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 range of behavior 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 concern 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 Janssens; 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 non-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. FeNiB) the finest microstructure is achieved at minimum 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 occur 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 FeNiB 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 inter 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 Recrystallization. See Bossuyt, A. and A. Lindsay Greer, Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; VUB-TW-MEMC, Vrije Universiteit Brussel, Brussels, 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 and a self-sustained 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-polymeric crystallization.

9:45 AM #MM1.4

Icosahedral short-range order (ISRO) is often presumed to dominate the structural features of liquid and amorphous metal, but has been used to explain micro-alloying effects on glass formation and stability, and to account for non-structure formation in the growing number of glasses that crystallize to quasicrystals. Frank first proposed the existence of ISRO over fifty years ago for liquid alkali metals, reporting a surprisingly high nucleation barrier to crystallization that had been masked by Turnbull. Recently, we present the first direct experimental demonstration of Frank’s hypothesis, clearly demonstrating the link between ISRO and crystallization. A growing icosahedral short-range order with decreasing temperature in a Ti36Zr36Ni28 liquid. The short-range order data were obtained using BESL, a new facility that allows synchrotron x-ray measurements on deeply undercooled electronically driven 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 discussed. K. F. Kelton, G. W. Lee, A. K. Gangopadhyay, R. W. Hyers, T. J. Grubh, J. R. Rogers, M. B. Robinson and D. S. Robinson, Phys. Rev. Lett., 90, 195504 (2003).

10:30 AM #MM1.5
Amorphization and devitrification of Al-rare earth transition metal alloys. L. Butazzoni, M. Baricco, M. Kusy, M. Palumbo, V. Ronto and P. Rizzii; Dipartimento di Chimica IFM, Università 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 deeutectic 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 be even surprising that these melts can undercool to the extent of forming glasses. The issue of amorphization is reviewed here considering transport and thermodynamic properties of the melt. Calculation of a ternary AlNiCe phase diagram is progressing with the inclusion of metastable phase equilibria involving the glass and intermetallic compounds. Some experimental data on metastable phases [glass transition temperature, 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 A187N87RE6 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

Recent studies have shown that a variety of crystallization reactions occur 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; in order to obtain a better understanding of the crystallization mechanisms of bulk-forming metallic glasses, we have investigated the early crystallization stages of Pd36Si14Ge9, Zr47.5Al15.5Ni16Cu14.5, Zr29.5Ti6.5Cu25Ni33.5Be12 and Zn40Al5Mg30Ni10Be20 alloys, all of which were reported to decompose into two glassy phases prior to crystallization. The major experimental challenge was to distinguish the glassy phase decomposition from nanocrystallization. Metal-atom amorphous ribbon of the above alloys were annealed right above the glass transition temperature, and the microstructure evolution was studied by transmission electron microscopy (TEM), three-dimensional tomography (3D-TEM), and small-angle x-ray scattering (SANS). Attention has been paid to separate chemical decomposition and structural transformation by the complementarity use of TEM, energy-filtered TEM, energy-filtered electron diffraction (EFED), 3D-TEM, and SANS. 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 ZrAl5Te24Gd40 metallic glass. Thus, differential scanning calorimetry (DSC) and x-ray diffraction clearly shows an inflection between the glass transition temperature ($T_g$) and the crystallization temperature ($T_c$), which used to be interpreted as $T_c$ for one of the two decomposed glassy phases. However, no evidence for the presence of glassy phases was confirmed by TEM and 3DAP observations.

Early Stages Of Al-Nanocrystal Formation in Al$_{80}$Sn$_{20}$. Gerhard Wilde$^1$, Harold Roese$^{2,3}$, Nancy Bouchard$^1$, Joe Hann$^2$, William S. Tong$^2$ and John H. Perepezko$^2$, $^1$ Institute of Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany; $^2$ Department 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 nucleated structure on nanocrystal synthesis. In this respect, the Al$_{80}$Sn$_{20}$ 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 using sensitive electronic 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, and the created phases and the transformed fractions were determined with a high accuracy for extended ranges of temperatures and times. As a result, the nanocrystal size distribution functions for melt-quenched Al$_{80}$Sn$_{20}$ 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 analyzed regarding the kinetics of the early stages of nanocrystallization and are additionally evaluated with respect to the origin of the nanocrystalline dispersion. The support by the DFG within the Emmy Noether program (WI 1899/1-3) and by the ARO [DAAD19-01-1-4486] is gratefully acknowledged.

Modification of the Phase Selection during the Nanocrystallization of Amorphous Al-Y-Fe. Nancy Bouchard$^1$, Harold Roese$^{2,3}$, Rainer J. Heber$^2$, John H. Perepezko$^2$ and Gerhard Wilde$^1$, $^1$ Institute of Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany; $^2$ Department 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 crystallization reaction upon heating that impedes the glass transition and stabilizes the amorphous 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 and cold-working, or the controlling 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/matrix interface and with respect to different nucleation mechanisms. The results indicate that the possibility for controlling the concentration gradient for new opportunities for an optimization. The support by the DFG [Emmy Noether program and center for functional nanostructures, CNF] and the ARO is gratefully acknowledged.

Thermal Tempering of Bulk Metallic Glasses. C. C. Aydiner$^4$, E. Ustundag$^5$, Bjoern B. Prinz$^6$ and Robert A. Winnholtz$^7$, $^1$ Materials Science, California Institute of Technology, Pasadena, California; $^2$ Liquidmetal 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 excellent absorption ability. Making such an ideal foam is a challenging task since they are highly unstable structures. Their properties strongly depend on the structures homogeneity. The kinetics of the foaming process, of the sedimentation of the bubbles, and the change 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 to 3 Pa·s. Therefore, the foaming kinetics of BMGs can be expected to be much larger. Thus better control over the foaming process can be gained by 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 amorphous forms and dimensions which are much larger than the critical freezing 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 much smaller dimensions than the critical 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.

Thermal Tempering of Bulk Metallic Glasses. C. C. Aydiner$^4$, E. Ustundag$^5$, Bjoern B. Prinz$^6$ and Robert A. Winnholtz$^7$, $^1$ Materials Science, California Institute of Technology, Pasadena, California; $^2$ Lujan Neutron Science Center, Los Alamos National Laboratory, Los Alamos, New Mexico; $^3$ Engineering Sciences and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico; $^4$ Department of Mechanical Engineering, University of Missouri, Columbia, Missouri. Multi-component metallic alloys with super high 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 stresses. The BMG processing typically involves casting an alloy into a mold followed by severe quenching. This procedure can cause 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]. The residual stresses were measured in BMG [2] and cylinders [3] via the crack compliance (or sitting) method. We also developed a viscoelastic model [3] that can predict the final residual stresses within 1-5% of the experimental values. In addition, neutron diffraction measurements in BMG [4] and 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." Metall. Mater. Trans., 32A, 270-271 (2001). 2. C. C. Aydiner, E. Ustundag, M. B. Prinz, and P. Körner, "Modeling and Measurement of Residual Stresses in a Bulk Metallic Glass Plane," J. Non-Cryst. Solids, 316 [1], 83-95 (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 (2004). 4. C. C. Aydiner, B. Claesen, E. Ustundag, J. C. Hanan, M. A. M. Bourke and R. A. Winnholtz, "Residual Stresses in a Bulk Metallic Glass / Stainless Steel Composite," submitted to Mater. Sci. and Eng. (2003).

O. M. Kino1, T. C. Hufnagel2 and T. P. Weihs3, 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 fuses as local heat sources. Reactive fuses are freestanding, nanoscale 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 melt, creating a self-propagating exothermic reaction. Bonding occurs between two metal glass components and igniting the reaction, the interfaces are heated rapidly and uniformly above their glass transition temperature, the glass freezes to a solid, 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 fuse contract and often fracture due to constraints from the surrounding glass components. Once cracking occurs, the viscous supercooled liquid flows over cracks, widening them and coating some 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 droplet, dragging the reacted fuse 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 heat of mixing) and the pressure pulse 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 macrostructure 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. Yang2, P. B. Wheeler3, J. Eckert2, U. Kuehn2 and D. J. Srolovitz2, 1Metal and Ceramics Program, Ames Laboratory, Iowa State University, Ames, Iowa, 2Naval Research Laboratory, Washington, DC, 3IBM Research, Almaden Research Center, San Jose, CA.

Recently developed Zr-based metallic glass compositions 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 boron phase precipitates were obtained by high pressure He gas atomization. Formation of the boron phase in amorphous matrix strongly depends on the material composition and on the processing parameters during crystallization. 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 processing parameters were characterized using X-ray diffraction, differential scanning calorimetry, optical, scanning and transmission electron microscopy. Amorphous powders were consolidated by warm extrusion. Temperatures for the extrusion were obtained from the region at which crystallization begins. Microstructural features 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, Sung Bok Lee and Nick 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 used to develop a computer model of the TTT diagrams. A more accurate prediction 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 simulations and it has been demonstrated 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. Min and Y. 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 using 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-bonded 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-Re-Si, Leonid A. Benderson 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 glassy phases by growth along a moving interface, as in a first-order transition, has been advanced. We present evidence of the growth of a metallic glass phase in the Al-Re-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-Re-Si phase diagram consistent with the microstructural and compositional 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 Tatarchovits, Materials and Processes Division, USM Inc, Dayton, Ohio.

