National Laboratory by the U.S. Department of Energy, BES. One of the author (A.B.) also acknowledges the financial support by the state of Niedersachsen via a "Lichtenberg Stipendium".

9:00 AM MM3.2

TEM and XAS Characterization of Hard Magnetic Phase in Nd-Fe Alloys. Golden Kumar¹, Juergen Eckert¹, Wolfgang Loeser¹, Paul Schilling², Evan Ma³, Christine Mickle¹, Juergen Thomas⁴ and Ludwig Schultz¹; ¹Institute for Metallic Materials, IFW Dresden, Dresden, Germany; ²Department of Mechanical Engineering, University of New Orleans, New Orleans, Louisiana; ³Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ⁴Institute for Solid State Research, IFW Dresden, Dresden, Germany.

Hard magnetic properties in as-cast Nd-rich Nd-Fe and Nd-Fe-Al alloys are often correlated to the phases with unidentified structures, hitherto known as A₁ and μ , respectively. The main difficulty in characterizing these alloys is the occurrence of a very fine microstructure and several metastable phases stabilized by impurities due to the high reactivity of Nd. According to the binary Nd-Fe phase diagram, two stable intermetallic phases i.e., Nd₂Fe₁₇ and Nd₅Fe₁₇ are known, which are magnetically soft. However, the formation of a NdFe₂ Laves-type phase under atmospheric conditions is not known with certainty due to the lack of structural data. In this work, Nd₆₀Fe₂₀ alloys were prepared by copper mold casting and directional solidification to obtain a coarse microstructure. The mold-cast samples exhibit a fine globular eutectic structure and show high room temperature coercivity (~ 4 kOe). The directionally solidified (ds) samples exhibit large grains (composition close to NdFe₂) in peritectic morphology but show no coercivity. The NdFe₂ grains (formed in the ds samples) show clear magnetic domains with uniaxial anisotropy indicating that NdFe₂ is not a cubic phase. Selected area diffraction (SAD) patterns from the NdFe₂ grains have been indexed with a triclinic structure. X-ray absorption spectroscopy (XAS) was used to analyse the local configuration around Fe atoms in the mold-cast samples. The XAS results do not match with the bcc and fcc standards, which supports the view that the Fe atoms are not in a cubic environment. Annealing experiments show that the NdFe₂ phase in the ds samples does not transform after heat treatment at 700 °C for 4 hrs. The possibility of stabilization of the NdFe₂ phase by oxygen or other impurities has been investigated by Auger spectroscopy. The correlation between the formation of the uniaxial-type NdFe₂ phase and the hard magnetic properties in Nd-Fe alloys is discussed.

9:15 AM MM3.3

Magnetic and Mechanical Properties of Amorphous and Nanocrystalline Fe(Co)NbB Alloys. Ivan Skorvanek¹, Tibor Krenicky¹, Jozef Kovac¹, Peter Svec², Rainer Gerling³ and Juergen Koetzier⁴; ¹Institute of Experimental Physics, SAS, Kosice, Slovakia; ²Institute of Physics, SAS, Bratislava, Slovakia; ³GKSS-Forschungszentrum Geesthacht GmbH, Geesthacht, Germany; ⁴Institute of Applied Physics, University Hamburg, Hamburg, Germany.

The nanocrystalline Fe-based and FeCo-based alloys prepared by devitrification of melt-spun amorphous precursors belong to an important group of soft magnetic materials. In this study, the formation of a nanocrystalline structure and its influence on the magnetic properties in series of (Fe_{1-x}Co_x)₈₁Nb₇B₁₂ (x=0, 0.25, 0.33, 0.5) alloys is investigated using different experimental methods. We show that the ternary FeNbB nanocrystalline alloys exhibit a variety of phenomena starting from spin-glass like behavior at cryogenic temperatures, followed by very soft magnetic behaviour at intermediate temperatures, and finally, approaching the Curie

temperature of the amorphous matrix, $T_c(\text{am})$, a marked magnetic hardening due to a decoupling between the nanograins occurs. Above $T_c(\text{am})$, the effects of superparamagnetic relaxations start become dominant, especially in the samples with lower volume fractions of nanocrystalline particles. Strikingly different behaviour is observed for Co-containing samples, where the α -FeCo nanograins remain well magnetically coupled up to high temperatures due to a significant increase of the Curie temperature of the residual amorphous matrix. The differences in the soft magnetic properties at elevated temperatures are discussed for the samples with different cobalt content and various volume fractions of nanocrystalline particles. The ductile/brittle behaviour of the thermally treated samples is studied by two different methods. The relative strain at fracture (ϵ_f) is determined by using simple bending tests. The elongation of the ribbon to failure (ϵ_{BP}) is determined by miniaturized Erichsen (ball punch) tests. It is shown that the embrittlement in our samples occurs predominantly in the temperature region 520 - 720 K, i.e. before the onset of nanocrystallization. The further increase of annealing temperature and subsequent crystallization has nearly no influence on the values of the relative strain at fracture and the elongation to failure. The Co-free alloy shows better resistance against the embrittlement in an amorphous phase as compared to the alloys containing cobalt.

9:30 AM MM3.4

Ultimate Stability of Nanocrystalline Materials: Grain Size Reduction Induced Amorphization in Multicomponent Solid Solutions. Guangping Zheng and Mo Li; School of Materials Science and Engineering, Georgia Tech, Atlanta, Georgia.

The effect of grain size on stability of multicomponent solid solution is of great technological and theoretical importance for preparation of metallic glasses and nanocrystalline materials. A critical solute concentration is known to play an essential role for amorphization; Microstructures such as grain size and grain boundary are also key factors determining the ultimate stability of the crystalline order. In this work, molecular dynamics simulation is carried out to investigate amorphization transition, or the ultimate stability of nanocrystalline phase of binary solid solution $A_{1-x}B_x$. Nanocrystalline materials with log-normal grain-size distribution is prepared using a method of grain-growth kinetics. It is shown that below the critical solute concentration ($x=0.2$), homogenous amorphous state is formed spontaneously when the grain size is reduced to several nanometers. At the critical grain size, the grain refinement induced crystal-to-glass transition is accompanied by significant softening of shear modulus and enhancement of low-frequency phonon density. Interface diffusion occurs with rapid growth of the amorphous phase originating from the grain boundaries near the critical grain size. The general relations among stability of nanocrystalline materials, micro-crystalline phase and glass formation will be discussed.

9:45 AM MM3.5

The Glass Transition Temperature T_g , Thermal Expansion Coefficients and Excess Free Volume in Metallic Glasses measured by Time-resolved Diffraction in Transmission. Alain Reza Yavari^{1,2,3}, Monica Tonegaru⁴, Nicoleta Lupu^{2,1}, Akihisa Inoue², Eiichiro Matsubara², Gavin Vaughan³, Ake Kvick³ and Walter Jose Botta F.^{4,1}; ¹ENSEEG, Institut National Polytechnique de Grenoble, St-Martin-d'Heres, France; ²IMR, Tohoku University, Sendai, Japan; ³European Synchrotron Radiation Facilities (ESRF), Grenoble, France; ⁴DEMa, Univ. Fed. Sao Carlos, Sao Carlos.

The glass transition T_g in metallic glasses can be studied by calorimetric techniques which show an endothermic event corresponding to a specific heat ΔC_p difference between the glassy and supercooled liquid states. In this work we show for the first time, that through thermal expansion measured by real-time diffraction using synchrotron light in transmission, the isochoric glass transition T_g can be detected for bulk metallic glass-forming alloys. This was impossible previously as metallic glasses with crystallisation temperature T_x near T_g crystallized during real-time diffraction experiments. This limitation does not hold for newly developed bulk metallic glasses (BMGs) with large supercooled regions $\Delta T = T_x - T_g$. Under such conditions, the variation of α -th, the volume coefficient of thermal expansion, has been measured for the first time by diffraction near T_g for a number of bulk glass-forming alloys. The variation of α -th is clearly detected in the same glass transition temperature range of ΔC_p for both metal-metalloid bulk glasses and metal-metal type bulk glasses. Structural relaxation and the annihilation of the excess free-volume has also been monitored by in-situ diffraction during annealing of the glass. The amount of excess free-volume is found to depend on the quench rate when comparing for example, specimen from the bulk glass and melt-spun glassy ribbons of the same alloy or for ribbons spun at different wheel speeds. Acknowledgements: This work was supported by the EU Network on BMGs (HPRN-CT-2000-00033), IFCAM, ESRF project ME-544 and CNPq-CNRS.

10:30 AM *MM3.6

Ultrasonic Investigation of Bulk Metallic Glasses.

Wei Hua Wang, Institute of Physics, Chinese Academy of Science, Beijing, China.

Microstructure, ultrasonic attenuation, acoustic, elastic and thermal properties as well as their pressure and temperature dependence of the Zr-, Cu-, Fe-, Pd-, Nd-, Pr-, Ni-based bulk metallic glasses (BMGs) and glassy composites have been systematically studied by using a pulse echo overlap method which is particularly sensitive to the microstructural change. The elastic constants and thermodynamic parameters as well as their temperature and pressure dependence have been determined for the BMGs and are compared with those of oxide glasses, other conventional metallic glasses and crystallized BMGs. Some unique acoustic characteristics upon pressure and temperature of the BMGs are found. The glass forming ability and elastic properties are found to have good correlation for the BMGs, oxide glasses and conventional metallic glasses. A striking softening of long-wavelength transverse acoustic phonons in the BMGs relative to its crystallized state is observed and contributed to the microstructural characteristics of the BMG. The volume-pressure equation of state and the Grueneisen constant for these BMGs was obtained. The compression curves of the BMGs are found to interpose among its components, and the BMGs exhibits much small volume changes upon pressure comparing with oxide glass, indicating that the BMG has similar atomic close-packed configurations with elements. The compression curve, the elastic constants and Debye temperature of the BMGs are also calculated based on a similarity of their properties between the glassy state and its corresponding crystalline state. These results confirm the theoretical predictions concerning the features of microstructure and interatomic bonding in the BMGs.

11:00 AM MM3.7

Modeling of Thermophysical Properties and Phase Diagrams of Multicomponent Metallic Alloys. Tahir Cagin, William A

Goddard, Peng Xu, Hyon-je Lee, Robin Koshy and Guoyun Zhang; California Institute of Technology, Pasadena, California.

The development and design of high performance structural materials is mostly considered to be either a trial and error endeavor or the artisan's property-performance correlations knowhow. But the recent developments and progress in theory and simulation methods, and the increasing pace of the growth in computational power have opened up opportunities for a theory and simulation supported rational design approach. In this presentation, we will describe our work on the properties of metallic systems: solid and liquid metals and alloys, using various levels of theory; quantum mechanics, force fields, molecular dynamics, non-equilibrium molecular dynamics, statistical mechanics and thermodynamics in studying their structure and properties (mechanical -elastic and plastic-, thermodynamic, and transport).

11:15 AM MM3.8

Ab-initio Calculation of the Diffusion Coefficients in Fe-based Liquids. Miguel Fuentes-Cabrera^{1,2}, Donald M Nicholson¹, Mike

Widom², Yang Wang² and Merek Mihalkovic³; ¹Oak Ridge National Lab, Oak Ridge, Tennessee; ²Carnegie Mellon University, Pittsburgh, Pennsylvania; ³Slovakia Academy of Science, Bratislava, Slovakia.

Fe-based Bulk Metallic Glasses (BMG) appear only in certain ranges of composition. Empirical rules have evolved as guides to the discovery of new glasses. Ab initio calculations can provide a foundation for existing empirical rules, reveal new rules, and give additional guidance to the determination of useful compositions. Our goal is to use ab-initio techniques to gain understanding and make useful predictions. We have studied the self-diffusion in liquid Fe₇₀X₅Zr₅B₂₀ (X=Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd). The 4d elements are the slow diffusers and play a critical role in preventing crystallization. Keeping the Zr composition fixed facilitates comparisons of 4d diffusion relative to Zr diffusion. Trends in diffusion are correlated with atomic size and bonding of the 4d element with Fe and B. Diffusion coefficients and partial pair distribution functions were determined from 20ps simulations done with the Vienna Ab-initio Simulation Package. Work supported by DARPA/ONR Grant N00014-01-1-0961 under DOE subcontract DEAC05-00OR22R725464 with UT-Battelle, LLC.

11:30 AM MM3.9

Early Crystallization Stages of Undercooled Zr-Cu-Ni-Al-Ti Melts with Different Oxygen Contents. Andreas A Kundig,

Tadakatsu Ohkubo and Kazuhiro Hono; Metallic Nanostructure Group, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Earlier studies on the crystallization behavior of Zr_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅ using XRD, DSC, SANS [1,2], TEM and

ASAXS [3] report composition fluctuations on the nanometer scale and nanocrystals at early and intermediate states of crystallization, respectively. For the underlying crystallization process different models such as "growth of (icosahedral) clusters present in the glass", "high rate classical nucleation" or "decomposition into amorphous phases on a nanometer scale" have been proposed. In the present work, investigations on the early crystallization stages by means of DSC, HREM and 3DAP show a low density of nanocrystals including quasicrystals. More detailed results will be reported in the talk and used to discuss the above mentioned models. In addition, the oxygen content of the alloy has been varied as it influences the crystallization mechanism. While oxygen generally reduces the glass forming ability upon cooling of Zr-based glass forming melts [4], it increases the glass transition temperature of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ for higher levels. Also, the first peak in DSC, which determines the nanocrystal formation, is shifted to higher temperatures and finally disappears in the second peak. The influence of oxygen on crystallization is discussed on the basis of its content in the crystalline phases. [1] Löffler JF, Bossuyt S, Glade SC, Johnson WL, Wagner W, Thiyagarajan P, Appl. Phys. Lett. 77 (2000), 525-527. [2] Hermann H, Mattern N, Kuhn U, Heinemann A, Lazarev N, J. non-cryst. Solids 317 (2003), 91-96. [3] Hufnagel TC, Gu XF, Munkholm A, Mater. Trans. 42 (2001), 562-564. [4] Lin XH, Johnson WL, Rhim WK, Mater. Trans. JIM 38 (1997), 473-477.

11:45 AM MM3.10

Viscosity of bulk metallic glass forming liquids close to the melting point. Tyler Shaw and Ralf Busch; Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon.

A high temperature high vacuum rotating cylinder viscometer was designed and built for the measurement of liquid viscosities in a high purity environment with a measurement range from .01 to 10 [Pa*s]. Using this viscometer the viscosity of bulk metallic glass forming alloys is studied in the vicinity of the melting point as a function of temperature. A series of Zr-based alloys with increasing amount of components is investigated. It includes binary Zr-Ni, ternary Zr-Ni-Al, quaternary Zr-Al-Cu-Ni and pentary Zr-Al-Cu-Ni-Nb glass formers. It is found that the viscosity increases with increasing amount of components in the melt, which is consistent with a larger fragility parameter D^* , and thus a stronger liquid with enhanced glass forming ability. Viscosities of the Zr-Al-Cu-Ni-Nb alloy are very similar to the Zr-Ti-Cu-Ni-Be that are about 3 orders of magnitude more viscous than pure metals. The high viscosities are attributed to the fact that the multicomponent eutectic glass formers exhibit compositions with very effective packing of the mixture of the different size atoms, leading to a small free volume. This also stabilizes the liquid thermodynamically with respect to the crystal and reduces the driving forces for crystallization.

SESSION MM4: Joint Session with LL6: Quasicrystals from Metallic Glasses
Chairs: Ken Kelton and Dan Sordelet
Tuesday Afternoon, December 2, 2003
Republic B (Sheraton)

1:30 PM *MM4.1

Icosahedral Transformation from Supercooled Liquid in Metal-Metal Type Bulk Glassy Alloys. Akihisa Inoue, IMR, Tohoku Univ., Sendai, Miyagi, Japan.

Since the first syntheses of metal-metal type bulk glassy alloys without metalloid element in Mg-, lanthanide- and Zr-based alloy systems for several years between 1988 and 1990, we have developed a number of bulk glassy alloys in metal-metal and metal-metalloid systems. It is well known that these bulk glassy alloys exhibit unique engineering properties such as high strength, large elastic elongation, high corrosion resistance, good soft magnetic properties and Newtonian flow. We have also noticed that the metal-metal type bulk glassy alloys have unique heating-induced phase transformation in which primary crystallization phase consists only of big cube or icosahedral phase. It has also been reported that the precipitation of icosahedral phase occurs in Zr-, Hf- and Cu-based alloy systems containing special additional elements such as Ag, Pd, Pt, Au, Ti or Nb leading to nearly zero or positive heats of mixing against the other constituent elements. In addition, the icosahedral phase precipitates homogeneously at very high nucleation rates from their supercooled liquid and their grain size is as small as 5 to 20 nm. The precipitation of the icosahedral phase in the alloys containing the special elements has been interpreted to result from an increase in instability of supercooled liquid accompanied by an ease of nucleation of icosahedral phase through the introduction of weak bonding sites in the supercooled liquid structure consisting mainly of short-range icosahedral atomic configurations. The first aim of this paper is to review alloy systems in which the icosahedral phase precipitates

during heating from supercooled liquid, kinetic behavior and microstructure for the precipitation of the icosahedral phase, and mechanical properties of icosahedral base alloys in the Zr-, Hf- and Cu-based alloys containing the special elements. The second is to investigate the reason for the role of the special elements in the precipitation of the icosahedral phase.

2:00 PM *MM4.2

Quasicrystals and Related Phases in Multicomponent Alloy Systems. J Eckert, U Kuehn, S Scudino and N Mattern; Institute of Metallic Materials, IFW Dresden, Dresden, Saxony, Germany.

