SYMPOSIUM L
Supercooled Liquid, Bulk Glassy, and Nanocrystalline States of Alloys

November 27 – 30, 2000

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*Invited paper
SESSION 11: ATOMIC AND ELECTRONIC STRUCTURE

Chairs: Hans-Joerg Fecht and Franz Fasch
Monday, November 27, 2000
Room 201 (Hynes)

8:45 AM AM 11.1
LOCAL ATOMIC STRUCTURES OF Zn-BASED BULK AMORPHOUS ALLOYS BY THE AXS AND EXAFS METHODS
Eiichi Matsuura, Institute for Materials Research, Tohoku University, Sendai, JAPAN; Shigeo Sato, Munezuki Inakaku, Junji Saida, Inoue Superluid Glass Project, ERATO, Sendai, JAPAN; Akihiko Issue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Zn-based alloys show very different crystallization processes depending on their constituent elements. For example, in a Zn-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 Zn-12.5Al-25Ni alloy. By replacing a part of Ni atoms with Pt atoms in a Zn-Al-Ni system, nano-meter sized quasicrystals are formed by annealing the quenched amorphous Zn-6.5Al-10%Ni-14%Pt alloy. In the present study, local atomic structures around certain constituent elements, such as Zn and Ni in the ternary amorphous and crystallized alloys, and Zn, 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 the 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, AXS and EXAFS methods of 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 structure. By analyzing these results with Pt and Zr pairs in the amorphous state as well as the quasicrystalline state has been confirmed.

9:15 AM AM 11.2
CRYSTALLIZATION BEHAVIOUR OF Zr_{1-x}V_{x}Cu_{20}Ni_{31}Al_{14}
BULK METALLIC ALLOYS BY IN-SITU NEUTRON DIFFRACTION
J. Louis, Soobeyroux, Nicolas Chret, Laboratoire de Cristallographie/CHETA, 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 Tg enables a good workability in a relatively wide range of temperature (80), up to the crystallization temperature Tx. We have performed in-situ neutron diffraction crystallization experiments on a Zr-Ti-Cu-Ni-Al alloy [3] and we have shown that the first phase appearing at the first DSC crystallization peak is an isochronal phase, meaning that in the glassy state the short range ordering must be of isotropic nature. We present the study of an enriched制作 of this alloy by varying the compositions in titanium and aluminium for 0 < 7.5 and 5 < 16. This work reports on various formulations of Zr-Ti-Cu-Ni-Al alloys studied by DSC experiments and in-situ neutron diffraction experiments. The crystallization experiments will be 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 crystallized phases. [1] W.L. Johnson, Mater. Sci. Forum, 225-227 (1996) 35. [2] A. Iwaki, T. Zhang and T. Masumoto, Mater. Trans. JIM, 31 (1990) 425. [3] J.L. Soobeyroux, J.M. Pelletier, R. Perrier de la Bache, Physica B 276-278 (2000) 905.

9:30 AM AM 11.3
SHORT RANGE CHEMICAL ORDERING IN BULK METALLIC GLASSES
P. Asbeck-Kumar, J.H. Hartley, R.H. Howell, P.A. Storey, T.G. Nieh, Lawrence Livermore National Laboratory, Livermore, CA; K.M. Florez, W.H. Fahrenholtz, R.H. Davis, Department of Materials Science and Engineering, Stanford University, Stanford, CA

We do provide experimental direct evidence for a non-random distribution of atomic constituents in Zr_{28}Ti_{42}Al_{14}Cu_{20}Ni_{14} bulk metallic glass using positron annihilation spectroscopy. The Ti content around the open-volume regions is significantly enhanced as the expense of Ni and Cu. Our results indicate that Ni and Cu atoms closely occupy the open-volume regions, surrounded by their neighboring Zr, 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 positrons is significantly affected by quenching or by crystallization. Theoretical calculations indicate that the observed elemental distribution is not consistent with the known crystalline phases Zr_{2}Cu and Ni_{2}Zr, while Al_{2}Zr 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 AM 11.4
STUDY OF THE ELECTRICAL RESISTIVITY CHANGE UPON PHASE TRANSFORMATION IN Zn-BASED METALLIC GLASS
Keiko Komiyama, Ruyji Tamura, Shin Takeuchi, Science Univ.of Tokyo, Dept. of Materials Science and Technology, Chiba, JAPAN; Tadaharu Shiozawa, Toyo Univ, Faculty of Engineering, Sabaura, JAPAN.