New Ca-based bulk metallic glasses have recently been discovered based on Senkov-Miracle topology 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 incentive to narrow the compositional range for searching new metallic glasses. In particular, according to this model, the atomic radii of the alloying elements should be roughly the 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 formulae Ca(Ni,Co)(Ge,Mn), 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 glass stability: Parting Glasses, Joseph B. Garbuz, 1 materials, University of Virginia, Charlottesville, Virginia, 2 materials.
Development of Amorphous Metals Using High Throughput Experiments. C. Eric Ramberg, Yongi Wang, Gran Fun, Erik McDermott, Jason Wang, Kirk Renyon 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 Tg, Ts, and Tm from differential scanning calorimetry (DSC) and differential thermal analysis (DTA). The advantages and challenges of using high throughput techniques will be discussed, using examples from different classes of amorphous metals.

Deactivation Of Aluminum-Rare Earth-Transition Metal Alloys, Alexandre I. Vanlier1, Mark Ando2, Martin J. Blackburn1 and Thomas J. Watson2; TMS, University of Connecticut, Storrs, Connecticut; 1Pratt & 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 deactivation 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 deactivation products appeared: spherical nanoscale α-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 α-Al or α-Al(RE) were formed with habit planes parallel to {100} of α-Al and consisting of ordered Al2TM or Al2TM(RE) rhombohedral. 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

Chair: Athilal Irwane and Yi Li

Tuesday Morning, December 2, 2003

Republic B (Sheraton)

8:30 AM MM3.1

From Hard To Soft Magnetic Properties in the Nd60Fe40Al1 alloy Composite: A Study on Microstructure in Bulk, Splat-Cooled and Thin Film. Alberto Bracci1, Susanne Schneiter1, Poppmann Thiirgen1, and Konrad Simon1; 1IV. Physikalisches Institut, University of Göttingen, Göttingen, Germany; 2IV. Physikalisches Institut, University of Göttingen, Göttingen, 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 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 Nd60Fe40Al1 alloy 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, and is used to solidify them. In this work, isothermal annealing experiments, bulk samples of nominal composition Nd60Fe40Al1 have been prepared by different solidification methods achieving cooling rates between 10^6 K/s and 10 K/s. Structure and magnetic properties have been studied by high-energy angle x-ray diffractometry, 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 modulations 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 a transverse dimension ranging between 20 and 200 nm 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 Nd60Fe40Al1 thin films.

Support by Deutsche Forschungsgemeinschaft via SFB 692 (TP A5). 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 authors (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, Evans Ma1, Christine Michel1, Juergen Thomas2 and Ludwig Schulte1; 1Institut fur Materialforschung, Deutsches Elektronen-Synchrotron, Hamburg, 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 the cast Nd-rich Nd4Fe and Nd4FeAl alloys are often correlated to the phases with unidentified structures, hitherto known as γ and γ, 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., Nd2Fe7 and Nd5Fe17 are known, which are magnetically soft. However, the formation of a Nd2Fe13-like phase under atmospheric conditions is not known with certainty due to the lack of structural data. In this work, Nd60Fe40Al1 alloys were prepared by copper mold casting and directional solidification to obtain a coarse microstructure. The 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 Nd2Fe13) in peritectic morphology but show no coercivity. The Nd2Fe13 grains (formed in the ds samples) show clear magnetic domains with uniaxial anisotropy indicating that Nd2Fe13 is not a cubic phase. Selected area diffraction (SAD) patterns from the NdFe2 grains have been indexed with a trigonal structure. X-ray absorption spectroscopy (XAS) was used to analyse the local configurations of Fe atoms in the 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 Nd2Fe13 phase in the ds samples does not transform after heat treatment at 700 °C for 4 h. 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-like Nd2Fe13 phase and the hard magnetic properties in Nd-Fe-AI alloys is discussed.

9:15 AM MM3.3

Magnetic and Mechanical Properties of Amorphous and Nanocrystalline Fe-based Alloys: Ivan Sladecek1, Tseren Dorjsuren2, Jozef Krenicky1, Jozef Kovac1, Peter Sece1, Rainer Gerling3 and Juergen Koetzler1; 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 Co-based-based alloys prepared by devitrification or 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 metallic glasses, (Fe70B10Cu10(Ni35Co30)(1-x)Mn10 (x = 0.25, 0.33, 0.5)) alloys is investigated using different experimental methods. We show that the ternary FeNb nanocrystalline alloys exhibit a variety of phenomena starting from spin-glass like behavior at cryogenic temperatures, following by very soft magnetic behaviour at intermediate temperatures, and finally, approaching the Curie
temperature of the amorphous matrix, Tc(asm), a marked magnetic hardening due to a decoupling between the nano-grains occurs. Above Tc(asm), the chain of magnetizationquisitions starts to be 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 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 contents and the influence of nano-fractions of crystalline phases. The ductile/brittle behaviour of the thermally treated samples is studied by two different methods. The relative strain at fracture (εf) is determined by simple bending tests. The elongation of the ribbon to failure (εp) is determined by miniaturized Ersharsen (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 to more than 800 K results in the ultimate yield point and ultimate tensile strength. The new findings are in line with the well-known dependence 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.

9:45 AM MM3.5
The Glass Transition Temperature Tg, Thermal Expansion Coefficients and Free Volume in Metallic Glasses measured by Time-resolved Diffraction in Transmission, Akin Bezn Yang1,2,3, Monica Tanegrush1, Nicola Lulup2,3, Akhis Inou2, Ichiro Matsubara2, Gwin Vaughan3, Ake Kocks3 and Walter Jose Eissen3. 1Institut National Polytechnique de Grenoble, ScMac/Inr, France; 2IMR, Tokio University, Sendai, Japan; 3European Synchrotron Radiation Facility (ESRF), Grenoble, France; 4DEMS, Univ. Fed. Sao Carlos, Sao Carlos.

The glass transition temperature Tg in metallic glasses can be studied by calorimetric techniques which show an endothermic event corresponding to a specific heat Tg-Dp difference between the glass 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 Tg can be detected for bulk metallic glass-forming alloys. This temperature is measured as metallic glasses with a similar composition to Fe50Ni50T = 320°C. Using such conditions, the variation of α(1-x)θ, the volume coefficient of thermal expansion, has been measured for the first time by diffraction near Tg for a number of bulk glass-forming alloys. The variation of α(1-x)θ is clearly detected in the same glass transition temperature range of Fe50Ni50T = 320°C for bulk metallic 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 does not depend on the quench rate when comparing for example, specimen from the bulk glass and melt-spinning glasses of the same alloy or for ribbons spun at different wheel speeds. Acknowledgements: This work was supported by the EU Network on BMG. (STREP-ICT-2010-1-218833), IFCAM, ESRH project ME-544 and CNPq-CNRS.

10:30 AM #MM3.6
Ultrasonic Investigation of Bulk Metallic Glasses, Wei Hun 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, Nio–P, Ni-based bulk metallic glasses (BMGs) and glassy composites have been systematically studied by using high frequency echo method which is particularly sensitive to the microstructural changes. The elastic constants and thermodynamic parameters as well as their pressure and temperature 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 glasses. A striking feature of long-wavelength transverse acoustic phonons in the BMGs relative to its crystallized state is observed and contributed to the microstructural characteristics of the BMGs. The volume-pressure equation of state and the Gruneisen constant for these BMGs was obtained. The compression curves of the BMGs are found to interpose among its components, and the BMGs exhibit much small volume changes upon pressure compared 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

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 know how. But the recent developments and progress in theory and simulation methods and the increasing pace of 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, ab initio mechanics and thermodynamics in studying their structure and properties (mechanical, elastic and plastic, thermodynamic, transport).

11:15 AM MM3.8
Ab-initio Calculation of the Diffusion Coefficients in B-based Liquids, Miguel Puentes-Cabrera1,2, Donnalli M Nicholson1, Mike Wixon3, Yang Wang4 and Merek Mihalkovic1,4, Oak 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 selfdiffusion in liquid Fe70X5ZrNi5Zr20 (X= Y, Zr, Ni, 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 N00014-01-1-0891 under DOE subcontract DEA05-00OR2275454 with UT-Battelle, LLC.