(Nano-)quasicrystalline, amorphous and nanocrystalline multicomponent Al- and Zr-based alloys are attractive materials for advanced high-strength applications. Further property improvements are achievable by designing multiphase composite materials with optimized length-scale, volume fraction and intrinsic properties of the constituent phases. Such alloys can be synthesized by quenching from the melt or by solid state reaction using mechanical alloying / ball milling techniques. Many studies suggest a linkage between the short-range order of the amorphous phase and the formation of quasicrystals or other related complex intermetallic compounds. These suggestions are based on the idea that the liquid prior to vitrification contains icosahedral short-range order or clusters, which are retained in the glass upon quenching, and even may stabilize the glassy state/supercooled liquid. Moreover, there are speculations that solid state synthesis does not provide the opportunity to form the initial short-range order as proposed in liquid-to-solid processing routes. We have investigated single-phase alloys and multiphase composites containing different volume fractions of (quasi-)crystalline or amorphous phases with different length-scale of the constituent phases prepared by quenching from the liquid as well as by solid state reaction. Examples for the phase formation and the development of the microstructure under different processing conditions, the short-range order and for the thermal stability of the metastable alloys will be given, and critically discussed by considering the underlying thermodynamics and kinetics of metastable phase formation. Data for the mechanical behavior will be presented, revealing that in particular the properties of composite materials in quasicrystal-forming systems can be tuned within a wide range of strength and ductility as a function of volume fraction, size and morphology of the different phases.

2:30 PM MM4.3

Quasicrystal Formation in Zr-Based Metallic Glasses: Influence of Ag. Lyudmila Lyubenova and Uwe Koster; Dept. Biochem. & Chem. Eng., University of Dortmund, Dortmund, Germany.

In the Zr-Cu-Ni-Al system one of the best bulk metallic glass forming alloys was found. But in a narrow concentration range around the composition of the best glass forming ability (e.g., $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$) formation of quasicrystals either by primary or polymorphic reaction is known to proceed during annealing [1]. Exchange of Cu or Ni by other late transition elements was found to stabilize or deteriorate quasicrystal formation. The reason for such an influence on the formation of quasicrystals are not known as yet. Recent papers mention for example some evidence that the quasicrystals in these alloys are a hybrid of two structural elements, i.e. the tetragonal Zr_2Ni (Al_2Cu) and the tetragonal Zr_2Cu ($MoSi_2$) structure, as well as the influence of a positive enthalpy of mixing for at least one of the interactions, namely that between TM and M. Whereas replacement of Cu by Ag is known to result in nanocrystallization of the quasicrystalline phase [2], small Ag additions in the range of 0.5 to 1 at.% reduces the number of nucleation sites significantly, thus allowing growth of rather large quasicrystals. This paper presents a detailed study on the influence of Ag additions on the formation of icosahedral quasicrystals. Combining electron microscopy with DSC as well as crystallization statistics allows the separation of the influence of Ag on the relevant crystallization parameter, for example the interfacial energy. Reasons for the observed behavior will be discussed in detail. The results may help to understand the ruling factors on the formation of quasicrystals in Zr-based glasses. [1] U.Köster, J.Meinhardt, S.Roos, H.Liebertz, Appl.Phys.Lett. **69** (1996), 179; [2] J.Saida, M.Matsushita, A.Inoue, Mater.Sci.Forum **360 – 362** (2001),73.

2:45 PM MM4.4

Influence of Al on quasicrystal formation in Zr-Ti-Nb-Cu-Ni-Al metallic glasses. S. Scudino¹, J. Eckert¹, U. Kuehn¹, H. Breitzke², K. Lueders² and L. Schultz¹; ¹Institut fuer Metallische Werkstoffe, IFW Dresden, Dresden, Germany; ²Fachbereich Physik, Freie Universitaet Berlin, Berlin, Germany.

Although Zr-based glassy alloys that form a metastable quasicrystalline phase upon partial devitrification have attracted much attention in the last years and several investigations have been

performed, the knowledge regarding quasicrystal formation is still incomplete. In order to clarify the role of Al, an element often present in quasicrystal-forming Zr-based alloys, on the formation of quasicrystals, the devitrification of glassy (Zr_{61.62}Ti_{8.64}Nb_{2.7}Cu_{15.03}Ni_{12.01})_{100-x}Al_x alloys with x = 0, 2.5, 5 and 7.5 at. % prepared by melt spinning was investigated. The crystallization behavior was studied by isochronal and isothermal thermal analysis, x-ray diffraction and electron microscopy. The devitrification of the ribbons is characterized by the formation of a metastable quasicrystalline phase during the first stage of the crystallization process, followed by successive transformation into intermetallic compounds at higher temperatures even for the alloy with x = 0. Therefore, Al is not essential for quasicrystal formation in the present alloys. However, it affects the properties of the amorphous as well as of the quasicrystalline phase. In fact, with increasing Al content, the range of stability of the quasicrystalline phase decreases whereas the stability of the amorphous phase increases together with a slight increase of the supercooled liquid region. Thus, it is concluded that although the addition of Al improves the properties of the glassy phase, it has no beneficial effect on the formation of quasicrystals.

3:30 PM *MM4.5

Topological and Chemical Short-Range Order in Undercooled and Stable Melts Forming Quasicrystals and Approximants.

Dirk Holland-Moritz¹, Thomas Schenk^{1,4}, Virginie Simonet² and Robert Bellissent³; ¹Institut fuer Raumsimulation, DLR, Koeln, Germany; ²Laboratoire Louis Neel, Grenoble, France; ³Centre d'Etudes Nucleaires, Grenoble, France; ⁴European Synchrotron Radiation Facility, Grenoble, France.

It was suggested already in 1952 by Frank that an icosahedral short-range order should be energetically favored in undercooled melts of systems consisting of atoms of spherelike geometrical symmetry. This hypothesis was recently experimentally confirmed by diffraction experiments on stable and undercooled melts of pure metals. In this work systematic in-situ investigations on the short-range order of deeply undercooled liquids of alloys forming quasicrystalline and polytetrahedral phases by elastic neutron scattering are presented. For Al₁₃(Co,Fe)₄ melts partial structure factors were determined which allow the analysis of both the topological and the chemical short-range order as a function of the temperature. These investigations indicate an icosahedral topological short-range order prevailing in the undercooled liquids which is accompanied by a pronounced chemical short-range order such that the first coordination shell around transition metal atoms consists preferentially of Al-atoms. An enhancement of the topological and the chemical short-range order is observed, if the temperature is decreased. The influence of this short-range order on the nucleation behavior of quasicrystalline phases in undercooled liquids is discussed.

4:00 PM *MM4.6

Metastable States During Devitrification of Metallic Glasses.

Matthew J. Kramer¹, Dan J. Sordelet¹ and Pete L. Lee²; ¹Ames Laboratory, Iowa State University, Ames, Iowa; ²Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

High energy-high temperature X-ray diffraction was used to investigate the time-temperature transformations in the short-range order (SRO) of Zr₇₀Pd₃₀ and Zr₇₀Pd₂₀Cu₁₀ alloys produced by rapid solidification (RS) and mechanical milling (MM). The differences in the total scattering function S(Q) as a function of time at a temperature ~ 50 K below the crystallization temperature were determined. After rapidly heating, diffraction data were taken at 5 min intervals for 180 min. The difference in the S(Q)/s over this time interval shown that both alloys undergo a structural relaxation prior to nucleation and growth. The RS alloys are shown to have SRO dominated by a random polyhedral configuration close to icosahedral symmetry. The MM samples have SRO to medium-range order (MRO) which is topologically similar to the MoSi₂-type structure (I4/mmm), but chemically closer to the Al₂Cu-type structure (I4/mcm). Reverse Monte Carlo (RMC) simulations of the experimentally measured atomic pair distributions were performed to identify the partial pair distributions and differences in local chemical ordering. At nucleation, the RS alloy is transformed to the icosahedral phase while the MM alloy forms the Al₂Cu-type structure. The differences in the transformation pathways between the RS and MM alloy can be understood in terms of the differences free energy of the SRO relative to the possible metastable structures. The work at Ames Laboratory was supported by the U.S. Dept. of Energy through Iowa State University under contract No. W-7405-ENG-82. The Midwest Universities Collaborative Access Team (MUCAT) sector at the APS is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, through the Ames Laboratory under Contract No. W-7405-Eng-82. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

4:30 PM MM4.7

Investigation by Transmission Electron Microscopy, EDX and EELS of Quasicrystal Phase in

Zr_{46.75}Ti_{8.25}Ni₁₀Cu_{7.5}Be_{27.5} and Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈

Alloys: Effect of the Be in the Quasicrystal Formation.

Bertrand Van de Moortele^{1,2}, Jean-Marc Pelletier¹, Won Tae Kim³, Thierry Epicier¹ and Jean-Louis Soubeyrou⁴; ¹GEMPPM, INSA de Lyon, Villeurbanne, France; ²IPMC, EPFL, Lausanne, Switzerland; ³Applied Science Division, Chongju University, Chongju, South Korea; ⁴CRETA, CNRS, Grenoble, France.

Since the first observation of quasicrystal phase in a rapidly quenched Al-Mn alloy by Shechtman et al., many materials containing quasicrystals were discovered. In particular, quasicrystal could be observed in metallic glasses during devitrification. Such phases are metastable and disappear when temperature or time of ageing increases. It is well known that an increase of Be-content between from Vit1 (22.5% Be) to Vit4 (27.5 %Be) alloy leads to the formation of a quasicrystal phase during ageing. Also stable quasicrystalline phase has been reported to form during crystallization of an amorphous Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈. In metallic glasses, the formation of quasicrystalline phase often takes place by a polymorphous transformation, i.e. that only a change of local order is necessary to go from the matrix to the quasicrystal. However very few chemical analyses have been performed on such phases to ensure that composition of these phases is similar to that of the amorphous matrix. The aim of this work is to compare the chemical evolution of two metallic glasses during crystallization with an emphasis of Be effect on the formation of quasicrystal. EDX and EELS analyses show that the quasicrystalline phase in the Zr_{46.75}Ti_{8.25}Ni₁₀Cu_{7.5}Be_{27.5} alloy (Vit4) does not contain Be, indicating that a chemical partitioning takes place during the precipitation. Measurements in the Ti₄₀Zr₂₅Ni₈Cu₉Be₁₈ alloy indicate an important change in the composition. This influence of the Be content on the quasicrystal formation is discussed.

4:45 PM MM4.8

The micromechanism of amorphous-to-quasicrystalline

transformation in a Zr-based bulk metallic glass. Lin Liu^{1,2}, K.

C. Chan¹, G. K. H. Pang³ and K. Z. Baba-kishi³; ¹Department of Industrial and System Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong; ²Department of materials Science and Engineering, Huazhong University of Science and technology, Wuhan, Hubei, China; ³Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong.

A Zr-based bulk metallic glass with a diameter of 2 mm was successfully prepared by copper-mould casting. The phase transformation of the glass was investigated by x-ray diffraction (XRD), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). It was found that the bulk metallic glass obtained exhibits two distinct exothermic reactions. The first one corresponds to the formation of quasicrystals from the amorphous phase, while the second reaction results from the formation of a stable intermetallic compound from the previously formed quasicrystals. In order to understand the micro-mechanism governing the amorphous-to-quasicrystalline transformation, high resolution TEM coupled with nano-scale EDX was employed to monitor the structural evolution of the glass with the increase of temperature. It was found that the amorphous-to-quasicrystalline transformation does not follow the traditional nucleation/growth mechanism. Instead, it undergoes a series of inter-processes with the formation of a set of metastable phases. The metastable phases are highly disordered and possess a high density of lattice defects, such as dislocations, stacking faults and nano-twins. The lattice ordering of the metastable phases gradually modified with the increase of temperature, and finally fell into the lattice array and symmetry of quasicrystal. EDS revealed that no change in the compositions was involved in the whole process of the phase transformation, suggesting that the amorphous-to-quasicrystalline transformation in the present bulk metallic glass is a non-polymorphous reaction, and the transformation seems to be governed by the lattice-self-modification.

SESSION MM5: Poster Session I
Chairs: Ralf Busch and Todd Hufnagel
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

MM5.1

Thermodynamics and Kinetics of the

Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3} at% Bulk Metallic Glass

Forming Liquid. Minalben Shah, Isabella Gallino and Ralf Busch;

Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon.

The $Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ at% alloy shows an improved bulk metallic glass forming ability compared to neighboring compositions in the Zr-Nb-Cu-Ni-Al system [1]. The critical cooling rate is less than 10K/s. In addition it exhibits a large supercooled liquid region, when the glassy alloy is heated above the glass transition. Thermodynamics of the bulk metallic glass forming $Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ at% liquid were investigated using differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The experiments lead to the determination of thermodynamic functions. We find a small entropy of fusions and small driving forces for crystallization. Isothermal relaxation and crystallization studies of

$Zr_{58.5}Nb_{2.8}Cu_{15.6}Ni_{12.8}Al_{10.3}$ bulk metallic alloy were performed using the DSC in the glass transition and the supercooled liquid region. The relaxation kinetics was studied using isothermal enthalpy relaxation experiments. The relaxation data obtained for temperatures below the onset of the glass transition temperature were fitted using a stretched exponential function. Results reveal that enthalpy does relax in a non-Arrhenius fashion. However the stretching exponents are close to unity, which indicates that the alloy is a rather strong glass former. This is confirmed by Vogel-Fulcher-Tammann fits to the heating rate dependence of the glass transition. Both, the small driving force for crystallization and the strong liquid behavior lead to the good glass forming ability. The time-temperature transformation (TTT) diagram is determined close to the glass transition when heated from room temperature to isothermal temperature. It is in good agreement with the diagram measured by electrostatic levitation [1], which was obtained by cooling to isothermal conditions from the liquid state. The large time and temperature window, in which the supercooled liquid is accessible close to T_g , makes this alloy very suitable for processing at low temperatures. [1] C.C. Hays et al., Appl. Phys. Lett., 79, 1605 (2001)

MM5.2

Thermodynamics of the $Pd_{43}Ni_{10}Cu_{27}P_{20}$ metallic glass forming alloy. Masahiro Kuno¹, Ralf Busch¹ and Jan Schroers²; ¹Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon; ²Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California.

Since $Pd_{43}Ni_{10}Cu_{27}P_{20}$ has a melting point below 1000K and a very low critical cooling rate of about 0.1 K/s, it can be undercooled below the melting point in a power compensated differential scanning calorimeter (DSC). It is therefore possible to measure the thermodynamic properties of the supercooled liquid with great accuracy. In this study, we measure the specific heat capacity c_p^l of the supercooled liquid and the enthalpy change ΔH^{l-x} upon crystallization in the same isothermal experiment for different amounts of undercooling. We thus obtained c_p^l and ΔH^{l-x} over the entire undercooled liquid region. Each experiment was calibrated individually with a reference run using a sapphire standard. After measuring the specific heat capacity of the crystal c_p^s , the difference in specific heat capacity $\Delta c_{p,l-x}$ can be integrated. In the case of this alloy we have the opportunity to compare this calculation with the measured enthalpy change. A very good match between measured enthalpy change and calculated values is found. This confirms that the approach that is commonly used to calculate the temperature change of the thermodynamic functions is a good approximation. The study also reveals that the alloy has a very small entropy of fusion and thus a very small driving force for crystallization. This suggests that nucleation probability rather than nucleation and growth kinetics determines the crystallization of this alloy. This is supported by the additional facts that (1) the alloy is a relatively fragile bulk metallic glass former and that (2) it crystallizes very fast upon undercooling once the first nuclei have formed. Both features indicate relatively fast kinetics.

MM5.3

On the Fragility of NbNi Based Bulk Metallic Glasses. Ludi A Shadowspeaker and Ralf Busch; Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon.

The heating rate dependence of the glass transition region and the crystallization of the $Ni_{65}Nb_{35}$, $Ni_{60}Nb_{35}Sn_5$, $Ni_{59.35}Nb_{34.45}Sn_{6.2}$, $Ni_{60}(Nb_{40}Ta_{60})_{34}Sn_6$, and $Ni_{57}Fe_{3}Nb_{35}Sn_5$ metallic glasses is investigated with differential scanning calorimetry (DSC) in a range between 0.0167 K/s and 3.333 K/s. The continuous heating diagrams for all alloys are constructed, showing that with increased number of components the temperature range of the supercooled liquid region increases. The fragility of the different alloys can be deduced by plotting the inverse heating rate for each DSC experiment versus inverse glass transition temperature normalized to the glass transition temperature for a rate of 0.0167 K/s (Angell plot). The fragility m is determined as the slope of the curve at the glass transition temperature for a heating rate of 0.0167 K/s. The data are also fitted with a Vogel-Fulcher-Tammann (VFT) type relation yielding the fragility parameter D^* as well as the VFT temperature T_0 . The

fragility parameter increases from the binary alloy ($D^* = 6.2$) to the ternary alloys ($D^* = 11.0$) and is the largest for the quaternary alloys ($D^* = 16$). The D^* increases linearly as the number of components in the alloy increases, yielding a fragility parameter of about $D^* = 2$, if we extrapolate down to a one component system, which is in good agreement with the estimated fragility of pure metals using their melt viscosity and apparent activation energies for flow. The data are compared with results on other bulk metallic glass forming alloys. The increase of the fragility parameter with the number of components in NbNi based alloys is also observed in Zr based alloys. It reflects the slowdown in kinetics and thus the increase in glass forming ability with the increase of the number of components.