Since the first report on precipitation of isochronal phase from Zn-based metallic glass by Koster et al. it has been found that in many Zn-based multicomponent systems metallic glasses are capable of forming the L-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 crystalline in Zn-based metallic glasses. 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 Zn_{70}Sn_{20}Pd_{10} shows two consequent exothermic peaks at 68K and 723K, respectively. X-ray diffraction measurements for the samples annealed at temperatures above the first peak and above the second one demonstrate formation of an isochronal phase and a Zr-Pd crystalline phase, respectively, indicating that the first peak and the second one in the DSC curve correspond to the phase transformation from amorphous to L-phase and from L-phase to crystalline phase, respectively. The electrical resistivity decreases monotonously from 12K to 68K and is followed by a sharp increase above 68K due to transformation to L-phase. The resistivity continues to increase with increasing temperature and suddenly drops at 723K owing to the transformation to crystalline Zr-Pd.

10:30 AM AM 11.5
CRYSTALLIZATION OF AMORPHOUS Cu_{34}Ti_{13}Zr_{11}Ni_{4}
S.C. Glade, J. Löffler, S. Bossay, W.L. Johnson, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA; M.K. Miller, Microscopy and Microanatomical Sciences Group, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN

The results of a study on the crystallization of amorphous Cu_{34}Ti_{13}Zr_{11}Ni_{4} 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 reveal their composition 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 a transformation and growth of a crystalline phase. The results from this study indicated this crystalline phase had a face centered cubic structure. Research at the Oak Ridge National Laboratory USER Facility was supported by the Division of Materials Science and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC, and through the SHARE Program under contract DE-AC05-76OR00000 with Oak Ridge Associated Universities.

10:45 AM AM 11.6
STRUCTURAL STUDY OF R-BASED GLASSY ALLOYS WITH A LARGE SUPERCOOLED LIQUID REGION
Munezuki Inakaku, Shigeo Sato, Inoue Superluid Glass Project, ERATO, JST, Sendai, JAPAN; Eiichi Matsuura, Akihiko Issue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Fe-based glassy alloys with a large supercooled liquid region have been found in Fe-based glassy alloys with a large supercooled liquid region have been found in many Fe-based metallic glasses, 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-58B (MgNb, Zr, W, Ta) and Fe-Co-La-B (La=Sm, Tb, Dy, Nd) glassy alloys were investigated using 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 structure of supercooled liquid state by comparing the local order changes between crystalline and glassy 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 into inserting La atoms. The crystalline phase, which was identified as Fe_{8}La_{5} type structure, requires the
ENHANCED GLASS FORMING ABILITY FOR MULTI-COMPONENT SUPERCOOLED LIQUIDS STUDIED BY MOLECULAR DYNAMICS SIMULATIONS. Zhi Jin, K. Lu. State Key Lab for USA, Institute of Metal Research, Chinese Academy of Sciences, Dalian, CHINA. F. Miu, Department of Materials Science and Engineering, Johns Hopkins Univ., Baltimore, MD.

The mechanism for the extraordinarily high glass-forming ability (GFA) of bulk metallic glass formers has attracted much interest recently, but still remains largely unexplored. 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 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 pairwise 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 the systems with different components. In systems with more than 4 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 effect of efficiency of the mobility of particles due to the multicomponent effect is responsible for the enhanced glass-forming ability of those bulk metallic glass formers.

SESSION L2: ATOMIC AND ELECTRONIC STRUCTURE (continued)
Chair: Eichiro Matsubara
Monday Afternoon, November 27, 2000
Room 200 (Hyers)

1:30 PM L2.1
DIFFUSION IN METALLIC GLASSES AND SUPERCOOLED LIQUIDS. Franz Faupel, Klaus Ritzke, Hartmut Ehrman, Peter Klugkist, Volker Zillmer. Institute for Materials Science, 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 $T_g$, well above the calorimetric glass transition temperature $T_c$. Below $T_g$, the theory predicts cooperative hopping processes. We present here results from isotope effect measurements [1] which 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. Despite 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. Zillmer, K. Ritzke, and F. Faupel, Phys. Rev. Lett. 84, 1407 (2000). 2. H. Ehrman, A. Heesemann, K. Ritzke, F. Faupel, and U. Geyer, Phys. Rev. Lett. 80, 4919 (1998). 3. P. Klugkist, K. Ritzke, S. Reiders, P. Troche, and F. Faupel, Phys. Rev. Lett. 80, 3298 (1998). 4. P. Klugkist, K. Ritzke, and F. Faupel, Phys. Rev. Lett. 81, 614 (1998).