11:30 AM Early MM3.9
Early Crystalization Stages of Undercooled Zr-Cu-Ni-Al-Ti Melts with Different Oxygen Contents, Andrea A Kundig, Tsukui Ohtsuka and Kusuhiro Hono; Metallic Nanostructure Group, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Earlier studies on the crystallization behavior of Zr52Cu26.5Ni14Al10Ti5 using XRD, DSC, SANS [1,2], TEM and


SESSION MM4: Joint Session with LL6: Quasicrystals from Metallic Glasses Chai K, Kolton D, Debrlelet B, Amon G, Zhu W, Republic B (Sherman) 1:50 PM MM4.1 Icosahedral Transformation from Supercooled Liquid in Metal-Metal Type Bulk Glassy Alloys, Akhiam Inoue, IMR, Tohoku Univ., Sendai, Miyagi, Japan. Since the first syntheses of metal-metal type bulk glassy alloys without metalloid element in Mg-Pd, U-Mn and Zr-Me alloys systems for several years between 1980 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, high elastic elongation, high corrosion resistance, high soft magnetic properties and Neutrinon flow. We have also noticed that the metal-metal type bulk glassy alloys have been identified as the transforming in which primary crystallization phase consists of only big cube or icosahedral phase. It has also been reported that the precipitation of icosahedral phase occurs in Zr-Hg 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, which 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 the supercooled liquid accompanied by an ease of nucleation of icosahedral phases 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, kinematic behavior and microstructure for the precipitation of the icosahedral phase, and metal-metalloid base alloys in the icosahedral Al-Co-Ni-Ti and Cu-base 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 Studino and N Mattner, Institute for Metallic Matter, IFW Dresden, Dresden, Saxony, Germany. [Nano-]quasicrystalline, amorphous and nanocrystalline multicomponent Al- and Zn-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 reactions using mechanical or hot rolling 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 intermetallic 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 the 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 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 transition 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. The mechanistic 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 Quasicrystalline Formation in Zr-Based Metallic Glasses: Influence of Ag, Lydmath Luscherm and Uwe Kuehler, Dept. Biochem. & Chem. Eng., University of Dortmund, Dortmund, Germany. In the Zr-Co-Ni-Al system one of the best bulk metallic glassy alloys was found. But in a narrow concentration range around the composition of the best glass forming ability (e.g., Zr60Cu28Ni6Al5) formation of quasicrystals either by primary or post-heat treatment is known. However, during amorphous to crystalline transformation, 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 yet. Recent papers mention for example the possibility that the quasicrystals in these alloys are a hybrid of two structural elements, i.e. the tetragonal Zr2Ni (Al2Cu) and the tetragonal Zr2Cu (MoSi2) 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 phases. Combining electron microscopy with DSC as well as crystallization statistics allows the separation of the intermetallic and the crystallization parameter, for example the interfacial energy. Reasons for the observed behavior will be discussed in detail. The results may help to understand the role of factors on the formation of quasicrystals in Zr-based glasses [1]. UKuehler, J Meinhart, S Roes, H Liersch, Appl. Phys. Lett. 69 (1996), 179; [2] J. Sajid, M. Matsushita, A. Inoue, Mater. Sci. Forum 360 - 363 (2001), 23. 2:45 PM MM4.4 Influence of AI on quasicrystalline formation in Zr-Ti-Nb-Cu-Ni-Al metallic glasses, S. Studino, J. Eckert, U. Kuehn, H. Breitkreuz, K. Luiders and L. Schultz, 1 Institut fuer Materialwissenschaftliche Werkstoffe, IFW Dresden, Dresden, Germany, 2 Fachbereich Physik, Freie Universitat Berlin, Berlin, Germany. Although Zr-based glassy alloys that form a metastable quasicrystalline phase upon partial detwinned 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 Zn-Mg-Zn-based alloys, on the formation of quasicrystals, the deactivation of gliss [Zn61.6Zn8.4Ni9.3Al11.0Cu8.7Si7.5B2.75Te9.4Bi0.6] alloys with x = 0, 2.5, 5.0 and 7.5 at.

Therefore, Al is not essential for quasicrystal formation in the present alloys. However, due to the decrease of microgravity, Al plays a role as a stabilizer in the formation of quasicrystals. In fact, with increasing Al content, the range of stability of the microgravity 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 microgravity phase undergoes a transformation to the metallic glass 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 Schenk1,4, Virginie Simonet3 and Robert Bellissent3, Institut für Strukturphysik, DLR, Köln, Germany, 1Laboratoire Louis Néel, Grenoble, France, 2Centre d’Etudes Nucléaires, Grenoble, France, 3European Synchrotron Radiation Facility, Grenoble, France.

It was suggested already in 1952 by Frank that an isochronal short-range order should be energetically favored in undercooled melts of systems consisting of atoms of spherical geometrical symmetry. This hypothesis was recently experimentally confirmed by diffraction experiments on stable and undercooled melts of pure metallic glasses.

In this work systematic in-situ investigations on the short-range order of deeply undercooled melts of Al-Mn and Al-Mg-Mn alloys forming quasicrystalline and polytetrahedral phases by elastic neutron scattering are presented. For Al1_xMg_x (Mg) melts partial structure factors were determined which allow the analysis of both the topological and the chemical correlation order as a function of the temperature. These investigations indicate an isochronal topological short-range order prevailing in the undercooled melts which is accompanied with 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 Deactivation of Metallic Glasses.
Matthew J. Kramer1, Dan J. Sarda1 and Pete L. Lee2, Ames Laboratory, Iowa State University, Ames, Iowa, 1Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

High energy-high temperature X-ray diffraction was used to investigate the structure transformation between the short-range order (SRO) of Zr52.5Ti26.5Cu19Nb5 and Zr52.5Ti19Cu19Nb5 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 near the crystallization temperature were determined. After rapid heating, diffraction data were taken at 5 min intervals for 180 min. The difference in the S(Q) at over this time interval showed that both alloys undergo a structural relaxation prior to nucleation and growth. The RS alloys are shown to be SRO dominated by a random polyhedral configuration close to isochronal symmetry. The MM samples show SRO to medium-range order (MRO) which is topologically similar to the Mo25Ti15 structure (M4/mmm). Isotopic and tracer experiments (14N/mcm), Raman spectroscopy (14/16N/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 isochronal phase while the MM alloy forms the AlCu2-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 metastable polycrystalline structures. The work at Ames Laboratory was supported by the U.S. Dept. of Energy through Iowa State University under contract No. W-7405ENG-82. The Midwest Universities Collaborative Access Team (MUCAT) sector at the APS is supported by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, through the Ames Laboratory under Contract No. W-7405ENG-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
Transmission Electron Microscopy, XRD and EELS of Quasicrystals, on Zr40.75Ti58.5Cu7.5Be18.
Alloys: Effect of the Be in the Quasicrystal Formation.
Bertrand Van de Meulebeeke1, Jean-Marc Pelletier2, Win Van Kim3, Thierry Eggier1 and Jean-Louis Soubyroy3, 1GEMPP, INSA de Lyon, Villeurbanne, France, 2IPIC, EPFL, Lausanne, Switzerland, 3Applied Science Division, Chungbuk University, Chungju, South Korea.

Since the first observation of quasicrystal phase in a rapidly quenched Al-Mn alloy by Shechtman et al., many materials containing quasicrystals have been discovered. In particular, quasicrystalline phases could be observed in metallic glasses during deactivation. Such phases are metastable and disappear when temperature or time of ageing increases. It is well known that an increase in Be content from V11 [22.5% Be] to V14 [27.5% Be] alloy leads to the formation of a quasicrystalline phase during deactivation. Also, the quasicrystalline phase has been reported to form during crystallization of an amorphous Zr40Ti25Ni8Cu18Be alloy. In metallic glasses, the formation of quasicrystalline phase often takes place by a polynuclear transformation, i.e. this 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 quasicrystals. XRD and EELS analyses show that the quasicrystalline phase in the Zr40.7Ti58.5Cu7.5Be alloy (V14) does not contain Be, indicating that a chemical partitioning takes place during the precipitation. Measurements in the T4025Ni8Cu18Be 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 microcrystallization of amorphous-to-quasicrystalline transition in a Zr-based bulk metallic glasses.
Lin Lu1,2, K. C. Chan3, G. K. H. Pang3 and K. Z. Babakhani4, 1Department of Industrial and System Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong, 2Department of Materials Science and Engineering, Hong Kong University of Science and Technology, Hong Kong, 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 electron diffraction in the EDS is employed to monitor the structural evolution of the glass with the increase of temperature. It was found that the quasicrystal-to-quasicrystalline transformation does not follow the traditional nucleation/growth mechanism. Instead, it undergoes a sequence of intermetallic phases in 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 microtwins. 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-polymorphic reaction, and the transformation seems to be governed by the lattice self-modification.
The $Zr_{54.5}Nb_{19.36}Cu_{15.5}Ni_{12.8}Al_{9.2}$ at% alloy shows an improved bulk metallic glass forming ability compared to compositions in the $Zr-Nb-Co-Ni-Al$ system [1]. The critical cooling rate is less than 10 K/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 $Zr_{54.5}Nb_{19.36}Cu_{15.5}Ni_{12.8}Al_{9.2}$ 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 fusion for the supercooled liquid region. Isothermal relaxation and crystallization studies of $Zr_{54.5}Nb_{19.36}Cu_{15.5}Ni_{12.8}Al_{9.2}$ 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 the enthalpy decays with an activation energy of 0.53 eV. 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 Thammus 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 at a rate of about 0.1 K/s, it is to isothermal temperature. It is in good agreement with the diagrams measured by electrospray levitation [1], which was obtained by cooling to isothermal conditions from the liquid state. The large time and temperature windows over 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 $Pd_{43}Ni_{10}Cu_{32}P_{20}$ metallic glass forming alloy. Masahiro Kuno, 1 Ralf Busch, 1 and Jan Schrecken, 1
1 Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon, 2 Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, California.