MM5.4

Viscous Flow of Glass-forming Liquids: A Cluster Approach. Guojiang Fan¹, Enrique Lavernia¹ and Hans Fecht²; ¹Chemical Engineering and Materials Science, University of California, Davis, California; ²Center for Micro- and Nanomaterials, University of Ulm, Ulm-89081.

The structures of a glass-forming liquid remain an unsolved problem. The free volume has been considered as a useful structural parameter for the glass-forming liquids. We previously developed a cluster model to account for the viscous flow of the glass-forming liquids (G. J. Fan and H. J. Fecht, J. Chem. Phys. 116, 5002 (2002)). We found that the kinetic fragility of a glass-forming liquid is quantitatively connected with its entropy of fusion ΔS_f , the value of its melting point T_m , and the structures of interfaces between clusters. Here, we will demonstrate that the proposed cluster model is in consistency with the energy landscape model of the glass transition. In contrast to the strong liquids, fragile liquids have a larger value of $\Delta S_f/T_m$, thereby, undergo steep change in the energy landscape when cooling from the melt into the glass. The stretched exponential relaxation, commonly observed in the glass-forming liquids, is due to the wide distributions of clusters with sizes in the range of nanometer scale. The glass-forming liquids consisting the nanometer-sized clusters may be responsible for the observed similarity in the mechanical properties between metallic glasses and nanostructured metals.

MM5.5

Abstract Withdrawn

MM5.6

Candidate Short-Range Atomic Configurations in the Structures of Metallic Glasses. Daniel B. Miracle and Kevin L. Kendig; Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio.

It has been experimentally well established that short-range atomic order is commonly observed in the structure of many metallic glasses. Specific atomic configurations have been proposed or measured for two classes of metallic glasses. A capped trigonal prism with a coordination number (CN) of nine has been discussed for metal-metalloid glasses, and icosahedral clusters with CN = 12 have been proposed for Al-based glasses with rare earth and transition metal solutes. Recent research has established the influence of the relative size of solute and solvent atoms on the constitution and stability of metallic glasses. That research has shown that specific ratios between solute and solvent atom radii, R^* , are preferred in the formation of metallic glasses. While each of the values of R^* correspond to a particular CN, the specific atomic configurations that may exist for each value of R^* and the corresponding CN have not been defined. The present research will describe a systematic exploration of the local atomic configurations that may exist for solute atom radii that range from about 60% of the solvent radius (CN = 8) to solute radii that are about 130% the radius of solvent atoms (CN = 18).

MM5.7

Exploration of New Bulk Metallic Glasses Based on the Ti-Ni-Si System. Daniel B. Miracle¹, Joseph Kell², Samad Firdosy² and Wynn Sanders¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio; ²Southern Ohio Council for Higher Education, Dayton, Ohio.

A recently developed topological model has shown that specific radius ratios between solute and solvent atoms are preferred in the constitution of bulk metallic glasses. Further, atomic size distribution plots (ASDPs) have shown that a reasonably well-defined topological relationship is preferred between the concentration of solute atoms and the solute atom sizes in bulk metallic glasses. Together, these two ideas can be used to guide the exploration of new bulk metallic glasses. Candidate solute species can be selected based on the preferred solute size relative to the solvent atoms, and the preferred solute concentrations can be selected so that the ASDP of the candidate alloy approximates the topological profile common for known bulk metallic glasses. In addition to these topological guiding

principles, thermodynamic assessments have been used to explore new bulk metallic glass alloys based on the Ti-Ni-Si system. Details of this approach will be described and the results will be presented.

MM5.8

Development of Bulk Aluminum Metallic Glass Using Revised Glass Forming Criteria. Wynn S. Sanders¹, Mike Scott², Daniel B Miracle¹, Ross E Dotzlar⁶, Sesh Tamirisa⁴ and Joseph W Kell³; ¹Air Force Research Laboratory, Wright-Patterson AFB, Ohio; ²UES, Inc., Dayton, Ohio; ³Southwestern Ohio Council of Higher Education, Dayton, Ohio; ⁴Ohio University, Athens, Ohio; ⁵California Polytechnic State University, San Luis Obispo, California; ⁶US Air Force Academy, Colorado Springs, Colorado.

This paper presents a strategy for the development of bulk aluminum metallic glass. Recent research has developed new insights into the criteria for bulk metallic glass formation. First, bulk metallic glasses obey a unique topological relationship as shown in atomic size distribution plots. Additionally, there are critical (preferred) radius ratios that are beneficial to efficient atomic packing. Finally, appropriate alloying element selection can depress the liquidus relative to the glass transition temperature. These revised criteria, in combination with thermodynamic modeling, are being used to guide efforts to develop new bulk metallic glasses based on aluminum. Composition space of known ternary marginal glass formers is being systematically explored via the addition of quaternary and higher order alloying elements based upon topological and chemical considerations. To date, this approach has resulted in an important increase in the glass forming ability of marginal aluminum glasses. The specific approach applied in this exploration study will be described and results will be presented.

MM5.9

A Transmission Electron Microscopy Study Of Devitrification Products in Al-Gd-Ni-(Fe,Co) Alloys. Alexandre L Vasiliev¹, Mark Aindow¹, Martin J Blackburn¹ and Thomas J. Watson²; ¹IMS, University of Connecticut, Storrs, Connecticut; ²Pratt & Whitney, East Hartford, Connecticut.

The Al-Gd-Ni-X alloys (where X = Fe or Co) are perhaps the most significant for the manufacture of Al-based metallic glasses because of the wide range of compositions for which amorphous phases can be produced. In the devitrified state these alloys exhibit nanocrystalline microstructures consisting of face-centered-cubic a-Al, binary Al₃Gd, and ternary Al-Ni-Fe or Al-Gd-Ni phases. There is, however, some uncertainty about the crystal structures exhibited by the ternary phases in such alloys. In the present paper we will present an overview of the transmission electron microscopy data acquired from several of these alloys in the devitrified state. A series of imaging, diffraction and energy-dispersive X-ray spectrometry experiments has been performed to identify the intermetallic phases present, and high-resolution lattice imaging together with image simulations has been used to confirm the results of these analyses. It was shown that the ternary Al-Gd-Ni phase is present as rods of the orthorhombic compound Al₁₉Ni₅Gd₃, but that particles of this phase contain embedded slabs of a Al₂₃Ni₆Gd₄ phase which has been reported previously by Gladyshevskii et al [1]. There is very little known about this latter phase. It is presumably metastable, but is retained in the microstructure even after annealing at high homologous temperatures. The morphology and microstructural development of these particles, and those of the binary phase, will be discussed. References 1. R.E.Gladyshevskii and E.Parthe Z. Kristallographie 198, 171-172 (1992).

MM5.10

Microstructure And Ternary Phases In Al-rich Al-Y-Ni Alloys. Alexandre L Vasiliev¹, Mark Aindow¹, Martin J. Blackburn¹ and Thomas J. Watson²; ¹Institute of Material Science, University of Connecticut, Storrs; ²Pratt & Whitney, Hartford, Connecticut.

Al-Y-Ni alloys processed through the amorphous state exhibit highly refined microstructures and significant improvements in strength over conventional Al alloys. As such, they are now being considered for aerospace applications. One possible complication with Al-RE-TM alloys is that the binary and ternary intermetallic compounds can lead to embrittlement. However, it has been shown that it is possible to define compositions and phase distributions in the Al-Y-Ni system that combine intermediate strength (700 - 800MPa) with quite high ductility. To understand how these mechanical properties are achieved, and what scope there is for further improvement, we have been investigating the structural and morphological features of various intermetallic phases that are formed. In this paper we will present the results of a transmission electron microscopy study on the crystal structures and morphologies exhibited by each of the phases in a set of four Al-rich Al-Y-Ni alloys which contain 1.7-4.5 at. % Y and 3.5-10.1 at. % Ni. It is shown that each alloy contains fcc-Al, a binary phase (either Al₃Ni or Al₃Y), and a ternary phase. The electron

diffraction data obtained from the ternary phase are consistent with those expected for the orthorhombic phase Al₁₆Ni₃Y reported by Rykhal et al. [1]. There has been considerable controversy about this phase in the literature and indeed the composition of the ternary particles measured by energy-dispersive X-ray spectrometry is not consistent with this stoichiometry. A combination of high-resolution lattice imaging and image simulations has been used to resolve the apparent contradiction between the diffraction and spectrometry data. It is shown that the phase is actually a metastable phase Al₁₉Ni₅Y₃ (C/mcm, a=0.4025 nm, b=0.799 nm and c= 2.689 nm, Al₁₉Ni₅Gd₃ structure type) which has not been reported previously. This phase is present in each of these alloys, even after annealing at high homologous temperatures. In many cases, the ternary particles also contain embedded slabs of the equilibrium Al₂₃Ni₆Y₄ phase. The precipitation sequence which leads to the development of these distinctive ternary particles will be discussed. References 1. R.M.Rykhal, O.S.Zarechnyuk Dopov.Acad. Nauk Ukr. SSR, Ser A 4, 375 (1975).

MM5.11

Effect of Hydrogen on the Stability of Mg-Based Metallic Glasses. Annett Gebert, Mariya Savyak, Margitta Uhlemann, Juergen Eckert and Ludwig Schultz; IMW/23, IFW Dresden, Dresden, Saxony, Germany.

Glass-forming magnesium-based alloys are very interesting regarding their interaction with hydrogen due to their short-range order and composition. Amorphous ribbons of a Mg-Cu-Y alloy were prepared by melt spinning and subsequently hydrogen-charged at constant current densities of i = -1 and -10 mA/cm²cm in 0.1 M NaOH solution with various hydrogen concentrations. The hydrogen content of the ribbon samples was determined using the hot extraction method. The microstructure and the thermal stability of as-quenched and differently hydrogen-charged samples were investigated by means of X-ray diffraction, scanning and transmission electron microscopy, differential scanning calorimetry and thermal desorption analysis. The amorphous Mg-Y-Cu alloy can absorb electrochemically up to about 3.7 weight percent hydrogen. With increasing hydrogen content a change from a fully amorphous to a very fine nanocrystalline microstructure was observed revealing that the amorphous alloy undergoes already at room temperature during electrochemical charging a disproportionation reaction. The effect of hydrogen on the thermal behavior, i.e. after heating charged samples to selected temperatures up to 723 K at a constant heating rate, which is at high hydrogen contents mainly governed by formation of hydrides and grain growth, will be discussed in detail.

MM5.12

Medium-Range Order and Crystallization in Zr₅₉Cu₂₀Al₁₀Ni₈Ti₃ and Zr₅₇Cu₂₀Al₁₀Ni₈Ti₃ Metallic Glasses investigated by NMR. Hergen Breitzke¹, Klaus Lueders¹, Sergio Scudino², Uta Kuehn² and Juergen Eckert²; ¹Fachbereich Physik, Freie Universitaet Berlin, Berlin, Germany; ²Institut fuer Metallische Werkstoffe, IFW Dresden, Dresden, Germany.

Medium-range order and quasicrystal formation in Zr₅₇Cu₂₀Al₁₀Ni₈Ti₃ and Zr₅₉Cu₂₀Al₁₀Ni₈Ti₃ metallic glasses are investigated by means of magnetic resonance (NMR). The samples are prepared by rapid solidification and annealed to induce primary quasicrystal formation. ²⁷Al and ⁶³Cu NMR spectra and spin relaxation curves are recorded before and after the annealing process. The ²⁷Al spin-lattice relaxation time in both metallic glasses is about two orders of magnitudes higher than in metallic Al. The spin-lattice relaxation time of ⁶³Cu exceeds the spin-lattice relaxation of metallic Cu by one order of magnitude indicating low densities of states at Al and Cu sites. The low densities of states together with relatively well structured ²⁷Al and ⁶³Cu NMR spectra can be taken as a proof for the presence of medium-range order in the investigated metallic glasses. By simulations of ²⁷Al and ⁶³Cu second moments in various binary Al and Cu compounds the medium-range orders L₁₂ AlZr₃ and C11₆ CuZr₂ can be identified in both as-quenched metallic glass. After heat treatment both metallic glasses show strong changes in the ⁶³Cu second moments, whereas the ²⁷Al second moments show only relatively small changes. Furthermore, the Cu second moment after heat treatment in Zr₅₇Cu₂₀Al₁₀Ni₈Ti₃ is about half as large as in Zr₅₉Cu₂₀Al₁₀Ni₈Ti₃ indicating different types of crystallization in both metallic glasses during heat treatment.

MM5.13

Local Ordering Induced by Elemental Doping and Its Effect on Glass Formation and Crystallization. Li-qian Xing¹, K. F. Kelton¹, Anindita Mukhopadhyay² and W. E. Buhro²; ¹Department of Physics, Washington University, St. Louis, Missouri; ²Department of Chemistry, Washington University, St. Louis, Missouri.

While difficult to test, it is often assumed that local ordering exists in liquid alloys and metallic glasses. The effects of this local ordering on

glass formation and crystallization, however, remain unclear. Oxygen has a strong chemical bonding potential with metal elements possibly inducing chemical short-range ordering; this has been demonstrated in Ti-3d transition metal-Si alloys, where the oxygen induces icosahedral ordering. In principle, then, oxygen could be used to investigate the effect of local ordering in metallic glasses, however in most cases it is difficult to distinguish the effects of local ordering from oxide formation, forming heterogeneous nucleation sites. We will show that oxygen does not alter glass formation of the $Al_{88-x}Y_7Fe_5(Ti, Zr, V)_x$ ($x = 0.5, 1, 1.5$) alloys significantly unless the oxygen concentration is greater than approximately 0.5 at.%. The oxygen changes the phases formed upon crystallization, favoring the formation of a bcc phase but depressing the formation of a metastable phase, demonstrating that the oxygen is not simply leading to the formation of heterogeneous nucleation sites. We further demonstrate that small additions of Ti, Zr and V (of order 0.5%) stabilize the metastable phase and depress the formation of the primary α -Al phase, increasing the glass forming ability. These results suggest that in these glasses micro-level doping leads to local ordering, insight that can be used in developing new metallic glasses.

MM5.14

Amorphous Alloy Formation in Immiscible Cu-Ta and Cu-W Systems by Atomistic Modeling and Ion-Beam Mixing. H.R. Gong, L.T. Kong and Baixin Liu; Dept. Mat. Sci. & Eng., Tsinghua University, Beijing, China.

For the immiscible Cu-Ta and Cu-W systems, realistic n-body potentials are derived under an embedded-atom method through fitting the cross potentials to some physical properties obtained from ab initio calculations for a few possible metastable Cu-Ta and Cu-W crystalline phases, respectively [1]. Based on the derived potentials, molecular dynamics simulations reveal that in the Cu-Ta system, 30 at. % of Ta in Cu is the critical composition for the crystal-to-amorphous transition in the Cu-rich Cu-Ta solid solutions, and that in the Cu-W system, amorphous alloys can be formed within the composition range of 20-65 at. % of W. Interestingly, amorphous alloys are indeed obtained by ion-beam mixing in the properly designed $Cu_{70}Ta_{30}$, $Cu_{65}Ta_{35}$, $Cu_{60}Ta_{40}$, and $Cu_{50}Ta_{50}$ multilayered films, while the crystalline Cu and Ta remain in the $Cu_{75}Ta_{25}$ multilayered sample [2], which matches well with the critical composition of 30 at. % of Ta predicted by simulation. Moreover, there have been experimental data [3], which are in support of the predicted composition range of the Cu-W system by simulations. References 1. H. R. Gong, L. T. Kong, W. S. Lai, and B.X. Liu, Phys. Rev. B 66, 104204 (2002). 2. H. R. Gong, L. T. Kong, W. S. Lai, and B.X. Liu, Acta Mater. (2003), in press. 3. B. X. Liu, W. S. Lai and Z. J. Zhang, Adv. Phys. 50, 367 (2001).

MM5.15

Direct Observation of Phase Transformation in Ag/Cu Alloy System. Hao Chen^{1,2} and Jian-Min Zuo^{1,2}; ¹Dept. of Materials Science & Engineering, University of Illinois at U-C, Urbana, Illinois; ²Frederick Seitz Materials Research Laboratory, Urbana, Illinois.

Here we report on the phase transformation process of Ag/Cu alloy from amorphous to crystalline phase separated nano-clusters. We synthesize the samples by co-sputtering of Ag and Cu onto amorphous carbon film support to form continuous Ag/Cu thin alloy films. As-deposited, the films are amorphous. The initially amorphous continuous alloy thin film transformed into crystalline structure when samples are heated from room temperature to 400 Celsius degree. This transformation is associated with phase separation of two phases (Ag-rich or Cu-rich), which was observed using Scanning Transmission Electron Microscope (STEM). The phase transformation temperature starts at about 150 Celsius degree, and the phase separation is obvious at about 200 Celsius degree, which is higher than the phase transformation temperature. We suggest that this temperature difference is due to the different diffusion processes that govern the different phenomena. In phase transformation process, surface diffusion is dominant, while in phase separation process, bulk diffusion is the controlling factor. As the surface diffusion is faster than the bulk diffusion, the corresponding phase transformation temperature is lower than the phase separation temperature.

MM5.16

Non-Equilibrium Technology Of Obtaining Nanoamorphous Metals. Razmik Malkhasyan, ATOM SPE, Yerevan, Armenia.