2:00 PM L2.2
SELF-DIFFUSION IN Zr$_5$Al$_4$Pd$_{25}$ AND Pd$_{4}$Co$_{20}$Ni$_{20}$P$_{20}$ BULK METALLIC GLASSES. Hiroshi Nakaizumi, T. Kojima, Osamu Ueki. Inst of Scientific and Industrial Research, Osaka Univ., Suita, Osaka, JAPAN, K. Nosaka, Iwate Univ, Dept of Materials Science and Technology, Moriock, 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$_5$Al$_4$Pd$_{25}$ and of Ni and Pd in Pd$_{4}$Co$_{20}$Ni$_{20}$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 $^{125}$Pd. The diffusion coefficients in the supercooled liquid region of Zr$_5$Al$_4$Pd$_{25}$ metallic glass are much higher than those extrapolated from the measured temperature data in the temperatures in the undercooled liquid regime. 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$_{4}$Co$_{20}$Ni$_{20}$P$_{20}$ 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 phase is due to single atomic process in both metallic glasses.

3:30 PM L2.3
MOLECULAR DYNAMICS SIMULATIONS OF SUPERCOOLED LIQUID METALS AND GLASSES. Hue-Jye Lee, Yue Qi, Thahir Çagm, 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 gas 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 solute/solvent atomic size mismatch effect on 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 higher-packed state in liquid phase has higher energy barrier to crystallization.

2:45 PM L3.4 EXAFS AND XEELS STUDY OF THE STRUCTURE AND STABILITY OF Pd-BASED BULK METALLIC GLASSES.

P. M. Alangari, H. Jiai, D.B. Williams, Lehigh Univ., Dept. of MSE, 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 cm. The importance of Pd in this system can be appreciated from the fact that both Pd-Ni-P and Pd-Co-P are BMGs whereas Ni-Co-P does not form bulk glass. We have explored the importance of Pd in the short range order in these systems and also in controlling the stability of the glass 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 as many as five or more elements. 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: Ralph Busch
Monday Afternoon, November 27, 2000
Room 200 (Hynes)

3:30 PM L3.1 GLASS FORMING ABILITY AND CRYSTALLIZATION OF HIGH-PURITY Pd-Co-Ni-P ALLOY. Nobuyuki Nishiyama, Mitsubishi Metals, Japan Science and Technology Corporation, ERATO Iron-Steel Glasses Promoting Project, JAPAN; Akihisa Inoue, IJMR, Tokohu Univ, Sendai, JAPAN

We have previously reported that a Pd$_4$Co$_{33}$Ni$_{26}$P$_{20}$ alloy exhibits an extremely high glass forming ability (GFA) and has a low cooling rate for glass formation (Rc) of 0.1 K/s. Furthermore, the high GFA of the alloy enabled us to prepare the bulk metallic glass with a thickness of 72 mm, which is believed to have the largest thickness in all metallic glasses. In this study, we have observed the formation of the amorphous phase in the undercooled liquid of the high-purity alloy by about 80 K below the melting point. 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 high-resolution transmission electron microscopy (HR-TEM) with a temperature controllable specimen holder. It is found that the undercooled liquid crystallized suddenly after heating for 318 K at 983 K. The grain size of the precipitated crystal was about 15 nm and no further grain growth was observed 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 Pd-Co-Ni-CALI GALLIUM ALLIAGES. B.R. Lu, C.P. Gorder, R. Willmacker, Inst fur Materialwissenschaften und DLR, Germany; H-J. Fecht, Uni University, Faculty of Engineering, Materials Division, Um, GERMANY

The metallic glass former PdNiP is well known for its pronounced stability against crystallization. Samples of this alloy vitreously complete 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 presently known for metallic glass formers. The high stability against crystallization during cooling allows for simultaneous measurements of its thermodynamic properties within the entire glass transition 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 rarely 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-Na-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, NUS Univ, Singapore, Republic of SINGAPORE.

