

SYMPOSIUM L

Supercooled Liquid, Bulk Glassy, and Nanocrystalline States of Alloys

November 27 – 30, 2000

Chairs

Reinhold H. Dauskardt

Dept of MS&E
Stanford Univ
Bldg 550 Rm 550G
Stanford, CA 94305-2205
650-725-0679

Akihisa Inoue

IMR
Tohoku Univ
Sendai, 980-8577 JAPAN
81-22-215-2110

William L. Johnson

Dept of Matls Sci
California Inst of Technology
MS 138-78
Pasadena, CA 91125
626-395-4433

A. Reza Yavari

Inst Natl Polytechnique de Grenoble
LTPCM-CNRS
St-Martin-Heres, 38402
FRANCE METROPOLITAN
33-4-76826516

Proceedings published as Volume 644
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

SESSION L1: ATOMIC AND ELECTRONIC
STRUCTURE

Chairs: Hans Joerg Fecht and Franz Faupel
Monday Morning, November 27, 2000
Room 200 (Hynes)

8:45 AM *L1.1

LOCAL ATOMIC STRUCTURES OF Zr-BASED BULK AMORPHOUS ALLOYS BY THE AXS AND EXAFS METHODS.
Eiichiro Matsubara, Institute for Materials Research, Tohoku University, Sendai, JAPAN; Shigeo Sato, Muneyuki Imafuku, Junji Saida; Inoue Superliquid Glass Project, ERATO, Sendai, JAPAN; Akihisa Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Zr-based alloys show very different crystallization processes depending on their constituent elements. For example, in a Zr-Al-Ni system, a bulk amorphous alloy exhibiting an extremely wide supercooled liquid region is produced. The temperature span of supercooled liquid region reaches 77 K in an amorphous Zr-15%Al-25%Ni alloy. By replacing a part of Ni atoms with Pt atoms in a Zr-Al-Ni system, nano-meter sized quasicrystals are formed by annealing the as-quenched amorphous Zr-6%Al-10%Ni-14%Pt alloy. In the present study, local atomic structures around certain constituent elements, such as Zr and Ni in the ternary amorphous and crystallized alloys, and Zr, Ni and Pt in the quaternary amorphous and quasicrystallized alloys, have been investigated by both of the anomalous X-ray scattering (AXS) method and the EXAFS method, so that their atomic structures have been revealed in the amorphous and crystallized or quasicrystallized states and the role of the constituent elements, especially Pt, in the formation of quasicrystals will be discussed from the structural points of view. In addition, atomic structures around Pt and Zr have also been studied in the binary Zr-Pt and ternary Zr-Ni-Pt systems, where a single quasicrystalline phase is also obtained. The system containing less elements enables us to determine further details of their atomic structures. By comparing these results with that in the quaternary system, the presence of a strong atomic correlation between Pt and Zr pairs in the amorphous state as well as the quasicrystalline state has been confirmed.

9:15 AM L1.2

CRYSTALLIZATION BEHAVIOUR OF $Zr_{65-x-y}Ti_xCu_{22}Ni_{13}Al_y$ BULK METALLIC ALLOYS BY IN-SITU NEUTRON DIFFRACTION. Jean-Louis Soubeyrou, Nicolas Claret, Laboratoire de Cristallographie/CRETA, BP 166, Grenoble, FRANCE.

New bulk metallic glasses are attractive due to their specific mechanical properties, in particular yield strength [1-2]. The occurrence of a glass transition at a moderate temperature T_g enables a good workability in a relatively wide range of temperature (80), up to the crystallisation temperature T_x . We have performed in-situ neutron diffraction crystallisation experiments on a Zr-Ti-Cu-Ni-Al alloy [3] and we have shown that the first phase appearing at the first DSC crystallisation peak is an icosahedral phase, meaning that in the glassy state the short range ordering must be of icosahedral type. We present the study of an enlarged area of stability of this alloy by varying the compositions in titanium and aluminium for $0 < x < 7.5$ and $5 < y < 16$ respectively. This work reports on various formulations of Zr-Ti-Cu-Ni-Al alloys studied by DSC experiments and in-situ neutron diffraction crystallisation experiments that have been performed at the same heating rates as the DSC experiments in order to attribute the different transitions to the apparition or disappearance of binary or ternary crystallised phases. [1] W.L. Johnson, Mater. Sci. Forum, 225-227 (1996) 35. [2] A. Inoue, T. Zhang and T. Masumoto, Mater. Trans. JIM, 31 (1990) 425. [3] J.L. Soubeyrou, J.M. Pelletier, R. Perrier de la Bathie, Physica B 276-278 (2000) 905.

9:30 AM L1.3

SHORT RANGE CHEMICAL ORDERING IN BULK METALLIC GLASSES. P. Asoka-Kumar, J.H. Hartley, R.H. Howell, P.A. Sterne, T.G. Nieh, Lawrence Livermore National Laboratory, Livermore, CA; K.M. Flores, D. Suh, R.H. Dauskardt, Department of Materials Science and Engineering, Stanford University, Stanford, CA.

We provide direct experimental evidence for a non-random distribution of atomic constituents in $Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$ bulk metallic glass using positron annihilation spectroscopy. The Ti content around the open-volume regions is significantly enhanced at the expense of Ni and Cu. Our results indicate that Ni and Cu atoms closely occupy the volume bounded by their neighboring atoms while Al, Ti, and Zr are less closely packed, and more likely to be associated with the open volume regions. The overall distribution of elements seen by the positron is not significantly altered by annealing or by crystallization. Theoretical calculations indicate that the observed elemental distribution is not consistent with the known crystalline phases Zr_2Cu and $NiZr_2$, while Al_3Zr_4 shows some of the characteristics seen in the experiment. Results from bulk metallic

glass subjected to stress, hydrogen charging, and annealing will also be presented. This work is performed under the auspices of the U.S. Department of Energy and Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

9:45 AM L1.4

STUDY OF THE ELECTRICAL RESISTIVITY CHANGE UPON PHASE TRANSFORMATION IN Zr-BASED METALLIC GLASS.
Keiko Komatsu, Ryuji Tamura, Shin Takeuchi, Science Univ of Tokyo, Dept of Materials Science and Technology, Chiba, JAPAN; Tadaharu Shibuya, Toyo Univ, Faculty of Engineering, Saitama, JAPAN.

Since the first report on precipitation of icosahedral phase from Zr-based metallic glass by Koster et al. it has been found that in many Zr-based multicomponent systems metallic glasses are capable of forming the I-phase in the supercooled region. The aim of the present work is to investigate resistivity changes induced by phase transformation from amorphous to quasicrystal and from quasicrystal to crystal in Zr-based metallic glass. Alloys produced by arc-melting under argon atmosphere were melt-spun to obtain an amorphous phase. For samples of an amorphous phase the electrical resistivity was measured by the four-probe method in the temperature range between 12K and 1073K. The result of the DSC measurement for $Zr_{70}Ni_{10}Pd_{20}$ shows two consequent exothermic peaks at 683K and 773K, respectively. X-ray diffraction measurement for the samples annealed at temperatures above the first peak and above the second one demonstrate formation of an icosahedral phase and a Zr_2Pd crystalline phase, respectively, indicating that the first peak and the second one in the DSC curve correspond to the phase transformation from amorphous to I-phase and from I-phase to crystalline phase, respectively. The electrical resistivity decreases monotonously from 12K to 683K and is followed by a sharp increase above 683K, due to transformation to I-phase. The resistivity continues to increase with increasing temperature and suddenly drops at 773K owing to the transformation to crystalline Zr_2Pd .

10:30 AM L1.5

CRYSTALLIZATION OF AMORPHOUS $Cu_{47}Ti_{34}Zr_{11}Ni_8$.
S.C. Glade, J. Löffler, S. Bossuyt, W.L. Johnson, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA; M.K. Miller, Microscopy and Microanalytical Sciences Group, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN.

The results of a study on the crystallization of amorphous $Cu_{47}Ti_{34}Zr_{11}Ni_8$ with the use of differential scanning calorimetry (DSC), transmission electron microscopy (TEM), X-ray diffraction (XRD), field ion microscopy (FIM), atom probe tomography (APT), and small-angle neutron scattering (SANS) are presented. These experimental techniques were used to characterize as-prepared samples and specimens heat treated at different temperatures around the glass transition temperature. SANS and APT revealed that the alloy decomposed into copper-enriched and titanium-enriched regions prior to nucleation and growth of a crystalline phase. TEM revealed that this crystalline phase had a face centered cubic structure. Research at the Oak Ridge National Laboratory SHaRE User Facility was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC, and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities.

10:45 AM *L1.6

STRUCTURAL STUDY OF Fe-BASED GLASSY ALLOYS WITH A LARGE SUPERCOOLED LIQUID REGION. Muneyuki Imafuku, Shigeo Sato, Inoue Superliquid Glass Project, ERATO, JST, Sendai JAPAN; Eiichiro Matsubara, Akihisa Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Fe-based glassy alloys with a large supercooled liquid region have been found in a number of multicomponent systems such as Fe-(Al, Ga)-(P, C, B, Si), Fe-(Nb, Mo)-(Al, Ga)-(P, B, Si), Fe-(Co, Ni)-Zr-B, Fe-(Co, Ni)-(Zr, Nb)-(Mo, W)-B, Fe-Co-(Nd, Sm, Tb, Dy)-B. According to the Inoue's empirical rules for bulk glass-forming ability, a kind of unique local atomic structure should play an important role in the suppression of nucleation and crystal growth in these alloys. In this study, the local atomic structures of the Fe-M-B (M=Nb, Zr, W, Ta) and Fe-Co-Ln-B (Ln=Sm, Tb, Dy, Nd) glassy alloys were investigated by the ordinary X-ray diffraction and the anomalous X-ray scattering (AXS) measurements. The crystallization behavior of the Fe-M-B alloys was also examined to investigate the stability of supercooled liquid state by comparing the local atomic structures between glassy and crystalline phases. The analyses of interference functions and radial distribution functions revealed that the local atomic structures of these alloys are essentially explained by the distorted dense network of the trigonal prisms with substituting M atoms or inserting Ln atoms. The formation of the primary crystalline phase, which was identified as $Fe_{23}B_6$ type structure, requires the

long-range rearrangement of the constituent atoms. We conclude therefore that the high thermal stability of the Fe-based glassy alloys results from the difficulty of the rearrangement of the trigonal prism network against crystallization.

11:15 AM L1.7

ENHANCED GLASS FORMING ABILITY FOR MULTI-COMPONENT SUPERCOOLED LIQUIDS STUDIED BY MOLECULAR DYNAMICS SIMULATIONS. Z.H. Jin, K. Lu, State Key Lab for RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, CHINA; E. Ma, Department of Materials Science and Engineering, Johns Hopkins Univ, Baltimore, MD.

The mechanism for the extraordinarily good glass-forming ability (GFA) of bulk metallic-glass formers has attracted much interest recently, but still remains to be fully understood. A cooperative mechanism of molecular motion is reportedly responsible for the glass transition, but not necessarily the single factor for a strong GFA. It is instructive and important to study the effects of factors such as different atomic species/sizes and the specific topological/chemical short-range orders (SRO) to better understand the transition from supercooled liquid to glass. In order to highlight these points, we carried out extensive molecular dynamics simulations on supercooled Be-containing ternary (Be-Ti-Zr) and higher-order (Be-Cu-Ni-Ti-Zr) liquid alloys, with pair-wise interactions among different atoms derived from a pseudopotential perturbation theory. The results indicated that in the multicomponent system the chemical SRO effect is weak and the structure can be regarded as "dense random packing of spheres" due to various sizes of different atomic species. No significant dependence was found of the nominal glass transition temperature on the number of components. However, the dynamic heterogeneity characterized by the mobility of particles at various temperatures is quite different for those systems with different components. For liquids with more components, the structural relaxation needs much longer time and leads to very low average mobility of particles even at high temperatures. We conclude that the efficient depression of the mobility of particles due to the multicomponent effect is responsible for the enhanced glass-forming ability of those bulk metallic-glass formers.

11:30 AM L1.8

EXPERIMENTAL STUDIES AND MOLECULAR DYNAMICS SIMULATIONS OF THE SLIDING CONTACT OF METALLIC GLASS. Xi-Yong Fu, D.A. Rigney, The Ohio State University, Department of MS&E, Columbus, OH; Michael L. Falk, Harvard University, Div of Engineering & Applied Sciences, Cambridge, MA.

Tribological properties of bulk metallic glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.6}Be_{22.5}$ were studied experimentally using a pin/disk geometry without lubrication. Experimental observations were compared with 2D molecular dynamics simulations of amorphous material in sliding contact. Wear tracks and wear debris were studied using microhardness, SEM/EDS and TEM. Friction coefficient and wear rate were found to vary with normal load, sliding speed and experimental environment. Combined chemical analyses and microhardness measurements of longitudinal and transverse cross-sections suggested that a series of subsurface structures was generated during sliding. Moving from the surface in toward the bulk material, these subsurface structures included first a mechanically mixed layer affected by the environment and then a mechanically sheared layer, sometimes with cracks. Molecular dynamics simulations were conducted with a two-component amorphous system consisting of 20,000 particles interacting via Lennard-Jones pair potentials. Friction coefficients decreased with increasing sliding speed. Mechanical mixing was observed at the interface. Subsurface displacement was found to decay exponentially into the substrate, which is consistent with experimental observations. Shear localization was observed and was found to be spatially correlated with a region of increased free volume near the sliding interface. It is suggested that this lower density region, observed in simulations, corresponds to the soft layer, observed experimentally, adjacent to the sliding interface.

11:45 AM L1.9

DECOMPOSITION AND NANOCRYSTALLIZATION OF DEEPLY UNDERCOOLED METALLIC LIQUIDS. Jörg F. Löffler and William L. Johnson, California Institute of Technology, W.M. Keck Laboratory, Pasadena, CA.

In situ small-angle neutron (SANS) and synchrotron small-angle x-ray scattering (SAXS) experiments are presented for various Zr based bulk amorphous alloys, Vit1 (Zr-Ti-Ni-Cu-Be), Vit105 (Zr-Ti-Ni-Cu-Al) and Vit106 (Zr-Nb-Ni-Cu-Al), at temperatures in the undercooled liquid regime. In all three materials, the scattering data resolve interference maxima, giving evidence for decomposition and nanocrystallization, as also detected by wide-angle x-ray diffraction (XRD). From the *in situ* experiments, we derive a chemical diffusion constant whose temperature dependence follows an Arrhenius law.

When normalizing the temperature to the glass transition of the respective material, the diffusion data of the three different materials are very similar. In addition, in Vit1, the chemical diffusion constants are comparable with expected self-diffusion data of Ti in Vit1, as determined in independent studies of diffusion. This gives evidence that Ti, respectively Nb, is involved in the decomposition. Indeed, when reducing the Ti content in Vit1, SANS experiments resolve a gradual increase of the characteristic length of the decomposition till finally the interference maximum vanishes. At that composition, XRD gives evidence for a coarse-grained microstructure.

SESSION L2: ATOMIC AND ELECTRONIC STRUCTURE (continued)

Chair: Eiichiro Matsubara

Monday Afternoon, November 27, 2000
Room 200 (Hynes)

1:30 PM *L2.1

DIFFUSION IN METALLIC GLASSES AND SUPERCOOLED MELTS. Franz Faupel, Klaus Rätzke, Hartmut Ehmeler, Peter Klugkist, Volker Zöllmer, Andreas Heesemann, University of Kiel, Dept of Materials Science and Engineering, Kiel, GERMANY.

Diffusion in metallic glasses and in the supercooled liquid state is of considerable technological and fundamental interest. Within the framework of the mode coupling theory the glass transition is a kinetic phenomenon characterized by the arrest of viscous flow at a critical temperature T_c well above the calorimetric glass transition temperature T_g . Below T_c the theory predicts cooperative hopping processes. We present results from isotope effect measurements [1] which indeed confirm the highly collective nature of diffusion in metallic glasses and suggest cooperative hopping processes to be closely related to the universal low-frequency excitations as observed in recent molecular dynamic simulations. In accord with the mode coupling scenario these cooperative hopping processes are also observed in the supercooled liquid state of the new bulk metallic glasses well above T_g [2]. The reported kink in the Arrhenius plot for diffusion of various elements is shown to be related to structural changes above T_g , e.g., an increase in free volume as probed by positron annihilation, but not to a change in the diffusion mechanism. Measurements of the activation volume of diffusion show that, depending on the structure of the glass, cooperative hopping may take place without assistance of thermally generated defects or via delocalized thermal defects [3,4]. Moreover, we provide evidence of the existence of an opposite Kirkendall effect in interdiffusion between certain amorphous alloys that combine slow diffusion via thermal defects and fast direct diffusion. 1. A. Heesemann, V. Zöllmer, K. Rätzke, and F. Faupel, Phys. Rev. Lett. 84, 1467 (2000). 2. H. Ehmeler, A. Heesemann, K. Rätzke, F. Faupel, and U. Geyer, Phys. Rev. Lett. 80, 4919 (1998). 3. P. Klugkist, K. Rätzke, S. Rehders, P. Troche, and F. Faupel, Phys. Rev. Lett. 80, 3288 (1998). 4. P. Klugkist, K. Rätzke, and F. Faupel, Phys. Rev. Lett. 81, 614 (1998).

2:00 PM *L2.2

SELF-DIFFUSION IN $Zr_{75}Al_{10}Ni_{10}Cu_{25}$ AND $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BULK METALLIC GLASSES. Hideo Nakajima, T. Kojima, Osaka Univ, Inst of Scientific and Industrial Research, Ibaraki, Osaka, JAPAN; K. Nonaka, Iwate Univ, Dept of Materials Science and Technology, Morioka, JAPAN; T. Zhang, A. Inoue, Tohoku Univ, Inst for Materials Research, Sendai, JAPAN; N. Nishiyama, ERAT, JST, Sendai, JAPAN.

Self-diffusion coefficients of Ni in $Zr_{75}Al_{10}Ni_{10}Cu_{25}$ and of Ni and Pd in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ bulk metallic glasses below and above the glass transition temperature T_g have been measured with an ion-beam sputter-sectioning technique using the radioactive isotopes ^{63}Ni and ^{103}Pd . The diffusion coefficients in the supercooled liquid region of Zr-Al-Ni-Cu metallic glass are much higher than those extrapolated from low temperature data in the amorphous region. The temperature dependence of the diffusion coefficients exhibits non-Arrhenius behaviour. Such significant increase in the diffusion coefficients in the supercooled liquid region is interpreted in terms of increase of the configurational entropy associated with viscous flow and the resulting change in the migration enthalpy. On the other hand, the diffusion coefficients in Pd-Cu-Ni-P metallic glass show less remarkable temperature dependence. It is suggested that diffusion in the supercooled liquid region takes place by cooperative motion of the surrounding atoms, while diffusion in the amorphous region is due to single atomic process in both metallic glasses.

2:30 PM L2.3

MOLECULAR DYNAMICS SIMULATIONS OF SUPERCOOLED LIQUID METALS AND GLASSES. Hyon-Jee Lee, Yue Qi, Tahir Çağın, Alejandro Strachan, William A. Goddard, III, and William L. Johnson, California Institute of Technology, Pasadena, CA.