In the given paper a new principle of obtaining nanosize amorphous metals (including single-component ones), that is worked out for the first time by us, is being discussed. Use of non-equilibrium technological processes and giving thermal (equilibrium) factors influence up is a main principle of the suggested method. The method is based on the comprehension of the different nature of two activation barriers. If the activation barrier of an elementary act of chemical transformation is possible at the expense of inner energy of

excitement at least of one of reagents, then it is possible to overcome the second activation barrier of the formation of crystalline embryo only at the expense of thermal energy (also including the energy that is isolated at the phase transition of the first kind). Thus, if the first elementary act of chemical endothermic transformation in a solid phase is carried out by non-equilibrium manner at the expense of inner energy of excitement of molecules or particles (for example, by molecules of hydrogen, vibrationally excited on different quantum levels - QChT), then it turned out simply that the energy is insufficient for overcoming of the second activation barrier in the system, and the products of the reaction remain in amorphous nanosize state. Nanosizeness is conditioned by the fact that the critical magnitude of a crystalline embryo does not exceed some nanometers, practically for all metals. One can say that the presented non-equilibrium principle of reaction conducting leads to creation of the "cold" atoms of reaction products, that are not capable to overcome the activation barrier of crystalline embryo - formation.

MM5.17

Mn effect on non-collinear magnetic structure of FeMn-B amorphous alloys. Yang Wang¹, Don Nicholson², Mike Widom¹, Miguel Fuentes-Cabrera^{1,2} and Marek Mihalkovic³; ¹Pittsburgh Supercomputing Center, Carnegie Mellon University, Pittsburgh, Pennsylvania; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee; ³Institute of Physics, Slovakia Academy of Sciences, Bratislava, Slovakia.

Fe-B amorphous alloys exhibit approximately collinear magnetic structure. When a certain amount of Fe atoms are replaced with Mn, the magnetic structure of the alloys is found to become non-collinear. In this presentation, we discuss the Mn effect on the magnetic structure of FeMn-B amorphous alloys. We performed electronic structure calculations using the locally self-consistent multiple scattering (LSMS) method for supercell samples generated by ab initio molecular dynamics simulation using the Vienna Ab-Initio Simulation Package. The magnetic structure including the distribution of moment sizes, angular distributions, and correlation between moments and local atomic environment in the samples are discussed. This work is supported by DARPA/ONR Grant N00014-01-1-0961 and is supported by DOE subcontract DEAC05-00OR22R725464 with UT-Battelle, LLC. The VASP and LSMS calculations were performed at Pittsburgh Supercomputing Center.

MM5.18

Indium as an Additive in GexSe1-x Glasses. L.C. Cai and P. Boolchand; Department of ECECS, University of Cincinnati, Cincinnati, Ohio.

The doping behavior of the group III additive Indium in GexSe1-x glasses is examined in temperature modulated DSC (MDSC) measurements. MDSC results on In doped GexSe1-x glasses over all ranges x, i.e. floppy ($0 < x < 0.20$), intermediate ($0.20 < x < 0.26$) and stressed rigid ($0.26 < x < 1/3$) reveal that the group III additives nanoscale phase separates as In2Se3 phase leaving behind a Ge-rich base glass. The observed slopes, dT_g/dy , in GexInySe1-y glasses can be in excellent accord with the predicted slopes based on a nanoscale phase separated model in which In is trivalent and is bonded to 3/2 Se atoms. The covalent radius of In exceeds that of Ge by 15%. These results demonstrate that large size mismatch between atoms can drive nanoscale phase separation in network glasses. These results were obtained using a thermal method that is not generally recognized as a structural probe of network glasses. In that respect these results are not only new but quite novel.

MM5.19

Grain Boundary Dissociation in Nanocrystalline Gold. Douglas L. Medlin¹, D. Cohen¹, G. Lucadamo¹ and S. M. Foiles²; ¹Thin Film and Interface Science Dept., Sandia National Laboratories, Livermore, California; ²Materials and Process Modeling Department, Sandia National Laboratories, Albuquerque, New Mexico.

A common structural relaxation at grain boundaries in low stacking-fault-energy metals is the spreading, or dissociation, of the interface by the emission of partial dislocations. This phenomenon is of particular importance in nanocrystalline materials because it increases the volume fraction of material associated with interfacial sites and because the constraints of geometric compatibility in such small-grained systems can locally promote the dissociation. Here, through HRTEM observations and atomistic simulations, we consider the structure of dissociated boundaries in nanocrystalline, [110]-textured Au films. Our analyses of the interfacial dislocation structures in these boundaries shows how the stacking arrangement within the dissociated layers is directly related to the intergranular misorientation. To illustrate, we discuss in detail the interfacial structure at 90°-related grains. Boundaries in this system dissociate to form a ~1 nm wide layer of material with close-packed planes arranged in the 9R stacking sequence (i.e., abc/bca/cab). Formation

of this non-FCC layer can be understood by considering the distribution of Shockley partial dislocations that are intrinsic to the interface: separation of the pure-edge (90°) and mixed character (30°) dislocations, which are present in a ratio of 2:1, produces a stacking fault every third plane and a characteristic local plane bending. Finally, we discuss how this approach is generalized to other orientations by varying the ratio of dislocation types and how the constraints arising at boundary junctions affect the separation of the interfacial dislocations, and, thus, the boundary width. This work is supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000 by the Office of Basic Energy Science, Division of Materials Science.

SESSION MM6: Shear Bands and Mechanical Properties I

Chairs: Katherine Flores and William L. Johnson
Wednesday Morning, December 3, 2003
Republic B (Sheraton)

8:30 AM *MM6.1

Quasi-static and Dynamic Indentation of Bulk Metallic Glasses. J Lu¹, W Zhang¹, G Ravichandran¹ and Subra Suresh²; ¹Division of Engineering and Applied Sciences, California Institute of Technology, Pasadena, California; ²Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

When bulk metallic glasses are subjected to mechanical loading, intense shear localization occurs. Indentation of metallic glasses offers a convenient means to suppress catastrophic failure and to investigate the post-yield deformation by confining shear band propagation. Such indentation studies of bulk metallic glasses also facilitate systematic studies of the effects of controlled strain rates (from quasi-static to dynamic loading) on overall deformation, damage and failure over multiple length scales (from the nano to the macro-scale). This work deals with experimental studies of quasi-static and dynamic indentation in bulk metallic glasses. First, it is shown that controlled quasi-static nanoindentation can lead to the formation of nanocrystalline particles during active deformation in the highly strained region surrounding the indent. By drawing an analogy with the deformation of amorphous polymers, it is reasoned that such nanocrystallization is an outcome of significantly enhanced diffusion along active shear bands introduced during indentation. Next dynamic indentation experiments capable of measuring the time-resolved depth and load response during the indentation process are developed so as to assess the dynamic rate sensitivity and pressure dependence of a bulk metallic glass Vitreloy 1 and its composite. The indentation responses are modeled numerically using both pressure-insensitive and pressure-dependent flow models. Both the materials were found to be strain rate insensitive and pressure (or normal stress) dependent for strain rates up to 2,000/s. Intense shear bands are observed in the indentation craters and are found to be responsible for the overall inelastic deformation. Some general strategies for dynamic indentation are discussed and are applied to extract insights into the effects of high strain rate and pressure on the deformation characteristics of bulk metallic glasses.

9:00 AM MM6.2

Discrete and Homogeneous Plasticity during Nanoindentation of Metallic Glasses. T. G. Nieh³, Christopher A. Schuh¹, Ali S. Argon² and Jeffrey Wadsworth⁴; ¹Materials Science and Engineering, MIT, Cambridge, Massachusetts; ²Mechanical Engineering, MIT, Cambridge, Massachusetts; ³Materials Science and Technology, Lawrence Livermore National Laboratory, Livermore, California; ⁴Battelle Memorial Institute, Columbus, Ohio.

Instrumented nanoindentation has become a valuable tool for the study of shear band formation in metallic glasses, because each shear band operation appears as a discrete burst of displacement in the load-depth curve. Here this phenomenon is discussed as a function of the indentation loading rate for a variety of metallic glass families. For all of the glasses investigated, we find that the occurrence of discrete plastic bursts is a highly rate-dependent phenomenon. For very slow indentations, plasticity can become ideally discretized, where each displacement burst is separated by regions of purely elastic behavior. In contrast, high applied indentation velocities appear to suppress the discrete nature of plasticity, leading to flow that is homogeneous in time. The experimental results are discussed within the framework of glass plasticity models, and are found to be consistent with the notion that shear band operation is nucleation-limited.

9:15 AM MM6.3

Indentation Topography in Nanocrystalline Metals. Benedikt Moser, Jun Mei and Subra Suresh; Dept of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We have performed indentation in various nanocrystalline (nc) and ultra-fine-crystalline (ufc) metals, with grain sizes in the 20-100 nm and 100-500 nm ranges, respectively. The topography of the residual imprint as well as of the indenter tip was analyzed using atomic force microscopy. The materials studied include electrodeposited nc and ufc Ni, electrodeposited ufc Cu, and equi-channel angular pressed ufc Ti. The effect of different materials (with distinct constitutive laws) and grain size as well as the influence of the tip geometry (i.e. included equivalent cone angle) on the pile-up formation is investigated. Specific features of the imprints such as pile-up volume, displaced material volume, pile-up height and flank angle were quantitatively measured. We found clear differences in the ratio between pile-up volume and displaced material volume among the different materials and a strong dependence on the indenter geometry. The ratio between pile-up volume and displaced material volume increases with decreasing cone angle. A special algorithm has been developed to perform these measurements in a repeatable way. Computational studies using axis-symmetric finite element simulation of the indentation process have also been performed. The effect of the material constitutive law (yield strength, strain-hardening rate), tip geometry (cone angle) and friction between indenter tip and specimen surface on the pile-up formation was investigated through a parametric study. While friction has only a minor influence on the measured load-displacement curve and is therefore often neglected in the analysis of load-displacement curves, it has a large influence on the formation of the pile-up and hence on the true contact area. The discrepancy between the hardness calculated using different approaches is examined. The predicted ratio between pile-up volume and displaced material volume agrees well with the experiments conducted on nanocrystalline nickel with different indenter geometries.

9:30 AM MM6.4

Molecular Dynamic Simulation of Nanoindentation of a Model Metallic Glass. Bulent Biner and J. R. Morris; Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa.

In this study, the localized plastic deformation behavior of amorphous solids were examined by molecular dynamic simulations of nanoindentation. The model system was two-dimensional and composed of a binary alloy with a two-body Lennard-Jones potential. These simulations enable us to clearly identify the events leading to inhomogeneous deformation in amorphous systems. It will be shown that the mechanism of shear localization and the formation of shear bands is a dynamic process balancing transient events of dilatation and contraction in regions involving a limited number of atoms. These shear localization regions were characterized in terms of the initial stress state and stiffness. A connection is also established with the serrated plastic flow that is seen during the nanoindentation experiments on metallic glasses. This work was performed for the United States Department of Energy by Iowa State University under contract W-7405-Eng-82. This research was supported by the Director of Energy Research, Office of Basic Sciences.

9:45 AM MM6.5

Strain Localization, Shear Softening and Structure in Molecular Dynamics Models of Metallic Glasses. Michael L. Falk, Fabio Albano and Yunfeng Shi; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Molecular dynamics investigations of the relationship between processing and mechanical properties in model metallic glasses demonstrate that the micromechanics of deformation can be directly related to particular features of higher order correlation functions that characterize the structure. Solid glass samples were abruptly quenched from liquids equilibrated at a number of temperatures above the mode coupling temperature of the glass. These model glasses exhibit a range of mechanical properties analogous to those observed in the laboratory including strain localization and shear softening. Using these simulation techniques the micromechanisms of the deformation process have been analyzed. We find that the mechanism of shear band slip in these simulations appears to be a dynamic process balancing transient events of dilatation and contraction 1-4 atomic diameters in size. The typical dilatation in these regions is small, approximately 1-5%. We have also measured the dependence of the localization process on strain rate, temperature and the thermal history of the glass. In addition we have observed structural changes that occur throughout the glass during shear, corresponding to generation and annihilation of free volume. We find that while the structure factor of the glass is insensitive to these rearrangements, higher-order correlation functions show signs of dramatic changes in medium-range order. These calculations can serve as a useful guide to interpreting fluctuation electron microscopy and positron annihilation spectroscopy data with the aim of characterizing metallic glass structure.

10:30 AM *MM6.6

Shear Banding in Bulk Nanostructured Metals and Multi-component Alloys. Evan Ma, Materials Sci & Eng, Johns Hopkins University, Baltimore, Maryland.

Shear banding is the predominant deformation mechanism in metallic glasses. Interestingly, enhanced propensity for shear flow localization is also found in some nanostructured metals, such as bcc Fe and W. The topic of localized deformation in the form of shear banding is therefore important for both of the two groups of alloys (amorphous and nanocrystalline) covered in this symposium. In this talk, we show several examples of shear band formation upon plastic deformation in bulk metals and alloys when the microstructure is brought down into the nanostructured regime. While not yet amorphous, such ultrafine microstructures are susceptible to localization because their strain hardening and strain rate hardening properties have been changed with respect to their conventional polycrystalline counterparts. Other factors contributing to the initiation and propagation of shear bands are related to the processing route used, such as consolidation, casting, and rolling (with corresponding texture development). We will discuss cases where the plastic instability needs to be controlled to improve plastic strains, such as in Ti-based multi-component alloy composites. We will also demonstrate cases where concentrated deformation in localized zones can be taken advantage of, for example in bcc metals and alloys based on W. Such nanostructured and amorphous materials, or their composites, have potential in certain critical applications.

11:00 AM *MM6.7

Deformation-Assisted Crystallization in an Amorphous Al-Rich Alloy. Michael Atzmon^{1,2} and Wenhui Jiang¹; ¹Dept. of NERS, University of Michigan, Ann Arbor, Michigan; ²Dept. of MSE, University of Michigan, Ann Arbor, Michigan.

In metallic glasses, there always exists a driving force for crystallization. However, the crystallization kinetics are typically too sluggish at room temperature to be observable. It was therefore surprising when nanocrystallites were observed to form in several Al-rich metallic glasses at shear bands resulting from plastic deformation.¹ It is known that irradiation or plastic deformation can produce nonequilibrium defects, which can enhance the diffusion kinetics. Such an enhancement was suggested as the cause of crystallization, but the possibility of a transient temperature spike was not ruled out. In this paper, we present the results of TEM investigations of the mechanisms of deformation-assisted crystallization in amorphous Al₉₀Fe₅Gd₅. Using nanoindentation, the effect of strain rate on nanocrystal nucleation and growth was investigated. The results suggest that free-volume is annihilated with kinetics of order higher than first, similar to results of published irradiation studies. In samples deformed by bending, nanocrystallization occurs in the predominantly-compressive region only. Using a combination of high-resolution TEM and spatial filtering,² we observe a high concentration of nanovoids in the shear bands of the tensile region only.³ While excess free volume is generated in the shear bands under either compression or tension, we suggest that, under tension, the excess free volume condenses into nanovoids and is therefore not available to enhance the atomic diffusion rate during plastic deformation. 1) H. Chen, Y. He, G. J. Shiflet and S. J. Poon, *Nature* **367**, 541 (1994). 2) P. D. Miller and M. J. Gibson, *Ultramicroscopy* **74**, 221 (1998), J. Li, Z. L. Wang and T. C. Hufnagel, *Phys. Rev. B* **65**, 144201 (2002). 3) W. H. Jiang and M. Atzmon, *Acta Materialia*, 2003, in press.

11:30 AM MM6.8

Structural Analysis of Shear Bands in Amorphous Materials by Fluctuation Electron Microscopy. Michael Foley, Steven Yaliso, John Mansfield and Ronald Gibala; University of Michigan, Ann Arbor, Michigan.

We have examined the structure of deformed ribbons of an Fe-Ni-Cr-P-B metallic glass (Metglas) by fluctuation electron microscopy, a transmission electron microscopy technique pioneered by Gibson and coworkers. The specific goal of the research has been to examine possible differences in structure of shear bands in the deformed material relative to regions not shear-banded in the immediate environs of the shear band. The technique of fluctuation electron microscopy was chosen for its ability to detect the presence of medium range order in amorphous solids and especially differences in medium range order in different regions of the same TEM foil examined at high resolutions. Metglas was chosen as a model material for its ability to display broad, profuse shear bands for easy examination by TEM. A statistically large number of TEM foils were examined by FEM from specimens which exhibited shear bands emanating from cracks initiated by bending deformation prior to foil preparation. Data in the form of normalized variance versus coherence parameter (in reciprocal nanometers) suggest the presence of medium range order within shear bands that does not exist outside the shear

bands. The structural results and the mechanistic implications of these results will be discussed.

11:45 AM MM6.9

High-density Liquid-like Component Facilitates Plastic Flow in Amorphous Silicon Simulated by Molecular Dynamics. Michael John Demkowicz and Ali S Argon; Mechanical Engineering, MIT, Cambridge, Massachusetts.

Simulations of plastic deformation in amorphous silicon—a model covalent network material—reveal striking differences from the plastic deformation characteristics of metallic glasses and glassy polymers. Plastic response in a-Si is very sensitive to the density of the initial unstressed state with the lowest density systems exhibiting a pronounced yield phenomenon, strain softening, and a dramatic drop in system pressure during deformation at constant volume. Systems of high initial density, however, do not have an unambiguous yield stress, do not strain harden or soften, and exhibit a rise in pressure with deformation at constant volume, just like metallic glasses. This range of plastic deformation behavior is explained in terms of the presence in every system of a certain concentration of solid-like and liquid-like components, the latter being denser and more amenable to plastic flow. Investigation of local atomic environments demonstrates that such a characterization is justified and can be carried out unambiguously. These results are a dramatic demonstration of the fact that free volume considerations alone cannot account for the nature of plastic flow in some amorphous materials and that an explanation based on pockets of liquid-like material would be more robust.