Glass forming ability can be represented by many parameters. The reduced glass transition temperature, Tg (Tg/Tf) 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 Tf often decreases. Thus, the interval between Tg and Tf generally decreases and the value of Tf 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 system in which the glass forming ability is higher is those with a deep eutectic or low lying Tf compared with the melting points of the host metals, which leads to high Tg. 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 Tg given by Tg/Tf of many bulk metallic glasses is found to show a stronger correlation with critical cooling rate or critical section thickness for glass formation than Tg given by Tg/Tf. Using Ln 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

Chair: Hsin-Hung Kao and Y. Li
Tuesday Morning, November 28, 2000
Room 200 (Hynes)

8:30 AM L4.1 BULK GLASS FORMING Mg-Co-Y ALLOYS IN THE AS-PREPARED, SUPERCOOLED LIQUID AND CRYSTALLINE STATES. Soren Linderoth, Nini Prads, Morten Eklund, Allan Schroeder Pedersen, Riso National Laboratory, Roskilde, DENMARK; Munro Olmsted, National Research Institute for Metals, Tohoku, JAPAN; Tien-Ju Zhou, Leif Gerard, Jianzhong Jiang, Technical University of Denmark, Lyngby, DENMARK; C. Linde, 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 crystallized state. In the as-prepared state, the diffraction of sub-millimeter sized regions were performed using a focused x-ray beam. The phase transition 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 alloys 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 crystalline transition temperature. The dependence of external pressure on the crystallization temperature has been investigated in situ high-temperature and high-pressure x-ray powder diffraction by synchrotron radiation. The investigation forms the basis for a selection of the optimum temperature in the supercooled liquid region for performing deformation/aging of the Mg-alloys.

9:00 AM I4.2
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 Material 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 interatomic potentials. We compared the calculated critical solubility of glassy NiZr and NiTi with the experiments performed in this study. The critical solubility, 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 critical solubility, i.e., 14-75 at. % Zr and 38-85 at. % Ti for the Ni-Zr and Ni-Ti systems, respectively, which are comparable with those from experiments and zr from Lindemann criterion. The kinetic of solid-state amorphization (SSA) was also investigated by MD simulation of the Ni-Zr [1] and Ni-Ti [2] alloys.

10:00 AM I4.5

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 glasses: alloys Zr65Al17Cu15Ni10, Zr65Al11Cu8Ni9Cd, Zr65Al11Cu8Ni9Cd. Properties included the specific heat and enthalpy of fusion, the thermal conductivity, and the temperature-dependent resistivity. The results exhibit very low thermal conductivity, in the undercooled melt. This is the key to the formation of thermal stability in the undercooled melt, compatible with a model predicting a change in the chemical short range order as a function of the melt temperature. The specific heat of the liquid Zr65Al17Cu15Ni10 and Zr65Al11Cu8Ni9Cd shows a pronounced concentration dependence with that of Zr65Al11Cu8Ni9Cd. The specific heat of the undercooled melt is about 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, 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.

10:30 AM I4.6
CHEMICAL COOLING RATE AND THERMAL STABILITY OF Zr-Ti Cu-NiBe ALLOYS. Theodore A. Winkler, Jan Schröer, W.L. Johnson, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

The crystalization 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 [Zr0.66Cu0.34Ni0.03] + [Ni0.02Cu0.98] + [Be0.40] + [Vd0.40] + [Vd0.40] show a continuous increase in the 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.

11:30 AM I4.7

The recent innovations in metallic glasses have led to new alloy classes that may be vitrified and re-examined for the commonly used
The thermal stability and crystallization behavior of melt spin amorphous Ta$_2$C$_3$O$_7$Ni$_5$S$_3$ alloys are investigated by thermal analysis and structural characterization with an intention to find alloys with high amorphous composition with wide supercooled liquid regime $\Delta T_c$. The $\Delta T_c$ of amorphous Ta$_2$C$_3$O$_7$Ni$_5$S$_3$ alloys increased with increasing Ni content, up to 15 at.% Ni, then decreased with further increasing Ni content. Maximum $\Delta T_c$ of 41 K was obtained in Ta$_2$C$_3$O$_7$Ni$_5$S$_3$ 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 at.% Cu, the supercooled liquid range increased from 573 to 776 K. The temperature of the crystallization exotherm increased from 763 to 804 K with increasing Sn content. This behavior is suggests that the amorphous Ta$_2$C$_3$O$_7$Ni$_5$S$_3$Sn$_x$ alloy exhibits $\Delta T_c$ of 73 K. The amorphous Ta$_2$C$_3$O$_7$Ni$_5$S$_3$ alloy crystallized by precipitation of supersaturated Ta$_2$(Ni,Cu) phase followed by decomposition into a mixture of higher temperature. Amorphous Ta$_2$C$_3$O$_7$Ni$_5$S$_3$Sn$_x$ phase crystallized by co-precipitation of Ta$_2$(Ni,Cu) and Ta$_2$Ni phases, followed by transformation into a mixture of TiNi, CuTi, Ta$_2$Ni phases.