We utilize MD simulations to describe the structural, thermodynamic and transport properties of pure metals and binary alloys in solid, liquid, and glass phases. Specifically, we characterize the changes in volume, energy, the pair correlation function, and diffusivity of the supercooled metallic liquid near the glass transition. Under constant temperature and pressure, these thermodynamic properties, as well as the structures of solid solutions, are mainly determined by the solute/solvent atomic size difference and solute concentration. Therefore, we first focus on describing the solvent/solute atomic size mismatch effect on the glass transition. Furthermore, we study the effect of varying solvent/solute concentration on the glass forming ability. The packing efficiency and energy of these solid solutions are studied as a function of temperature and concentration. We find that the glass forming tendency is correlated with the packing efficiency in the liquid state; because the highly-packed state in liquid phase has higher energy barrier to crystallization.

2:45 PM L2.4

EXAFS AND EXELFS STUDY OF THE STRUCTURE AND STABILITY OF Pd-BASED BULK METALLIC GLASSES.

F.M. Alamgir, H. Jain, D.B. Williams, Lehigh Univ., Dept. of MS&E, Bethlehem, PA; R.B. Schwarz, O. Jin, Los Alamos National Lab., Los Alamos, NM.

Pd-(Ni, Cu)-P is one of the best known bulk metallic glass (BMG) formers with minimum dimensions exceeding 7 cms. The importance of Pd in this system can be appreciated from the fact that both Pd-Ni-P and Pd-Cu-P are BMGs whereas Ni-Cu-P does not form bulk glass. We have explored the importance of Pd in the short range order in these systems for increasing the stability of the glassy phase. With only three or four constituent elements, a study of the atomic-scale structure of these alloys still remains tractable in comparison to other BMG systems with at least five components. We have examined the changes in coordination environment as well as the structural disorder around the transition metals in Pd-(Ni,Cu)-P glasses using extended X-ray absorption fine structure (EXAFS). We have done similar studies around the coordination of P using electron energy loss fine structure (EXELFS). We find that the Pd-based glasses are not simply solid solutions of the binary phosphide phases. We also find that the proximity of the glass structure to stable crystalline counterparts is important in increasing the stability of the glassy phase.

SESSION L3: GFA AND THERMAL STABILITY OF BMG I

Chair: Ralf Busch
Monday Afternoon, November 27, 2000
Room 200 (Hynes)

3:30 PM *L3.1

GLASS-FORMING ABILITY AND CRYSTALLIZATION OF HIGH-PURITY Pd-Cu-Ni-P ALLOY. Nobuyuki Nishiyama, Mitsuhide Matsushita, Japan Science and Technology Corporation, ERATO Inoue Superliquid Glass Project, Sendai, JAPAN; Akihisa Inoue, IMR, Tohoku Univ, Sendai, JAPAN.

We have previously reported that a Pd₄₀Cu₃₀Ni₁₀P₂₀ alloy exhibits an extremely high glass forming ability (GFA) and has a low critical cooling rate for glass formation (R_c) of 0.1 K/s. Furthermore, the high GFA of the alloy enabled us to prepare the bulk metallic glass with a diameter of 72 mm, which is believed to have the largest thickness in all metallic glass systems reported up to date. With the aim of eliminating heterogeneous nucleation and enhancing GFA of the alloy, high-purity phosphorus was used in the alloy preparation. In the case of continuous cooling, it is found that the degree of undercooling of the high-purity alloy is larger by about 80K than that of the ordinary-purity alloy. This improvement of stability for the high-purity alloy is assumed to result from the reduction of quenched-in nuclei. In order to clarify the early stage of crystallization in the undercooled high-purity liquid, an in-situ observation was carried out by a high-resolution transmission electron microscope (HR-TEM) with a temperature controllable specimen holder. It is found that the undercooled liquid crystallized suddenly after heating for 3180 s at 683 K. The grain size of the precipitated crystal was about 15 nm and no further grain growth was recognized during isothermal annealing. Based on these data, the origin for the high GFA of the alloy will be discussed kinetically and structurally.

4:00 PM L3.2

INVESTIGATIONS ON THE THERMAL STABILITY OF BULK GLASS FORMING PdCuNiP ALLOYS. I.-R. Lu, G.P. Górlér, R. Willnecker, Inst. fuer Raumsimulationand, DLR, Cologne, GERMANY; H.-J. Fecht, Ulm University, Faculty of Engineering, Materials Division, Ulm, GERMANY.

The metallic glass former PdNiP is well known for its pronounced stability against crystallization. Samples of this alloy vitrify completely at low cooling rates down to 0.1 K/s. The addition of copper to this alloy system reduces further the crystallization kinetics significantly. Investigations on critical cooling rates were performed on PdNiCuP alloys of different concentration by means of isothermal nucleation experiments. The results indicate a critical cooling rate in the order of 10⁻³ K/s, which is the lowest one presently known for metallic glass-formers. The high stability against crystallization during cooling allows for simultaneous measurements of its thermodynamic properties within the entire temperature range from the regime of the liquid to the glassy state. Heat capacity measurements were carried out by differential heat-flow calorimetry and the coefficient of thermal expansion was determined by applying sessile drop technique. The results can be consistently discussed within the free-volume model.

4:15 PM L3.3

DYNAMIC SPECIFIC HEAT OF A METALLIC GLASS-FORMER.

G. Wilde, Forschungszentrum Karlsruhe, Institute of Nanotechnology, Karlsruhe, GERMANY.

Frequency-dependent measurements on deeply undercooled liquids can reveal the characteristics of the relaxation modes of the liquid state that are related to the occurrence of the glass transition upon continued cooling. Heat capacity spectroscopy is an especially powerful tool concerning the monitoring of the intrinsic relaxation times of the undercooled melt since the dynamic specific heat couples to all modes of molecular movement in contrast to e.g. dielectric loss spectra that probe the response of polarization-sensitive modes only. Nevertheless, such data is only scarcely available for metallic glass formers and has not yet been quantitatively analyzed with respect to the intrinsic relaxation times of the deeply undercooled liquid state. In this contribution, we report on modulated temperature calorimetry measurements on a bulk glass-forming Pd-Ni-P alloy in the frequency range between 1/(10 s) and 1/(1000 s). The results, that reveal the typical behavior known for dissipative systems are evaluated with respect to the temperature dependence of the mean relaxation time as well as the shape of the relaxation-time spectrum. In addition, the frequency-dependence of the dynamic specific heat is compared to results of dynamic mechanical compliance measurements that have been performed on the same material at similar modulation frequencies.

4:30 PM *L3.4

NEW GLASS FORMATION WITH HIGH REDUCED GLASS TEMPERATURE. Y. Li, Natl Univ of Singapore, REPUBLIC OF SINGAPORE.

Glass forming ability can be represented by many parameters. The reduced glass transition temperature, Trg (Tg/Tl) is one of the widely used indicators of glass forming ability of alloys. As the alloy concentration increases, Tg generally has a weak dependence on composition and Tl often decreases. Thus, the interval between Tl and Tg generally decreases and the value of Trg increases with increasing alloying concentration so that the probability of being able to cool through the interval without crystallization is enhanced. i.e. the glass forming ability is increased. Accordingly, the alloy systems for which the glass forming ability is higher, are those with a deep eutectic or low lying Tl compared with the melting points of the host metals, which leads to high Trg. Bulk metallic glass formation has been found to be most effective at or near their eutectic points and less effective for off-eutectic alloys. Reduced glass transition temperature Trg given by Tg/Tl of many bulk metallic glasses is found to show a stronger correlation with critical cooling rate or critical section thickness for glass formation than Trg given by Tg/Tm. Using La and Pd based alloy systems as model systems, we will demonstrate that the large glass forming alloys are usually around a eutectic system and new bulk glass formation has been obtained in these alloys.

SESSION L4: GFA AND THERMAL STABILITY OF BMG II

Chairs: Hin-Wing Kui and Y. Li
Tuesday Morning, November 28, 2000
Room 200 (Hynes)

8:30 AM *L4.1

BULK AMORPHOUS Mg-Cu-Y ALLOYS IN THE AS-PREPARED, SUPERCOOLED LIQUID AND CRYSTALLINE STATES.

Soren Linderoth, Nini Pryds, Morten Eldrup, Allan Schroder Pedersen, Riso National Laboratory, Roskilde, DENMARK; Masato Ohnuma, National Research Institute for Metals, Tsukuba, JAPAN; Tie-Jun Zhou, Leif Gerward, Jianzhong Jiang, Technical University of Denmark, Lyngby, DENMARK; C. Lathe, HASYLAB am DESY, Hamburg, GERMANY.

Bulk Mg-Cu-Y alloys, prepared by casting into a wedge-shaped copper mould, have been studied in the as-prepared, the supercooled liquid, and the crystalline states. In the as-prepared state micro x-ray diffraction of sub-millimeter sized regions were performed using a focused x-ray beam. The phase composition of the cross section as well as of the surface of the wedge-shaped specimen was investigated as a function of position. The cooling history of the alloy was examined experimentally and compared to results of a control-volume finite-difference modelling study. The experimentally determined and the calculated cooling rates were compared to the observed amorphous/crystalline structure. The transition from an amorphous to a crystalline state has been followed by x-ray diffraction studies as function of time at specific temperatures in the region between the glass transition and the crystallisation temperature. The dependence of external pressure on the crystallisation temperature has been investigated by in situ high-temperature and high-pressure x-ray powder diffraction by synchrotron radiation. The investigations form the basis for a selection of the optimum temperature in the supercooled liquid region for performing deformation/shaping of the Mg-alloys.

9:00 AM L4.2

CALCULATION OF GLASS FORMING ABILITY IN THE Ni-Zr AND Ni-Ti SYSTEMS FROM INTERATOMIC POTENTIALS. W.S. Lai and B.X. Liu, Tsinghua University, Dept of Materials Science and Engineering, Beijing, CHINA.

To investigate the glass forming range of the Ni-Zr and Ni-Ti systems, molecular-dynamics (MD) simulation was conducted with realistic n-body potentials to compare the relative stability of terminal solid solutions versus the corresponding amorphous states as a function of solute concentrations. It turned out that the terminal solid solutions transformed into an amorphous state spontaneously when the solute concentrations were beyond the maximum allowable values, i.e. the critical solubilities, determined to be 14 at% Zr in Ni and 25 at% Ni in Zr for Ni-Zr system and 38 at% Ti in Ni and 15 at% Ni in Ti for the Ni-Ti system, respectively. The glass-forming ranges were therefore bounded by the respective critical solubilities, i.e. 14-75 at% Zr and 38-85 at% Ti for the Ni-Zr and Ni-Ti systems, respectively, which are compatible with those from experiments and/or from Lidenmann criterion. The kinetics of solid-state amorphization (SSA) was also investigated by MD simulation of the Ni-Zr [1] and Ni-Ti multilayers. It was found that SSA did take place upon annealing at 773 K and that the growth of the amorphous interlayer followed exactly a square-root t law. Interestingly, different asymmetric growth behaviors were observed that the growing speed of amorphous interlayer towards Ni was greater than that directed to the Zr lattice, while it was smaller than that to Ti side. As shown above, the lower the maximum solid solubility the less stable the metal lattice, implying that the metal with lower solid solubility collapsed faster than its partner under SSA. We therefore named it as solubility criterion, which also works for the observations in the Cu-Ta bilayer with a positive heat of formation [2].

Reference:

- [1] W.S. Lai and B.X. Liu, Phys. Rev. B 58, 6063 (1998).
 [2] K.W. Kwon, H.J. Lee and R. Sinclair, Appl. Phys. Lett. 75, 935 (1999).

9:15 AM *L4.3

KINETICS OF BULK METALLIC GLASS FORMING LIQUIDS. Ralf Busch, Oregon State University, Dept. of Mechanical Engineering, Corvallis, OR.

This talk gives an overview of the kinetics of bulk metallic glass forming liquids. The viscosities of these alloys are high in the entire supercooled liquid region, which is indicative for strong liquid behavior and slow crystallization kinetics. This strong liquid nature also determines the relaxation in the glass transition region as it has been measured by the heating rate dependence of T_g , viscosity relaxation, and enthalpy relaxation. Atomic mobilities are likely to follow the behavior of the viscosity at high temperatures. In the glass transition region, however, mobilities depend on the atomic size. Small and medium sized atoms show much faster diffusivities than it would be expected from the relaxation behavior. This affects the thermal stability of the material when it is reheated into the supercooled liquid region. Primary crystallization upon heating is usually determined by the mobility of the second slowest element in the alloy.

10:15 AM L4.4

PHASE EQUILIBRIA AND GLASS FORMING ABILITY IN THE Zr-Cu-Ni-Al SYSTEM. Douglas Swenson and Sreenivas Bhattiprolu, Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI.

Alloys within the Zr-Cu-Ni-Al system exhibit some of the largest values of T_{rg} and ΔT_x among the bulk metallic glasses. While several researchers have studied the properties of these quaternary alloys in

the glassy form, there is very little information available pertaining to these alloys in the equilibrium state. In this paper, the results are presented of a combined experimental and computational study of phase equilibria in the $Zr_{66.7}Cu_xAl_yNi_{33.3-x-y}$ quaternary isopleth (for $0 \leq x, y \leq 33.3$), a compositional range of special interest for bulk metallic glass formation in this system. Experimental work includes isothermal phase equilibrium data obtained from samples equilibrated at 800°C, using electron probe microanalysis and X-ray diffraction, and high temperature differential scanning calorimetry (DSC) of both melt-spun (amorphous) and equilibrated samples to obtain solidus and liquidus temperatures. These data, along with thermodynamic data reported in the literature, have been utilized to develop a CALPHAD model of phase equilibria in the isopleth. The results of the phase diagram modeling are correlated with the glass forming abilities of alloys of various compositions within the isopleth section.

10:30 AM L4.5

THERMOPHYSICAL PROPERTIES OF BULK METALLIC GLASSES IN THE STABLE AND UNDERCOOLED LIQUID - A MICROGRAVITY INVESTIGATION. Hans-J. Fecht, Rainer K. Wunderlich, University of Ulm, Faculty of Engineering, Ulm, GERMANY; Stephen J. Glade, William L. Johnson, California Institute of Technology, Keck Laboratory for Engineering Materials, Pasadena, CA.

Non-contact calorimetry in an electromagnetic levitation device has been used under conditions of reduced gravity on board spacelab for an investigation of the thermophysical properties in the liquid phase of a series of bulk metallic glass forming alloys: $Zr_{65}Al_{17.5}Cu_{17.5}Ni_{10}$, $Zr_{60}Al_{10}Cu_{18}Ni_9Co_3$, $Ti_{34}Zr_{11}Cu_{47}Ni_8$, and $Zr_{57}Cu_{15.4}Ni_{12.6}Nb_5Al_{10}$. Properties included the specific heat and enthalpy of fusion for calculation of the thermodynamic functions, thermal conductivity and total hemispherical emissivity, and the electrical resistivity. The specimens exhibited excellent stability in the undercooled melt allowing for this type of alloys for the first time specific heat measurements at significant undercooling by cooling from stable melt. Combined with cP data of the glass and highly undercooled melt the specific heat of the alloys $Zr_{65}Al_{17.5}Cu_{17.5}Ni_{10}$ and $Zr_{60}Al_{10}Cu_{18}Ni_9Co_3$ appears to exhibit a nonmonotonous temperature dependence in the undercooled melt, compatible with a model predicting a change in the chemical short range order as function of temperature. The driving force for nucleation as obtained from the difference in the Gibbs free energy between the undercooled melt and an equilibrium crystalline phase mixture exhibits a pronounced concentration dependence with that of $Zr_{57}Cu_{15.4}Ni_{12.6}Nb_5Al_{10}$ being the lowest correlating very well with critical cooling rates observed in the laboratory. The total hemispherical emissivity of $Zr_{65}Al_{17.5}Cu_{17.5}Ni_{10}$ and $Zr_{60}Al_{10}Cu_{18}Ni_9Co_3$ exhibits a temperature dependence not in accordance with the free electron model applied to the measured bulk resistivity indicating surface segregation at a well defined temperature 50 K above the liquidus. The electrical resistivity in the liquid phase, up to a small undercooling of 20 K, is characterized for all alloys investigated by a negative temperature coefficient typically a factor 10 larger than that observed in the glassy phase. A possible explanation in terms of a temperature dependent chemical short range order affecting the density of states at the Fermi level is currently investigated by x-ray absorption methods.

10:45 AM L4.6

CRITICAL COOLING RATE AND THERMAL STABILITY OF Zr-Ti-Cu-Ni-Be ALLOYS. Theodore A. Waniuk, Jan Schroers, W.L. Johnson, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

The crystallization behavior of a series of alloys in the Zr-Ti-Cu-Ni-Be system is studied. Upon cooling from the molten state with different rates, alloys with compositions ranging along a tie line from $(Zr_{75}Ti_{25})_{55}(Ni_{45}Cu_{55})_{22.5}Be_{22.5}$ (Vit1) to $(Zr_{85}Ti_{15})_{55}(Ni_{57}Cu_{43})_{17.5}Be_{27.5}$ (Vit4) show a continuous increase in the critical cooling rate to suppress crystallization. In contrast, thermal analysis of the same alloys shows that the undercooled liquid region, the temperature difference between the glass transition temperature and the crystallization temperature, is largest for compositions midway between the two endpoints, revealing that glass forming ability does not correlate with thermal stability. The relationship between the composition-dependent glass forming ability and thermal stability is discussed with reference to a chemical decomposition process.

11:00 AM *L4.7

SYNTHESIS AND STABILITY OF AMORPHOUS Al ALLOYS. J.H. Perepezko, R.I. Wu, R. Hebert, Univ. of Wisconsin-Madison, Dept. Mat. Sci. and Eng., Madison WI; G. Wilde, Forschungszentrum Karlsruhe, INT, Karlsruhe, GERMANY.

The recent innovations in metallic glasses have led to new alloy classes that may be vitrified and a re-examination of the commonly used

criteria for glass formation and stability. The new alloy classes are usually at least ternary systems and often higher order that can be grouped into two general categories. In one case large, bulk volumes may be slowly cooled to the glassy state which signifies a nucleation controlled synthesis. The other important class is represented by some Al and Fe based glasses that can be synthesized only by rapid solidification processes such as melt spinning. These glasses are often called marginal glass formers that are synthesized under growth controlled kinetic conditions. With marginal glass forming alloys the termination of the amorphous state upon heating is often not characterized by a clear glass transition signal, T_g , but instead by the rapid onset of a primary crystallization reaction that represents the partial crystallization into a high number density of nanocrystals of the major component (i.e. Al or Fe) dispersed within a residual amorphous matrix. However, a closer examination by modulated or dynamic differential scanning calorimetry (DDSC) has identified a true reversible T_g signal that confirms the amorphous state and has revealed additional relaxation behavior that impacts the overall thermal stability and microstructure evolution. At the same time, alternate synthesis strategies involving deformation alloying by intense cold rolling reveal that the primary crystallization reaction can be bypassed. In addition, rolling deformation has also been shown to influence the crystallization and stability of melt spun amorphous ribbons. Alternatively other approaches have demonstrated that by suitable alloying it is possible to inoculate the primary crystallization reaction and increase the density of primary nanocrystals by about an order of magnitude. These developments represent a major level of microstructure control that have an impact on the structural performance and stability and the understanding of glass formation. The support of the ARO (DAAG55-97-1-0261) is gratefully acknowledged.