SESSION MM7: Shear Bands and Mechanical Properties II

Chairs: Evan Ma and Subra Suresh
Wednesday Afternoon, December 3, 2003
Republic B (Sheraton)

1:30 PM *MM7.1

Deformation and Free Volume Changes in Bulk Metallic Glasses. Katharine M. Flores, Materials Science and Engineering, Ohio State University, Columbus, Ohio.

At low temperatures, plastic deformation of metallic glasses occurs by the formation of shear bands. However, the precise mechanisms of shear band formation and propagation remain uncertain. For example, the role of stress state, the effect of adiabatic heating, and the extent of local structural rearrangement are under active investigation. In this work we investigate shear band formation in the vicinity of a sharp crack tip after loading. Previous investigations of crack tip deformation under tensile loading reveal significant increases in fracture toughness to more than 80 MPa \sqrt{m} , 4-5 times the inherent toughness of the alloy, due to the formation of a large damage zone. Controlling the formation of such a damage zone is integral to the optimization of bulk metallic glass composites. The magnitude and distribution of free volume is thought to play a central role in the flow behavior of metallic glasses. To elucidate the influence of free volume, structural changes after plastic deformation and thermal relaxation have been investigated. Positron annihilation spectroscopy studies on a Zr-Ti-Cu-Ni-Be alloy suggest that most of the free volume is associated with the larger solvent atoms (Zr and Ti) and that plastic deformation results in a net free volume increase and redistribution. Similar investigations of Cu-based alloys have been undertaken and will be discussed.

2:00 PM MM7.2

Formation and Annihilation of Free Volume during Homogeneous Flow of a Metallic Glass. Marc Heggen², Michael Feuerbacher² and Frans Spaepen¹; ¹Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; ²Institute for Solid State Physics, Forschungszentrum Juelich, Juelich, Germany.

Compression tests in the creep mode (constant stress) have been performed on a PdNiCuP metallic glass in the homogeneous flow mode. At high stresses, the strain rate increases with time, which means that flow defects, or free volume, are being created. At lower stresses, the strain rate decreases with time, which means that annihilation of defects or free volume dominates. These two processes can be analyzed separately. Although the bimolecular annihilation mechanism is well-established, the creation mechanism is still under study. Our results allow a test of different models for free volume creation. Identification of this model is important for an accurate description of inhomogeneous flow, which arises due to runaway creation of defects.

2:15 PM MM7.3

Dilatation of metallic-glass matrix composites under uniaxial

compression. Cang Fan¹, Tong Jiao², R T Ott¹, L J Kecskes³, K T Ramesh² and T. C. Hufnagel¹; ¹Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ²Department of Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland; ³US Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Plastic deformation in single-phase metallic glasses under uniaxial compression occurs by the initiation and propagation of a relatively small number of shear bands. Each shear band creates a slip step with a significant shear offset on the surface of the specimen, and causes an abrupt drop in the measured stress-strain curve. In (Zr₇₀Cu₂₀Ni₁₀)₈₂Ta₈Al₁₀ metallic-glass matrix composites, in contrast, the crystalline Ta particles both promote the initiation of shear bands and hinder their propagation, leading to a dramatic increase in the shear band density as deformation proceeds. The shear strain on each shear band is much smaller, and there are no discernible load drops in the early stages of plastic deformation. As a result, the macroscopic character of the plastic deformation is much more homogeneous than for the single-phase glass. In order to further understand the mechanical behaviours of these composites, we designed and performed a method to measure the diameter of specimens during uniaxial compression. Both the engineering stress-strain curves and "true" stress-strain curves (calculated assuming homogeneous plastic deformation) fail to accurately describe the behaviour of the composites. Instead of the previously reported monotonic strain hardening, we observe strain hardening only in the initial stages of plastic deformation. We also observe dilatation of the specimens during plastic deformation, associated with an increased free volume in the shear bands. We will discuss the implications of these observations for the mechanical behaviour of composites and our understanding of shear localization in metallic glasses.

2:30 PM MM7.4

Yield Criteria of Nanocrystalline and Amorphous Metals: Simulation Results and Experimental Suggestions.

Christopher A. Schuh and Alan C. Lund; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

For metallic alloys, the amorphous state is often regarded as the limiting structure as grain size is reduced towards zero. One interesting consequence of this limit is that the properties of the finest nanocrystalline metals must begin to resemble those of metallic glasses. In this work we focus upon the nature of the plastic yield criterion of these materials, and seek to identify commonalities and disparities in the nature of plastic yield in glasses and nanocrystals. Using molecular statics simulations, we first establish that the yield criterion of an idealized metallic glass is asymmetric according to the Mohr-Coulomb relation, with higher strengths in compression as compared to tension. These results are discussed with reference to a fundamental unit model of glass plasticity as well as available experimental data. We also discuss the extension of these simulations to the finest nanocrystalline materials with grain sizes up to 5 nm, and compare with the metallic glass case. The simulation results are finally compared with the available experimental data for nanocrystalline metals.

2:45 PM MM7.5

Ratcheting of Bulk Metallic Glasses. Wendelin J. Wright, R H Dauskardt and W D Nix; Materials Science and Engineering, Stanford University, Stanford, California.

The major mechanical shortcoming of bulk metallic glasses is their limited ductility at room temperature. Monolithic metallic glasses sustain only a few percent plastic strain when subjected to uniaxial compression and essentially no plastic strain under tension. By subjecting a metallic glass sample to cyclic torsion, the glass will be brought to the yield surface; the superposition of a small tensile stress (much smaller than the yield stress) should then produce increments in plastic strain along the tensile axis. This accumulation of strain during cyclic loading, commonly known as ratcheting, has been extensively investigated in stainless and carbon steel alloys, but not in bulk metallic glasses. Various forms of ratcheting may have potential as manufacturing techniques to overcome the limited ductility of monolithic metallic glasses and achieve large plastic strains at room temperature. We have successfully demonstrated the application of this ratcheting technique of cyclic torsion with superimposed tension for polycrystalline Ti-6Al-4V, and our stability analyses demonstrate that the plastic deformation of materials exhibiting elastic-perfectly plastic constitutive behavior such as metallic glasses should be stable under cyclic torsion. Experimental results will be presented for amorphous Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}, and the observed mechanical behavior will be discussed in terms of the free volume theory of deformation.

3:30 PM MM7.6

Deformation Mechanisms in Bulk Metallic Glass Matrix

Composites. Ersan Ustundag¹, Bjoern Clausen², Seung-Yub Lee¹, Gregory S. Welsh¹ and Mark A. M. Bourke²; ¹Materials Science, California Institute of Technology, Pasadena, California; ²Lujan Neutron Science Center, Los Alamos National Laboratory, Los Alamos, New Mexico.

Bulk metallic glasses (BMG) have superb mechanical properties: yield strength of above 2 GPa, fracture toughness of up to 140 MPa.m^{1/2} and elastic limit of 2%. BMGs can also be processed into intricate shapes similar to polymers. Unfortunately, monolithic BMGs fail catastrophically under unconstrained deformation by forming shear bands. To overcome this problem, BMG matrix composites with fiber and particulate reinforcements were proposed. We have recently investigated the deformation behavior of composites with W, Mo, Ta and Fe fibers [1,2], W and Ta particles [3] as well as an in-situ composite with crystalline dendritic inclusions [4]. Loading measurements were performed using in-situ neutron or high-energy X-ray diffraction to determine the lattice strains in the crystalline reinforcements. The diffraction data were then combined with finite element and self-consistent modeling to determine the behavior of the matrix. It was shown that usually the reinforcements yield first, then start transferring load to the matrix. The reinforcements possess different yield strengths, elastic constants, interface strengths and coefficient of thermal expansion (CTE) values. The effects of these parameters on the overall composite deformation will be described with an aim to identify the "ideal" reinforcement and its morphology. References 1. B. Clausen, S. Y. Lee, E. Ustundag, C. C. Aydiner, R. D. Conner and M.A.M. Bourke, "Compressive Yielding of Tungsten Fiber Reinforced Bulk Metallic Glass Composites," Scripta Mater., 49 [2], 123-128 (2003). 2. S. Y. Lee, B. Clausen, E. Ustundag, H. Choi-Yim, C. C. Aydiner and M.A.M. Bourke, "Compressive Behavior of Wire Reinforced Bulk Metallic Glass Matrix Composites," submitted to Mater. Sci. and Eng. (2003). 3. D. K. Balch, E. Ustundag and D. C. Dunand, "Elasto-Plastic Load Transfer in Bulk Metallic Glass Composites Containing Ductile Particles," in press: Metall. Mater. Trans. (2003). 4. B. Clausen, S. Y. Lee, E. Ustundag, C. P. Kim, J. C. Hanan, D. W. Brown and M.A.M. Bourke, "Compressive Deformation of In-Situ-Formed Bulk Metallic Glass Composites," submitted to Acta Mater. (2003).

3:45 PM MM7.7

Nanoscaled Deformation mechanism on PLD nanocrystalline Ni. Zhiwei Shan¹, J.A. Knapp² and Scott X. Mao¹; ¹Mechanical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²MS 1056, Sandia National Labs, Albuquerque, New Mexico.

The nanocrystalline Ni thin film with an average grain size of ~20nm and a narrow grain size distribution prepared by pulsed laser deposition (PLD) is studied by means of mechanical tensile loading, in situ transmission electron microscope tensile test combined with micro beam diffraction technique as well as high resolution TEM observation. Particular attention was devoted to the characterization of grain boundary structure at atomic level and the plastic deformation around the crack tip during the crack propagation process. The observations clearly reveal that grain rotation/grain boundary sliding not only exist but also has considerable contribution to the plastic deformation. Failure mechanism also studied by SEM.

4:00 PM MM7.8

Fabrication and Properties of Tungsten Reinforced Zr Based Metallic Glass Composites. Ibrahim Karaman, K.Ted Hartwig, Jae-Taek Im, Suveen N. Mathaudhu, Anish A. Simon and Robert E. Barber; Department of Mechanical Engineering, Texas A&M University, College Station, Texas.

Warm equal channel angular extrusion (ECAE) is used to consolidate Vitreloy 106a (Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}) plus 60, 70, and 80 vol.% pure tungsten blended powders at temperatures between T_g and T_x for the glassy metal phase. The effects of extrusion temperature, number of extrusion passes and can material were investigated. In certain cases, a fully dense, 12 mm diameter bar of metallic glass matrix composite is achieved after only one extrusion. Microstructure and hardness of the ECAE consolidates were examined and compared with those of the initial powder and consolidated pure metallic glass. Metallography results show good infiltration of the amorphous Zr-based alloy in between crystalline particles and uniform consolidation. Hardness and DSC measurements indicate retention of amorphous character in the metallic glass phase. Tension and compression experiments were conducted on selected samples at room temperature. Fracture surface investigations reveal that although the bonding between the glass and tungsten particles is quite good overall, there is occasional local tungsten particle pull out which is attributed, in some cases, to tungsten particle agglomerates. Deformation in tungsten regions is also observed. Experimental results will be presented. ECAE appears to be a viable process for consolidating bulk metallic glass matrix composite materials. The research is supported by a grant from U.S. DOD Defense Advanced

4:15 PM **MM7.9**

Anomalous Low Fatigue Endurance Limit of a Zr-Based Bulk Metallic Glass. Brian Menzel and Reinhold H. Dauskardt; Stanford University, Stanford, California.

In order to explore the anomalously low fatigue endurance limits that have been reported for bulk metallic glasses, a stress-life fatigue study was conducted on a $Zr_{41.25}Ti_{13.75}Ni_{10}Cu_{12.5}Be_{22.5}$ bulk metallic glass using a four-point bend configuration. The early stages of damage initiation and propagation on the maximum tensile surface of the specimen were recorded in situ during testing using a surface replicating technique. High resolution SEM and AFM characterization of the resulting replicas and final fracture surfaces were used to identify possible fatigue initiation and growth mechanisms. Generally, damage could be traced back from final fracture surfaces to either surface imperfections such as second phase inclusions or surface roughness that was present on the specimen surfaces prior to testing. It is demonstrated that the apparent lack of a damage initiation stage during the fatigue process may account for the low endurance limit of $\sim 1/10$ of the ultimate tensile strength. Surface damage, in the form of either shear bands or surface cracks, were observed to grow initially under mixed mode loading conditions in approximately the maximum shear stress direction. At a characteristic size, the surface shear bands or cracks abruptly changed orientation with respect to the loading axis and continued to grow as mode I cracks. The resulting "small" fatigue crack growth rates were carefully characterized and shown to be consistent with "long" crack growth rate behavior indicating the absence of significant crack tip shielding. Fatigue life was estimated from the initial defect sizes determined from the surface replicas. The resulting predictions are shown to be consistent with measured stress life data.

4:30 PM **MM7.10**

Transient Fatigue Crack-Growth Behavior and Damage Zones in Zr-Based Bulk Metallic Glass. Peter A. Hess and Reinhold H. Dauskardt; Materials Science and Engineering, Stanford University, Stanford, California.

Fatigue crack propagation mechanisms of bulk metallic glasses (BMGs) are not well understood, limiting their use in safety-critical structural applications particularly where complex fatigue loading may occur. Accordingly, the present study examines the effects of variable amplitude fatigue loading associated with block loading and tensile overloads on fatigue crack-growth rates in a Zr-based BMG. Crack growth studies were conducted on compact tension specimens using computer control of the applied stress intensity range, ΔK . Fatigue crack closure loads, which represent the initial contact of mating crack surfaces during the unloading cycle, were continuously monitored during testing. Abrupt drops in ΔK were found to significantly decrease fatigue crack-growth rates far below equilibrium values, arresting growth completely at a ΔK twice the nominal fatigue threshold, ΔK_{TH} . Conversely, an abrupt increase in ΔK was found to accelerate fatigue crack-growth rates. The effects of roughness-induced crack closure were assessed and found to be consistent with the suppression or acceleration of growth rates. However, in order to fully explain the observed transient growth rate response, other mechanisms that may be related to the fatigue mechanism itself were also considered. Specifically, the nature of the fatigue crack tip damage zone was also investigated. As BMGs lack distributed plasticity at low temperatures, the plastic zone differs greatly from that seen in ductile crystalline materials, and its role in fatigue crack propagation mechanisms is examined.

4:45 PM **MM7.11**

Fatigue Study of a Zr-Ti-Ni-Cu-Be Bulk Metallic Glass. Gongyao Wang¹, P. K. Liaw¹, A. Peker², B. Yang¹, M. L. Benson¹, W. Yuan¹, W. H. Peter¹, L. Huang¹, M. Freels¹, R. A. Buchanan¹, C. T. Liu³ and C. R. Brooks¹; ¹Materials Science and Engineering, The University of Tennessee, Knoxville, Tennessee; ²LiquidMetal Technologies Inc., Lake Forest, California; ³Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

High-cycle fatigue (HCF) studies were performed on zirconium (Zr)-based bulk metallic glasses (BMGs): $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$, in atomic percent. The HCF experiments were conducted using an electrohydraulic machine at a frequency of 10 Hz with a R ratio of 0.1 and under tension-tension loading, where $R = \sigma_{min.}/\sigma_{max.}$, where $\sigma_{min.}$ and $\sigma_{max.}$ are the applied minimum and maximum stresses, respectively. The test environment was air and vacuum. A high-speed and high-sensitivity thermographic-infrared (IR) imaging system has been used for nondestructive evaluation of temperature evolution during fatigue testing of BMGs. Limited temperature evolution was observed during fatigue. However, no sparking phenomenon was found at the final

fracture moment of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$. At high stress levels (the maximum stress > 864 MPa), the fatigue lives of Batch 59 are longer than those of Batch 94 due to the presence of oxides in Batch 94. Moreover, the fatigue-endurance limit of Batch 59 (703 MPa) is somewhat greater than that of Batch 94 (615 MPa) in air. The vein pattern and droplets with a melted appearance were observed in the apparent melting region. Fracture morphology indicates that fatigue cracks initiate from some defects. The fatigue lives in vacuum are generally comparable with those in air. The cracking shapes on the fatigue surfaces were analyzed and predicted. The present work is supported by the National Science Foundation (NSF), the Combined Research-Curriculum Development (CRCD) Program, under EEC-9527527 and EEC-0203415, the Integrative Graduate Education and Research Training (IGERT) Program, under DGE-9987548, and the International Materials Institutes (IMI) program under DMR-0231320, With Ms. M. Poats, and Drs. P. W. Jennings, L. S. Goldberg, and C. Huber as contract monitors.

SESSION MM8: Poster Session II
Chairs: Ralf Busch and Todd Hufnagel
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

MM8.1

Synthesis and Characterization of Amorphous Metallic Alloy Thin Films for MEMS Applications.

Senthil Nathan Sambandam^{1,2}, Shekhar Bhansali¹ and Venkat R. Bhethanabotla²; ¹Electrical Engineering, University of South Florida, Tampa, Florida; ²Chemical Engineering, University of South Florida, Tampa, Florida.

Microstructures of multi-component amorphous metallic glass alloys are becoming increasingly important due to their excellent mechanical properties and low coefficient of friction. In this work, thin films of Zr-Ti-Cu-Ni-Be have been deposited by DC magnetron sputtering in view of exploring their potential technological applications in fields such as MEMS. Their structure, composition, surface morphology, mechanical properties viz., hardness and Young's modulus were analyzed using X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Nanoindentation. Influence of the deposition parameters of sputtering pressure and power upon the composition and surface morphology of these films has been evidenced by SEM, XPS and AFM analysis, showing that such a process yields very smooth films with target composition at low sputtering pressures (~ 0.6 Pa). Films prepared at lower sputtering pressures (~ 0.6 Pa) showed a higher hardness and Young's modulus compared to those prepared at the higher pressures of (~ 13 Pa) which is in correlation with changes in film composition. XRD patterns revealed amorphous as-deposited films. Sputter process simulations yielded predictability of property variation and established correlation between process parameters and film properties.