Since $Pd_{43}Ni_{10}Cu_{32}P_{20}$ has a melting point below 1000K and a very low 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 possible to measure the thermodynamic properties of the supercooled liquid with great accuracy. The study was performed with supercooled liquid at a temperature $T_0$ below the glass transition temperature $T_g$, and the enthalpy change $\Delta H^\text{cool}$ upon crystallization in the same isothermal experiment for different amounts of undercooling. We thus obtained $\Delta S_0$ and $\Delta H^\text{cool}$ over the entire undercooled liquid region. Each experiment was calibrated individually with a reference run using a magnesium standard. After measuring the specific heat capacity of the crystal $c_p$, the difference in specific heat capacity $\Delta c_p$, the specific heat capacity $c_p$, and the enthalpy change $\Delta H^\text{cool}$, the values are integrated. This confirms that the approach is commonly used to calculate the temperature dependence of the thermodynamic functions is a good approximation. The study made use of very small enthalpy changes between measurements 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 high kinetics.

**MM5.3**
On the Fragility of NbNi Based Bulk Metallic Glasses. Ludi A. Shukle-Bopp 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 $Ni_{63}Nb_{37}$, $Ni_{60}Nb_{35}Sn_{5}$, $Ni_{62}Sn_{35}In_{8}$, $Ni_{60}Ti_{40}Cu_{15}In_{8}$, and $Ni_{60}Fe_{30}Sn_{31}In_{9}$ 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 driving force for crystallization and supercooled liquid region decreases. The fragility of the different alloys can be deduced by plotting the inverse heating rate for each DSC experiment versus the glass transition temperature, normalizing to the glass transition temperature for a rate of 0.0167 K/s (Angell plot). The fragility 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-Tammus (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 ($D^* = 16$). This $D^*$ increase is similarly observed in the alloy decreases, 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 melting point and their energy of formation. 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 the increase in glass forming ability with the increase of the number of components.

**MM5.4**
1 Chemical Engineering and Materials Science, University of California, Davis, California, 2 Center for Micro- and Nanomaterials, University of Ulm, Ulm, Germany.

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. 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 $\Delta S_f$, 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 consistence 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. Helling; 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 copped trigonal prism with a coordination number (CN) of nine has been discussed for many metallic glasses, and for intermetallic clusters with CN = 12 have been proposed for Al-based glasses with both solid and transition metal solutes. Recent research has established the influence of the relative size of solute and solvent atoms on the structure and stability of metallic glasses. This 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 a solute atom radii that range from about 80% of the solvent radius (CN = 8) to solute radii that are about 130% of the radius of solvent atoms (CN = 18).

**MM5.7**
Exploration of New Bulk Metallic Glasses Based on the Ti-Ni-Si System. Daniel B. Miracle, 1 Joseph Kell, 2 Samuel Findley, 2 and Wynn Sanders; 1 Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio, 2 Southern Ohio Council for Higher Education, Dayton, Ohio.

A recently developed topological model has shown that specific ratios between solute and solvent atoms are preferred in the composition of bulk metallic glasses. Further, atomic size distribution plots (ASDPs) have shown that 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 measurements have been used to explore new bulk metallic glass alloys based on the TiNi-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, Wyn S. Sanders, 1 America, MnScn, 1 Air Force Research Laboratory, Wright-Patterson AFB, Ohio; 2University of Dayton, Dayton, Ohio; 2Southwestern Ohio Council of Higher Education, Dayton, Ohio; 2Ohio University, Athens, Ohio; 3California Polytechnic State University, San Luis Obispo, California; 4US Air Force Academy, Colorado Springs, Colorado.

This paper presents a study for the development of bulk aluminum metallic glasses. 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 patterns. High critical [preferred] radius ratios that are beneficial to efficient atomic packing. Finally, appropriating alloy 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 metallic glasses 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 metallic glasses. The specific approach applied in this investigation study will be described and results will be presented.


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 addition, these alloys exhibit nanocrystalline microstructures consisting of faccentered cubic (f.c.c) Al, binary Al3Gd, and ternary Al-Ni-Fe or Al-Gd-Ni phases. It 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 deformed state. A series of imaging, diffraction, and energy-dispersive X-ray spectroscopy 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 a very close to the orthorhombic compound Al12Ni2Gd4 but that part of this phase contains embedded silts of Al2NiGd4 phase that 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 of these deformed nanocrystalline microstructures. The morphology and microstructural development of these particles, and those of the binary phase, will be discussed. References: 1. H.E. Gladyshevskii and E.Parthe Z. Kristallographie 1/8, 171-172 (1959).


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 high ductility[2]. 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 present the results of a transmission electron microscopy study on the crystal structures and morphologies exhibited by each of these phases in a set of four Al-Au-Y-Ni alloys which contain 1.74.5 at. % Y and 3.5-10 at. % Ni. It is shown that each alloy contains Au-Al, a binary phase (either Al3Au5 or Al5Au3), and a ternary phase. The electron diffraction data obtained from the ternary phase are consistent with those expected for the orthorhombic phase AI11Au5Ni3 reported by Rydhal 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 spectroscopy is not consistent with this stoichiometry. A combination of high-resolution lattice imaging and imaging conditions 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 AI11Au5Ni3, (Cmcm, a=0.4025 nm, b=0.789 nm and c=2.809 nm, Al11Au5Ni3 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 silts of the equilibrium Al11Au5Ni3 phase. The precipitation sequence which leads to the development of these distinctive ternary particles will be discussed. References: 1. R.M. Rydhal, 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. Annet Gelart, Marlyn Scoville, Margaret Uhlemeyer, Juergen Eckert and Ludwig Schulz, IMW 731, IFW 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 spining and subsequently hydrogen-charged at constant current densities of 1.5 - 1.0 mA/cm² 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 quenched and dehydrogenated 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, is that 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 Zr52Cu21Al15Ni10 and Zr55Cu20Al15Ni10, Metallic Glasses investigated by NMR. Hagen Brezloka, Klaus Lueders, Sergo Scudinno, Uta Kuehn and Juergen Eckert, 1Forschungszentrum, Freie Universitat Berlin, Berlin, Germany; 2Institut fuer Metallische Werkstoffe, IFW Dresden, Dresden, Germany.

Medium-range order and quasicrystal formation in Zr52Cu21Al15Ni10 and Zr55Cu20Al15Ni10 metallic glasses are investigated by means of magnetic resonance (NMR). The samples are prepared by rapid solidification and annealed to induce primary quasicrystal formation. 7Al and 63Cu NMR spectra and spin relaxation curves are recorded before and after the annealing process. The spin-lattice relaxation time in both amorphous and crystalline phases is of two orders of magnitude 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 7Al and 63Cu NMR spectra can be taken as a proof of the presence of medium-range order in the investigated metallic glasses. By simulations of 7Al and 63Cu second moments in various binary and Cu compounds and other medium-range order metals Al12Co2 and C114 CoZr2 can be identified in both as-quenched metallic glass. After heat treatment both metallic glasses show strong changes in the 63Cu second moment, whereas the 7Al second moment shows only relatively small changes. Furthermore, the Cu second moment after heat treatment in Zr52Cu21Al15Ni10 is about half as large as in Zr55Cu20Al15Ni10 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. Jingxin Xing, K. F. Kelton, 1Anindita Mukhopadhyay, 2W. E. Buhl, 3Department of Materials, 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 simultaneous change ordering (formation of a new oxide phase) in Ti3d transition metal-Si alloys, where the oxygen induces incosddedral 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 (Al44.3+Y45.7)Fe10(Ti, Zr, V3+ (x = 0.5, 1, 1.5) alloys significantly until 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 inducing a change in the crystallization temperature of the metallic glasses, with an increased nucleation strength. 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 these glasses micro-level doping leading to local ordering, insight that can be used in developing new metallic glasses.

**MM5.14**


For the immiscible Cu-Ta and Cu-W systems, realistic n-body potentials are derived under an embedded-atom method through fitting the structural properties 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 can be homogenized over a critical composition of 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 Cu51Ta49, Cu42Ta58, Cu44Ta56 and Cu47Ta53 multilayered films, while the crystalline Cu and Ta remain in the Cu72Ta28 multilayered sample [2], which matches well with the critical composition of the 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.


**MM5.15**

**Direct Observation of Phase Transformation in Ag/Cu Alloy System.** Hao Chen1,2 and Jin-Min Zuo1,2.

*1Dept. of Materials Science & Engineering, University of Illinois at Urbana-Champaign; 2Frederick Seitz Materials Research Laboratory, Urbana, Illinois.*

Here we report on the phase transformation process of Ag/Cu alloy from amorphous to crystalline phase separation. Amorphous alloy samples were synthesized 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 film transformed into crystalline structure when samples were heated to 800 Celsius degrees. 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 Nanomorphous Metals.** Ruzvik Malkhazyan. ATOM SPE, Erevan, Armenia.