11:30 AM L4.8

QUATERNARY AND QUINTERNARY Ni-BASED BULK AMORPHOUS ALLOYS IN THE Ni-Ti-Zr-X-Y (X=Al, Si, P, Y=Sn, Mo, Y) SYSTEM. Myoung Hyun Lee, Seunghoon Yi, Tae Gyu Park, Won Tae Kim and Do Hyang Kim Yonsei Univ., Center for Noncrystalline Materials, Dept. of Metallurgical Engineering, Seoul, KOREA.

A number of bulk amorphous alloys has been developed as a potential engineering material that has unique properties attributed to the atomic structure of amorphous phase. Development of Ni-based bulk amorphous alloys is expected to expand the application fields of the amorphous alloys. Recently, fully amorphous rods with the maximum diameter of 1mm have been prepared in the Ni-Nb-Cr-Mo-P-B system. In the present study, new Ni-based bulk amorphous alloys in the alloy system Ni-Ti-Zr-X-Y (X=Al, Si, P, Y=Sn, Mo, Y) are developed through systematic alloy design based upon the empirical rules for high glass forming alloys. The empirical rules are; 1) multicomponent system; 2) large atomic size differences; 3) negative heat of mixing among the elements. Based on the empirical rules, the ternary Ni-Ti-Zr system is selected due to large atomic size differences (>12%) as well as large negative heats of mixing among the elements. Also, amorphous phase formations by rapid quenching techniques have been reported in the binary systems Ni-Zr and Ni-Ti. Alloying effects on the glass forming ability (GFA) and the undercooled liquid region (ΔT_x) of the alloys Ni-Ti-Zr-X-Y are systematically studied using a differential scanning calorimetry. Fully amorphous rods with the diameter of up to 2mm in diameter that have large ΔT_x (>50 K) can be fabricated by a copper mold casting method. The new Ni-based bulk amorphous alloys extend the maximum dimension of Ni-based amorphous alloys that can be cast from liquid state. Further scaling up the amorphous materials is possible through various processing routes including warm processing at temperatures within the large ΔT_x .

11:45 AM L4.9

GLASS FORMING ABILITY AND CRYSTALLIZATION BEHAVIORS OF THE Ti-Cu-Ni-(Sn) ALLOYS WITH LARGE SUPERCOOLED LIQUID REGION. Yu-chan Kim, Seunghoon Yi, Won Tae Kim, Do-hyang Kim, Center for Noncrystalline Materials, Dept. of Metallurgical Eng., Yonsei Univ., Seoul, KOREA; Dept. Physics, Chongju Univ., Chongju, KOREA.

The thermal stability and crystallization behavior of melt spun amorphous Ti-Cu-Ni-(Sn) alloys are investigated by thermal analysis and structural characterization with an intention to find alloy composition with wide supercooled liquid regime ΔT_x . The ΔT_x of amorphous $Ti_{50}Cu_{50-x}Ni_x$ alloys increased with increasing Ni content up to 15 at% and then decreased with further increasing. Maximum ΔT_x of 41 K was obtained in $Ti_{50}Ni_{15}Cu_{35}$ alloy. Partial replacement of Cu by Sn improved thermal stability of amorphous phase and supercooled liquid range. With increasing Sn content from 0 to 7, onset temperature of the crystallization exotherm increased from 739 to 776 K for the first exotherms and from 753 to 804 K for the second exotherms. ΔT_x $Ti_{50}Cu_{32}Ni_{15}Sn_3$ alloy exhibits ΔT_x of

73 K. The amorphous $Ti_{50}Cu_{35}Ni_{15}$ alloy crystallized by precipitation of supersaturated Ti(Ni,Cu) phase followed by decomposition into a mixture of TiCu and TiNi at higher temperature. Amorphous $Ti_{50}Cu_{32}Ni_{15}Sn_3$ phase crystallized by co-precipitation of Ti(Ni,Cu) and Ti_2Ni phases, followed by transformation into a mixture of TiNi, CuTi, Ti_3Sn phases.

SESSION L5: CRYSTALLIZATION AND DECOMPOSITION

Chairs: John H. Perepezko and Kazuhiro Hono
Tuesday Afternoon, November 28, 2000
Room 200 (Hynes)

1:30 PM *L5.1

CRYSTALLIZATION DURING CONTINUOUS HEATING AND COOLING OF SUPERCOOLED BULK GLASS FORMING MELTS. Jan Schroers, William L. Johnson, California Institute of Technology, Keck Laboratory of Engineering Materials, Pasadena, CA.

The crystallization of bulk glass forming melts is studied under different heating and cooling rates. A large asymmetry in the crystallization kinetics is found. Heated amorphous samples crystallize more rapidly than samples cooled from above the liquidus temperature. The difference between the critical heating and cooling rate is discussed within a model that cumulates the nuclei formed during cooling and heating and calculates their subsequent growth according to classical nucleation theory and diffusion limited growth. The calculated difference between the critical heating and cooling rate can be explained by the fact that nuclei formed during cooling and heating are exposed to different growth rates.

2:00 PM L5.2

CRYSTALLIZATION KINETICS IN Zr-Ti-Cu-Ni-Be BULK GLASS. J.Z. Jiang, Technical University of Denmark, Dept of Physics, Lyngby, DENMARK.

In this work, we present experimental results obtained from synchrotron radiation X-ray diffraction, TEM, DSC, and acoustic measurements on structural change from amorphous to crystalline state in bulk metallic ZrTiCuNiBe glass with and without pressure. Quasicrystals were formed during early stage of crystallization. We found that the pressure reduces the atomic diffusion process and shifts the TTT diagram, but, does not enhance the crystallization temperature estimated by XRD with a stepwise enhancement of temperature (10 K). Possible mechanisms for the crystallization kinetics will be addressed.

2:15 PM *L5.3

CONTROLLED CRYSTALLIZATION OF METALLIC GLASSES THROUGH JOULE HEATING. Marcelo Knobel, Rafael Piccin, Fabio C.S. da Silva, Inst. de Fisica Gleb Wataghin, Univ. Estadual de Campinas (UNICAMP), Campinas, SP, BRAZIL; Walter J. Botta Filho, Dept. de Materiais, Universidade Federal de Sao Carlos, SP, BRAZIL; Alain Reza Yavari, LTPCM-CNRS, Inst. Nat. Polytechnique de Grenoble, Grenoble, FRANCE.

It is well known that suitable thermal treatments can improve and stabilize the physical properties of amorphous materials produced by rapid solidification techniques. The soft magnetic properties of ferromagnetic amorphous materials (both ribbons and wires) are further improved either by low-temperature anneals which induce structural relaxation or by high temperature thermal treatments, leading to surface crystallization and/or nanocrystallization. Besides an enhancement on the magnetic properties, fast-heating treatments can lead to materials with better mechanical properties [1]. In particular, techniques which explore the heat released by an electrical current flowing through the sample (Joule heating) have emerged as one of the most promising methods to obtain materials with optimized physical properties. Joule heating (also known as flash annealing) is conceptually simple and experimentally versatile, allowing one to follow the structural transformation of the samples through on-line monitoring the materials resistance during annealing [2]. In this work, a brief review of Joule heating, both from the experimental and theoretical viewpoints will be given. Recent results of linearly varying current Joule heating (LVC-JH) on the following amorphous alloys will be presented: $Al_{90}Fe_5Nd_5$, $Al_{90}Fe_3Nd_3Cu_4$, $Al_{88}Fe_5Nd_2Cu_5$, $Al_{88}Fe_1Ni_6Nd_5$, $Al_{85}Fe_4Nd_6Cu_5$, $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$, $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}Pd_{10}$, $Zr_{69.5}Al_{7.5}Ni_{11}Cu_{12}$. Each different sample displays a typical resistance versus current curve, with different discontinuities which mark the different crystallization stages. It was possible to stop the annealing in different points of the crystallization process, and samples with different phases were therefore produced. These samples were studied at room temperature by means of X-ray diffractometry

and transmission electron microscopy, and a systematic control of the final structure was attained. The advantages of this method will be discussed. [1] P. Allia, M. Knobel, P. Tiberto and F. Vinai, J. Magn. Mater. 133, 243 (1994). [2] P. Allia, M. Baricco, P. Tiberto and F. Vinai, Rev. Sci. Instr. 64, 1053 (1993); F.C.S. da Silva, E.F. Ferrari, and M. Knobel, J. Appl. Phys. 84 5366 (1999).

3:15 PM *L5.4

FORMATION OF NANOSTRUCTURED ALLOYS BY LIQUID STATE SPINODAL DECOMPOSITION. H.W. Kui, Dept of Physics, Chinese University of Hong Kong, Shatin NT, Hong Kong, PR CHINA.

If the like species in an alloy melt attracts each other more, it was found the system undergoes liquid state spinodal decomposition at a temperature T that is substantially below its liquidus T_1 . The wavelength λ of the decomposed networks decreases with undercooling ΔT that is defined as $\Delta T = T_1 - T$. Most interestingly, λ can enter the nanometer regime at large undercoolings. As soon as an original homogeneous undercooled melt decomposes into liquid networks with $\lambda \leq 100$ nm, if isothermal annealing is simultaneously introduced, the liquid networks, driven by surface tension, would break up into tiny liquid droplets of diameter ≤ 100 nm. The system of tiny liquid droplets is then allowed to crystallize at various quenching rates and the final product is a nanostructure. The constituent grains can be amorphous or crystalline. There are three important features about an as-prepared ingot: (1) bulk in size with a diameter > 1 cm; (2) porosity free; (3) controllable grain size; and (4) the constituent grains are rather uniform in size.

3:45 PM L5.5

SPATIAL LOCALIZATION OF THE NUCLEATION RATE IN DEEPLY UNDERCOOLED LIQUIDS. S. Bossuyt, W.L. Johnson, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

In bulk metallic glass forming alloys cooled slightly faster than the critical cooling rate for glass formation, the nucleation density is observed to be spatially inhomogeneous; there are spherical clusters with a high density of nanocrystals in an amorphous matrix. This is attributed to the combined effect of recalescence due to the heat of crystallization and the fact that in deeply undercooled liquids the nucleation rate increases with increasing temperature. A linear stability analysis of the non-linear differential equations describing temperature-dependent nucleation and growth reveals that a recalescence instability exists when the heat release rate due to crystallization reaches a threshold level ω when the nucleation rate increases with increasing temperature. Therefore, in deeply undercooled liquids the recalescence instability develops even during the early stages of crystallization. As a result, fluctuations due to the statistical nature of nucleation are amplified, leading to regions with local increases in both the nucleation rate and the growth rate. It is postulated that the interaction of these regions, causing them to coalesce, determines the critical cooling rate for glass formation.

4:00 PM L5.6

INFLUENCE OF DECOMPOSITION ON THERMAL STABILITY IN THE BULK GLASS FORMING SYSTEM Zr-Ti-Cu-Ni-Al. Andreas A. Kündig, Jörg F. Löffler, William L. Johnson, California Institute of Technology, W.M. Keck Laboratory, Pasadena, CA.

Different bulk glass forming alloys in the neighborhood of $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ (Vit105) have been investigated by differential scanning calorimetry (DSC), x-ray diffraction (XRD) and small-angle neutron scattering (SANS). Along the Al/Ti line in composition space, $Zr_{52.5}Ti_{5-x}Cu_{17.9}Ni_{14.6}Al_{10-x}$ with $-5 < x < 2.5$, the glass transition temperature, T_g and the undercooled liquid regime, $\Delta T = T_x - T_g$ (T_x = crystallization temperature) continually decrease with increasing x . SANS measurements on the annealed alloys show interference maxima, giving evidence for decomposition on the nanometer scale, up to a critical temperature T_c . In contrast to T_g , T_c increases with x and thus intercepts with T_g at a certain composition. At that composition, significant changes in DSC traces and XRD patterns are observed. Therefore, we conclude that the critical temperature T_c determines the crystallization behavior and the thermal stability of these bulk metallic glasses.

4:15 PM *L5.7

IMPROVED OXIDATION RESISTANCE OF Zr-Cu-Ni-AL METALLIC GLASSES BY ALLOYING OR NANOCRYSTALLIZATION. Uwe Köster, Dept of Chemical Engineering, University of Dortmund, Dortmund, GERMANY.

Bulk metallic glasses are a new class of materials with very promising properties, e.g. the superior mechanical properties as used for golf clubs. Zr-Cu-Ni-Al belongs to the best glass forming systems known.

Recent work, however, realized fast oxidation in air as compared to Be-containing bulk glasses. From crystalline materials it is known that oxidation resistance can be improved by alloying with elements, which either are strong oxide formers or exhibit a different valency thus increasing electrical resistivity. Sn, Si, Y as well as Mo were chosen in order to improve the oxidation resistance. Oxidation of $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$, as a quaternary glass or alloyed with 2at.% of Si, Sn, Mo or Y as well as nanocrystalline alloys of same composition was studied in the temperature range between 300 and 400°C by means of thermogravimetry in dry air, x-ray diffraction, SEM and TEM as well as Auger depth profiling. In all glasses oxidation kinetics was observed to follow a parabolic law. In the quaternary glass oxidation kinetics seems to be controlled by oxygen diffusion in the scale towards the ZrO_2 /glass interface. The scales formed consist mainly of tetragonal ZrO_2 , but incorporate all the Cu, Ni and Al in the same ratio as in the glass. Whereas Sn and Si additions were observed to reduce the oxidation kinetics significantly, Mo and Y exhibited only minor influences. Alloying, however, not only increases oxidation resistance, but also changes crystallization kinetics and phase selection: Si, Sn and Mo additions increase thermal stability. Whereas Si leads to the formation of tetragonal Zr_2Ni and Mo to the formation of the fcc big-cube phase, Y seems to improve the formation of quasicrystals. Controlled nanocrystallization prior to oxidation was observed to reduce the oxidation rate significantly. Reasons for the improved oxidation resistance by alloying or nanocrystallization will be discussed in detail.

4:45 PM L5.8

NANOCRYSTALLIZATION AND HYDROGENATION OF AMORPHOUS $Zr_{60}Ni_{25}Al_{15}$. Daniela Zander, Uwe Köster, Dept of Chemical Engineering, University of Dortmund, Dortmund, GERMANY.

Zr-Ni-Cu-Al is not only one of the best glass forming system, but exhibits also excellent hydrogen absorption properties. In order to understand this behavior in more detail, the properties of closely related ternary systems are of large interest. Only very recently hydrogen absorption from the gas phase of $Zr_{60}Ni_{30}Al_{10}$ amorphous alloys has been studied in detail by Inoue et al. [1]. Glassy $Zr_{60}Ni_{25}Al_{15}$ was prepared by melt-spinning. It exhibits a very reasonable thermal stability as observed by DSC. Around 450°C nanocrystallization was observed leading to an extreme microstructure with mean grain sizes below 5 nm. Coarsening and transformation into the stable crystalline phases proceed during further annealing. Kinetics of crystallization was studied by DSC, its micromechanism by systematic TEM as well as crystallization statistics; the crystalline phases formed were analyzed by means of x-ray and nanobeam electron diffraction. The influence of hydrogenation on thermal stability and nanocrystallization was studied in detail. Hydrogenation up to an hydrogen content of $H/M = 0.9$ was done electrochemically in a phosphoric acid/glycerol electrolyte and followed by length as well as weight increase or changes in the x-ray diffraction. As indicated by TDA and DSC there is some evidence for hydrogen desorptions above about 400°C. Results on the crystallization, hydrogenation as well as on the influence of hydrogen on the crystallization will be compared in detail with the behavior of the quaternary Zr-Ni-Cu-Al glasses. [1] X.G. Li, T. Otahaara, S. Takahashi, T. Shoji, H.M. Kimura, A. Inoue, J. Alloys Compounds 297 (2000), 303-311.

SESSION L6/K10: JOINT SESSION

QUASICRYSTAL

Chair: Uwe Koester

Wednesday Morning, November 29, 2000

Room 200 (Hynes)

8:30 AM *L6.1/K10.1

FORMATION OF NANO ICOSAHEDRAL QUASICRYSTALLINE PHASE IN Zr-BASED BINARY AND TERNARY GLASSY ALLOYS. Junji Saida, Mitsuhide Matsushita, Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation (JST), Sendai, JAPAN; Akihisa Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Since the reproducible formation of an icosahedral quasicrystalline phase as a primary precipitation phase from an amorphous state has been discovered in the Zr-Al-Ni-Cu-Ag alloy, the correlation between the icosahedral phase and a short-range ordering in the glassy state has attracted much attention in the aspects of the high glass-forming ability. The effect of constitutional elements on the formation of the icosahedral phase is also of importance in relation with the atomic configurations in the glassy state. Recently, we have found that a nano icosahedral phase in the diameter below 50 nm is formed as a primary phase in the crystallization reaction of the Zr-Ni-M (M=Pt, Au or Pd) and Zr-TM-Pd (TM=Fe, Co, Ni or Cu) ternary glassy alloys. These results imply that the formation and/or stabilization of

the icosahedral phase is attributed to the existence of two kinds of strong chemical pairs of Zr-M and Zr-TM. Very recently, we have also found that a nano icosahedral phase is formed even in the Zr-(Pd and Pt) binary alloys. It indicates that the dominant factor for the formation of the icosahedral phase is Zr-M pair. These results also suggest that an icosahedral short-range ordering exists in the Zr-(Pd or Pt) alloys. In this paper, we intend to present the transformation behavior of the nano icosahedral phase from the glassy state in the Zr-based binary and ternary glassy alloys.

9:00 AM L6.2/K10.2

QUASICRYSTALS AND NANO-QUASICRYSTALS IN ANNEALED Zr-Al-Ni-Cu-Ag BULK METALLIC GLASSES. M.W. Chen, I. Dutta, Naval Postgraduate School, Dept of Mechanical Engineering, Monterey, CA; A. Inoue, T. Sakurai, Tohoku University, Institute for Materials Research, Sendai, JAPAN.

Quasicrystals and nano-quasicrystals were discovered in annealed Zr-Al-Ni-Cu-Ag bulk metallic glasses by systematic transmission electron microscopic analysis. Selected area electron diffraction and micro-beam diffraction patterns corresponding to five-, three-, and two-fold rotational symmetry were obtained, demonstrating that the precipitated phases in the primarily devitrified bulk metallic glasses are icosahedral quasicrystalline phases. The formation of nano-quasicrystals is attributed to the high nucleation density. Moreover, the addition of Ag benefits the formation of the nano-quasicrystalline phase since energy-filtered elemental maps show that Ag slightly enriches into the nano-quasicrystals. The preliminary results of electron-energy-loss spectroscopy and phase transformation kinetics exhibit an interesting relationship between the bulk metallic glasses and the icosahedral quasicrystalline phases, which strongly supports that the local atomic structure is similar for the two solid states.

9:15 AM *L6.3/K10.3

NANOQUASICRYSTALLIZATION OF Zr-BASE METALLIC GLASSES. B.S. Murty, D.H. Ping and K. Hono, National Research Institute for Metals, Tsukuba, JAPAN.