MM8.2

Development of Milling Maps for the Bulk Metallic Glass forming Alloys. Jatin Bhatt and B.S. Murty; Met. & Mater. Eng., Indian Institute of Technology, Kharagpur, Kharagpur, India.

Mechanical alloying (MA) is a versatile method for the synthesis of stable and metastable materials with novel microstructures and properties. However, synthesis of various phases during MA is strongly influenced by milling parameters such as milling speed, type and size of balls, ball to powder weight ratio, etc. All the milling parameters can be combined into two energy parameters, namely, the impact energy of the ball and total milling energy. In a milling map, which is a two dimensional map of the above energy parameters, one can identify the domain of conditions for the synthesis of any phase by MA. In the present study, an attempt has been made to develop milling maps for the bulk glass forming alloys such as $Zr_{65}Al_{17.5}Cu_{17.5}Ni_{10}$, $Ti_{50}Cu_{23}Ni_{20}Sn_7$, $Cu_{60}Zr_{30}Ti_{10}$, $Fe_{56}Co_{7}Ni_{7}Zr_{10}B_{20}$, $Ni_{60}Nb_{20}Ti_{12.5}Zr_{7.5}$. The MA of the elemental blends has been carried out in Fritsch Pulverisette P5 planetary ball mill using WC milling media. Milling parameters such as milling speed, ball to powder weight ratio have been varied over wide ranges in order to have a wide range of milling energies. The progress of amorphization in mechanically alloyed powder has been monitored using x-ray diffractometry, differential scanning calorimetry, scanning and transmission electron microscopy. The results indicate that total energy of milling has a decisive role than the impact energy of the ball in the formation of the amorphous phase. The paper compares the glass forming abilities of the various bulk glass forming compositions in terms of the milling maps.

MM8.3

Bicrystal Interfaces. Chien H Wu, Civil and Materials Engineering,

An elastic crystal is characterized by a set of crystal-structure parameters that is usually expressed in terms of three edge lengths and three interaxial angles, in addition to its anisotropic elastic moduli. For many alloy crystal structures, a composition can vary from the stoichiometric value without altering the type of structure, although the edge lengths and interaxial angles change somewhat with composition. This fact may be quantified into the statement that the molar crystal structure is a function of the local concentrations. Thus, nonuniform concentrations lead to a nonuniform crystal structure, which, in turn, generates a state of geometrically necessary eigentransformation as well as an associated state of elastic transformation. The elastic transformation defines the (traditional) stress-associated elastic deformation, which is well understood in classical continuum mechanics. The eigentransformation is a direct result of the nonuniform composition and may, therefore, be interpreted as a material or configurational deformation. The product of the (traditional) stress and the deformation rate is the density of working in classical continuum mechanics. It is shown in [1,2,3] that the product of a generalized energy momentum tensor and the aforementioned eigentransformation rate also contributes to the density of working. For this reason, the energy momentum tensor obtained by Eshelby may be termed a material stress or configurational stress. At the same time, the question whether the chemical potential for a solid should be a tensor or scalar becomes mute, as a part of the scalar potential is actually the product of two tensors. In the classical theory of anisotropic elasticity, a bicrystal interface is merely the intersection of two elastic bodies of different moduli over which the continuities of displacement and traction are to be enforced. These conditions must now be augmented by the new material traction and the geometric incompatibility between the crystals, together with the possibility that the interface may actually evolve with time. References: [1] Wu, C.H., 2001. The role of Eshelby stress in composition-generated and stress-assisted diffusion. *J. Mech. Phys. Solids* 49, 1771-1794. [2] Wu, C.H., 2002. Chemical potential and energy momentum tensor in single phase mixtures. *Mech. Research Communications* 29, 493-499. [3] Wu, C.H., 2003. A crystal structure-based eigentransformation and its work-conjugate material stress. *EUROMECH COLLOQUIUM 445*, University of Kaiserslautern, May 21-24, 2003.

MM8.4

Hardness and Plastic Deformation in Bulk Metallic Glasses. Saumyadeep Jana¹, Y. Kawamura², Kamania Chattopadhyay¹ and Upadrasta Ramamurty¹; ¹Department of Metallurgy, Indian Institute of Science, Bangalore, KA, India; ²Department of Mechanical Engineering and Materials Science, Kumamoto University, Kumamoto, Japan.

Experimental investigation into the Vickers hardness and the associated plastic deformation in as-cast and systematically annealed (to induce partial to full crystallization) Pd₄₂Ni₄₀P₁₈ and Zr₅₇Cu₂₇Al₁₁Ni₅ bulk metallic glasses was conducted. Results show that the hardness/yield strength ratio for these materials is ~3.2, indicating pressure sensitivity. In addition to the bulk indentation behavior, the deformation morphology underneath the indenter and its variation with annealing was examined by employing the bonded interface technique. Results show that the as-cast as well as the partially-crystallized alloys deform appreciably through the shear band mechanism, with semi-circular and radial shear band morphologies. Extensive cracking is observed when the alloys are fully crystallized. For both the bulk and the interface indentation, the trends in the shear band induced plastic deformation zone sizes with load agree well with those predicted from the expanding cavity model. The subsurface deformation morphology also leads to this conclusion. However, the yield strength extracted from the indentation data is higher than that measured in uniaxial compression, indicating the need for incorporating Mohr-Coulomb type yield criterion into the deformation model. These observations are compared with similar studies made on ductile metals and silicate glasses. Implications of this study in understanding the constitutive response of metallic glasses and their derivatives will be discussed.

MM8.5

Mechanical Properties of Zr/Hf Based Bulk Metallic Glasses. Hao Li¹, Ghatu Subhash¹, Laszlo J. Kecskes² and Robert J. Dowding²; ¹Department of Mechanical Engineering and Engineering Mechanics, Michigan Technological University, Houghton, Michigan; ²Weapon and Materials Research Directorate, U. S. Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Quasistatic and dynamic uniaxial compression tests on cylindrical specimens of Zr/Hf based metallic glasses with compositions (Hf_xZr_{1-x})_{52.5}Ti₅Ni_{14.6}Cu_{17.9}Al₁₀ (x=0, 0.2, 0.4, 0.6, 0.8, 1.0) and (Hf_xZr_{1-x})₅₇Ti₅Ni₈Cu₂₀Al₁₀(x=0, 0.4) revealed that the failure strengths for all the alloys decreased with increasing strain rate in

certain range of strain rate. The failure strength of these alloys increased with increasing Hf content when the sum of Hf and Zr contents were held fixed. These alloy compositions exhibited larger inelastic strains under quasistatic conditions and the samples broke into 2 pieces with smooth fracture surfaces at an average angle of 42.4 degree to the specimen axis. Under dynamic conditions, the failure strains were significantly lower and the samples broke into multiple fragments of irregular shapes and sizes with relatively rough fracture surfaces. The rapid temperature rise associated with the multiple shear band formation during high strain rate deformation and the absence of dislocation activity have been postulated to contribute to the negative strain rate sensitivity of failure strength in these metallic glasses.

MM8.6

Infiltration Processing of Tungsten Particle-Reinforced Bulk-Amorphous Metal Matrix Composites. Laszlo Kecskes, Brian Edwards and Robert Woodman; AMSRL-WM-MD, US Army Research Laboratory, Aberdeen Proving Ground, Maryland.

High-density tungsten (W) powder reinforced bulk amorphous metal (BAM) matrix composites have been fabricated by a pressure infiltration methodology. A Hf-based BAM with a density of 11 g/cm³ has been used to infiltrate open-porosity W-powder performs to create W-BAM composites with densities reaching 16 g/cm³. Because of the considerably higher liquidus temperature of Hf-based BAM alloys, special techniques were developed to suppress the interaction of the BAM with the fixture components and the W preform as well as to reduce the formation of undesirable intermetallic phases in the composite. The roles of infiltration pressure, soak temperature, and time at temperature on the composite structure were of primary interest. The structure and quality of the composites were determined with simple mechanical tests, scanning electron microscopy, X-ray diffraction, and differential thermal analysis. The fabrication procedure steps and the characteristics of the composites are discussed.

MM8.7

Microstructure, Thermal Stability and Mechanical Properties of Slowly Cooled Zr-based Composites Containing Dendritic bcc Phase Precipitates. Nicole Radtke, Juergen Eckert, Mihai Stoica and Ludwig Schultz; IFW Dresden, Dresden, Germany.

We report about the microstructure, thermal stability and the mechanical properties of slowly cooled Zr-Nb-Cu-Ni-Al alloys with ductile bcc phase precipitates embedded in a glassy or a nanocrystalline matrix. The samples were prepared in form of rods by injection casting into a cooper mould. The phase formation and the microstructure of the composite material are investigated by X-ray diffraction, EDX-analysis, scanning and transmission electron microscopy. The thermal stability was examined by differential scanning calorimetry and the mechanical behaviour was investigated by compression tests und quasistatic loading at room temperature. The formation of bcc phase dendrites and a glassy or a nanocrystalline matrix is strongly governed by the alloy composition and the actual cooling rate during solidification. Besides, changes in composition and cooling rate lead to different volume fraction and size of the bcc phase precipitates and, hence, to different values of yield strength, elastic and plastic strain. The sample with a nanocrystalline matrix shows a homogeneous distribution of the bcc phase precipitates over the whole cross-section. The formation of a nanocrystalline matrix depends on the melting temperature of the alloy and, hence, the cooling rate. The higher the melting point, the lower the cooling rate and the higher the volume fraction of the bcc phase precipitates. Surprisingly, these sample exhibits higher yield strength and plastic strain than the samples containing an amorphous matrix. Illustrated by the presented results we show the possibility of obtaining tailored mechanical properties by control of composition and, hence, solidification conditions.

MM8.8

Nano-mechanical study of mechanically alloyed Zr-Cu-Al-Ni glass composite containing second-phase ZrC particles. German Alcalá, Sonia Mato, Stefano Deledda, Jurgen Eckert, Annett Gebert and Ludwig Schultz; Institute for Metallic Materials, IFW Dresden, Dresden, Germany.

Metallic glasses exhibit generally high hardness and elastic modulus values at the expense of very limited plasticity. The incorporation of crystalline particles within an amorphous metallic matrix has been widely reported to improve the performance of these materials by reducing crack propagation. The present work analyzes the influence of nanometer-size ZrC particles on the nano-mechanical behavior of mechanically alloyed Zr₅₅Cu₃₀Al₁₀Ni₅ glassy matrix composites. The volume fraction of ZrC particles ranged from zero up to 30 vol. %, showing a critical change in the mechanical behavior between 10 and 20 vol. %, being the elastic response particularly affected. The results

are compared with mechanically alloyed Zr-Cu-Al-Ni-C glasses to account for possible C dissolution during ball milling. This allows separating the effects of the ZrC particles from compositional changes of the matrix. Additionally, features such as the plastic deformation response, both during nanoindentation and nanoscratch, have been investigated by combination of the nano-mechanical tests and scanning probe microscopy.

MM8.9

Mechanical Behavior of Bulk Glassy

Fe_{65.5}Cr₄Mo₄Ga₄P₁₂C₅B_{5.5}, M. Stoica¹, N. Radtke¹, J. Eckert¹, S. Roth¹, G. Alcalá¹, A. Gebert¹, L. Schultz¹, W. H. Wang² and Y. H. Zhao²; ¹Metastable and Nanostructured Materials, IFW Dresden, Institute for Metallic Materials, Dresden, Germany; ²Institute of Physics, Chinese Academy of Sciences, Beijing, China.

The bulk amorphous Fe-based alloy with the nominal composition Fe_{65.5}Cr₄Mo₄Ga₄P₁₂C₅B_{5.5} was obtained by copper mold casting in different shapes: cylindrical rods with diameters up to 2.5 mm, rectangular rods 2x2 mm or 2x1 mm and discs, 10 mm in diameter and 1 mm in thickness. This alloy exhibits good soft magnetic properties: for as-cast samples, the coercivity H_c is below 10 A/m, the polarization at saturation is 0.8 T and the magnetostriction λ = 9 ppm. Using electrochemical investigations we found that the corrosion resistance of this alloy is better than that of usual FeSi steel used for magnetic applications. Beside magnetic properties and corrosion resistance, this alloy exhibits also good mechanical properties. These were investigated by compression tests, nanoindentation and by an ultrasonic technique. The Young's modulus E was found to be around 150 GPa, the yield strength σ_y around 3 GPa and the fracture strength σ_f around 3.23 GPa, together with elastic strain ε_e = 2% and fracture strain ε_f = 2.3%. The Vickers hardness H_v was found to be around 1000. This paper will discuss in detail the values for as-cast and annealed samples as a function of geometrical dimension, as well as in comparison with other published data for different amorphous alloys.

MM8.10

Thermal Stability and Mechanical Behavior of Bulk

(ZrHf)/TiCuNiAl Amorphous Alloys. Hongwen Zhang¹, Ghatu Subhash² and Laszlo J Kecskes³; ¹Dept of Material Science & Engineering, Michigan Technological University, Houghton, Michigan; ²Dept of MEEM, Michigan Technological University, Houghton, Michigan; ³US Army Research Laboratory, Weapons and Materials Research Directorate (AMSRL-WM-MD), Aberdeen Proving Ground, Maryland.

The thermodynamic behavior and mechanical properties of bulk Zr/Hf based amorphous alloys with composition (Hf_xZr_{1-x})_{52.5}Ti₅Ni_{14.6}Cu_{17.9}Al₁₀ (x=0, 0.2, 0.4, 0.6, 0.8, 1) were investigated. It was found that the crystallization and glass transition temperatures increased with the substitution of Zr by Hf. It was also observed that their thermal stability increased although their glass forming abilities tend to decrease moderately. The hardness and the modulus as measured by nano-indentation and micro-hardness tests, revealed an increasing trend with increasing Hf content. Formation of shear bands around the indents accounts for the severe deformation during indentation. It is postulated that the observed strengthening and hardening might result from the microstructural changes with increasing Hf content.

MM8.11

Microstructure, Phase Formation and Mechanical Properties in Ti-Based, Nanocrystalline-Dendrite Composites.

T.G. Woodcock¹, G. He¹, E. Ma², Q.L. Dai³, M.L. Sui³, G. Alcalá¹, W. Loeser¹ and J. Eckert¹; ¹IFW Dresden, Dresden, Germany; ²Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ³Shenyang National Laboratory for Materials Science, Chinese Academy of Sciences, Shenyang, China.

The addition of refractory elements (e.g. Nb, Ta) to Ti-base, bulk metallic glass (BMG) forming alloys such as Ti-Cu-Ni-Sn results in a composite microstructure consisting principally of primary dendrites in a nanocrystalline matrix [1]. The dendrite phase in Ti₆₀Cu₁₄Ni₁₂Sn₄Nb₁₀ has been previously found to be the ternary solid solution beta-Ti(Nb,Sn) [1] and TEM results, presented here, show that the nanocrystalline matrix consists of a eutectic of two phases of the bcc structure. The presence of the dendrites acts as a barrier to shear band propagation thus introducing significant ductility into an otherwise brittle material [1]. Previously published data showed compressive plastic strain greater than 14% in Ti₆₀Cu₁₄Ni₁₂Sn₄Nb₁₀ [1]; however, tensile tests, presented here, show much smaller values (up to 6%) for the same alloy. The explanation for this lies in retained casting porosity in many samples and this is supported by tensile results from samples with different levels of porosity. High temperature thermal analysis and thermodynamic models have been used to obtain various thermophysical parameters

for the above alloy in order to investigate the possibility of reduction of porosity by casting at a lower temperature in the semi-solid range but above the melting point of the matrix. The mechanical properties of the constituent phases have been measured using nano-indentation, in order to more fully describe the mechanical behaviour of the materials. [1] G. He, J. Eckert, W. Loeser and L. Schultz, Nature Materials, 2003, 2, 33-37

MM8.12

Synchrotron Strain Measurements for In Situ Formed Metallic Glass Matrix Composites. R.T Ott¹, F Sansoz², J.F Molinari², C Fan¹ and T.C Hufnagel¹; ¹Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ²Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

Metallic glass matrix composites exhibit unique mechanical properties including high yield strengths and large plastic strains. For example, we have found that the (Zr₇₀Cu₂₀Ni₁₀)_{90-x}Ta_xAl₁₀ (6 < x < 12) series of alloys which consists of an amorphous matrix reinforced with in situ formed Ta-rich particles display large plastic strains prior to failure (> 10%) in compression while maintaining the high yield strength (~1.75 GPa) of the monolithic metallic glass. Additionally, we have found that volume fractions of the ductile phase as low as 4% significantly increases the plasticity compared to the monolithic metallic glass. Unlike typical metal matrix composites, the crystalline reinforcing phase is stiffer and exhibits a lower yield strength than the amorphous matrix. Therefore, during loading the weaker crystalline phase is first to yield via dislocation motion followed by yielding in the amorphous matrix by shear band formation. In order to study the micromechanics associated with these composite alloys, we have used high-energy synchrotron X-ray scattering to perform in situ strain measurements on the Ta-rich particles during uniaxial compression. By measuring the lattice strains present in the crystalline reinforcing phase, we have examined the load partitioning that occurs during uniaxial loading. We have also investigated the load partitioning as a function of the volume fraction of crystalline particles. Additionally, we have performed in situ strain measurements on composite alloys containing both the ductile Ta-rich phase along with a hard intermetallic phase. We compare the experimental measurements of load partitioning between the amorphous matrix and the crystalline phases with the predicted results obtained from finite element modeling.