In the given paper a new principle of obtaining nanosize amorphous metals has been presented that works 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 assumption that the corresponding crystal structure with a low degree of order in the diffraction patterns may be responsible for the activation barriers. If the activation barrier of an elementary act of chemical transformation is possible at the expense of inner energy of excitation 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 internal energy of excitation (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 internal energy of excitation of one of reagents participating in it, then the second elementary act of the same reaction can be carried out by transforming the amorphous embryo into the crystalline phase.

**MM5.17**

**Mn effect on non-collinear magnetic structure of FeMn-B amorphous alloys.** Yang Wang1, Don Nicholson2, Mike Widom3, Miguel Puentes-Osornio3,4 and Marek Mihailovic3,5.

*1Pittsburgh Supercomputing Center, Carnegie Mellon University, Pittsburgh, Pennsylvania; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee; 3Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia.*

Fe-B amorphous alloys exhibit approximately collinear magnetic structure. When a certain amount of Mn 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 selfconsistent multiple scattering (LSMS) method for supercell samples generated by ab initio molecular dynamics simulations performed using the IMPACT 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 No.N00014-01-1-0961 and is supported by DOE subcontract DE-AC05-76OR00000. The VASP and LSMS calculations were performed at Pittsburgh Supercomputing Center.

**MM5.18**

**Indium as an Additive in Ge0.78-xSb0.22x Glasses.** L.C. Cui and P. Boldsmith.

*Department of ECECS, University of Cincinnati, Cincinnati, Ohio.*

The doping behavior of the group III additive Indium in Ge0.78-xSb0.22x glasses over all ranges x, i.e. floppy (0 < x < 0.25), intermediate (0.25 < x < 0.26) and stressed rigid (0.26 < x < 1.3) reveals that the group III additives introduce phase separations in Ge0.78xSb0.22x phase leaving behind a Ge-rich base glass. The observed phase diagrams, Figs. 1, in Ge0.78xSb0.22x 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 Sb atoms. The common radius of In exceeds that of Ge by 15%. These results demonstrate that the In 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 this report is not only new but quite novel.

**MM5.19**

**Grain Boundary Dissociation in Nanocrystalline Gold.** Douglas L. Medlin1,2,3,4,5.

*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 of particular importance in nanocrystalline materials because it increases the volume fraction of material associated with interface 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 dissociation boundary structures described in these boundary structures show how the stacking arrangement within the dissociated layers is directly related to the interfacial misorientation. To illustrate, we discuss in detail the interfacial structure at 90° related grains. Boundaries in this system dissociate to form α-1 nm wide layer of material with close-packed planes arranged in the 4H stacking sequence (i.e., abc/abc/abc). Formation
of this non-FCC layer can be understood by considering the distribution of Shockley partial dislocations that are intrinsic to the interface separation, and with grain sizes in the range of 100 to 500 nm, respectively. The topography of the residual imprint as well as that of the interfacial layer was measured using atomic force microscopy. The materials studied include electrodeposited nc and Uf Ni, electrodeposited wc and Ti, and electroplated uf carbon. Different types of information about 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-AC03-76SF00098 by the Office of Basic Energy Science, Division of Materials Science.

SESSION MM6: Shear Bands and Mechanical Properties I
Chair: 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. Liu1, W. Zhang2, G. Buchholz1 and S. 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-indentation 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 macro to the micro 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 nanindentation can lead to the formation of nanoscale shear bands during active deformation in the highly strained region surrounding the indenter. 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, the effect of 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 Vitrex 1 and its composite. The indentation response models are developed numerically using both pressure-sensitive and pressure-dependent flow models. Both the materials were found to 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 crater 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 Nanindentation of Metallic Glasses. T. G. Nieh1, C. A. Shuh1, S. A. Argos2 and J. W. Walsh1,
1Materials Science and Engineering, MIT, Cambridge, Massachusetts; 2Mechanical Engineering, MIT, Cambridge, Massachusetts.

Instrumented indentation 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 glassy materials. 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 plastic deformation, 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. Benedict Moser1, Jun Mei1 and Suresh Suresh1; Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We have performed indentation in various nanocrystalline (nc) and ultra-nanocrystalline (uln) metals in the size ranges of 100 nm and 100-500 nm, respectively. The topography of the residual imprint as well as that of the interfacial layer was measured using atomic force microscopy. The materials studied include electrodeposited nc and uln Ni, electrodeposited wc and Ti, and electroplated uln carbon. Different types of information about the constraints arising at boundary junctions affect the separation of the interficial dislocations, and, thus, the boundary width. This work is supported by the U.S. Department of Energy under contract No. DE-AC03-76SF00098 by the Office of Basic Energy Science, Division of Materials Science.

SESSION MM6: Molecular Dynamics Models of Metallic Glasses.
Chair: Michael L. Falk, Fabio Alibano and Yunfeng Shi, Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

9:45 AM MM6.5
Molecular Dynamic Simulation of Nanoindentation of a Model Metallic Glass. Bulent Birer1 and J. R. Morris, Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa.

In this study, the localized plastic deformation behavior of amorphous solids was examined by molecular dynamic simulations of nanoindentation. The model system was a two-dimensional and composed of a binary alloy with a two-body Leonard-Jones potential. These simulations enable us to clearly identify the processes 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 delamination and contraction in regions involving a limited number of atoms. These shear localization regions are 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-Eg-82. This research was supported by the Director of Energy Research, Office of Basic Sciences.
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 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 nano-crystalline) concerned in this branch of metal forming. 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 nanostructure 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 lubricating role of gas bubbles, impurities, including gas bubbles, impurities, and impurities, which can be seen in several alloy compositions. We will also demonstrate how the occurrence of localized deformation in localized zones can be taken advantage of, for example, in certain metallic and amorphous materials, or their compositions, have potential in certain critical applications.

11:40 AM #M6.7 Deformation-Assisted Crystallization in an Amorphous AI-Rich Alloy. Michael Atzmüller1,2 and Wenwu Jiang1. 1Dept of NERI, 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 amorphous alloys were shown to form in several Al-rich metallic glasses at shear bands resulting from plastic deformation. 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 Al$_7$Fe$_3$O$_5$. Using nano-indentation, 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 boding, nanocrystallization occurs in the predominantly, compressive region only. Using a combination of high-resolution TEM and spatial filtering, we observe a high concentration of nanovoids in the shear bands of the tensile region only. While excess free volume is generated in the shear bands at 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.

SESSION MM7: Shear Bands and Mechanical Properties II

1:30 PM #M7.1 Deformation and Free Volume Changes in Bulk Metallic Glasses. Katherine 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 unclear. For example, the role of stress state, the effect of intrinsic healing, 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.m$^{1/2}$, 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 glasses compositions. 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$_2$Ti$_2$Cu$_5$Be$_2$ 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 #M7.2 Formation and Annihilation of Free Volume during Homogeneous Flow of a Metallic Glass. Marc Heggen1, Michael Federhofer2 and Frede Spenger1. 1Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; 2Institute for Solid State Physics, Forschungszentrum Jülich, Jülich, Germany.

Compression tests in the creep mode (constant stress) have been performed on a PdNiCu metallic glass in the homogeneous flow mode. At high stresses, the strain rate increases with time, which means that flow, free volume, and free volume dominate. At lower stresses, the strain rate decreases with time, which means that annihilation of defects is associated. 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 #M7.3 Brittle Fracture of metallic-glass matrix composites under uniaxial
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 angular shift in the measured stress-strain curve. In 
(Fe70Cu20Ni10)27Ta5Si10 metallic-glass matrix composites, in contrast, the crystalline Ta particles both promote the initiation of shear bands and control 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 discernable load drops in the early stages of plastic deformation. As a result, the mechanical behavior of the bulk metallic glass is far more homogeneous than for the single-phase glass. In order to further understand the mechanical behavior 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 behavior 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 behavior 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. Laud; MateriScience 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 and amorphous 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 to the available experimental data for nanocrystalline metals.

2:45 PM MM7.5

Ratchetting of Bulk Metallic Glasses, Wendelin J. Wright, R H Dussard and W D Nim; MateriScience 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 torsion, commonly known as ratchetting, has been extensively investigated in stainless and carbon steel alloys, but not in bulk metallic glasses. Various forms of ratchetting may have potential for manufacturing techniques to overcome the limited ductility of monolithic metallic glasses and achieve large plastic strains or room temperature. We have successfully demonstrated the application of this ratchetting technique of cyclic torsion with superimposed tension for polycrystalline Ti-Nb4-V, and our stability analyses demonstrate that the plastic flow behavior of monolithic metallic glasses is an important parameter in the plastic constitutive behavior such as metallic glasses should be stable under cyclic torsion. Experimental results will be presented for amorphous Zr41.5Ti4.5Cu25Ni10Be22.5, 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, Eric Ustundag, Bjorn Clause, Seung-Yub Lee, Gregory S. Walsh and Mark A. M. Bourke; Materials Science, California Institute of Technology, Pasadena, and Lujan Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico.