Recent investigations revealed that nanoquasicrystallization occurs in a number of Zr based metallic glasses. This paper reports our recent studies on the influence of various elements in the icosahedral phase formation in Zr-based metallic glasses for the purpose of understanding the essential conditions for nanoquasicrystallization. Icosahedral phase is formed in the first stage of crystallization reaction of the $Zr_{65-x}Cu_{27.5}Al_{7.5}O_x$ amorphous alloys beyond a critical oxygen level, suggesting that oxygen is a factor to stabilize icosahedral phase formation in Zr-Cu(-Ni)-Al based metallic glasses. 3DAP results have clearly shown that oxygen is enriched in the icosahedral phase. On the other hand, Zr-based alloys containing Pd do not require oxygen for icosahedral phase formation. In the presence of Pd, even binary $Zr_{100-x}Pd_x$ ($x=30$ and 35) alloys show nanoquasicrystallization in the course of amorphous to crystal transformation. Based on 3DAP and TEM observation results together with kinetics analysis results, the quasicrystallization modes that occur during crystallization of Zr-based metallic glasses are discussed.

SESSION L7: SOFT MAGNETIC PROPERTIES

Chair: K. V. Rao
Wednesday Morning, November 29, 2000
Room 200 (Hynes)

10:15 AM *L7.1

CORE LOSSES AND SOFT MAGNETIC PROPERTIES OF NANOCRYSTALLINE Fe-Zr-Nb-B ALLOYS WITH ZERO-MAGNETOSTRICTION. Akihoro Makino¹, Akihisa Inoue², and Tuiyoshi Masumoto³. ¹Department of Machine Intelligence and System Engineering, Faculty of Systems Science and Technology, Akita Prefectural University, Honjo, JAPAN; ²Institute for Materials Research, Tohoku University, Sendai, JAPAN; ³The Research Institute of Electrical and Magnetic Materials, Sendai, JAPAN.

The nanocrystalline Fe-rich Fe-M-B (M = Zr, Hf, Nb) alloys produced by crystallizing of melt spun amorphous ribbons are known as a new kind of soft magnetic material with a high saturation magnetic induction (Bs) and high permeability. The alloys consist of nanoscale bcc-Fe grains about 10-15 nm in size embedded in a residual amorphous minority matrix containing a large amount of M elements and B. Owing to strong ferromagnetic exchange interaction between the grains, the net crystalline anisotropy is canceled. This is a reason why the nanocrystalline Fe-M-B alloys exhibit the good soft magnetic properties. The Fe90Zr7B3 (Bs = 1.7 T, permeability = 30,000 at 1 kHz, core loss = 0.21 W/kg at 1.4 T and 50 Hz) and Fe84Nb7B9 (Bs = 1.5 T, permeability = 51,000 at 1 kHz, core loss = 0.14 W/kg at 1.4 T and 50 Hz) alloys are typical examples of the nanocrystalline

ternary Fe-M-B alloys.

The nanocrystalline ternary Fe-M-B alloys exhibit small but non-zero magnetostriction. Therefore, it is expected that the soft magnetic properties of the nanocrystalline Fe-M-B alloys can be improved further by achieving zero-magnetostriction. Since the magnetostriction is negative for the Fe-Zr-B alloys and positive for the Fe-Nb-B alloys, it is expected that zero-magnetostriction can be obtained by mixing Zr and Nb and adjusting the amount of Zr + Nb and of B. The compositional dependence of the soft magnetic properties of the nanocrystalline Fe-Zr-Nb-B alloys has been studied. The magnetostriction and grain size of the Fe-Zr-Nb-B alloys show intermediate values between those of the Fe-Zr-B and the Fe-Nb-B alloys. The high permeability of 60,000 at 1 kHz has been obtained for Fe85.5Zr2Nb4B8.5 alloy. The alloy exhibits a high Bs of 1.64 T and zero-magnetostriction, simultaneously. Furthermore, the Fe-Zr-Nb-B alloys also exhibit a very low core loss of less than 0.1 W/kg at 1.4 T and 50 Hz. This value is extremely lower than that of Fe-Si-B amorphous alloys and oriented Si-steels. The nanocrystalline Fe-Zr-Nb-B alloy also has a good thermal stability of the magnetic properties. The nanocrystalline Fe-Zr-Nb-B alloys are therefore suitable for a core material for the pole transformers.

10:45 AM L7.2

PREPARATION AND CHARACTERIZATION OF THE SOFT MAGNETIC FeCo-BASED AMORPHOUS ALLOY WITH ENHANCED PROPERTIES AND THERMAL STABILITY. V.I. Tkatch, S.I. Khartsev and Alex Grishin, Department of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN.

Alloying of Co is known to enhance the saturated magnetization as well as the thermal stability of the Fe-based amorphous alloys. We have studied the effect of Ni replacing with Co in well-known metallic glass of nominal composition $Fe_{40}Ni_{40}P_{14}B_6$. Fabricated FeCo-based alloy has melting temperature of 1313 ± 5 K and demonstrates a good casting properties. 8 mm wide and 15-25 micrometer thick amorphous ribbons were prepared by melt-spinning onto a copper wheel. As-spun ribbons have superior soft magnetic properties compared with those of $Fe_{40}Ni_{40}P_{14}B_6$: coercive field is found to be almost the same, while the saturated magnetization $4\pi M_s = 14.2 \pm 0.3$ kGs and maximum permeability are about 1.7 and 3 times higher. Co alloying appears to substantially enhance thermal stability of amorphous state. The crystallization temperature of the FeCo-based melt-spun ribbons under continuous heating was found to be as much as almost 60 K higher than that of the FeNi counterpart and the activation energy for crystallization estimated by Kissinger technique was as high as 47800 K. The investigated metallic glass crystallizes by eutectic reaction $\gamma-(Fe,Co) + (Fe,Co)_3(P,B)$ via highly non-steady state homogeneous nucleation and linear growth of colonies. The comprehensive quantitative analysis of kinetics of crystallization has been performed and it has been established that improved thermal stability of the FeCo-based metallic glass in comparison with that of $Fe_{40}Ni_{40}P_{14}B_6$ is due to both lowered diffusion coefficient and increased value of the specific free energy of the nucleus-melt interface. This work was supported in part by Swedish Royal Academy of Sciences.

11:00 AM L7.3

EFFECT OF BORON ON CRYSTALLIZATION, FORMING ABILITY AND MAGNETIC PROPERTIES OF Fe-BASED AMORPHOUS ALLOY. Bin Yao, Xiang Hu, Lun Shi, Hao Tang and Yi Li, National University, Faculty of Science, Department of Materials Science, Singapore, SINGAPORE.

$Fe_{91-x}Zr_5B_xNb_4$ ($x=0-30$) (FZBN) amorphous alloys were prepared by melt spinning. They crystallized in primary crystallization mode when the boron (B) content, X_B was smaller than 20 at%, and in eutectic one when $X_B > 20$ at%. Their glass-transition temperature, T_{gi} , onset crystallization temperature, T_x , supercooled liquid region ($\Delta T_x = T_x - T_{gi}$), and reduced supercooling, T_{gi}/T_m changed with concentration of B in the same rule, that is, they increased with increasing X_B when $X_B < 20\%$, increased sharply in the content range of B of $20\% < X_B < 22.5\%$ at%, in which the crystallization mode of the amorphous FZBN change from primary mode to eutectic one, and did not change approximately in the content range of B from 22.4at% to 27 at%, but increase again when $X_B > 27$ at%. The largest values for T_{gi} , T_x , ΔT_x and T_{gi}/T_m were obtained in the amorphous $Fe_{61}Zr_5B_{30}Nb_4$ alloy to be 880K, 923K, 43K and 0.623, respectively. Magnetic properties of the amorphous FZBN alloys were measured using vibrated sample magnetometer. It is very interesting that the saturated magnetization of the amorphous FZBN alloys increased with increasing content of B, that is quite different from the cases observed previously in the amorphous alloys formed by transit metals and metalloid metals, such as $Fe_{1-x}P_xB_x$ and $Fe_{1-x}B_x$, etc., and that the change rule of their saturated magnetization with boron content is the same as that of T_{gi} , T_x , ΔT_x , and T_{gi}/T_m . Above results indicated that the crystallization of the amorphous FZBN was influenced by B content and the amorphous FZBN crystallizing in

eutectic mode had high stability and amorphous forming ability, and that electrons of boron atom in the amorphous FZBN did not move to 3d shell of iron but may restrain electrons of Nb to move to iron. The mechanisms lead to these results.

11:15 AM *L7.4

DOMAIN STRUCTURE AND THERMAL DEPENDENCE OF THE COERCIVE FIELD IN NANOCRYSTALLINE FeZrBCu.

Antonio Hernando, Juan Arcas, Instituto de Magnetismo Aplicado (UCM, RENFE).

Nanocrystalline Fe_{87.2}Zr_{7.4}B_{4.3}Cu_{1.1} samples have been obtained by annealing melt-spun ribbons during 1 h at temperatures ranging between 713 K and 923 K. The samples have been submitted to a complete structural characterization by means of X ray diffraction and thermomagnetic analysis and they consist of Fe nanocrystals embedded in an amorphous matrix. The coercive field has been measured by a Förster coercimeter at temperatures ranging between 50 K and 300 K, and the room temperature domain structure has been monitored by magneto-optical Kerr effect. The samples as cast and annealed above 813 K display soft magnetic properties at room temperature, exhibiting a coercive field below 10 A/m, and wide regular domains. In contrast, the sample annealed at 748 K, corresponding to the beginning of the crystallization process, undergoes a dramatic magnetic hardening, showing a coercive field of 150 A/m and a dull domain pattern. When this sample is cooled down to 250 K its coercivity is reduced. Thus, the magnetic hardening is attributed to the exchange decoupling between crystallites, due to the proximity of the Curie temperature of the amorphous phase.

SESSION L8: HARD MAGNETISM

Chair: Antonio Hernando

Wednesday Afternoon, November 29, 2000
Room 200 (Hynes)

1:30 PM L8.1

CRITICAL BEHAVIOUR OF THE Fe₃Nd CLUSTER GLASS PHASE IN BULK GLASSY Nd₆₀Fe₃₀Al₁₀ HARD MAGNETS.

R.J. Ortega-Hertogs, K.V. Rao, Dept. of Materials Science

-Tmfy-MSE, Royal Institute of Technology, Stockholm, SWEDEN; and A. Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

The magnetic properties of novel bulk glassy Nd₆₀Fe₃₀Al₁₀ magnets around the transition to the paramagnetic state have been studied by magnetization measurements at constant dc-fields in the range 2.4–44 kA/m, at temperatures in the range 440–570K, and by magnetic thermogravimetry at fields ≈ 80A/m. Analysis of our data in the Curie-Weiss regime (effective moment and paramagnetic Curie temperature), as well as analyses of the critical behaviour of the isothermal susceptibility and magnetic isotherms suggest a transition from a low field state to a ferromagnetic-like or asperomagnetic state upon the application of high enough magnetic fields ≈ 28 kA/m. The ferromagnetic-like state is evidenced by a scaling of the magnetization curves with critical exponents $\gamma = 1.5(1)$, $\beta = 0.65(5)$, and $T_C = 465$ K, which correlates well with the expected exponents describing weak random magnetic anisotropy systems. A preliminary phase diagram for the cross over to the critical regime will also be presented.

1:45 PM L8.2

MICROSTRUCTURE CONTROLLED MAGNETIC PROPERTIES OF THE HARD MAGNETIC BULK GLASS Nd₆₀Fe₃₀Al₁₀.

S. Schneider, K. Samwer, I. Phys. Institut, U Goettingen, GERMANY; M. Seibt, IV. Phys. Institut, U Goettingen, GERMANY; A. Inoue, Tohoku University, Sendai, JAPAN; K.V. Rao, Royal Inst. of Technology, Stockholm, SWEDEN.

Among the growing family of bulk metallic glasses a number of ferromagnetic systems is known. While many of these show soft magnetic behavior, the Nd-Fe-Al alloy can have coercivities, as high as a few hundred kAm⁻¹ when cast into mm-sized samples. We report a combination of small angle neutron scattering (SANS), wide angle x-ray diffraction (XRD), and analytical transmission electron microscopy (TEM) studies on a 3mm Nd₆₀Fe₃₀Al₁₀ rod with pronounced hard magnetic behavior. These investigations show the existence of an in situ formed fine-dispersed crystalline phase which is Nd-rich. SANS data exhibit a power law behavior with an exponent of -2.5. This indicates the formation of a mass fractal and suggests that the crystalline Nd-rich phase forms a network embedding nm-sized Fe-rich clusters. Such a microstructure can explain the observed high as well as the low-temperature magnetic behavior. Convection flow patterns in the TEM images and the small crystal size indicate the formation of the primary phase in the undercooled liquid where the driving force for crystallization is high but the atomic mobilities are low. Consequently, the formation of the observed microstructure

should be suppressed at higher cooling rates in accordance with experimental data.

2:00 PM L8.3

LOCAL MAGNETIC STRUCTURE AND MAGNETIC PROPERTIES OF Nd₅₀Fe₄₀Si_{10-x}Al_x BULK GLASSY HARD MAGNETS. Horia Chiriac, Nicoleta Lupu, National Institute of Research and Development for Technical Physics, Iasi, ROMANIA; Robert Vandenberghe, Department of Subatomic and Radiation Physics, Gent University, Gent, BELGIUM; K.V. Rao, Department of Materials Science, Royal Institute of Technology, Stockholm, SWEDEN.

The local magnetic structure and magnetic properties of melt-spun amorphous ribbons with thicknesses up to 150 μm and bulk rods of 2 mm in diameter prepared by suction casting, of nominal compositions Nd₅₀Fe₄₀Si_{10-x}Al_x (x = 0; 10), were investigated with VSM, SQUID magnetometer, ac-susceptometer and Mossbauer measurements, in the temperature range 5K < T < 700 K. The large values of the intrinsic coercive force of over 2.5 kOe at room temperature and over 7.5 kOe at 200 K measured in low magnetic fields (up to 1.5 T) for the “X-ray amorphous” rapidly quenched ribbons and bulk rods, and its dependence on the temperature and the cooling rate are ascribed to the existence of very small clusters embedded in an antiferromagnetic Nd-rich matrix. That is in accordance with Fourier analysis of XRD spectra and with the results obtained by Mössbauer spectra, which indicate Fe-rich regions within the Nd-rich matrix. The size and the number of these clusters can be controlled and improved by applying proper annealing to the molten alloy before ejection or suction. The differences obtained between zero-field cooled (M_{ZFC}) and field cooled (M_{FC}) magnetization curves and the presence on the M_{ZFC} curves of one cusp and its displacement towards low temperatures with the increase of the applied field is related to the coexistence of ferromagnetic long-range order and short-range spin-glass-like behavior, even at room temperature.

2:15 PM L8.4

PROCESSING AND HARD MAGNETIC PROPERTIES OF NANOCRYSTALLINE Sm(Co,Zr)₇ MAGNET POWDERS. H. Tang, J. Zhou, Y. Liu, D.J. Sellmyer, Center for Materials and Analysis, University of Nebraska, Lincoln, NE.

Nanocrystalline Sm(Co,Zr) permanent magnet powders with TbCu₇ type structure has been synthesized by mechanically milling Sm_{12.5}Co_{87.5-x}Zr_x alloys (x = 0, 1, 2, 3) and subsequently appropriate annealing. Magnetic properties, structure and microstructure have been investigated by using VSM, SQUID magnetometer, XRD and TEM. The mechanical milling process of the alloys and the formation of nanocrystalline Sm(Co,Zr)₇ powders have been investigated. Hard magnetic properties have been found enhanced in the isotropic powders after milling and annealing due to the formation of nanocrystalline hard phase (grain size around 15–50 nm). Compared with the parent alloy (x = 0), the hard magnetic properties (coercivity H_{ci}, remanence M_r, maximum energy-products (BH)_{max}) have been enhanced greatly in the alloys with a small amount of Zr addition. For example, Sm_{12.5}Co_{87.5-x}Zr_x alloys milled for 20 hrs and subsequently annealed, have optimal values of room temperature H_{ci} of 13.50 kOe (x = 2), M_r of 73.36 emu/g (x = 1), M_r/M_s of 0.71 (x = 1), (BH)_{max} of 13.0 MGOe (x = 2), improved greatly compared with the parent alloy (x = 0) with optimal values, H_{ci} of 9.64 kOe, M_r of 71.93 emu/g, M_r/M_s of 0.66, (BH)_{max} of 11.05 MGOe. The hard magnetic properties are found to be sensitive to the mechanical milling time. The optimal value of H_{ci} of 18.65 kOe (M_r of 66.77 emu/g) for the Sm_{12.5}Co_{85.5}Zr₂ alloys milled for 10 hrs, is much higher (lower) than the value of H_{ci} of 13.50 kOe (M_r of 73.36 emu/g) for alloys milled for 20 hrs. The enhancement of remanence in this series of Sm_{12.5}Co_{87.5-x}Zr_x alloys is owing to the effective exchange coupling between the nano-sized grains. The hard magnetic properties are discussed with correlation to the structure and microstructure developed in the Zr-containing nanocrystalline Sm(Co,Zr) alloys.

SESSION L9: MECHANICAL PROPERTIES

Chair: Jurgen Eckert

Wednesday Afternoon, November 29, 2000
Room 200 (Hynes)

3:00 PM L9.1

MICROSTRUCTURES AND PROPERTIES OF METAL REINFORCED Zr₅₇Nb₅Al₁₀Cu_{15.4}Ni_{12.6} BULK METALLIC GLASS COMPOSITES. H. Choi-Yim, R.D. Conner and W.L. Johnson, W.M. Keck Lab of Engineering Materials, California Institute of Technology, Pasadena, CA.

To increase the toughness of a metallic glass with the nominal

composition $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$, it was used as the matrix in continuous fiber composites reinforced with W and also in particulate composites reinforced with W, W/Re, Ta, Mo, and Nb. Structure and microstructure of the composites are studied by X-ray diffraction, scanning electron microscopy, and electron microprobe. The metallic glass matrix remains amorphous after adding up to 80 vol.% of wires or 50 vol.% of particles. Dynamic deformation behavior of the composites is studied in ballistic tests. The tests were performed firing composite rods into 6061 T651 aluminum targets. The composite rods failed by localized adiabatic shear banding and exhibited self-sharpening behavior. Penetrator performance was 10 to 20% better than tungsten heavy alloy penetrators of comparable aspect ratio.

3:15 PM L9.2

BULK METALLIC GLASS MATRIX COMPOSITES CONTAINING IN SITU FORMED DUCTILE PHASE DENDRITE DISPERSIONS. C.C. Hays, C.P. Kim, and W.L. Johnson, Division of Engr. and Applied Science, California Institute of Technology, Pasadena, CA.