MM8.13

Tensile Creep Deformation Behavior and Microstructural Evolution in Zr_{41.2}-Ti_{13.8}-Cu_{12.5}-Ni₁₀-Be_{22.5} Metallic Glass. Bulent Biner, D. J. Sordelet, D. K. Rehbein and X. Yang; Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa.

Constant load tensile creep tests were performed on Zr_{41.2}-Ti_{13.8}-Cu_{12.5}-Ni₁₀-Be_{22.5} (atomic %) at 325 °C at different stress levels up to 300 hours. Nanoindentation with Berkovich indenter on the gauge section of the crept samples consistently gave higher effective modulus values than the ones seen for the initial condition and also on the samples having the same thermal history of those creep specimens. The microstructural evolution during the creep deformation was characterized with detailed thermal analysis and electron microscopy in order to understand this apparent increase in the modulus. The stress dependency of the creep exponent of Norton's power law for this glass system is also correlated in terms of back-stress concepts that were developed earlier for composite microstructures. This work was performed for the United States Department of Energy by Iowa State University under contract W-7405-Eng-82. This research was supported by the Director of Energy Research, Office of Basic Sciences.

MM8.14

Plasticity in Ni-based metallic glass matrix composites reinforced by brass-fibers synthesized by warm extrusion of powders. Donghyun Bae and Minha Lee; Metallurgical System Engineering, Yonsei University, Seoul, South Korea.

The study is aiming at understanding the deformation behavior of centimeter-scale Ni-based metallic glass matrix composites (MGMCs) reinforced by brass-fiber at room temperature. The MGMCs are synthesized by warm extrusion of gas-atomized powders. Throughout the extrusion process, all blended spherical powders in the range of 10 to 70micrometer are well consolidated, in which all powders are elongated along the extrusion direction. The metal-fibers are well distributed in the metallic glass matrix up to 0.4 in volume fraction for the MGMCs. With increasing the metal content, elastic modulus and strength decrease due to the relative softness of the metal, but enhanced macroscopic plasticity is observed due to the formation of multiple shear bands, initiated from the interface between metal-fiber and metallic glass matrix, as well as their confinement between the metal-fibers. These behaviors are not observed in the sample

synthesized by warm extrusion of only metallic glass powders. The detailed mechanisms for shear band formation and its propagation in the matrix are presented.

MM8.15

Synthesis and Processing of Metal Alloy and Semiconductor Nanoparticles. Peter N Njoki, Jin Luo, Mathew M Maye, Li Han and Chuan-Jian Zhong; Chemistry, SUNY-Binghamton, Binghamton, New York.

The ability to synthesize and process the size and composition of metal alloy and semiconductor nanoparticles is critical for the exploration of these nanomaterials in sensor, catalytic, and nanoelectronic applications. This presentation discusses recent results of an investigation of the refinement of the synthetic and processing protocols for the control of size and shape of metal alloy and semiconductor nanoparticles. The work is aimed to understand the fundamental basis of the control parameters. The preparation of Au-containing alloy nanoparticles and GaAs nanoparticles is investigated. Transmission electron microscopy, infrared reflection spectroscopy and atomic force microscopy have been used to characterize the size, structural and morphological properties of the nanostructures. The alloy composition in the nanostructure determined by direct current plasma-atomic emission spectroscopy has been correlated with the synthetic feed composition. Implications of the results to the design of binary functional nanomaterials will also be discussed.

MM8.16

Abstract Withdrawn

MM8.17

Molding of fine surface features into bulk metallic glass. Ivan McCracken and Ralf Busch; Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon.

The focus of this study was to explore the size down to which a feature in the mold could be replicated into a bulk metallic glass (BMG) surface. A mold casting device was built, in which the melt is cast into a die under controlled melt and mold temperature as well as mold and molding pressure of argon. Micro and nanometer size features were engraved into polished Cu and steel substrates, that were inserted into the mold. The BMG used was Vitreloy 1, ($Zr_{41.24}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$). The minimum size and quality of the replication depends on the substrate material, substrate (mold) temperature as well as the pressure in the mold. Best results were obtained with steel substrates, when the mold was held at a temperature close to the glass transition and at very low argon pressures. Replication of substrate features was possible down into the submicron range. This has been verified with SEM micrographs of both the mold surfaces and the BMG parts. Processing variables, including the injection temperature of the molten BMG and the atmosphere in which it is molded, appear to have a great effect on the ability to reproduce fine features.

MM8.18

Deposition of Silver Nanoparticles on Yttrium Manganese Oxide Powders. Citlali Roman L., Maria A. Castellanos R. and David Diaz; Facultad de Quimica, Universidad Nacional Autonoma de Mexico, Mexico, D. F., Mexico.

Citlali Roman L., Maria A. Castellanos R. and David Diaz., Facultad de Quimica, Universidad Nacional Autonoma de Mexico, 04510, Mexico, D. F., MEXICO. Following a novel silver nanoparticle synthesis pathway spontaneous reduction of silver 2-ethylhexanoate takes place in dimethyl sulfoxide (DMSO) at 50° C. Sodium citrate was used as capping agent (1). Pre-synthesized silver nanoparticles (4.4 nm of average diameter) were deposited on a substrate of yttrium manganese oxide. Silver nanoparticles dispersions mixed with yttrium manganite were kept for 20 days, at room temperature, in a wrapped aluminum foil Erlenmeyer flask. Pure yttrium manganese oxide was prepared by solid state reaction of stoichiometric mixtures, containing manganese carbonate (Alfa Products 99.9%) and yttrium trioxide (Aldrich 99.99%) as chemical reagents. The mixtures were homogenized by wet grinding, in an agate mortar, using acetone as dispersion medium. We used pellets made of dried reaction mixtures, of one centimeter in diameter, pressed at 2.5 bar for one minute. The pellets were calcined from 500° to 1200° C. XRD analysis was performed on the sintered samples. The complete characterization of the samples involves the following methods HR-TEM, SEM-EDS and BET. (1) G. Rodriguez-Gattorno et al, J. Phys. Chem. B **2002**,106, 2482-2487. We want to thank the financial support from DGAPA-UNAM PAPIIT, projects IN105102 and IN110800. C. R. thanks CONACyT for a scholarship. Also, we thank C. Salcedo, I. Puente-Lee, Carlos Flores and Luis Rendon-Vazquez for their technical assistance.

MM8.19

The heating and structural disordering effects of the nonlinear viscous flow in a Zr55Al10Ni5Cu30 bulk metallic glass. Hidemi Kato¹, Akihisa Inoue¹ and H.S. Chen²; ¹Institute for Materials Research, Tohoku University, Sendai, Miyagi, Japan; ²Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

The heat evolution of stress-induced structural disorder, ΔH_s , of a Zr55Al10Ni5Cu30 bulk metallic glass (BMG) during constant strain-rate deformation at the glass transition region ($T_g = 680$ K) was deduced from in-situ measurements of temperature change of the deforming sample. At the transition from the linear to nonlinear viscoelasticity, the behavior of viscosity change with strain, $\eta(\epsilon)$, is qualitatively consistent with the enthalpy evolution of the structural disordering, $\Delta H_s(\epsilon)$, but not with the temperature change, $\Delta T(\epsilon)$. It is concluded that the initial softening deformation is due to the stress-induced structural disordering. The change in the nonlinearity, $-\log(\eta/\eta_N)$, is found to be proportional to the ΔH_s and the slope of $\Delta H_s(-\log(\eta/\eta_N))$ can be estimated to 400 J/mol, where η_N is the Newtonian viscosity. On the other hand, the temperature raise, ΔT , is pronouncedly delayed as compared with the η and ΔH_s at the transition, but is determined by the product of stress and strain rate, and is nearly proportional to it at the steady-state. The slope of ΔT -the product curve can be estimated to 0.052 K mol/W.

SESSION MM9: Structure and Solid-State Reactions

Chairs: Annett Gebert and A. R. Yavari

Thursday Morning, December 4, 2003

Republic B (Sheraton)

8:30 AM *MM9.1

Positrons, atoms and molecules as probes in metallic, oxidic and polymeric glasses. Reiner Kirchheim, Institut fuer Materialphysik, University of Goettingen, Goettingen, Germany.

Interatomic or intermolecular sites which can be occupied by small particles differ with respect to available volume and/or the chemical nature of the surrounding atoms. Small particles behave different in different sites and their properties can be used to get information about the sites, i.e. the structure of glasses. Thus the lifetime of positrons in polymers depends on site volume which can be used to determine site density and to show that no new sites are formed at the glass transition. Mechanical relaxation of small molecules in polymers reveals information about the topology of the sites. The chemical potential of hydrogen in metallic glasses and its dependence on concentration provides information about short range order of the metal atoms. Examples for binary and multi-component metallic glasses will be presented. In silicate glasses structural changes caused by network modifiers strongly effect the diffusion of ions and gas atoms. The concept of using small particles as probes can be applied to any disordered material including nanocrystalline metals. This way an average thickness of grain boundaries has been determined in nanocrystalline palladium and a structural change of the grain boundary structure in nanocrystalline nickel was observed around 200 C.

9:00 AM MM9.2

Atomic structure of Al-based metallic glasses through the glass-liquid transition. Kyungsoo Ahn¹, Despina Louca¹ and G. J. Shiflet²; ¹Physics, University of Virginia, Charlottesville, Virginia; ²Materials Science, University of Virginia, Charlottesville, Virginia.

Al amorphous alloys with an Al content of ~ 90 at% and with good specific strength have been discovered within the Al-TM-RE (TM = transition metal, RE = rare-earth metal) system. Neutron scattering studies on the Al-Ni-Nd system using the isotope difference pair density function (PDF) analysis suggested that the Al-TM local atomic environment is quite different from the Al-RE environment due to differences in the interactions of Al with the TM and the RE. In the case of Ni, the interactions with Al are strong, indicated by shortening of the Al-Ni bonds while Ni plays an important role in forming a strong glass. Ni enhances cluster formation evidenced by the presence of a pre-peak in the structure function. With Nd however, evidence for clustering is weak and the Al-Nd bonds are as expected assuming metallic bonding. Our recent high temperature structure studies on this system from the glass to the liquid state showed that the coherence length of Ni-Al clusters continuously increases with heating. This indicates the presence of persistent clustering in the liquid phase. We will present the local atomic structure of the Al glass and how it changes as it goes through the phase transition.

9:15 AM MM9.3

Efficient Local Packing in Metallic Glasses. Daniel B. Miracle, Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio.

The recent development and validation of a simple topological model has shown that efficient atomic packing is a fundamental principle in the formation of metallic glasses. An approach for defining and quantifying the local packing efficiency, P , was developed in this earlier work for solute-centered clusters that contained only solvent atoms in the first coordination shell. In the present research, this methodology is extended to allow quantification of P when more than one atomic species is present in the first coordination shell. This analysis is applied to several metallic glasses using assessed values of atom radii and published experimental data of partial coordination numbers. It is shown that packing is generally very efficient in the structure of metallic glasses, and that the values of P obtained for assessed metallic glasses are essentially identical to the values obtained from a similar analysis of the competing crystalline structures. These results are consistent with frequent earlier reports of topological short range ordering in metallic glasses, and are inconsistent with a structural model based on dense random packing of atoms.

9:30 AM MM9.4 Medium-Range Order in High Al-content Metallic Glasses Measured by Fluctuation Electron Microscopy.

William Gregory Stratton, Paul M Voyles, Joe Hamann and John H Perepezko; Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

Fluctuation electron microscopy (FEM) is a quantitative microscopy technique for determining medium-range order (MRO) at nanometer length-scales in amorphous materials. It depends on statistical analysis of the diffracted electron intensity from nanoscale volumes [1]. Here we apply FEM to a high Al-content metallic glass, $Al_{92}Sm_8$ to determine the magnitude and type of MRO, which may be a structural precursor to primary crystallization. Samples of this glass formed by rapid quenching (melt-spinning) show a high density of pure Al nanocrystals ($>10^{20} m^{-3}$) at low temperatures ($<200^\circ C$) upon devitrification. In samples formed by deformation (cold-rolling), primary Al-crystallization does not occur [2]. This difference in devitrification behavior suggests an underlying structural difference in the glassy state. We use FEM measurements on melt-spun and cold-rolled glass to explore this difference. This work is supported by the Army Research Office (DAAD 19-01-1-0486 and DAAD 19-02-1-0245). 1. P. M. Voyles, J. M. Gibson, M. M. J. Treacy, J. Electron Microscopy 49, 259 (2000). 2. G. Wilde, H. Sieber, J. H. Perepezko, Scripta Mat., 40, 779 (1999).

9:45 AM MM9.5 On the Structural Characterization of a Series of Novel Ni-Nb-Sn Refractory Alloy Glasses. Michelle Tokarz and John Billelo; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Recently refractory alloy glasses of varying Ni, Nb and Sn concentrations were prepared and studied via several characterization methods, including x-ray diffraction via standard lab and synchrotron radiation sources, SEM, and other complementary techniques. A comparison between x-ray diffraction results obtained from synchrotron sources vs. standard lab sources, shows the necessity of a low-divergence source in order to distinguish nanoscale crystallites present within an amorphous matrix. The divergence of both sources was studied by comparing the diffraction patterns of a LaB6 standard and noting the deviation from infinitely thin Bragg peaks. This was manifested as distinct peak widths, which were measured and analyzed. The crystallites in these glasses comprised between 0 and 10 percent by volume, depending upon the specific composition. The results presented here also show a very good sample to sample consistency for any given alloy composition. While x-ray diffraction results give information about the average structure, SEM was also performed to understand aspects of individual crystallite size and distribution. These results, in addition to other complementary analyses, are also presented. By studying results from varying concentrations, it is seen that a very small composition range exists for near-perfect glass formers (as defined by a near zero percentage crystallinity). Radial distribution analysis was also performed for each composition and compared to hard sphere models for each alloy composition. This analysis indicates the presence of some intermediate range order beyond the first nearest neighbors as indicated by the divergence of the experimental reduced radial distribution functions from that predicted by the accompanying hard sphere models. This work was performed with support from DARPA under contract number: DAAD19-01-1-0525, DOE for use of synchrotron facilities at SSRL (Stanford Synchrotron Radiation Laboratories).

10:30 AM MM9.6 Structural Relaxation and Crystallization in a $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG. Rejin Raghavan¹, Upadrasta

Ramamurty¹, Joysurya Basu¹, Srinivasa Ranganathan^{1,2} and N. Nishiyama²; ¹Metallurgy, Indian Institute of Science, Bangalore, KA,

India; ²Institute for Materials Research, Tohoku University, Sendai, Japan.

The stability of a $Pd_{40}Cu_{30}Ni_{10}P_{20}$ bulk metallic glass (BMG) is investigated by isothermal annealing heat treatments below and above its glass transition temperature, T_g , for varying periods. Dynamic differential scanning calorimetry (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM) were utilized in probing the structural changes that occur during the annealing. DSC scans of the samples annealed below the T_g exhibit a sharp endotherm that coincides with the T_g , irrespective of the annealing temperature. The excess endotherm, which appears to be a result of a first order phase transition, is found to increase in intensity with the annealing time and the temperature and is attributed to enthalpy relaxation as a result of compositional short range ordering during annealing, involving the rearrangements of metal-metal and metal-metalloid atoms. When the samples were annealed above T_g (at $1.1 T_g$), crystallization ensues with the volume fraction of the crystallites increasing with annealing time. TEM reveals that the crystalline phases to be faceted with Pd_2Ni_2P , $Pd_{15}P_2$, Ni_3P and Cu_3P compositions. In-situ heating of the samples was carried in order to identify the sequence of the phase evolution and the compositional variation during annealing. These results are discussed in the context of structural relaxation and crystallization behavior of the BMGs.

10:45 AM MM9.7 Evidence of Polymorphism in Vitreous Boron Oxide under Pressure. Jason Nicholas^{1,2}, Stanislav Sinogeikin³, John Kieffer⁴ and Jay Bass^{2,3}; ¹Materials Science and Engineering, University of California, Berkeley, California; ²Materials Science and Engineering, University of Illinois, Urbana, Illinois; ³Geology, University of Illinois, Urbana, Illinois; ⁴Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Samples of vitreous boron oxide ($v\text{-}B_2O_3$) have been compressed at room temperature to 57 GPa (more than three times the limit reported in previous studies). Structural and mechanical properties were examined using Brillouin and Raman Spectroscopic measurements along the compression and decompression paths. Upon compression, the shear and longitudinal sound velocities gradually increased and the 808 cm^{-1} boroxol ring breathing mode gradually disappeared. Above 14 GPa no Raman modes were observed. Upon decompression the sound velocities followed a very different path, remaining substantially higher and exhibiting less of a pressure dependence than during compression. At 3 GPa a sharp discontinuity of 3 km/s in the longitudinal velocity and 2 km/s in the shear velocity was observed, bringing the velocities back to the magnitudes observed during compression. During decompression no Raman modes were observed above the discontinuity at 3 GPa. After the transition, the 808 cm^{-1} boroxol ring breathing mode suddenly reappeared, along with a new mode near 881 cm^{-1} . Both modes remained stable upon further decompression. Subsequent compression-decompression cycles produced the same behavior. Our results suggest that there are at least two low-density vitreous B_2O_3 polymorphs and one high density disordered phase. The discontinuity at 3 GPa coincides with the transformation between trigonally and tetrahedrally-coordinated phases in crystalline B_2O_3 . Thus, we surmise that upon pressure increase the boroxol rings gradually break up as the boron becomes tetrahedrally-coordinated. Upon pressure decrease the high-density, tetrahedrally-coordinated phase persists down to 3 GPa when it becomes unstable and reverts to a trigonally-coordinated phase made up of boroxol rings and a yet unknown additional structural member. This work is the first time vitreous polymorphs have been seen in a three-coordinated glass.