Bulk metallic glasses (BMG) have superb mechanical properties: yield strength of about 2 GPa, fracture toughness of up to 140 MPa m1/2 and elastic limit of 2%. BMGs can also be processed into intricate shapes similar to polymers. Unfortunately, monolithic BMGs fail catastrophically under uncontrolled deformation by forming shear bands. To overcome this brittleness of BMG matrix composites with fiber and particulate reinforcements were proposed. We have recently investigated the deformation behavior of composites with W, Mo, Ta and W-Ta fibers [1, 2] as well as in-situ composite with crystalline denticryl inclusions [3]. Tensile measurements were performed using in-situ neutron or high-energy X-ray diffraction to determine the lattice strains in the crystalline reinforcements. The difficulties in characterizing the composite material are then combined with finite element and self-consistent modeling to determine the behavior of the matrix. It was shown that the usual reinforcement 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 I. B. Clause, 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], 123-129 (2003); 2. S. Y. Lee, B. Clause, E. Ustundag, H. Choi, C. C. Aydiner, R. D. Conner and M.A.M. Bourke, "Composite Behavior of Wire Reinforced Bulk Metallic Glass Matrix Composites," submitted to Scripta Mater. [2003]; 3. D. K. Balch, E. Ustundag and D. C. Dunand, "Elastic-Plastic Load Transfer in Bulk Metallic Glass Composites during Axial Strain," Metall. Mater. Trans. (2003); 4. B. Clause, S. Y. Lee, E. Ustundag, C. C. Aydiner, R. D. Conner 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

Nanoscale deformation mechanism on PLD nanocrystalline Ni (Hupei Sheng1, J A Knap2, and Scott X Mag3); Materials Science Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania. 4 Materials Science Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania. 5 MS 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 the 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 Kirkin, K Ted Hartwig, Jui-Tsung Lin, Steven N. Mathias, Amish 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 108a (Zr58.5Sc6.5Ni11.5Ga21.5) plus 80, 70, and 80 vol.% pure tungsten blended powders at temperatures between Tg and Tm for the glassy metal phase. The effects of extrusion temperature, amount of extrusion passes and can material were investigated. In certain cases, the fine and dense, 12 mm diameter composites of metallic glass matrix composite is achieved after only one extrusion. Microstructure and hardness of the ECAE consolidated were examined and compared with those of the initial powder and consolidated pure metallic glasses. Metallography results show good infiltration of the amorphous Zebased 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 on selected extruded 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-rich 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 Research Projects Agency.

4:15 PM MM7.9
Anomalous Low Fatigue Endurance Limit of a Zr-Based Bulk Metallic Glass. Brian Mensel 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 Ti_{56}Zr_{44}Cu_{27}Be_{16} using a four-point bend configuration. The early stages of damage initiation and propagation on the maximum tensile surface of the specimens 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 precipitates 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 ~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 crack growth rates at a 2k times the nominal fatigue threshold. 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. Hsu 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. In particular, complex fatigue loading can occur in BMGs. The present study examines the effects of variable amplitude fatigue loading associated with block loading and tensile overload loading on fatigue crack growth rates in a Zr-based BMG. Crack growth studies were conducted on compact tension specimens using a computer control of the applied stress intensity range, \( \Delta K \). 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 \( \Delta K \) were found to significantly decrease fatigue crack growth rates for lower yield strength, and an increase in load at a k time the nominal fatigue threshold, \( \Delta K_{\text{fat}} \). Conversely, an abrupt increase in \( \Delta K \) was found to accelerate fatigue crack growth rates. The effects of crack closing load and crack closure load were 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 carefully assessed. As BMGs are band directed 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

High-cycle fatigue (HCF) studies were performed on zirconium (Zr)-based bulk metallic glasses (BMGs): Zr_{60}Ti_{15}Cu_{27}Be_{16}, Zr_{60}Ti_{16}Cu_{25}Be_{18}, and Zr_{60}Ti_{17}Cu_{20}Be_{13}. In all experiments, a high-speed mechanical testing machine was used at a frequency of 10 Hz with a R ratio of 0.1 and under tension-tension loading, where \( R = \sigma_{\text{min}} / \sigma_{\text{max}} \), where \( \sigma_{\text{min}} \) and \( \sigma_{\text{max}} \) are the applied minimum and maximum stresses, respectively. The test environment was air and vacuum. High-speed high-sensitivity thermographic-infrared (IR) imaging system has been used for nondestructive evaluation of temperature evolution during fatigue testing. BIMD evolution was observed during fatigue. However, no sparking phenomenon was found at the final fracture moment of Zr_{60}Ti_{15}Cu_{27}Be_{16}. At high stress levels (the maximum stress > 864 MPa), the fatigue lives of Zr_{60}Ti_{15}Cu_{27}Be_{16} were lower than those of Zr_{60}Ti_{16}Cu_{25}Be_{18} or Zr_{60}Ti_{17}Cu_{20}Be_{13}. Moreover, Zr_{60}Ti_{17}Cu_{20}Be_{13} is somewhat greater than that of Zr_{60}Ti_{17}Cu_{20}Be_{13} in air. The fatigue lives in vacuum are generally comparable with those in air. The cracking behavior of the BMG during fatigue was analyzed and predicted. The present work is supported by the National Science Foundation (NSF) and the Joint Materials Research Foundation (JMRF) Program under DGE-09039188, and the International Materials Institute (IMI) program under DMR-0231320. With Ms. M. Posts, and Drs. P. W. Jennings, L. S. Goldberg, and C. Huber as contract monitors.

SESSION MM8: Poster Session II
Chairs: Ralph Busch and Todd Huthaug
Wednesday Evening, December 3, 2003

Exhibition Hall D (Hynes)

MM8.1
Senthil Nathan Sambandam ¹, Sherkat Bhansali¹ and Venkat R. Bleihamanbad², Electrical 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, the mechanical properties, hardness and Young’s modulus were studied in Zr-Ti-Cu-Ni-Be films deposited by DC magnetron sputtering in view of exploring their potential technological applications in fields such as MEMS. The structure, composition, surface morphology, mechanical properties viz., hardness and Young’s modulus were characterized 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 on the composition and surface morphology of these films has been established by SEM, XPS and AFM analysis, showing that such a process yields very smooth films with target composition at lower 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 higher pressures (~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

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 Zr60Ti17Cu12Sn10, Ti60Cu20Ni20Sn8, Cu70Zr30Ti10, Fe56Co7Ni7Zr10B20, Ni60Ni20Ti12Zr2Fe7.5, and Fe56Co7Ni7Zr10B20. The MA of the elemental blend has been carried out in a Fuchs Pomeritter 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 diffraction, differential scanning calorimetry, scanning electron microscopy and electron microscopy. The results indicate that the 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 by the statement that the molar crystal structure is a function of the local concentrations. Thus, a nonuniform alloy composition leads to a nonuniform crystal structure, which, in turn, generates a state of geometrically necessary eigenstrain as well as an associated state of elastic transformation. The elastic transformation is defined as the (traditional) stress-associated elastic deformation, which is well understood in classical continuum mechanics. The eigenstrain transformation is a direct result of the nonuniform composition and may, therefore, be interpreted as a material or configurational deformation. The process of the [traditional] transformation rate is the deformation rate 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 transformation rate is the density of works. 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 bivariate interface is merely the intersection of two elastic bodies of different moduli over certain coordinates, and the eigenstrains are to be enforced. Those 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 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, 1771-1784. [2] Wu, C.H., 2002. Chemical potential and energy momentum tensor in single phase mixtures. Mech. Research Commun. 29, 493-499. [3] Wu, C.H., 2003. A crystal structure-based eigenstrain transformation 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.**


Experimental investigation into the Vickers hardness and the associated plastic deformation in as-cast and subsequently annealed [to induce partial to full crystallization] Pd$_4$N$_2$P$_{14}$ and Zr$_2$Co$_7$Al$_4$:Ni$_4$ bulk metallic glasses was conducted. Results show that the hardness of bulk metallic glasses is ~3.2 GPa, indicating pressure sensitivity. In addition to the bulk indentation behavior, the deformation morphology underwent the indentation and its variation with annealing was examined by employing the bonded indentation 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 being created. The results illustrate that when the alloys are fully crystallized, for both the bulk and the indentation loading, 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 adds 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 Mehdi-Coulomb type yield criterion into the deformation models. These observations are compared with similar studies made on ductile metals and silicone 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/HA Based Bulk Metallic Glasses.**

Hao Li, Ghata Shishak L, Lanzo J. Keeskes, and Robert J. Dowding.

Quasi-static and dynamic uniaxial compression tests on cylindrical specimens of Zr/HA-based metallic glasses with compositions [Hf$_{87}$Zr$_{22}$SG55Ni$_{66.6}$Co$_{19.2}$Al$_{10.4}$] (x = 0.2, 0.4, 0.6, 0.8, 1.0) and Zr$_{100}$ (x = 0.2, 0.4, 0.6, 0.8, 1.0) revealed that the failure stresses for both the glasses decreased with increasing strain rate in the 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 higher incipient 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 influence of shear band nucleation on the negative strain rate sensitivity of failure strength in these metallic glasses.