The recently developed families of Zr-based bulk metallic glass alloys show great promise as engineering materials. However, the application of these novel materials has been restricted by their limited ductility under unconfined loading conditions; i.e., specimens loaded in a state of uniaxial or plane stress fail catastrophically on one dominant shear band and show little global plasticity. Considerable success has recently been achieved in toughening bulk metallic glasses using in situ formed ductile phase dendrites in a metallic glass matrix [1]. In this paper we present the results of thermal analysis, x-ray diffraction, microstructural (SEM and TEM), and mechanical property measurements for a ductile metal reinforced bulk metallic glass matrix composite based on bulk glass forming compositions in the Zr-Ti-Cu-Ni-Be system. Primary dendrite growth accompanied by solute partitioning in the molten state yields an equilibrium microstructure consisting of ductile Ti-Zr-Nb dendrites in a Zr-Ti-Nb-Cu-Ni-Be bulk metallic glass matrix. Under mechanical loading the microstructure imposes constraints on the glassy matrix that leads to the generation of highly organized shear band patterns throughout the sample, where the shear band spacing is coherent with the periodicity of the dendrite dispersions. This results in a dramatic increase in the plastic strain to failure, impact resistance, and toughness of the metallic glass. These results are the first to show how microstructural inhomogeneities can be used to control the initiation and propagation of localized shear bands in metallic glasses under unconstrained loading conditions. [1]. C.C. Hays, C.P. Kim, and W.L. Johnson, Phys. Rev. Lett. 84, 2901 (2000).

3:30 PM L9.3

INTERNAL STRESSES IN BULK METALLIC GLASS MATRIX COMPOSITES. Ersan Ustundag, Danut Dragoi, Bjoern Clausen, California Institute of Technology, Dept. of Materials Science, Pasadena, CA; Dorian Balch, David C. Dunand, Northwestern University, Dept. of MS&E, Evanston, IL; Mark A.M. Bourke, Los Alamos National Laboratory, Los Alamos, NM.

Composites made of bulk metallic glass (BMG) matrices reinforced with metallic fibers and particulates (e.g., tungsten-W) have been shown to have superior mechanical properties compared to monolithic BMGs. However, the thermal expansion mismatch between the reinforcements and the matrix generate thermal residual stresses. Neutron diffraction and high-energy X-ray diffraction were used to measure these stresses in W/BMG composites. Next, the composites were loaded in tension and compression and the in-situ deformation of the reinforcements was investigated with the same methods. The results will be presented with an attempt to understand the mechanical behavior of the composites.

3:45 PM *L9.4

BULK AMORPHOUS AND NANOSCALE STRUCTURES IN TRANSITION METAL- AND RARE EARTH-BASED ALLOYS. J. Eckert, U. Kühn, G.J. Fran, W. Löser, S. Roth, IFW Dresden, Institute of Metallic Materials, Dresden, GERMANY.

Bulk amorphous alloy ingots have been prepared by copper mold casting in the Zr-(Ti/Nb)-Al,Cu-Ni and (Nd/Sm)-Fe-Co-Al systems. Depending on the actual alloy composition, quenching conditions and annealing treatment, either fully amorphous or nanocrystalline/amorphous, (nano)quasicrystalline/amorphous or nanocrystalline alloys with different grain size and volume fraction of nano-phases can be obtained. For several different alloys, ultrafine phase mixtures and microstructures with a scale of about 2 nm can be achieved, which yield a high stability against transformation into the equilibrium phases or coarsening. The thermodynamic and kinetic factors governing metastable phase formation in these complex systems will be discussed, considering the role of pronounced short-range ordering and possible phase separation in the melt. The role of quenched-in short-range/medium-range order clusters produced at different

quenching rates, strong liquid behavior and small driving force for crystallization as important parameters for nanostructure formation upon quenching or annealing will be critically assessed. This will be illustrated for selected transition metal- and rare earth-based systems. For Zr-based alloys, results for the deformation behavior at different temperatures and strain rates will be given for single-phase alloys and specimens with different size and volume fraction of nanophases. The contributions of different phases/volume fractions to the overall mechanical behavior will be critically assessed and linked to the microstructure of the material, focusing on the possibility of achieving a high room temperature strength combined with good ductility. For (Nd/Sm)-Fe-Co-Al alloys, the magnetic properties of samples prepared at different quenching rates will be compared. Whereas bulk cast samples are hard magnetic, rapidly quenched ribbons are magnetically rather soft. These findings will be linked to the tendency for developing pronounced short-range order/clustering in comparison to a random amorphous structure, and discussed in terms of magnetic exchange coupling interaction between structurally and chemically different heterogeneities.

4:15 PM L9.5

FRACTURE AND FATIGUE CRACK GROWTH OF BULK METALLIC GLASS ALLOYS AND THEIR COMPOSITES.

Katharine M. Flores, Reinhold H. Dauskardt, Department of MS&E, Stanford University, Stanford, CA.

The recent development of bulk metallic glasses allows their mechanical behavior to be observed and modeled under a variety of loading conditions and stress states. In this study we focus on the fracture and fatigue crack growth mechanisms of a Zr-Ti-Ni-Cu-Be bulk metallic glass and its composites. The monolithic alloy exhibits failure strengths on the order of 2 GPa and toughness values of 10-30 $MPa\sqrt{m}$ with remarkably little plastic deformation. Intense shear bands, associated with localized changes in free volume, form and propagate seemingly unimpeded through the material. Although under typical loading conditions shear band formation causes immediate failure, in the vicinity of a crack tip shear bands form stable damage zones where they can be studied more extensively. If properly stabilized, these zones increase the apparent toughness to more than 80 $MPa\sqrt{m}$. By modeling the damage zone as an array of branch cracks, we show that the intrinsic toughness of the material is on the order of 15 $MPa\sqrt{m}$, consistent with estimates based on Taylor's fluid meniscus instability. This has important implications for the design of bulk metallic glass matrix composites. The fracture and fatigue crack growth behavior of one such composite family utilizing a ductile particle reinforcement phase has been examined and is compared with that of the monolithic alloy. The second phase blocks the propagation of shear bands and distributes the plastic deformation over a larger volume. This gives rise to extensive stable crack growth at stress intensities double the intrinsic toughness of the unreinforced bulk metallic glass. More powerful toughening strategies, including crack bridging, will also be discussed.

4:30 PM L9.6

Abstract Withdrawn.

4:45 PM L9.7

SYNTHESIS AND CHARACTERIZATION OF IN-SITU BULK METALLIC GLASS MATRIX COMPOSITES. C.P. Kim, W.L. Johnson, California Institute of Technology, Keck Laboratory of Engineering Materials, Pasadena, CA.

A new class of bulk metallic glass matrix composites are prepared by rule of mixture combination of a metal or metal alloy with a good bulk metallic glass (BMG) forming composition in the Zr-Ti-Cu-Ni-Be system. The formula for such a mixture is given by $BMG(100-X)M(X)$, where M is Ta, Nb, V, or Mo. Upon cooling from high temperature of melt, the molten mixture undergoes partial crystallization by nucleation and subsequent dendritic growth of nearly pure M dendrites, with β phase symmetry, in the remaining liquid. The remaining liquid subsequently freezes to the glassy state producing a two-phase microstructure containing M rich β phase dendrites in an amorphous matrix. Differential cooling can produce oriented dendrites of ductile metal phase in an amorphous matrix. The orientation of dendrites influences the direction of strain in the composite and the direction of failure. By controlling the orientation of the dendrites, one can influence the direction of strain and failure. X-ray diffraction, scanning electron microscopy, and microprobe analysis results are presented.

SESSION L10: MECHANICAL AND OTHER PROPERTIES

Chairs: Robert O. Ritchie and A. Lindsay Greer
Thursday Morning, November 30, 2000
Room 200 (Hynes)

8:30 AM *L10.1

COMPARISON OF THE MECHANICAL BEHAVIOR AND QUALITY OF METALLIC GLASSES IN RIBBON AND BULKY SHAPES. M. Calvo-Dahlborg, Laboratoire de Science et Génie des Matériaux Métalliques (LSG2M), CNRS UMR7584, Ecole des Mines, Nancy, FRANCE.

A short history on the appearance of metallic glasses of large dimensions, so-called "bulks", is recalled. The quality and mechanical behavior of metallic glasses in the shape of ribbons is reviewed. The problems encountered for their technological applications and especially connected to their small dimensions and to the production conditions are detailed. It is emphasized how much the need of thick samples of good quality is also important from a theoretical point of view, especially in terms of fracture mechanics. What was expected with the "bulks" from the reported good properties of the ribbons is discussed. The quality and mechanical behavior of the presently produced bulk amorphous alloys is reviewed from the numerous studies reported in the literature. The reality is compared with the hopes, both in terms of quality and of mechanical behavior as well as in relation to the production conditions. Conclusions are drawn from this comparison.

9:00 AM L10.2

IN-SITU OBSERVATIONS OF SHEAR BAND DEVELOPMENT DURING DEFORMATION OF A BULK METALLIC GLASS. P. El-Deiry, R.P. Vinci, Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA; T.C. Hufnagel, The Johns Hopkins University, Department of Materials Science and Engineering, Baltimore, MD.

This work comprises a study of the development of shear band structure in a $Zr_{57}Ti_{15}Cu_{20}Ni_8Al_{10}$ bulk metallic glass during deformation. It is well known that low temperature plastic deformation in metallic glasses is concentrated into narrow regions called shear bands. In certain geometries, such as uniaxial tension, the resulting deformation is unstable. Hence, brittle failure follows shortly after the onset of yielding. In other geometries, such as bending and uniaxial compression, multiple shear bands can form. This results in behavior that is apparently "elastic-perfectly plastic". One feature of interest that has been observed in stress-strain curves from quasistatic uniaxial compression tests is the presence of "serrated-flow" in the plastic regime.

In order to investigate the relationship between shear band development and serrated flow, we performed three-point bend tests in an environmental scanning electron microscope. During the deformation, load-deflection data and surface images were simultaneously recorded. We observed that the appearance of the first shear bands coincided with the onset of plastic deformation. However, there was no evidence for "homogeneous" plastic deformation. As the load increased, the number of shear bands forming increased dramatically up to the point of maximum load. In the load-deflection data, yield drops or "serrated-flow" appeared to be correlated with new shear band initiation. Continued deformation beyond the point of maximum load occurred primarily as the result of slip along existing shear bands. As slip occurred, new secondary shear bands initiated at the previously existing primary bands. Results from in-situ uniaxial compression tests will be compared to those of the three-point bend tests.

9:15 AM L10.3

EFFECTS OF HYDROGEN ON THE CRYSTALLIZATION AND MECHANICAL BEHAVIOR OF A Zr-Ti-Ni-Cu-Be BULK METALLIC GLASS. Daewoong Suh and Reinhold H. Dauskardt, Department of Materials Science and Engineering, Stanford University, Stanford, CA.

Hydrogen is a well-known embrittling species in a wide range of crystalline metals. A great deal of research has been undertaken leading to several viable mechanisms of hydrogen embrittlement in crystalline metals. Previous studies of metallic glasses in the form of thin ribbons suggest that they are susceptible to similar deleterious effects of hydrogen embrittlement. Understanding of hydrogen embrittlement in amorphous metals is, however, far from complete compared to the considerable progress that has been achieved in crystalline metals. The objective of the present work is, therefore, to investigate the effects of hydrogen on the deformation and fracture behavior of a Zr-Ti-Ni-Cu-Be bulk metallic glass, specifically hardness and crack-propagation behavior under both monotonic and cyclic loading. Microstructure, glass transition and crystallization kinetics of the hydrogen-charged metallic glass were examined using high-resolution electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and differential scanning calorimetry to identify the microstructural origin of hydrogen effects in the amorphous microstructure. It was found that hydrogen shifted glass transition (T_g) and crystallization (T_x) temperatures to higher values and significantly retarded crystallization kinetics measured by

isothermal transformation study. These results suggest sluggish atomic relaxation process for plastic flow of hydrogen-charged amorphous microstructure. This retarded atomic relaxation process is believed to be responsible for increased flow stress and degraded toughness. Mechanisms are discussed in terms of changes of microstructure, short-range structure and defect concentration caused by hydrogen charging.

9:30 AM *L10.4

ABRASIVE WEAR RESISTANCE OF BULK METALLIC GLASSES. A. Lindsay Greer, Univ of Cambridge, Dept of Materials Science & Metallurgy, Cambridge, UNITED KINGDOM.

Wear resistance can be an important property, even for applications based on non-mechanical (for example, magnetic) properties. Recent measurements of microhardness and abrasive wear resistance of bulk metallic glasses are presented, in the context of tribological studies of metallic glasses in general which now extend over several years. The focus of the work is on bulk glasses based on Zr, La, Pd and Mg. The glasses have a ratio of wear resistance to hardness which places them in the category of hardened conventional metallic alloys. The ratio is smaller than for pure metals, but larger than for typical ceramics. This correlates well with the lack of work-hardening and local plastic flow in the glasses. The hardness and wear resistance of the glasses scale with the Young's modulus of the glass. The prospects for improving the hardness and wear resistance are reviewed; both devitrification (partial or complete) and addition of ceramic dispersions are considered. Overall, the high hardness and wear resistance of the glasses suggest their potential use as coatings for tribological applications.

10:30 AM *L10.5

NEWTONIAN FLOW IN BULK METALLIC GLASSES. T.G. Nieh, Lawrence Livermore National Lab, Livermore, CA; C.T. Liu, Oak Ridge National Lab, Oak Ridge, TN.

Bulk metallic glasses have good mechanical formability in viscous states. The good formability offers a great advantage of fabricating near-net-shape structural components. Whereas large tensile ductility has been observed in metallic glasses in the supercooled liquid region, the exact deformation mechanism, and particularly whether such alloys deform by Newtonian viscous flow ($m=1$, where m is the strain rate sensitivity exponent) or not, remains a controversial issue. In this paper, existing data are analyzed and the apparent controversy is discussed. Results obtained from two amorphous alloys (composition: $Zr_{10}Al_5Ti_{17.9}Cu_{14.6}Ni$ and $Zr_{10}Al_5Ni_{30}Cu$, both in at.%) are presented. Dynamic structural evolution is characterized using electron microscopy and focus x-ray. It is demonstrated that the observed non-Newtonian behavior is a result of stress-induced crystallization of the amorphous structure.

11:00 AM L10.6

ELASTIC PROPERTIES OF TWO BULK METALLIC GLASSES: EVOLUTION VERSUS TEMPERATURE IN THE GLASS TRANSITION REGION AND INFLUENCE OF CRYSTALLIZATION. Bertrand Van de Moortèle, Jean-Marc Pelletier, GEMPPM, INSA, Villeurbanne, FRANCE; Jean-Louis Soubeyroux, CNRS, Grenoble, FRANCE; Ing-Ru Lu, DLR, Köln, GERMANY.

The mechanical behavior of non-crystalline solids (polymers, oxide glasses, ...) depends strongly on temperature. In metallic glasses, various studies were reported on this behavior. However, due to their limited thermal stability, investigations in the supercooled liquid region (SLR) are difficult to achieve. In the present study, two "classical" bulk metallic glasses were investigated: Zr-Ti-Cu-Ni-Al and Pd-Ni-Cu-P. Experiments in DSC were made with different heating rates to determine the beginning and the end of glass transition (T_{g1} and T_{g3} , respectively) and the onset of crystallization (T_x). The complex shear modulus $G^*(i\omega) = G'(i\omega) + iG''(i\omega)$ was measured versus temperature (between 20 and 600°C) and versus angular frequency ($\omega = 2\pi f$, $10^{-4} < f < 1$ Hz) (G' : storage modulus, G'' : loss modulus).

In the Zr-base alloy, it is generally admitted that the SLR spreads over about 30-50K; however this value refers to the difference between T_x and T_{g1} . While, considering the effective onset of this region (T_{g3}), leads to a much more limited interval. Various experiments (X-ray diffraction, small angle X-ray scattering, transmission electron microscopy) were performed to investigate the onset of crystallization and they confirm the poor stability of this material against crystallization.

In contrast, in the Pd-base alloy, a wide effective SLR is observed. The existence of this region allows to compare the evolution of the elastic modulus through the glass transition in this metallic glass with that reported in other amorphous materials (polymers, oxide glasses, ...). A similar behavior is observed, i.e. a large decrease of the storage modulus (G') (about three decades) and a maximum of the loss modulus (G'').

Crystallization leads to a very important increase of the shear modulus. Finally, a physical analysis of these phenomena is presented.

11:15 AM **L10.7**

ON THE HIGH TEMPERATURE CREEP AND RELAXATION BEHAVIOR OF Zr-BASED BULK METALLIC GLASSES.

M. Heilmaier, B.S.S. Daniel, A. Reger-Leonhard, J. Eckert and L. Schultz, IFW Dresden, Institut für Metallische Werkstoffe, Dresden, GERMANY.

Bulk metallic glasses processed at very low cooling rates of 1-10 Ks⁻¹ to vitrify without crystallisation have attracted much interest regarding their atomic structure and the ensuing properties. These multi-component alloys also exhibit a wide supercooled liquid region which provides excellent stability against crystallisation, enabling fabrication of components with the smallest dimension of 10 mm using conventional casting technique. In the present study, 50 mm long ingots with diameters ranging from 3 to 5 mm of Zr₅₅Cu₃₀Al₁₀Ni₅ metallic glass were produced by casting into a copper mould under argon atmosphere from which cylindrical samples of 6 mm length were cut for compression testing. Additionally, microstructures consisting of a metallic glass matrix with nanometer sized crystallite precipitates of different shapes were synthesized. Creep tests under constant load as well as constant true strain rate were carried out at temperatures near T_g to study the time dependent flow behavior. In a particular experiment, the cross-head of the machine was stopped at different strain levels and an attempt was made to correlate the stress decay with the generation and annihilation of free volume in the amorphous structure. The log $\dot{\epsilon}$ - log σ relation over a wide $\dot{\epsilon}$ -range (10⁻⁷ to 10⁻² s⁻¹) was established for different temperatures. Both, the amorphous and partially crystalline alloys exhibit homogeneous shape change and truly Newtonian viscous flow (stress exponent of $n = 1$) at low strain rates. The appearance of its breakdown ($n > 1$) at higher applied strain rates and/or lower temperatures is connected with a transition towards inhomogeneous flow behavior. The observed deformation behavior including its temperature dependence can be described within the framework of the transition state theory.

11:30 AM ***L10.8**

DEFORMATION BEHAVIOR IN BULK METALLIC GLASSES.

Yoshihito Kawamura, Akihisa Inoue, IMR, Tohoku Univ., Sendai, JAPAN.

Deformation Behavior in Bulk Metallic Glasses Yoshihito Kawamura and Akihisa Inoue IMR, Tohoku Univ, Sendai, JAPAN Deformation behavior of Bulk Metallic Glasses was investigated by constant strain-rate stretching in Zr-Al-Ni-Cu, Pd-Ni-P, La-Al-Ni and Pt-Ni-P glasses. Deformation in metallic glasses was divided into three modes, inhomogeneous mode, and homogeneous modes with and without stress overshoot by the appearance of stress-strain curve. Yield stress, steady flow stress, stress overshoot and elongation to failure, as well as the deformation mode, were strongly dependent on temperature and strain rate. In the homogeneous deformation mode, the supercooled liquid exhibited Newtonian viscous flow that corresponds to equilibrium viscosity, and the transition to non-Newtonian flow occurred at critical strain rate. On the other hand, the glassy solid exhibited only non-Newtonian flow. The viscosity was expressed by a stretched exponential function. The stress overshoot in stress-strain curves was a characteristic feature in the non-Newtonian flow region. The stress overshoot was dependent on temperature and strain rate. Moreover, the stress overshoot appeared again after stress relaxation, which increased with the stress-relaxation fraction. A change in strain rate during plastic deformation, furthermore, gave rise to stress overshoot or undershoot which was sensitive to the increment in the strain-rate change. The stress overshoot seemed to be caused by a change in atomic mobility due to yielding. In the supercooled liquid state, the metallic glasses exhibited high-strain-rate superplasticity. Both the crystallization and non-Newtonian transition restricted the elongation to failure, and the maximum elongation was obtained at the critical strain rate of the Newtonian viscosity at each temperature. The well-known Vogel-Fulcher-Tammann formulation was insufficient to describe the equilibrium viscosity data over the wide temperature interval ranging from the glass transition regime to the melting regime. On the contrary, Cohen-Grest formulation gave a good approximation to the experimental data over the entire temperature range. The equilibrium viscosity of the supercooled liquid in the metallic glasses exhibited an intermediate fragility between the strong and fragile glasses.