11:00 AM MM9.8 Amorphous Product Formation by Self-Propagating Reactions in Nanoscale Multilayered Foils. Alan Duckham¹, Albert J Swiston¹, Jon Trenkle¹, Etienne Besnoin², Omar M Knio², Todd C Hufnagel¹ and Timothy P Weihs¹; ¹Materials Science and Engineering, The Johns Hopkins University, Baltimore, Maryland; ²Mechanical Engineering, The Johns Hopkins University, Baltimore, Maryland.

We present a novel method for forming amorphous metal structures: self-propagating exothermic reactions in freestanding multilayered foils. The heats generated by the self-propagating reactions are often sufficient to melt the products temporarily, and the cooling is often rapid enough so that the liquid phase can undergo a glass transition to the amorphous phase. The foils examined in this study were sputter deposited to contain hundreds of nanoscale layers. The nanoscale thickness of the deposited layers facilitates atomic diffusion, so that when an energy impulse initiates local mixing (and an associated release of heat), the formation reaction becomes self-propagating as atoms diffuse normal to the layers and heat diffuses parallel to the layers. We have investigated several Zr/Al/CuNi multilayer systems, which release different amounts of heat and also produce different

amorphous, ZrAlCuNi alloys, which are known to be bulk glass formers. For each alloy system, the heat of reaction and the melting temperature are critical in determining melting and are measured using calorimetry techniques. Whether or not a given system forms a glass is determined by the average foil composition and the initial cooling rate. Cooling rates are predicted by numerical modeling and they are validated by time-dependent temperature measurements. Furthermore, the cooling rate is varied by placing the foils between materials with different thermal conductivities. The structure of the foil following reaction is characterized by x-ray diffraction and transmission electron microscopy.

11:15 AM MM9.9

Mechanically-Induced Amorphization of Cementite in Iron-Cementite Nanocomposite. Eugene Petr Yelsukov and Gennady Alexeevich Dorofeev; Non-equilibrium Metallic System Laboratory, Physical-Technical Institute UrB RAS, Izhevsk, Russian Federation.

Mössbauer spectroscopy, X-ray diffraction and magnetic measurements were used to study the evolution of the phase composition, structure and magnetic properties of the α -Fe+60 at. % Fe₃C nanocomposite during mechanical grinding in a planetary ball mill. The α -Fe/Fe₃C nanocomposite with the grain sizes of 50 nm for α -Fe and 30 nm for Fe₃C was produced by mechanical alloying of the Fe and C powder mixture in the atomic ratio of 85:15 followed by annealing at 500°C for 1 hour. At the initial stage of mechanical grinding decrease of grain sizes ($\langle L \rangle < 10$ nm), transformation from the cementite with ordered local atomic arrangement - Fe₃C into the deformation-distorted cementite - (Fe₃C)_D accompanying of the coercivity H_C decreasing almost 2 times were observed. The specific saturation magnetization σ_S did not change at this stage and was 170 emu/g. The second long-time stage of mechanical grinding was characterized by further decrease of the grain sizes and by coexistence of three phases: α -Fe, (Fe₃C)_D and amorphous Am(Fe-C) phase, the C concentration in which was close to 25 at. %. The α -Fe amount remained unchanged, the Am(Fe-C) amount increased at the expense of decreasing the amount of the (Fe₃C)_D cementite. At this stage H_C decreased almost 3 times, and σ_S increased up to 190 emu/g. The final product of mechanical grinding was the α -Fe+Am(Fe-C) nanocomposite with grain sizes of a few nm, but with the particle size of ~ 10 nm being equal to that of the initial particle size of the α -Fe/Fe₃C nanocomposite. We suppose that with unchanged particle size and α -Fe amount during grinding the transformation (Fe₃C)_D→Am(Fe-C) takes place when the (Fe₃C)_D grain size reached some critical value. With the distribution of the grain size existing, the transformation (Fe₃C)_D→Am(Fe-C) does not take place at a certain moment of grinding time, but it is a long-time process. This work has been supported by the Russian Fund for Basic Research (project 03-03-32081).

11:30 AM MM9.10

Transition metal effects on amorphization, crystallization, and mechanical behavior of amorphous aluminum alloys. Tim Wilson¹, Hahn Choo^{1,2}, Scott A. Speakman² and Peter K. Liaw¹; ¹Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; ²Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

High-energy ball milling has been performed to synthesize aluminum-based amorphous alloys to better understand amorphization, crystallization, and mechanical behavior. The focus of this study is to determine the compositional effects of transition metals (TM) on the synthesis and properties of Al-Y-Fe-TM alloys (TM = Fe, Ni, Co, Cu). The effects of milling parameters, such as time and temperature, on the amorphization process were also examined. Crystallization kinetics of the amorphous powders was studied using differential scanning calorimetry and in-situ high-temperature x-ray diffraction. Mechanical behavior of the amorphous aluminum alloys at various stages of amorphization and crystallization processes was investigated using an indentation technique.

11:45 AM MM9.11

Aluminum Based Nanocomposites by Mechanical Alloying. B.S. Murty and S.S. Nayak; Met. & Mater. Eng., Indian Institute of Technology, Kharagpur, Kharagpur, India.

Mechanical alloying is a high-energy ball milling process to synthesize materials with homogeneous microstructure and novel properties. Mechanical alloying is used as a tool to synthesize a number of stable and metastable phases, such as supersaturated solid solutions, intermetallics, amorphous phases, nanocrystalline and quasicrystalline materials. In the present study, Al based nanocomposites were synthesized using mechanical alloying of elemental blends in a Fritsch P5 Planetary ball mill using WC vials and balls at 300rpm in toluene medium with a ball to powder weight ratio of 10:1. Attempts have

been made to synthesize nanocrystalline L12-Al3Ti and Al3Zr intermetallics and nanocomposites of these phases in an Al matrix. Al3Ti phase has DO22 structure under equilibrium conditions, which has poor ductility. Ternary additions such as Cu, Cr, Fe, Ni, Co and Mn can stabilize the L12 form of this phase, which has good ambient ductility. The influence of various ternary additions on the stability of L12 phase has also been studied in detail. Similarly, nanocomposites have also been synthesized with nanoquasicrystalline phase dispersed in Al matrix by mechanical alloying and subsequent annealing in Al-Fe-Cr-Ti system. The thermal stability of the nanocomposites and their grain coarsening behavior has been studied in detail. Both the as milled and heat treated powders were characterized using XRD, SEM/EDX microanalysis and TEM. Thermal studies were carried out using DSC. The crystallite size and strain in the lattice were calculated by separating their peak broadening contributions in terms of Cauchy and Gaussian components of peak profiles, respectively, using Voigt analysis.

SESSION MM10: Applications and Environmental Effects

Chairs: Jurgen Eckert and Daniel Miracle
Thursday Afternoon, December 4, 2003
Republic B (Sheraton)

1:30 PM *MM10.1

Applications of Bulk Amorphous Alloys. Atakan Peker, Liquidmetal Technologies, Lake Forest, California.

Amorphous alloys have been known to exhibit favorable properties such as high strength and good corrosion resistance. However, the use of amorphous alloys in general engineering applications was limited, as the section thickness of those alloys were bounded by very high cooling rates required to form the amorphous phase. In the last decade, there have been exciting developments in the field with the development of bulk-solidifying amorphous alloys. Some of these alloys are now developed and marketed for commercial use by Liquidmetal Technologies under the trade name of Liquidmetal Alloy. The leading family of these alloys, Zr-Ti-Ni-Cu-Be system, is such an exceptional system that fully amorphous objects with section thickness up to 30 mm can be prepared. With the development of bulk-solidifying amorphous alloys, other unique characteristics have also been noted for additional benefits in engineering applications. One such unique aspect is the availability of desired mechanical properties (up to 1,900 MPa yield strength) in as-cast condition. Furthermore, the unique casting characteristics of bulk-solidifying amorphous alloys provide near-to-net shape component fabrication with reduced post-finishing processes. As such, these alloys can provide enabling solutions in several engineering applications. A brief history of the development of bulk-solidifying amorphous alloys will be presented. Then, commercial development efforts led by Liquidmetal Technologies will be discussed. Various issues and challenges during the commercial development efforts will be highlighted, such as the realization of attributed mechanical properties in commercially developed processes. Finally, specific engineering properties and potential applications of bulk amorphous alloys will be discussed.

2:00 PM *MM10.2

Electrochemical Reactivity of Zr-Based Bulk Metallic Glasses. Annett Gebert, IMW/23, IFW Dresden, Dresden, Saxony, Germany.

Due to their short-range ordered atomic structure and to their composition of early and late transition metals Zr-based bulk glass-forming alloys exhibit very interesting electrochemical properties, e.g. fast uniform anodic oxidation and high reactivity for cathodic hydrogen reduction and absorption. Amorphous Zr-Ti-Al-Cu-Ni alloy samples were prepared by melt-spinning and copper mould casting in an argon atmosphere and characterized regarding their microstructure and thermal behavior by XRD, SEM, TEM and DSC. Their oxidation behavior in aqueous environments with pH= 0.5 - 13 was studied by static and dynamic electrochemical polarization techniques in combination with surface analytical investigations, i.e. SEM/EDX, AFM and AES. In halogenide solution the macroscopic corrosion resistance of bulk amorphous alloys is affected by the presence of concentrated cluster zones of selected components and of crystalline defects. Pitting phenomena are studied in neutral and acidic chloride solutions and in result a local corrosion mechanism is proposed. The cathodic reactivity of selected alloy samples at different microstructural states and after pre-etching in fluorine solutions was investigated applying potentiodynamic polarization techniques and impedance spectroscopy. After pre-etching melt-spun amorphous samples exhibit a significant increase in surface reactivity as expressed by a drastic increase in exchange current densities and in electrochemical capacities as well as by a significant reduction of overpotentials for the hydrogen generation reaction. The hydrogen sorption behavior was studied on samples galvanostatically

charged at various cathodic current densities by means of XRD, DSC, TEM and thermal desorption analysis TDA. At room temperature Zr-based alloys absorb hydrogen up to $H/M=1.65$ mainly by interstitial solution of hydrogen atoms in the amorphous structure. However, small hydrogen concentrations can lead to an improvement of the materials plasticity due to a hydrogen-driven cluster formation. The effect of absorbed hydrogen on the thermal stability and the crystallization behavior is described in detail.

2:30 PM MM10.3

Bulk metallic glasses for industrial products; New structural and functional applications. Nobuyuki Nishiyama¹ and Akihisa Inoue²; ¹RIMCOF Tohoku Univ. Lab., RIMCOF, Sendai, Miyagi, Japan; ²IMR, Tohoku Univ., Sendai, Miyagi, Japan.

Bulk metallic glasses (BMGs) exhibit unique and excellent properties such as ultra-high strength, good ductility, exceptional low Young's modulus, high corrosion resistance and good soft magnetic properties. Origins of these properties come from their dense-random packing (DRP) structure of atoms, which is quite different from conventional crystalline alloys. Newly developed products constructed by BMG parts will have superior structural and functional potential. In addition, viscous flow deformability and nano-printability with extremely low flow stress of BMGs enable us to produce near-net or net shaped parts and it lead to solve the global problem for energy saving and environmental. However, BMG forming systems and compositions with high glass-forming ability were relatively limited for Zr-, Pd-, La-, Mg-based alloys. If the BMGs are composed of commercial metal element, the application of BMGs will be extended. On this point of view, we try to prepare industrial parts using new Ni-, Cu- and Fe-based BMGs as high strength and soft magnetic materials. This paper is intended to introduce new application of BMGs such as magnetic yoke, micro-gear and some sensing device. Furthermore, the performance of these products made by BMG parts will be discussed.

2:45 PM MM10.4

Nanostructured Titanium and Ti6Al4V Surfaces Increase Bone Cell Functions. Thomas Jay Webster and Jeremiah Ejiolor; Biomedical Engineering, Purdue University, Lafayette, Indiana.

The average lifetime of an orthopedic implant (such as hip, knee, etc.) is 10 - 15 years. Although there are many reasons contributing to implant failure, insufficient bonding of the prostheses to juxtaposed bone clearly results in biomaterial loosening and possible eventual failure. Traditional orthopedic implants are composed of metals (usually titanium and/or titanium alloys) that possess constituent particle sizes greater than several tens of microns. Despite this fact, osteoblasts (bone-forming cells) are accustomed to interacting with nanostructured (not micron-structured) materials in the body. Specifically, the major inorganic and organic components of bone (hydroxyapatite and collagen, respectively) have nanofiber grain sizes. For these reasons, the objective of the present in vitro study was to synthesize and determine the potential of nanostructured titanium and titanium alloys (specifically, Ti6Al4V) to serve as orthopedic implants. Results of this study provided the first evidence of increased osteoblast adhesion and proliferation on nanostructured compared to conventional grain size titanium and Ti6Al4V. Longer-term functions of osteoblasts on such novel nanostructured metals will also be reported. Enhanced functions of osteoblasts leading to greater amounts of calcium deposition have also been demonstrated for nano-structured compared to conventional ceramics, polymers, and composites thereof. For this reason, results of this study adds another novel property of metals with particles sizes in the nanometer regime. In doing so, this study provides evidence that nanostructured titanium and titanium alloys should be further investigated for bone implant applications

3:00 PM MM10.5

Catalytic Properties of High-Density Monodispersive Metal Nanostructures. Irina N Yassievich¹, Vladimir M Kozhevnikov¹, Tat'yana N Rostovshikova², Denis A Yavsin¹, Michail A Zabelin¹, Pavel A Tret'yakov¹, Vladimir V Smirnov² and Sergei A Gurevich¹; ¹Centre of nanoheterostructure physics, Ioffe Physico-Technical Institute, St.Petersburg, Russian Federation; ²Moscow State University, Moscow, Russian Federation.

We report on ultra-high catalytic activity of high-density monodisperse Cu and Ni nanostructures fabricated by newly developed laser electrodispersion technique. In these structures the size of Cu particles is 5 nm, while Ni particles are 2.5 nm in diameter. In both cases the particle size dispersion is less than 20%. Deposited on oxidized silicon support one layer films have maximum particle surface density 410^{12} cm^{-2} for Cu and $1.610^{13} \text{ cm}^{-2}$ for Ni. Both Cu and Ni particles have amorphous structure. The catalytic properties of copper nanostructures were studied in chlorohydrocarbons transformations reactions. The activity of densely packed one-layer

film was found three orders of magnitude larger than the activity of currently available industrial catalysts and about order of magnitude larger than that offered by the best-known nanostructure based Cu catalyst. The activity of Ni structures was tested in the reaction of nonan hydrogenation. The maximal activity was also observed for high density films and it was more than 20 times higher than the activity of the best Pd-based catalyst. We believe that the observed extremely high activity is due to interparticle interaction, which results in the appearance of negatively and positively charged particles in densely packed granulated films. These charges are generated due to thermally activated interparticle electron tunneling. Strong local electric fields related with these charges (field strength up to $4 \times 10^6 \text{ V/cm}$) offer further the enhancement of the structure activity. The significant role of the particle charge and strong electric fields has been studied theoretically and proved in the experiments, which demonstrate drastic increase of the catalytic activity with the increase of dielectric permittivity of the reactant solution. Thus, the observed high catalytic activity seems to be general property of the densely packed thin nanostructure films fabricated by the laser electrodispersion technique.

3:15 PM MM10.6

Oxidation of Zr-Based Metallic Glasses. Lioba Jastrow and Uwe Koster; Dept. Biochem. & Chem. Eng., University of Dortmund, Dortmund, Germany.

Zr-alloys are among the most promising systems for bulk glass formation. These bulk metallic glasses are of increasing interest due to their excellent properties, e.g. high elastic limit or catalytic activity. For some applications (golf clubs, hydrogen storage) good oxidation resistance is necessary; in other cases (catalysis) fast oxidation is required. In order to use for example Zr-based metallic glasses instead of crystalline alloys as a repository for deuterium or tritium desorption has to be avoided, e.g. by formation of a dense oxide scale. Oxidation kinetics for example of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ glasses seems to be controlled by oxygen diffusion through the scale towards the ZrO_2 /glass interface and can be slowed down significantly by Be or small additions of some other alloying elements, e.g. Sn or Si. The continuous scales consist of tetragonal ZrO_2 ; Cu, Ni and Al forming nanocrystals between the ZrO_2 nodules are enclosed in the same ratio as in the glass. Zr-Au or Zr-Pd melt-spun glasses, on the other hand, exhibit "catastrophic" oxidation even at temperatures far below their glass transition. On as-cast surfaces of these glassy ribbons which are probably protected by a thin native ZrO_2 layer localized nucleation of the oxidation reaction was studied in detail, in particular by cross sectional TEM revealing a rather complicated microstructure of the oxide islands. In order to understand the influence of structure, the oxidation behavior of these metallic glasses was compared with that of nanocrystalline as well as coarse crystalline alloys of similar composition. Some evidence was found for highest oxidation resistance in the nanocrystalline material. Segregation at crystal surfaces or grain boundaries might be responsible by forming barriers with a higher oxidation resistance.