**MM8.6**

**Infiltration Processing of Woven Metal Matrix Composites.**

Lance Sklansky, Brian Edwards and Robert Woodman.

AMRL-W-MM-003, 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/cm$^3$ has been used to infiltrate open-porosity W powder to create W-BAM composites with densities reaching 10 g/cm$^3$. 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. Once solid, sintered nanocrystalline BAM, the time at temperature on the composite structure was 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 Rastke, Juergen Eckert, Milun Stoja and Ludwig Schultz.

We report about the microstructure, thermal stability and the mechanical properties of slowly cooled Zr-Ni-Cu-Ni-Al alloys with ducile bcc phase precipitates embedded in a glassy or a nanocrystalline alloy matrix. The samples were prepared in form of rods by injection casting into a copper mould. The phase formation and the microstructure of the composite material were investigated by X-ray diffraction, DIL analysis, scanning and transmission electron microscopy. The thermal stability was examined by differential scanning calorimetry and the mechanical behaviour was investigated by compression tests and quasistatic loading at room temperature. The formation of bcc phase dendrites and a glassy or a nanocrystalline alloy 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 phase fraction and size of the bcc phase precipitates as well as to differences in 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 samples exhibit 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-Co-Al-Ni glass composite containing second-phase ZrC particles.**

German Alcala, Sonin Mato, Stefano Decker, Jurgen Eckert, Annett Gehrert and Ludwig Schultz.

Institute for Metallic Materials, IPFW 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 approached to improve the performance of these materials by reducing crack propagation. The present work analyses the influence of a nanometer-size ZrC particles on the nano-mechanical behavior of mechanically alloyed Zr55Co22Al15Ni9 glassy matrix composites. The volume fraction of ZrC particles ranged from zero up to 30 vol. % and showed 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-Ga-AlN-G 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 nan indentation and nanocrack, have been investigated by combination of the nano-mechanical tests and scanning probe microscopy.

**MMR 0**

**Mechanical Behavior of Bulk Glasses**

B. Cla, Cr,Mg,Ga,P, C, S, M. Steina, N. Rudicka, J. Eckerta, S. Roth, G. Alexha, A. Gebert, L. Schultz, W. H. Wang2 and Y. H. Zhao,

2Metastable and Nanostructured Materials, IPFW Dresden, Institute for Metallic Materials, Dresden, Germany; 3Institute of Physics, Chinese Academy of Sciences, Beijing, China.

The bulk amorphous Fe-based alloy with the nominal composition Fe〈2.5〉Cr〈5〉Mg〈15〉Ga〈15〉P〈22〉S〈10〉 was obtained by copper mold casting in diamond dies. The rectangular rods 1 cm x 2 mm or 2 cm x 1 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 Hc is below 10 Oe, the magnetic anisotropy is 8 to 10 T and the magnetostriiction <3 ppm. Using spectroscopic 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, nanodeformation, and by an ultrasonic technique. The Young’s modulus E was found to be around 150 GPa, the yield strength σy around 3 GPa and the fracture strength σf around 5 GPa, together with elastic strain εy = 2% and fracture strain νf = 2.3%. The Vickers hardness HV 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 dimensions, as well as in comparison with other published data for different amorphous alloys.

**MMR 10**

**Thermal Stability and Mechanical Behavior of Bulk (ZrHf)TiCuNiAl Amorphous Alloys. Hongwen Zhang1, Ghauri Subhrai2 and Linaco J. Keskes1,**

1Dept of Material Science & Engineering, Michigan Technological University, Houghton, Michigan; 2Dept of MLE, Missouri University of Science and Technology, Rolla, Missouri; 3US Army Research Laboratory, Weapons and Materials Research Directorate [AMSLR-WMD], Aberdeen Proving Ground, Maryland.

The thermodynamic behavior and mechanical properties of bulk Zr/Hf-based amorphous alloys with composition (Hf,Zr)〈52.5〉Ti〈14〉Cu〈15〉Ni〈15〉Al〈10〉 (z=80, 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 nanoindentation and microhardness 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 may result from the microstructural changes with increasing Hf content.

**MMR 11**


1IPFW 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 glasses (BMG) forming alloys such as Ti-Cu-Ni-Sn results in a composite microstructure consisting principally of primary dendrites in a nano-crystalline matrix [1]. The dendrite phase in Ti46Cu34Ni14Sn10 has been previously found to be the ternary solid solution beta-Ti(Nb,Sn) [1] and TEM results, presented here, show that the nano-crystalline matrix consists of a eutectic of two phases of the bcc structure. The presence of the dendrites acts as a barrier to the grain propagation resulting in significantly ductility in another otherwise brittle material [1]. Previously published data showed compressive plastic strain greater than 14% in Ti46Cu34Ni14Sn10 [1], however, tensile tests, presented here, show much smaller values (5%) 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 thermostapical 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 choose the melting temperature. 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, 38-47

**MMR 12**

**Synchrotron Strain Measurements for In Situ Formed Metallic Glass Matrix Composites. R.T. Ott, F. Sistare, J. F. Molinari, C. Pan’ and T. C. Hufnegel,**

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 (Ni,Al)〈50〉Cu〈30〉Al〈20〉 series of alloys which consists of an amorphous matrix reinforced with in situ formed Ti-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 are 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 shearing band formation. In order to study the micromechanics associated with these composite materials, we have used high-energy synchrotron X-ray scattering to perform in situ strain measurements on the Ti-rich particles during uniaxial compression. By measuring the lattice strains present in the crystalline reinforcing phase, we have examined the phase 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 Ti-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.

**MMR 13**

**Tensile Creep Deformation Behavior and Microstructural Evolution in Zr41.2-Ti18.8-Cu12.5-Ni10-Be22.5 Metallic Glasses. Balent Biner, D. J. Sivadek, D. K. Rebhien and X. Yang;**

1Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa.

Concurrent tensile creep tests were performed on Zr41.2-Ti18.8-Cu12.5-Ni10-Be22.5 (atomic %) at 325 °C at different stress levels up to 300 hours. Nanoindentation with Berkovich indenter on the gauge section of the creep samples 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 dependence of the creep exponent of Newton’s power law for this glass system is also correlated in terms of brittle fracture 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.

**MMR 14**

**Plasticity in Ni-based metallic glass matrix composites reinforced by brass-fiber were synthesized by atomization of powders. Donghyun Bae and Minha Lee;**

1Metallurgical System Engineering, Yeonsu University, Seoul, South Korea.

The study is aiming at understanding the deformation behavior of centimeter-scale Ni-based metallic glass matrix composites (MGCs) reinforced by brass-fiber at room temperature. The MGCs are synthesized by warm extrusion of gas-atomized powders. Throughout the extrusion process, all bimodal spherical powders in the range of 10 to 70 micrometer 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 the volume fraction for the MGCs. 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 their configuration during deformation is the melt-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.


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 Ag-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, Ivo Mccracken and Ralf Bauch, Department of Mechanical Engineering, Oregon State University, Corvallis, Oregon.

The focus of this work 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 polycrystalline Cu and then plated with steel substrates, that were inserted into the mold. The BMG used was Vitrelloy 1, 

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 with Cotton L. Maria A. Castellanos R. and David Diaz, Facultad de Química, Universidad Nacional Autónoma de Mexico, Mexico, D.F., Mexico.

Cotila Romi L., Maria A. Castellanos R. and David Diaz, Facultad de Química, Universidad Nacional Autónoma de Mexico, 04510, Mexico, D.F., MEXICO. Following a novel silver nanoparticle synthesis pathway spontaneous reduction of silver tetrahexamethionate 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 manganese 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%]. The mixtures were homogenized by wet grinding, in an agate mortar, using nacette as dispersion medium. We used pellets made of dried react ion mixtures, of one centimeter in diameter, pressed at 2.5 bar for one minute. The pellets were calcined from 500°C to 1200°C 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).

SESSION MM8: Structure and Solid State Reactions

Chair: Annet Gerber and A. R. Yasuri

Thursday Morning, December 4, 2003

Republic B (Sheraton)

8:30 AM **MM8.1** Positrons, atoms and molecules as probes in metallic, oxide and polymeric glasses. Heiner Kreisheimer, Institut fuer Materialphysik, Universitaet of Goeppingen, Goeppingen, Germany.

Interatomic or intermolecular sites which can be occupied by small particles differ with respect to the possible intervention of 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 all the lifetime of positrons in polymers depends on the site where it is located. Laser induced positronium formation in polyethylene. The POSE investigation showed that positronium formation is sensitive to the chemical environment. The capture and annihilation of positrons can be used to probe structural changes and metal atomic environment.

9:00 AM **MM8.2** Atomic structure of AI-based metallic glasses through the glass-liquid transition. Kyungsoo Ahn1, Despin Louca2 and G. J. Shiflet2. 1Physics of University of Virginia, Charlottesville, Virginia; 2Materials Science of University of Virginia, Charlottesville, Virginia.