SESSION L11: MECHANICAL AND OTHER PROPERTIES (continued)

Chairs: T. G. Nieh and Ricardo B. Schwarz
Thursday Afternoon, November 30, 2000
Room 200 (Hynes)

1:30 PM ***L11.1**

LOCAL ATOMIC STRUCTURES AND PLASTIC DEFORMATION MODES IN THE SUPERCOOLED LIQUID STATE OF

La₅₅Al₂₅Ni₂₀. Tadakatsu Ohkubo, Yoshihiko Hirotsu, Osaka Univ, Inst. of Sci. & Ind. Res., Osaka, JAPAN; Akihisa Inoue, Tohoku Univ, Inst. of Mater. Res., Sendai, JAPAN.

Amorphous La₅₅Al₂₅Ni₂₀ alloy has an excellent superplasticity in the stable supercooled liquid state between temperatures from about 470 to 515K. These temperatures, 470 and 515K, correspond to those of the glass transition (T_g) and the crystallization (T_x), respectively. We have recently performed an *in-situ* electron diffraction and HREM study of this alloy by annealing up to T_x using specimen-heating stage in TEM. Diffraction intensities were recorded on imaging plates. In order to avoid inelastic scattering, energy-filter was used. Any appreciable change was observed by HREM on heating across the temperature T_g. However, atomic radial distribution function analysis revealed that a clear structural change proceeds in the temperature range between T_g and T_x on an atomic level. The structural change is concerned with a local phase separation due to strong atomic correlations especially for La-La and Al-Ni. On the basis of the above structural data, several structure models for the structures at temperatures between T_g and T_x were constructed using molecular dynamics (MD) simulation and reverse Monte-Carlo (RMC) simulation techniques. The MD simulation was used to set up initial structures for the RMC simulations. These constructed structure models were then utilized for MD simulations of plastic deformation in the supercooled liquid state. The simulations with and without the structural periodic boundary conditions showed a difference in the plastic deformation phenomenon especially in relation to diffusion rates of constituent atoms. A larger elongation was obtained for the structure near T_g, but for the structure near T_x the elongation was relatively smaller, due to the local phase separation. These simulation results correspond to the experimental elongation behaviors in superplastic deformation that the elongation is enhanced near T_g but suppressed as the temperature is increased towards T_x.

2:00 PM **L11.2**

STRAIN SOFTENING IN BULK METALLIC GLASSES. Ou Jin, Carl M. Cady, Ricardo B. Schwarz, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

The recent advent of bulk metallic glasses has attracted great interest in these materials because of their potential applications. However, the brittle nature of bulk metallic glasses below the glass transition temperature limits their applicability and requires further investigation. At temperatures approaching the glass-transition temperatures, the mechanical properties of bulk metallic glasses may involve free volume relaxation, short-range re-ordering and phase separation. As shear defects are harder to detect in amorphous than in crystalline materials, mechanical tests may lend us some understandings on the nature of the microscopic defects responsible for plastic deformation. We have studied the mechanical properties of Pd-Cu-Ni-P bulk glasses at temperatures 80 to 40K below the glass transition temperature. Constant strain-rate compression and creep tests revealed a strain-softening phenomenon. The stress-strain curve measured at the constant strain-rate exhibited a pronounced yield peak at around 2% plastic strain, followed by homogeneous flow without apparent stress increase. The yield peak was larger in samples pre-annealed at the deformation temperature. However, when the sample was loaded to a constant load below the yield point, the strain slowly accelerated, taking the sample across the yield peak. The strain acceleration rate increased with the increase of the load applied to the sample. The experimental results are discussed in terms of the generation and annihilation of short-range order during the deformation. This study suggests that bulk metallic glasses may be shaped by forging at temperatures well below their glass transition temperatures.

2:15 PM **L11.3**

INTERNAL FRICTION AND ELASTIC MODULUS CHANGE ASSOCIATED WITH STRUCTURAL RELAXATION AND CRYSTALLIZATION IN AMORPHOUS Mg-Ni-Y ALLOYS. Yakov Soifer, Nikolai Kobelev, Inst of Solid State Physics, Chernogolovka, Moscow Region, RUSSIA; Eli Korin, Leonid Soifer, Dmitrii Mogylanskii, Armond Bettelheim, Dept of Chemical Engineering, Ben-Gurion Univ of Negev, ISRAEL.

Mechanical spectroscopy techniques has been applied to investigation of structural relaxation and crystallization of Mg-Ni-Y amorphous alloys. The composition of the alloys was varied due to change of yttrium concentration from 0 to 9 at.%. at corresponding magnesium decrease. The internal friction and Young's modulus of amorphous Mg-Ni-Y alloys obtained by the melt spinning technique have been measured by a vibrating reed method at frequency of 250 Hz at heating and cooling runs in the temperature range from 300K to 650K. The structural relaxation and different stages of crystallization as can

seen through the changes of the Young's modulus and internal friction spectrum of the sample as a function of temperature has been studied. These results have been compared with x-ray and DSC measurements. The study has revealed a strong correlation between the internal friction and DSC spectra. It has been found that The transition from amorphous to nanocrystalline state in the Mg-Ni-Y alloys has been revealed to go through several stages with origination of intermediate phases. It has been studied kinetics of the different crystallization stages, the structure stability of intermediate phases, and their dependence on chemical composition of the alloys investigated. The special attention has been focused on the enhanced mechanical properties (microhardness and rigidity modulus) of the intermediate phase. It has been established the connection of this phenomena with yttrium concentration in alloy and conditions of the heat treatment. The internal friction spectra and accompanying Young's modulus of the alloys have been analyzed from the point of view of structure relaxation and crystallization from amorphous to nanocrystalline state and related to the interface micro-sliding mechanism.

2:30 PM *L11.4

STRESS RELAXATION, GLASS TRANSITION AND VISCOSITY OF Zr-Al-Ni-Cu THIN FILMS. U. Geyer, M. Bicker, I. Physikalisches Institut, U Goettingen, GERMANY.

By means of a very sensitive technique we determine stress formation and stress relaxation in thin films with thicknesses down to a few nm. This allows to quantitatively measure density changes due to structural relaxation or crystallization. Furthermore, in thin films prepared from bulk metallic glass forming alloys one can observe the glass transition. Thin Zr-Al-Cu-Ni films are prepared by magnetron sputtering under compressive stresses, and the relaxation of these stresses during linear heating ramps is investigated. Different stress effects are found and can be attributed to thermal expansion of the glass, structural relaxation and annealing-out of excess volume, the glass transition, thermal expansion of the undercooled liquid and crystallization. In the glass transition regime compressive stresses quickly relax to zero until the equilibrium undercooled liquid is reached. Comparison with differential scanning calorimetry of micron-thick sputtered films verifies that the observed stress relaxation is a fingerprint of the glass transition. Isothermal stress relaxation following a step-like temperature change makes viscosity measurement possible. We demonstrate how the stress measurement technique can be used to search for a possible size (=thickness) dependence of the glass transition in these metallic systems.

3:30 PM L11.5

THE SHEAR MODULUS OF $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (VIT 1) IN THE SUPERCOOLED LIQUID AND GLASSY STATE. A.S. Bains, C.A. Gordon, A.B. Lebedev¹, A.V. Granato, Physics Dept., University of Illinois, Urbana, IL; M.A. LaMadrid², W.L. Johnson, Dept. of Materials Science and Engineering, California Institute of Technology, Pasadena, CA. ¹Ioffe PhysicoTechnical Inst; ²Univ of Washington.

Using an EMAT technique, we have measured the temperature dependence of the infinite frequency shear modulus of this five component alloy at constant heating rate in the glassy and supercooled liquid states. Values of the shear softening fragility parameter $-\ln(G/G_g)/d(T/T_g)$ are compared with those obtainable from frequency dependent shear moduli, specific heat and viscosity measurements, using the Interstitial Theory of Condensed Matter States. There is overall agreement found between these independently measured values. Supported by NSF Grant DMR9705750.

3:45 PM L11.6

SERRATED PLASTIC FLOW IN $Zr_{40}Ti_{14}Ni_{10}Cu_{12}Be_{24}$ BULK METALLIC GLASS. Wendelin J. Wright and William D. Nix, Department of MS&E, Stanford University, Stanford, CA.

We have studied the serrated plastic flow observed in the $Zr_{40}Ti_{14}Ni_{10}Cu_{12}Be_{24}$ bulk metallic glass alloy when it is tested in uniaxial compression. Serrated flow, which is characterized by repeating cycles of a sudden stress drop followed by elastic reloading, is due to the propagation and arrest of shear bands. Multiple serrations are observed in every compression test. Quantitative measurements with sufficient temporal resolution to record the fine-scale structure of the data are reported. The unloading rate, the displacement rates (total, elastic, and plastic), and the time elapsed during unloading are analyzed for each serration. These mechanical measurements are corroborated with optical and scanning electron microscopy. A possible failure criterion for this alloy will be discussed. The results of combined compression and torsion experiments will also be presented.

4:00 PM L11.7

SERRATED FLOW AND FRACTURE OF Zr-Ti-Cu-Ni-AL BULK

AMORPHOUS ALLOY. Li-qian Xing, Todd C. Hufnagel, Dept of MS&E, Johns Hopkins Univ, Baltimore, MD; K.T. Ramesh, Dept of Mechanical Engineering, Johns Hopkins Univ, Baltimore, MD.

We have investigated deformation and fracture of Zr-Ti-Cu-Ni-Al bulk amorphous alloys under quasi-static uniaxial compression. The "serrated plastic flow" that occurs in these alloys is composed of repeated sections of elastic deformation followed by abrupt load drops. By compressing the specimens to various strains short of failure in the plastic region and examining the sample surface microscopically, we observed the development of the shear band structure and conclude that the sudden load drops are due to formation of shear bands that propagate across the sample but do not cause failure. By measuring the acoustic emission that occurs during fracture, we found that fracture occurs in a manner of discrete bursts. These pauses between the bursts may be due to pause in the crack propagation. Microscopic analysis shows that bunches of shear bands, small cracks, or both can be initiated ahead of the main crack tip. These release the stress concentration at the crack tip and may therefore cause the pauses in the crack propagation.

4:15 PM L11.8

A DERIVATION OF THE VOGEL-FULCHER-TAMMANN RELATION FOR SUPERCOOLED LIQUIDS. A.V. Granato, Physics Dept. University of Illinois, Urbana, IL.

It has been known for about 75 years that the 3-parameter non-Arrhenius Vogel-Fulcher-Tammann relation for the viscosity η , $\ln\eta/\eta_0 = U_0/k(T-T_0)$ describes simply one of the most characteristic features of supercooled liquids. Using the Interstitial Theory of Condensed Matter (Phys. Rev. Lett. vol 68, 974 (1992)) and the Dyre, et al (Phys. Rev. vol B53, 2171 (1996)) Shoving Model for diffusion, we derive this relation and obtain $T_0/T_g = \gamma/(\gamma - 1)$, and $U_0 = U(T_g)/(\gamma - 1)$, where γ is a softening parameter given by $\gamma = -\ln G/d(T/T_g)$ with G the shear modulus and $U(T_g)$ the interstitial migration energy at the glass temperature T_g . γ is related to the normalized fragility parameter by $\gamma - 1 = f = F/\log(\eta_g/\eta_0)$, where F is the Angell fragility $d\log\eta/d(T_g/T)$. Work is supported by the National Science Foundation under Grant DMR 97-05750

4:30 PM L11.9

SYNTHESIS AND VISCOELASTICITY OF Zr-BASED BULK GLASSY ALLOY CONTAINING ZrC PARTICLES. Hidemi Kato, Tomoya Hirano, Yoshihito Kawamura, Akihisa Inoue, IMR, Tohoku Univ, Sendai, JAPAN; Ho-Sou Chen, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

The recent developments of glassy alloys that have high glass-forming ability and high thermal stability against crystallization allow us to use them for fundamental investigations and practical uses. The multicomponent Zr-Al-TM (TM= transition metals) alloy system is known to be one of the best glass formers. Although the bulk glassy alloys exhibit high strength of almost 1.8GPa, the plastic strain is nearly zero. With the aim of improving the mechanical properties without macroscopic elongation, we have studied the synthesis and mechanical properties of bulk glassy $Zr_{55}Al_{10}Ni_5Cu_{30}$ composite materials containing ZrC particles. Recently, we have found that an in-situ reaction between Zr metal and graphite to form ZrC particles during preparation is effective for improvement of the mechanical properties of the composite glassy alloy because the in-situ reaction achieves good wettability and homogenized dispersion of the filler particles. This paper is intended to demonstrate the good effect of the in-situ reaction method on the synthesis of the composite glassy alloy and to examine the feature of its viscoelasticity in comparison with that of the $Zr_{55}Al_{10}Ni_5Cu_{30}$ single glassy phase.

4:45 PM L11.10

HYDROGEN-DOPED BULK METALLIC GLASSES AS HIGH DAMPING MATERIAL. Teruaki Yagi, Rikiya Oguro, Ryuji Tamura, Shin Takeuchi, Science Univ of Tokyo, Dept of Materials Science and Technology, Chiba, JAPAN.

Bulk metallic glasses have extremely high strength and high ductility and are quite useful as structural material. Many of bulk metallic glasses are based on Zr, Ti and Pd; these elements have a high affinity for hydrogen and hence the bulk metallic glasses can contain a high density of hydrogen atoms. It is known that hydrogenized amorphous metals, as well as hydrogenized metallic crystals, exhibit Snoek-type relaxation, and hence metallic glasses containing a high density of hydrogen can have a high internal friction. In the present experiments, internal friction measurements have been performed for Zr-based and Pd-based metallic glasses doped with a variety of hydrogen concentrations. It is shown that the peak value of the internal friction reaches the order of 10^{-2} with the average activation energy of about 0.5eV in Zr-based bulk metallic glasses which have the fracture strength as high as 1.5GPa. Thus, we have shown that

hydrogen-doped bulk metallic glasses can be used as a high-strength, high-damping material.

SESSION L12: POSTER SESSION
Chairs: Yoshihiko Hirotsu and Ulrich Geyer
Thursday Evening, November 30, 2000
8:00 PM
Exhibition Hall D (Hynes)

L12.1

CORRELATION BETWEEN RESISTIVITY CHARACTERISTICS AND ELECTRONIC STRUCTURE PARAMETERS OF THE Ni-Pd-P AMORPHOUS ALLOYS. Mykola Babich, Olesya Nakonechna, Mykhailo Semen'ko, Gennady Yermenko, Mykola Zakharenko, Taras Shevchenko National University, Dept. of Physics, Kyiv, UKRAINE; Alain R. Yavari, LTPCM-CNRS, INPG, St. Martin-d-Heres, FRANCE.

The temperature dependencies of resistivity $R(T)$ of the Ni-Pd-P-based amorphous alloys (P content varied from 14 to 23 at.%) have been measured in a wide temperature range using the standard four-probe method. The linear character of $R(T)$ curves permits us to use the Faber-Ziman theory to describe the obtained dependencies. The temperature coefficients of resistivity (TCR) have been calculated. TCR value is decreased with P content increasing and becomes negative for alloy with 23 at.% of P. On the other side TCR value is increased with Pd content increasing while P content is not changed. Such behavior could be attributed to the electronic transfer effect from Ni to Pd and from P to Ni. This leads the Fermi level shift according to d-band edge and to the influence of the Mott's localized states contribution. The peculiarities caused by structural relaxation processes have been observed at the temperature range of 550 - 620 K. This effect is the most noticeable for the glasses with the lowest P content. The relaxation process was shown to be at least two stages. The first stage corresponds to the free volume exhausting and the second one - to the short range chemical ordering due to P migration.

L12.2

PHASE EVOLUTION IN Fe/Ag-Sm NANOCOMPOSITES. Victor Kuncser, Adrian Jianu, Radu Nicula, Eberhard Burkel, Rostock Univ, Dept of Physics, Rostock, GERMANY.

The case of magnetic nanometer scale granular particles embedded in a metallic immiscible matrix were extensively studied recently due to their peculiar mechanical, electrical and magnetic properties with important technological applications. An innovative approach for obtaining atomic-scale intermixing of immiscible elements using interlinking chemical species was attempted for the difficult case of the silver-iron pair. A metastable state of the components was first obtained by non-equilibrium alloying methods. The separation of phases and the grain growth processes were promoted by subsequent procedures, e.g. by annealing treatments. We here report on the possibility of intermixing various contents of iron in a silver matrix by high-energy ball-milling. The intermixing process and the evolution of phases was monitored vs. the milling time by electron microscopy, high-resolution X-ray diffraction and Mössbauer spectroscopy. Both X-ray diffraction and Mössbauer spectroscopy results indicate a rapid intermixing process between the initial Fe powder and the Ag₈₅Sm₁₅ alloy ribbons obtained by rapid-quenching. After 50 hours milling time at a milling frequency of 250 rpm only approx. 10% of the initial bcc iron phase could be evidenced. Information about the structural coherence length of the Ag-Sm-Fe solid solution were obtained from the evolution of the X-ray diffraction linewidths. The effect of the embedding Ag-based matrix on the bcc iron phase during the ball-milling process was clarified using both X-ray diffraction and Mössbauer spectroscopy methods. Magnetic interactions among the nanoparticles were analysed from temperature-dependent Mössbauer spectra. The local atomic configuration around Fe atoms as well as the degree of homogeneity of the different solid solutions were obtained from the distribution of hyperfine parameters. The stability of the solid solutions with temperature under applied pressures in the GPa range was investigated via in-situ X-ray scattering experiments performed in transmission mode at the Deutsches Elektronen Synchrotron HASYLAB/DESY (Hamburg, Germany).

L12.3

ANOMALOUS X-RAY SCATTERING ON MOLYBDENUM-GERMANIUM ALLOYS. Hope Ishii, Sean Brennan, Arthur Bienenstock^a, Stanford University, Stanford Synchrotron Radiation Lab, Stanford, CA; ^acurrently on leave at Office of Science and Technology Policy, Washington, DC.

Contrary to early implicit assumptions, vapor-deposited amorphous metal-germanium samples are not always single phase. In the composition range between 0 and 23% Mo, two phases with

compositions of approximately Ge and MoGe₃ have been observed. When alloyed with Ge, a tremendous array of metallic elements, M, across the periodic table (including M=Mo, Fe) form crystalline digermanides as the Ge-rich equilibrium phase. The chemical bond typically dominates in amorphous systems as well. It is presumed that this 1:2 M-to-Ge stoichiometry provides the most stable phase in the amorphous state as in the crystalline state. Therefore, the 1:3 Mo-to-Ge stoichiometry discovered in the Mo-Ge system is unexpected. We apply anomalous x-ray scattering (AXS) to *a*-MoGe₃, the metal-rich endpoint for phase separation in the sputtered Mo-Ge amorphous alloy system. Near the atomic absorption edges of the elements in the sample, the atomic scattering factor can be changed by varying the incident x-ray energy. The resulting changes in diffracted intensities can be extracted as chemically-specific structural information in the form of differential and partial distribution functions (DDFs and PDFs). The solution to the problem, however, is "ill-conditioned" and small errors in measurements lead to large errors in the PDFs. To address this sensitivity, sources of error were removed experimentally where possible: Anomalous scattering factors were directly measured, and a variable-focus graphite analyzer crystal was used to disperse scattered radiation onto a position-sensitive linear detector. The result is low background and sufficient energy resolution to allow direct removal of K_{β} resonant Raman scattering and Compton scattering over most of the reciprocal space range investigated. Using these improved experimental methods, DDFs and PDFs are obtained. Reliability and structural interpretations of these distribution functions will be discussed with the goal of understanding the metastability of the *a*-MoGe₃ phase.

L12.4

STRUCTURAL AND THERMODYNAMIC CHARACTERISTICS OF AMORPHOUS ALLOYS CREATED IN AN IMMISCIBLE SYSTEM. J.H. He¹, H.W. Sheng¹, P.J. Schilling², and E. Ma¹.

¹Department of MS&E, Johns Hopkins University, Baltimore, MD; ²Department of Mechanical Engineering, University of New Orleans, New Orleans, LA.

While the majority of amorphous alloys produced to date are in systems exhibiting a negative heat of mixing, there have also been occasional reports of amorphous phases in systems with a positive heat of mixing. However, the nature of these latter amorphous alloys, invariably created through extremely nonequilibrium processing routes, has seldom been probed on the atomic level. It is thus not understood as to exactly what kind of amorphous alloys have been obtained in experiments. Particularly interesting is the recent observation that amorphous alloys obtained in immiscible systems can exhibit heat of mixing of different magnitude and even sign, which must have its origin in the details of the internal local environments. Such systems are also of relevance to the multi-component bulk metallic glass forming liquids, because the latter alloys often involve elements with positive heat of mixing such that miscibility gaps and (spinodal) decomposition processes play an important role in controlling the glass forming ability. In this work, we report a detailed study of the atomic-level structure and its correlation with the measured thermodynamic properties of Ag-Ni amorphous alloys. We show XRD, TEM, EXAFS, and DSC evidence that under certain co-sputtering conditions at cryogenic temperatures amorphous alloys can be obtained in this highly immiscible system. The amorphous phase exhibits a low crystallization temperature and small crystallization enthalpy in calorimetry measurements, indicating that the alloy is in an unexpectedly low energy state. Our analyses of the local structures based on the EXAFS data, via reverse Monte Carlo (RMC) simulations, demonstrate that strong short-range clustering tendencies exist in these amorphous alloys and are responsible for the enthalpy state observed. The low energy state is further confirmed by calculations using the RMC configuration and EAM potential.

L12.5

THE GLASS TRANSITION AND LOW ENERGY EXITATIONS IN SUPERCOOLED METALLIC LIQUIDS AND GLASSES.

Ikuzo Kanazawa, Tokyo Gakugei Univ, Dept of Physics, Tokyo, JAPAN.

Although there are many interesting studies for the dynamics of supercooled liquids and the structural glass transition, a satisfactory theory of the glass transition in supercooled liquid is not yet confirmed so far. Recently Kivelson et al(1) present an important theoretical approach, which is referred as the frustration-limited domain (FLD) theory. In this theory, the frustration, which is described by Coulombic form of long-range interaction, plays an important role in the properties of supercooled liquids. In this study, adopting the theoretical formula(4-5) extended from the Nelson-Sachdev-Sethna formula(2-3), we will propose the theory of supercooled metallic liquids and glasses, based on the gauge invariant Lagrangian with spontaneous breaking. Using this theoretical formula, the mean field theory with the replica method is proposed to represent the metallic glass system. We introduce the order

parameter, which identifies the glass phase, by using the topological number of the hedgehog-like solitons, and introduce the equation similar to one in FLD theory(1). Furthermore, on the basis of the present theoretical formula, the new picture of low energy excitations (the boson peak) in glasses and supercooled liquids will be discussed. (1) D. Kivelson, G. Tarjus, and S.A. Kivelson, Prog. Theor. Phys. Suppl. 126, 289 (1997). (2) J.P. Sethna, Phys. Rev. Lett. 51, 2198 (1983). (3) S. Sachdev and D.R. Nelson, Phys. Rev. Lett. 53, 1947 (1984). (4) I. Kanazawa, Phys. Lett. A176, 246 (1993). (5) I. Kanazawa, Prog. Theor. Phys. Suppl. 126, 397 (1997).

L12.6

KINETIC STABILITY OF FAR FROM EQUILIBRIUM BULK ALLOY STATES. M.T. Clavaguera-Mora, J. Rodriguez-Viejo, D. Jacovkis, Grupo de Fisica de Materiales I. Dep. Fisica, Univ Autonoma de Barcelona, Bellaterra, SPAIN; N. Clavaguera, Departamento de Estructura y Constituyentes de la Materia. Univ Barcelona, Barcelona, SPAIN.

The supercooled liquid state is viewed as the initial state of an alloy in the temperature interval between glass transition temperature and liquidus temperature. The stabilization on cooling of the system into a homogeneous bulk glass depends critically on the kinetic impediment of precipitation of primary/eutectic crystalline phases. Previous studies in Al-rich alloys of the Al-Cu-Ni-Nd system include kinetic evaluation of FCC-(Al) nanocrystallisation and subsequent eutectic transformation by heat treatment under continuous heating and isothermal regime. A consistent picture of the kinetic data has been obtained when including evaluation of the free energy driving force for FCC-(Al) crystal formation and eutectic precipitation. These data were obtained from extrapolation of thermodynamic data of the Al corner of the quaternary system by the CALPHAD method. Derived quantities are crystal-interfacial energy, viscosity of the supercooled liquid alloys and mean diffusion coefficients. In this paper all the previous evaluated quantities are used to compute the formation of glassy, nano- or poly-crystalline states as a function of the solidification path. For that purpose, the kinetic competition in between primary crystallisation of the FCC-(Al) and/or the stoichiometric compounds is obtained by considering the specific metastable liquidus temperature, or degree of supercooling/supersaturation of each of the several crystalline phases and assuming homogeneous nucleation. The relative importance of each of the underlying kinetic mechanisms on changing the composition of the alloy is discussed.

L12.7

CRYSTALLIZATION MECHANISMS OF Pd₄₃Ni₁₀Cu₂₇P₂₀ METALLIC GLASS. Evgenia Pekarskaya, Jan Schroers, William L. Johnson, Keck Laboratory of Engineering Materials, California Institute of Technology, Pasadena, CA.

An exceptional stability of the undercooled liquid with respect to crystallization observed in Pd-Ni-Cu-P metallic glasses attracted a lot of attention in the last decade. The critical cooling rate of these alloys was determined to be as low as 0.1-0.3 K/s. The nose of the time-temperature-transformation diagram, which indicates the onset of crystallization in an isothermal experiment, is located at 200 s for the Pd₄₃Ni₁₀Cu₂₇P₂₀ samples fluxed with B₂O₃. The reasons of such high thermal stability as well as crystallization process of Pd-Ni-Cu-P metallic glasses have not been yet fully understood. Mechanisms of crystallization of Pd₄₃Ni₁₀Cu₂₇P₂₀ alloy are studied in the present work. The alloy prepared by induction melting was subjected to isothermal annealing experiments in the undercooled temperature region. Evolution of the microstructure during crystallization was studied by electron microscopy, X-ray diffraction and differential thermal analysis. Initiation of the crystallization process, types of phases formed, their morphology and chemical content are analyzed. Thermodynamic stability of the phases formed on early stages of crystallization is discussed. An important issue of the crystallization asymmetry which manifests itself in substantially different critical cooling and heating rates to bypass crystallization is investigated. To study this phenomenon two types of experiments were performed. The alloy was allowed to crystallize at a certain temperature upon cooling from the melt and upon heating from the amorphous phase. The microstructure of the alloys were then analyzed and compared.

L12.8

BULK METALLIC GLASS AND QUASICRYSTAL FORMATION IN Zr-Ti/Nb-Cu-Ni-Al ALLOYS. Uta Kühn, Jürgen Eckert, Ludwig Schultz, IFW Dresden, Institute of Metallic Materials, Dresden, GERMANY; Norbert Mattern, IFW Dresden, Institute for Solid State Analysis and Structural Research, Dresden, GERMANY.

The recently developed multicomponent Zr-Ti-Cu-Ni-Al and Zr-Nb-Cu-Ni-Al systems exhibit bulk glass forming ability for a variety of compositions [1-3]. For both alloy systems, we systematically investigated the tendency for bulk glass formation for

alloys with different Ti or Nb content, respectively. The samples were prepared via arc melting and injection into a metal mold as well as via melt spinning. The structure of the as-cast and melt-spun samples was characterized by X-ray diffraction and transmission electron microscopy. The glass transition and crystallization behavior were examined by differential scanning calorimetry. The results show that the bulk glass forming range of the alloys is limited by the formation of intermetallic or quasicrystalline phases. Special emphasis is placed of the nature and the size of the competing crystalline phases formed upon casting or annealing. For some of the alloys almost single-phase quasicrystalline material with grains in the micrometer range forms directly upon cooling from the melt. In contrast, nanosized quasicrystals with grain sizes on the order of 5 to 10 nm were observed as primary phase upon crystallization of as-quenched amorphous specimens. At higher temperatures, the metastable nano-quasicrystals transform into intermetallic compounds. Besides the difference in quasicrystal grain size for the differently prepared samples there are some differences in the composition of the quasicrystals between quasicrystals nucleated from the melt upon slow cooling and the nano-quasicrystals produced via annealing in the supercooled liquid region. This will be discussed with respect to the thermodynamics and kinetics of metastable phase formation under different processing conditions. References: [1] X.H. Lin and W.L. Johnson, Mater. Trans., JIM 38, 475 (1997); [2] X.H. Lin, Ph.D. Thesis, California Institute of Technology, 1997; [3] L.Q. Xing, J. Eckert, W. Löser and L. Schultz, Appl. Phys. Lett. 74, 664 (1999)

L12.9

NANO CRYSTALLINE STATES AND STABILITY OF MELT SPUN Mg-Ca-Zn ALLOYS. P.M. Jardim, I.G. Solurzano, Department of Material Science and Metallurgy, PUC-Rio, Rio de Janeiro, BRAZIL; J.B. Vander Sande, Department of Material Science and Engineering, MIT, Cambridge, MA; B.S. You, W.W. Park, KIMM, KOREA.

Alloys, with six different compositions in the system Mg-Ca-Zn were produced by melt spinning. The aging behavior of alloys was investigated by measuring the changes in microhardness after isochronal aging and the microstructure was analyzed by means of Transmission Electron Microscopy (TEM), Energy Dispersive X-Ray Spectrometry (EDS), Scanning Transmission Electron Microscopy (STEM) and Scanning Electron Microscopy (SEM). All six compositions in the as-solidified condition show a difference in microstructure between the wheel contact side (zone A) and the free surface side (zone B) as a result of the differences in the solidification rate across the ribbons. One of the alloys was chosen to be more deeply investigated in this work as it exhibited grain boundary films and presented the highest peak hardness among the low Ca alloys. The comparison between the two microstructural zones in this alloy can aid in understanding of the phase transformation steps during cooling with a model which is proposed here.

L12.10

INTERMETALLIC PHASES IN Ti-Ag-Zr-Ni ALLOYS. Radu Nicula, Adrian Jianu, Victor Kuncser, Gerd Holzhueter, Eberhard Burkel, Rostock Univ, Dept of Phys, Rostock, GERMANY.

Ti/Zr-based metallic glasses and crystalline intermetallic compounds with improved mechanical properties are presently a field of intense application oriented research. The formation and stability of nanocrystalline phases in Ag-substituted Ti-Zr and Ti-Zr-Ni alloys was followed using in-situ synchrotron radiation diffraction experiments performed under high-pressure/high-temperature conditions. The substitution of silver significantly enhances the formation of amorphous and/or nanostructured phases during rapid solidification. High-resolution synchrotron powder diffraction measurements and electron microscopy investigations show that in the as-quenched state the alloys are either amorphous or in a mixed nanostructured state. Upon heating, the alloy structure transforms to a fine mixture of crystalline phases depending on the applied pressure and thermal processing parameters. Differential scanning calorimetry studies were performed in order to identify the nature and sequence of the observed structural phase transitions. The experimental results are discussed with respect to the non-equilibrium synthesis and processing of bulk amorphous and bulk nanocrystalline materials in Ti/Zr-based alloys.

L12.11

SIMULATION OF CRYSTALLIZATION AND STRESS RELAXATION IN METALLIC GLASSES. Yoshiaki Kogure and Masao Doyama, Teikyo University of Science and Technology.

Materials of the glassy state, a quenched state of liquid, are known to show peculiar properties, which is related with the disordered configuration of atoms. The crystallization of glassy state is one of the useful processes to make a nanophase material. Fundamental mechanism of crystallization of glassy metals and alloys of noble metals (Cu, Ag, Au) are investigated by means of molecular dynamics

simulations. The simulation systems contain several thousands of atoms and the periodic boundary condition is adopted. Embedded atom method potentials for the materials developed by the present authors are adopted in the simulation. As an initial condition atomic system is kept in molten state, then the system is quenched to a glassy state. The structure of the glassy state is investigated through the radial distribution function. The temperature of the material is increased and the process of crystallization is monitored by the local crystalline order and the potential energy of individual atom. Distribution of internal stress in the glassy state and crystallized state is evaluated from the configuration of the nearest neighbor atoms and the potential energy of individual atoms. A relaxation of the internal stress during the crystallization is observed.

L12.12

METAMAGNETIC TRANSITION IN Nd-Al(Fe, Co, Cu) METASTABLE ALLOYS. Patricia Crespo Instituto de Magnetismo Aplicado, Madrid, SPAIN; Golden Kumar, S. Ram, Materials Science Center, Indian Institute of Technology, Kharagpur, INDIA; Stefan Roth, Jürgen Eckert, Karl-Hartmut Müller, Ludwig Schultz, IFW Dresden, Institute of Metallic Materials, Dresden, GERMANY.

Metastable NdAl(Fe, CoCu) alloys were prepared in the form of rods, 3 mm in diameter, by casting in a cold copper mold, and in ribbon shape, of about 20 to 30 μm thickness, by melt spinning. X-ray diffraction showed that the melt-spun ribbons were completely amorphous while the as-cast rods contained a certain amount of crystallites. Magnetization as a function of temperature and field was measured between 300 and 600 K for fields up to 2 T. The as-cast rods were hard magnetic with a coercivity of 0.2 to 0.3 T, whereas the as-quenched ribbons were considerably softer with a coercivity lower than 0.03T. Annealing of the ribbons at different temperatures does not lead to a hardening of the material and after fully crystallization, a paramagnetic behavior is observed. It is observed that after annealing some of the mold cast alloys exhibit a field induced metamagnetic transition at room temperature and under an applied field of about 1T. In addition, it has been observed that by adjusting the casting conditions it was possible to stabilize the metamagnetic phase in the as-cast state as well. Preliminary magnetoresistance measurements give values around 0.3% at room temperature. A similar behavior was recently reported by Ding et al. [1]. They observed a metamagnetic transition in Nd₃₃Fe₅₀Al₁₇ at temperatures below 140 K and fields ranging from 2 to 4 T. It should be pointed out that in our case the transition occurs at room temperature and at fields which may easily be reached with electro- or permanent magnetic devices. In this work the main features of the metamagnetic transition as a function of the composition and/or the thermal treatments will be presented. In addition, magnetoresistance measurements will be presented. [1] J. Ding, L. Si, Y. Li, and X.Z. Wang, Appl. Phys. Lett. **75** (1999) 1763

L12.13

THERMAL STABILITY AND MAGNETIC PROPERTIES OF Fe-BASED BULK GLASSY ALLOYS PREPARED BY A POWDER CONSOLIDATION METHOD. Akihisa Inoue, Tao Zhang, IMR, Tohoku Univ, Sendai, JAPAN; Takao Mizushima, Alps Co Ltd, Central Res Lab, Nagaoka, JAPAN.

Since the first synthesis of a bulk glassy alloy in Fe-(Al,Ga)-(P,C,B) system by copper mold casting in 1995, Fe-based glassy alloys have attracted much attention because of the expectation of their practical uses as highly efficient soft magnetic materials which can be produced in a final bulk form from the melt. Up to date, Fe-based bulk glassy alloys have been synthesized in Fe-Ga-(P,C,B), Fe-(Cr,Mo,Nb)-(Al,Ga)-(P,C,B), Fe-(Cr,Mo,Nb)-Ga-(P,C,B), Fe-(Zr,Hf,Nb)-B, Fe-(Zr,Nb)-(Cr,Mo,W)-B and Fe-(Cr,Mo)-(C,B) systems. The maximum sample thickness reaches about 5 mm. The above-described Fe-based glassy alloys also exhibit a large supercooled liquid region reaching 95 K before crystallization. By the use of viscous flowability in the supercooled liquid region, a fully dense bulk glassy alloy is expected to be formed from glassy powders. The resulting Fe-based bulk glassy alloys are also expected to exhibit good soft magnetic properties, even though there have been no data on the synthesis of Fe-based bulk glassy alloys with good soft magnetic properties by the powder consolidation method. Besides, the development of the process is expected to lead to the elimination of the critical thickness for glass formation of Fe-based glassy alloys. This paper is intended to present the formation of fully dense bulk glassy Fe-based alloys by the warm consolidation process and their soft magnetic properties.

L12.14

EFFECT OF PREPARATION ON GLASS FORMATION AND MAGNETIC PROPERTIES OF Nd-Fe-Co-Al-B ALLOYS. G. Kumar, S. Ram, Materials Science Centre, Indian Institute of Technology, Kharagpur, INDIA; Jürgen Eckert, Li Quiang Xing, Albert Güth, Stefan Roth, Wolfgang Löser, IFW Dresden, Institute of Metallic Materials, Dresden, GERMANY.

The effect of alternative preparation methods on glass formation and properties of Nd₄₀Fe₄₀Al₈Co₅B₇ and Nd₅₇Fe₂₀Al₁₀Co₅B₈ alloys has been revealed. Bulk amorphous samples and thin amorphous ribbons have been achieved by copper mould casting and melt spinning, respectively. Amorphous powders have been prepared by mechanical alloying from elemental powder blends as well as ball milling of crystalline ingot precursors. The increase of Fe content leads to a reduced glass forming ability of Nd-Fe-Co-Al-B alloys which may give rise to needle-like Nd₂Fe₁₄B crystals in as-cast Nd₄₀Fe₄₀Al₈Co₅B₇ amorphous rods. Samples prepared by different processing routes exhibit different phase transformation behaviour in DSC runs. The cast Nd₅₇Fe₂₀Al₁₀Co₅B₈ rod exhibits crystallization at 790 K succeeded by the endothermic peak due to melting at 810 K. Neither appreciable endothermic reaction caused by glass transition nor a supercooled liquid region have been observed. Elemental milled powders and milled prealloys display two exothermic peaks at roughly the same temperatures. The $J - H$ hysteresis loops of materials synthesized via different routes show that the unique atomic order responsible for hard magnetic properties can only be accessed by moderate cooling rates of melts realized in metal mould casting. Rapidly quenched ribbons, elemental milled powders and milled ingots do not show hard magnetic properties at room temperature. From thermomagnetic investigations a Curie temperature $T_C = 474$ K has been extrapolated for Nd₅₇Fe₂₀Al₁₀Co₅B₈ rods, whereas the M(T) plot of Nd₄₀Fe₄₀Al₈Co₅B₇ samples exhibits a two-phase behaviour with $T_C = 476$ K for the glassy matrix and $T_C = 576$ K similar to Nd₂Fe₁₄B. The investigation has proved that amorphous samples with different local order can be prepared by different processing routes.