AI amorphous alloys with an AI content of ~ 90% by weight and with specific structure have been discovered within the Al-TM-Ni (TM = transition metal, RE = rare-earth metal) system. Neutron scattering studies on the Al-Ni-Nb system using the same 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 strongly dependent on the Al-Ni bond, while Ni plays an important role in forming strong Al-Ni bonds. Ni enhances the formation of the Al-Ni bond, enabling the use of Al-Ni glasses. Al-Ni glasses are expected to have a high local atomic environment, which is quite different from the Al-RE environment due to differences in the interactions of Al with the TM and the RE. These differences indicate the presence of a strong glass transition in the liquid phase. The local atomic structure of the Al glass and how it changes as it goes through the glass transition.

9:15 AM **MM8.3** Efficient Local Packging In Metal 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 electron beam 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. The present research extends this methodology 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 measured values of atomic radii and the experimentally determined solute atomic 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 measured 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-containing Metallic Glasses Measured by X-ray Microscopy
William Gregory Straton, Paul M Voyles, Joe Haimann and John H Pettepeto; 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 diffraction electron intensity from nanoscale volumes. [1] Here we use a high Al-content metallic glass 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 (melting) show a high density of pure Al nanocrystals at low temperatures (ca. 293°C) due to 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 19-01-1-0886 and DAAD 19-01-1-0895). P. M. Voyles, J. M. Gibson, M. M. J. Treacy, J. Electron Microsc. Tech. 250 (2001) 160-167 and H. Wilde, H. Sieber, J. H. Pettepeto, Scripta Mater. 40, 779 (1999).

9:45 AM MM9.5 On the Structural Characterization of a Series of Novel Ni-Nb-Sn Refractory Alloy Glasses, Michelle Tokoy 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, synchrotron radiation sources, SEM, and other complementary techniques. A comparison between x-ray diffraction results obtained from synchrotron sources vs. standard lab sources showed the necessity of a low-background x-ray 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 analysis, were presented. By studying results from glasses of different composition, it is seen that a very small composition range exists for new-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 neighbor as indicated by the divergence of the experimental reduced radial distribution functions from those predicted by the accompanying hard-sphere models. This work was performed with support from DARPA under contract number: DAAD19-03-1-0525, DOE for use of synchrotron facilities at SRSRL (Stanford Synchrotron Radiation Laboratories).

10:30 AM MM9.6 Structural Relaxation and Crystallization in a PD44Cu18Ni3P2 bulk metallic glass, Rejin Rajgopal, Upadhyata Ramamurthy, Joyasurya Basu, Srinivasan Ranganathan and N. Nichiyama; Materials Science and Engineering, Stanford, CA.

The stability of a PD44Cu18Ni3P2 bulk metallic glass (BMG) is investigated by isothermal annealing heat treatments below and above the glass transition temperature, Tg, for varying periods. Dynamic differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) were utilized in probing the structural changes that occur during annealing. DSC scans of the samples annealed below the Tg exhibit a sharp endotherm that collapses with the Tg of the sample. 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 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 Tg (at 1.1 Tg), crystallization ensues with the volume fraction of the crystallites increasing with annealing time and temperature. TEM reveals that the constituent phases are to be faced with PD44Ni3P4, PD44Cu18P2, Ni3P and Cu3P compositions. In-situ heating of the samples was carried in order to identify the sequence of the phase evolution and the compositional variation during crystallization. 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 Nicholls1,2, Stanislav Sinogeikin3, John Kieffer1 and Jay Bass1,2; 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-B2O3) 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 spectroscopy and measurements along the compression and decomposition paths. Upon compression, the shear and longitudinal sound velocities gradually increased and the 808 cm⁻¹ boron 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 decomposition no Raman modes were observed above the discontinuity at 3 GPa. After the transition, the 808 cm⁻¹ boron 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 polymorphs and lab synchrotron density-limited phases present within the density-disordered phase. The discontinuity at 3 GPa coincides with the transformation between trigonally and tetrahedrally-coordinated phases in crystalline B2O3. Thus, we surmise that upon pressure increase the boron 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 boron rings and a metal 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 Films, Alan Duckham1, Albert J Switzer2, Jon Trenkle3, Etienne Benaon4, Omar M Kno5, Todd J Huftagel1 and Timothy P Wells6; 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 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 and reaction over an area that is large enough that when an energy impulse initiates local mixing and an associated release of heat, the formation reaction becomes self-propagating in an atom diffuse normal to the layers and heat diffuses parallel to the layers. We have investigated several molar ZrAlO3/B2O3 nanomeshes, 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 were determined 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 verified by independent measurements. Furthermore, the cooling rate is varied by placing the foil 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 Stressed Amorphization of Cementite in Iron-Cementite Nanocomposite, Eugene Pet Yelshakov and Gennady Alexeevich Dorofeev, Non-equilibrium Metallic System Laboratory, Physical-Technical Institute URL RAS, Izhevsk, Russia, 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 Fe-C alloy at 600°C under equilibrium and non-equilibrium conditions. The structure and magnetic properties were determined using the amorphization under stress. The degree of amorphization was calculated using the amorphization according to the magnetic characteristics of the samples and their dependence on the stress. The results of the calculations were compared with the results of the x-ray diffraction and magnetic measurements. The degree of amorphization was found to be dependent on the stress and the temperature of the samples.

SESSION MM10: Applications and Environmental Effects
Chair: Jurgen Paul and Daniel Miracle
Thursday, December 4, 2003

1:30 PM MM10-1
Applications of Bulk Amorphous Alloys, Akshon 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 engineering applications has been limited, as the mechanical properties of these alloys are not as well understood. The mechanical properties of amorphous alloys are affected by their composition, their microstructure, and the processing techniques used to produce them. The mechanical properties of amorphous alloys can be tailored to meet specific engineering requirements by controlling the composition, microstructure, and processing conditions. The mechanical properties of amorphous alloys can be characterized by their yield strength, tensile strength, and fatigue properties. These properties are important in determining the suitability of amorphous alloys for specific applications. The mechanical properties of amorphous alloys can be optimized for specific applications by controlling the composition, microstructure, and processing conditions. The mechanical properties of amorphous alloys can be tailored to meet specific engineering requirements by controlling the composition, microstructure, and processing conditions.
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 10% 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 desorbed 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. Nobuaki Nishiyama1 and Akihisa Imoue2, 1RIM COF Tohoku Univ., Lab., RIMCOF, Sendai, Miyagi, Japan; 2IMR, Tohoku Univ., Sendai, Miyagi, Japan.

Bulk metallic glasses (BMGs) exhibit unique and excellent properties such as ultrahigh 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, viscosity 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, Pt, In, Mg-based alloys. If the BMGs are composed of commercial metal elements, the application of BMGs will be extended. On this point of view, we try to prepare industrial products using new Ni, Cu, and Pb-based BMGs for 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 Eifreij, Biomedical Engineering, Purdue University, Lafayette, Indiana.
The average lifetime of an orthopedic implant (such as hip, knee, etc.) is 10-15 years. However, 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 nanometer 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 nanostructured compared to conventional ceramics, polymers, and composites thereof. For this reason, results of this study add 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 orthopedic implant applications.

3:00 PM MM10.5
Catalytic Properties of High-Density Monodisperse Metal Nanostructures. ILSN Vasilyev1, Vladimir M Kozhevnik1, Tat’yana N Rostoshchikova1, Denis A Yasyn2, Mikhail A Zakhar1, Pavel A Tret’jakova1, Vladimir V Smirnov2 and Sergei A Gurevich1; 1 Centre of nanomaterials, University of Technology, St Petersburg, Russian Federation; 2 Moscow State University, Moscow, Russian Federation.

We report on ultrahigh-catalytic activity of high-density monodisperse Cu and Ni nanostructures fabricated by newly developed liner electrodeposition technique. In these techniques 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 4·10^17 cm^-2 for Cu and 1.6·10^13 cm^-2 for Ni. Both Cu and Ni particles have amorphous structure. The catalytic properties of copper nanostructures were studied in ethanol/water 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 nanostructured Cu catalyst. The activity of Ni structures was tested in the reaction of naphthalene 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 activity is due to interparticle interaction, which results in the appearance of negatively charged particles in densely packed platinum films. These changes are generated due to thermally activated interparticle electron tunneling. Strong local electric fields related with these charges (field strength up to 4·10^9 V/cm) offer further 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 electrodeposition technique.

3:15 PM MM10.6

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 description has to be avoided, e.g. by formation of a dense oxide scale. Oxidation kinetics for example for Zr60Cu20Ni20Al5 glasses seems to be controlled by oxygen diffusion through the scale towards the ZrO2 glass interface and can be slowed down significantly by Be or other additions of some other alloying elements, e.g. Sn or S. The continuous scales consist of tetragonal ZrO2; Cu, Ni and Al forming monocrystals between the ZrO2 glass, which are probably protected by a thin native ZrO2 layer localized nucleation of the oxidization 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 monocristalline as well as coarse crystalline alloys of similar composition. Some evidence was found for highest oxidation resistance in the monocristalline material. Segregation at crystal surfaces or grain boundaries might be responsible for forming barriers with a higher oxidation resistance.