L12.15

MAGNETIC BEHAVIOR OF CRYSTALLIZED PHASES OF A METALLIC GLASS. INTERNAL HYPERFINE FIELD EVOLUTION WITH TEMPERATURE STUDIED WITH MOSSBAUER SPECTROSCOPY. V. Marquina, R. Gomez, R. Ridaura, M.L. Marquina, Facultad de Ciencias, UNAM, Mexico D.F., MEXICO.

We report the temperature variation of the hyperfine field in a crystallized sample of Metglas 2605 SC, from 673 K up to 933 K, where the system becomes paramagnetic (Curie temperature), as measured by Mossbauer Spectroscopy (MS). The hyperfine fields of the different phases, identified as a-Fe, Fe₂B and Fe₃Si by X-ray diffraction, vary as predicted by the molecular field theory of Weiss with a total spin moment of 3/2 (a-Fe) and 5/2 (Fe₂B and Fe₃Si). The majority phase in the crystallized Metglas corresponds to a-Fe, and the 3/2 value of the total spin is in contrast with the 5/2 value obtained for the amorphous phase, indicating that the crystalline field changes the electronic distribution around the Fe atoms.

L12.16

PREPARATION AND MECHANICAL PROPERTIES OF HAFNIUM-BASED BULK METALLIC GLASSES. Xiaofeng Gu, Li-qian Xing, Todd C. Hufnagel, Johns Hopkins Univ, Dept of MS&E, Baltimore, MD.

We have prepared bulk metallic glasses of composition (Hf_xZr_{1-x})_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅ (with x=0-1) by an arc melting/suction casting method. The density of these alloys increases by nearly 67% with increasing Hf content, which is required for their potential use as kinetic energy armor-piercing projectile materials. The glass transition temperature and the melting temperature increase linearly with increasing Hf content. The reduced glass transition temperature (T_g/T_m) decreases, from 0.64 (x=0) to 0.62 (x=1), indicating reduced glass-forming ability for the Hf-based alloy. The yield strength in uniaxial compression at quasistatic strain rates also increases with Hf content, reaching ~2.2 GPa for Hf_{52.5}Cu_{17.9}Ni_{14.6}Al₁₀Ti₅.

L12.17

MOLECULAR DYNAMICS SIMULATIONS OF FRACTURE IN AMORPHOUS Ni. Diana Farkas, Dept. of MS&E, Virginia Polytechnic Institute and State University, Blacksburg, VA.

A simulation of the structure of amorphous Ni was performed by quenching the liquid state using molecular dynamics techniques. The simulations use an embedded atom potential based on ab-initio calculations for various metastable structures. Fracture behavior was studied using the same interatomic potential and a technique that allows the calculation of fracture toughness. The results show ductility even at very low temperatures. The typical behavior of the crack tip region results in a blunted rounded crack tip morphology. This morphology is significantly different from what is found in crystalline Ni.

L12.18

FRACTURE MECHANISMS OF BULK AMORPHOUS METAL UNDER IMPACT AND FATIGUE LOADING. Takao Kobayashi and

Advanced fractographic methods were used to investigate the fracture mechanisms of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk amorphous metal fractured under impact and fatigue loading conditions. Topographs of conjugate fracture surfaces were juxtaposed and analyzed (the FRASTA technique) to reconstruct the fracture process and graphically display details of the deformation and microfailure processes occurring at the crack front. A fast Fourier transform was applied to the surface roughness data to obtain a parameter (the elevation power spectrum density) that could be related to fatigue loading conditions. The fracture surfaces near the notch tip of a Charpy impact specimen showed distinctive smooth islands whose surfaces were suggestive of molten flow. FRASTA results indicated these were failure surfaces of ligaments that once joined the opposing crack faces and had elongated as much as $100\ \mu\text{m}$ before rupturing. This finding suggests a contributory mechanism for the high values of measured toughness and implies that rapid straining and rupture of ligaments might raise the temperature sufficiently to melt material locally. Fracture surfaces produced by fatigue loading were populated by similar smooth islands, but which were distributed in size and had a consistent aspect ratio (about 2) and orientation (long axis parallel to the crack propagation direction). The sizes of the islands decreased with decreasing ΔK and eventually became undetectable near the ΔK threshold. FRASTA confirmed that these smooth islands were surfaces of broken ligaments, although the stretch before rupture was not as large as in the impact specimen and melt features were not seen. The surface roughness as indexed by the square root of the elevation power spectrum density varied linearly with ΔK , suggesting that load parameters such as ΔK may be obtainable from roughness measurements. This relationship and the insight regarding activity within the crack tip process zone provide the basis for fracture model development.

L12.19
MICROSTRUCTURAL CHARACTERIZATION OF SHEAR BANDS IN Zr-BASED METALLIC GLASSES. Jing Li, Xiaofeng Gu, Liqian Xing, Todd C. Hufnagel, Johns Hopkins University, Department of MS&E, Baltimore, MD.

Microstructural characterization of shear bands in metallic glass is important for understanding the mechanism of inhomogeneous deformation. To date, relatively little work has been done in this area, and in particular the nature of the atomic-scale structural changes in shear bands in metallic glasses is unknown. We have investigated microstructural changes in shear bands in Zr-based bulk metallic glasses and binary alloys using transmission electron microscopy (TEM). In particular, we have used an axially aligned dark field technique, with the objective aperture placed to collect the electrons from several different areas of the diffraction patterns, to image the shear bands. We frequently observe shear bands in the form of plastic zones ahead of micro cracks caused by deformation of the TEM foils of both binary and bulk Zr-based glasses. We have also examined shear bands formed during mechanical testing (three-point bend and uniaxial compression) of bulk metallic glasses. There are significant differences in the electron diffraction contrast between the deformed and undeformed regions. The plastic zones produce enhanced low-angle scattering of electrons and an apparent broadening of the amorphous halo, suggesting increased disorder in the deformed zone. These results are consistent with an increased degree of atomic-scale disorder in highly deformed regions, which may provide a partial explanation of the manner in which shear localization occurs in metallic glasses.

L12.20
SHAPING OF BULK METALLIC GLASSES BY SIMULTANEOUS APPLICATION OF ELECTRICAL CURRENT AND LOW STRESS. Alain Reza Yavari, Institut National Polytechnique de Grenoble, LTPCM CNRS umr 5614, St-Martin d'Heres Campus, FRANCE; Marcelo de Oliveira and Walter J. Botta F., DeMa, Universidade Federal de Sao Carlos, SP, BRASIL.

It is well known that bulk metallic glasses have large supercooled regions between the glass transition temperatures T_g and the crystallisation temperatures T_x up to some hundred degrees higher. In this range, the undercooled liquid in principal deforms in a Newtonian way, allowing thermomechanical shaping in the low viscosity range as applied to oxide glasses. However, such deformation is slow near T_g and requires very high stresses and expensive dies. At higher temperatures near T_x , the deformation is fast at low applied stresses but crystallisation intervenes easily. A new Electromechanical shaping process has been developed for the shaping of Bulk metallic glasses (BMG) and BMG-based composites into various complex forms. The Electromechanical shaping technology allows rapid shaping at low applied stresses by eliminating the thermal mass of the furnace and the need to heat the deformation dies. Joule heating is efficiently

used thanks to the high electrical resistivity of bulk metallic glasses. It is shown that large shape changes (high deformations) can be achieved without crystallisation. For example, crosses and other mechanically resistant complex forms are achieved from two amorphous rods or an amorphous rod and a crystalline bar. Other composite forms are also demonstrated. The maintenance of the fully amorphous character of the complex shapes after electromechanical processing is confirmed using non-destructive testing by synchrotron x-ray diffraction techniques in transmission geometry.

L12.21
THERMAL EXPANSION OF GLASS-FORMING Zr-BASED ALLOYS IN THE MELT, THE UNDERCOOLED LIQUID AND THE DIFFERENT SOLID STATES. K. Samwer, B. Damaschke, Univ. Göttingen, I. Physikalisches Institut, Göttingen, GERMANY; M. Krause, P. Ryder, Univ. Bremen, Institut für Werkstoffphysik und Strukturforchung, Bremen, GERMANY.

The thermal expansion coefficients of glass-forming Zr-based alloys were measured in the melt, the undercooled liquid and the glassy/crystalline state. Due to the high reactivity of the liquid material the experiments were performed containerless in an electrostatic levitator. We used an optical method where the samples were imaged with a high-resolution CCD-camera and the volume of the samples was evaluated by digital image processing. The coefficients of thermal expansion in the liquid and in the solid state could be determined from the volume versus temperature curves. The results can be compared with measurements in the electromagnetic levitation facility TEMPUS performed under microgravity conditions in the mission MSL-1 [1] and ground based DMA-measurements [2]. The thermal expansion data can be interpreted in terms of the free volume model.

[1] B. Damaschke and K. Samwer, Appl. Phys. Lett. 75, 2220 (1999)

[2] N. Geier, M. Wei, M. Moske, and K. Samwer, Eur. Phys. J. B 13, 37 (2000)

This work was supported by DLR/BO, Bonn, Germany and the DFG, SPP 'Unterklhte Metallschmelzen'.

L12.22
BULK METALLIC GLASSES AND AMORPHOUS-NANOCRYSTALLINE COATINGS. Tetyana Shmyreva, Praxair-TAFA, Concord, NH.

Bulk Metallic Glasses were obtained by detonation spraying with eutectic iron based alloys. Amorphous-nanocrystalline structures were produced in nickel and cobalt based alloys under action of concentrated energy sources such as detonation, plasma, electric spark through the liquid rapid solidification. The investigation showed that hydrogen concentration could be increased about 100 times than the equilibrium concentration. Hydrogen is in form of solid solution in amorphous phase. Hydrogen can act on amorphous-nanocrystalline phase transformation temperature and kinetics, and can improve the hardness up to 20%.

L12.23
CONSOLIDATION OF AMORPHOUS GAS ATOMIZED Ti-Cu-Zr-Ni POWDERS BY WARM EXTRUSION. Daniel Sordelet, Matthew Besser, Metallurgy and Ceramics Program, Ames Laboratory, Iowa State University, Ames, IA.

A feasibility study was performed to produce bulk metallic glass with Cu-Ti-Zr-Ni alloys by warm extrusion of gas atomized powders. Results based on differential scanning calorimetry, X-ray diffraction, transmission and scanning electron microscopy, optical microscopy, scanning Auger microscopy and indentation hardness testing are presented. During warm extrusion at temperatures between the glass transition and primary crystallization events, the amorphous structure of the gas atomized powders is retained after consolidation using extrusion ratios of 5, 9 and 13. The onset of the glass transition and crystallization temperatures of the starting powder ($\sim 415^\circ$ and 475°C , respectively) are observed at lower temperatures following extrusion. Comparing the thermal behavior of the extruded bulk metallic glass samples, the glass transition and crystallization temperatures increase as the extrusion ratio increases. A very thin layer of a nanocrystalline phase rich in Ti and Zr was observed at some of the particle boundaries of extruded samples. Although the gas atomized powders contain approximately 700 ppm by weight O, parallel energy loss spectroscopy did not detect any O within the nanocrystalline phase. The microhardness values of extruded samples (~ 6.0 GPa) are similar in transverse and longitudinal directions and are comparable to those of Ti-Zr-Cu-Ni bulk metallic prepared by other techniques.

L12.24
A NEW METHOD FOR PRODUCING AMORPHOUS ALLOY WIRES. Tao Zhang, Akihisa Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Rotating disk continuous casting as a new method of producing amorphous alloy wires has been developed. The rotating disk, which is made of copper, has a semicircular groove on its upside surface. The wires with a large diameter larger than 0.5 mm in bulk amorphous forming alloy systems, such as Zr-, Ti- and Fe-based alloy systems, have been prepared by the new method. The wire cross-section is nearly circular, because the melt is quenched to amorphous state when contacts the inner surface of the groove of rotating disk. The rotating disk continuous cast amorphous alloy wires exhibit the same thermal stability and mechanical properties with those for the melt-spun amorphous alloy ribbon and copper mold cast cylinder with the same composition. Therefore, the present success of forming amorphous wires with a large diameter is attributed to the high glass-forming ability of the alloys. In any event, the success of forming amorphous alloy wires by this new continuous cast method is important for further extension of application fields of amorphous alloys.

L12.25

IMPROVEMENTS OF DUCTILITY AND STRENGTH IN Zr-BASED BULK METALLIC GLASS BY DISPERSION OF NANOCRYSTALLINE PARTICLES. Cang Fan, Inou Superliquid Glass Project, Japan Science and Technology Corporation, Sendai, JAPAN; Akihisa Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

It is generally known that high strength and good bending ductility of melt-spun amorphous alloys are lost by annealing-induced crystallization. However, for the last decade, a substantial increase in strength has been reported in a number of multiphase nanocrystalline alloys, especially in bulk nanocrystalline glassy alloys. Nevertheless, there are only a few reports on the ductility of bulk nanocrystalline alloys. Recently, we investigated mechanical properties and microstructure of a $Zr_{60}Cu_{20}Pd_{10}Al_{10}$ bulk nanocrystalline alloy prepared by annealing the glassy alloy. The compressive strength increases with increasing volume fraction of nanocrystals, from 1760 MPa at $V_f=0\%$ to 2060 MPa at $V_f=70\%$. The plastic strain increases significantly and the maximum value of about 4.5%, which is much larger than that of as-cast glassy alloys (such as $Zr_{55}Ni_5Cu_{30}Al_{10}$ glassy alloy showing a typical high glass-forming ability exhibits no recognizable plastic deformation), is obtained in the early stage of nanocrystallization. High-resolution TEM images reveal that the partially crystallized alloy having the maximum plastic strain consists of nanocrystals with grain sizes of 2-3 nm embedded in the glassy matrix. Thus, the existence of nanocrystals with a few nanometers in diameter dispersed in the glassy matrix is concluded to be effective for an increase of ductility as well as strength.

L12.26

ULTRASONIC INVESTIGATION OF BULK METALLIC GLASSES. Wei Hua Wang, R.J. Wang, Y. Zhang, D.Q. Zhao, M.X. Pan, P. Wen, Institute of Physics & Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing, CHINA.

Zr-Ti(Nb)-Cu-Ni(Fe)-Be, Zr-Ti(Nb)-Cu-Ni-Al, Zr-Al-Ni-Cu(Y), Nd-Al-Fe-Co, and Pd-Ni-Cu-P bulk metallic glasses (BMGs) were formed by quenching methods. Acoustic velocities and their pressure and temperature dependence of the BMGs have been measured by using a pulse echo overlap method, which is particularly sensitive to the microstructure. The temperature and pressure dependent acoustic velocities can provide critical information on the microstructural characteristics and evolution as well as the elastic and thermal properties during the processes of relaxation, glass transition and crystallization of the BMG. The elastic constants and thermodynamic parameters as well as their temperature and pressure dependence have been determined for the Zr-based BMGs. The volume-pressure equation of state for the BMGs was obtained. The obtained elastic constants, thermodynamic parameters and ultrasonic attenuation are compared with those of oxide glasses, other conventional metallic glasses and crystallized BMG, the differences among them are discussed in the microstructural point of view. Some unique acoustic characteristics upon pressure and temperature of the BMGs are found. The microstructure, glass forming ability, and elastic properties are found to have good correlation for the BMGs oxide glasses and conventional metallic glasses. The findings assist the understanding of the excellent glass forming ability and properties in the bulk glass forming system. A striking softening of long-wavelength transverse acoustic phenomenon is not simply attributed to small density difference between the two states. The origin for the phenomenon is discussed from the microstructural point of view. A sudden change of the density, acoustic velocities, elastic constants and thermodynamic parameters near the glass transition temperature, and anomalous density, acoustic and elastic behavior in the supercooled liquid region are observed in Zr-based BMGs.

L12.27

NANOCRYSTALLISATION BEHAVIOR OF Al-Ni-Sm BASED ALLOYS. M. Gich, T. Gloriant, S. Suriñach, M.D. Baró, Universitat Autònoma de Barcelona, Departament de Física, Bellaterra, SPAIN.

Al-TM-RE metallic glass alloys have attracted a great interest since the last decade because of their good mechanical properties. These mechanical properties can be further improved by a thermally induced devitrification treatment producing a particular structure consisting of a random distribution of a-Al nanoparticles in an amorphous matrix. The aim of this work is to study the nanocrystallisation process of $Al_{88}Ni_4Sm_8$ and $Al_{88}Ni_6Sm_6$ melt-spun ribbons by means of X-ray diffraction, transmission electron microscopy and differential scanning calorimetry (DSC). The crystallization process during continuous heating takes place in several stages. The apparent activation energy of the first stage, corresponding to the α -Al nanocrystallization, was evaluated using the peak's method, and is higher for $Al_{88}Ni_4Sm_8$ than for $Al_{88}Ni_6Sm_6$. Isothermal DSC scans revealed the existence of quenched-in nuclei in both amorphous alloys. These quenched-in nuclei are probably due to the melt-spinning process and the crystalline structure after devitrification is strongly dependent on them. A detailed discussion of the different metastable and stable crystalline phases found, on further heating, is presented.

L12.28

PHASE EQUILIBRIA DETERMINING THE CRYSTALLIZATION OF SUPERCOOLED LIQUID Al-Ni-Nd ALLOYS. Reinhard Lück, Tilo Gödecke, Wen Shen Sun, Max-Planck-Inst f. Metallforschung, Stuttgart, GERMANY, Ke Lu, Lab RSA, Inst Met Res, CAS, Shenyang, P.R. CHINA.

Phase equilibria in the Al-rich portion of the Al-Ni-Nd phase diagram were investigated in detail by DTA, micrographs, and XRD. It was found that stable and metastable phase equilibria can be observed depending on heat treatment. The metastable phase diagram represents the ternary eutectic reaction $L = (Al) Al_3Ni Al_{11}Nd_3$ whereas the stable diagram is characterized by the ternary eutectic reaction $L = (Al) Al_7Ni_2Nd Al_{11}Nd_3$ and the transition reaction $L Al_3Ni = (Al) Al_7Ni_2Nd$. Supercooled liquid samples produced by meltspinning are found in a certain composition range. The transformation of supercooled liquid alloys into stable state during heat treatment were monitored by magnetic measurements and DSC, the crystallization products were characterized by XRD. The crystallization follows mainly the metastable and partly the stable phase equilibria depending on composition (as well as on temperature and heating rate). These composition ranges will be described and related to the phase diagram.