1:30 PM - 5.1.5 CRYSTALLIZATION DURING CONTINUOUS HEATING AND COOLING OF SUPERCOOLED BULK GLASS FORMING ALLOYS.

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. Quadrupoles were formed during early stage of cooling. We find 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 - 5.1.5 CRYSTALLIZATION KINETICS IN Zr$_2$Ti$_2$Cu$_2$Ni$_5$B$_2$ BULK GLASS.

J. Z. Jiang, Technical University of Denmark, Dept. of Physics, Lyngby, DENMARK.

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 wires and ribbons) are further improved either by low-temperature anneals induced by structural relaxation or by high temperature thermal treatments, leading to surface crystallization and/or nanocrystallization. Besides an enhancement of the magnetic properties, fast-heating treatments can lead to materials with better mechanical 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. In this work, we present results of the effects of Joule heating (LVC-JH) on the following amorphous phases: Cu$_6$Al$_{60}$Fe$_{10}$Ni$_{10}$Cu$_{10}$, Cu$_{60}$Al$_{20}$Fe$_{10}$Ni$_{10}$Cu$_{10}$, Cu$_{60}$Al$_{20}$Fe$_{10}$Ni$_{10}$Zn$_{10}$Cu$_{10}$, Cu$_{60}$Al$_{20}$Fe$_{10}$Ni$_{10}$Zn$_{10}$Cu$_{10}$, and Cu$_{50}$Al$_{25}$Fe$_{10}$Ni$_{10}$Zn$_{10}$Cu$_{10}$, with different sample displays a typical resistance versus current curve, with different disconnections which mark the different crystallization stages. It was possible to stop the annealing at 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.

3:15 PM L5.4 FORMATION OF NANOSTRUCTURED ALLOYS BY LIQUID STATE SPINODAL DECOMPOSITION. H.W. Kim, Dept of Physics, Chungnam University of Hong Kong, Shek Tin, Hong Kong, PR CHINA.

If the like species in an alloy melt attract each other more, it was found the system undergoes liquid state spinodal decomposition at a temperature $T_0$ that is substantially below its liquidus $T_l$. The wavelength $\lambda$ of the decomposed networks decreases with undercooling $\Delta T$ which is defined as $\Delta T = T_l - T$. Most interestingly, $\lambda$ can enter the nanometer regime for liquid undercoolings. As a result, original homogeneous undercooled melt decomposes into liquid networks with $\lambda < 100 \text{ nm}$, if isothermal annealing is simultaneously introduced, the liquid networks, driven by surface tension, would break up into tiny liquid droplets of diameter $< 10 \text{ nm}$. 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 $> 1 \text{ cm}$; [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. Bassett, 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 recrystallization due to 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 recrystallization instability exists when the heat release rate due to crystallization reaches a threshold level or when the nucleation rate increases with increasing temperature. Therefore, in deeply undercooled liquids the recrystallization 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 DECOUPLING ON THERMAL STABILITY IN THE LARGE GLASS FORMING SYSTEM Zr$_2$Cu$_4$Ni$_4$Al$_2$. Andrew A. Kündig, Jörg F. Leijer, William L. Johnson, California Institute of Technology, W.M. Keck Laboratory, Pasadena, CA.

Different bulk glass forming alloys in the neighborhood of Zr$_2$Cu$_4$Ni$_4$Al$_2$ (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, $Zr_{30}Ti_{30}Cu_{30}Ni_{30}Al_{20}$, with $-5 < x < 2.5$, the glass transition temperature, $T_g$ and the undercooled liquid regime, $\Delta T = T_g - T_c$ (at crystallization temperature) continually decrease with increasing $x$. SANS measurements on the glassy and alloyed melts show inverse master curves, giving evidence for decomposion 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 $T_c$ 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 Koester, 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 gear wheels. Zr-Cu-Ni-Al belongs to the best glass forming systems known. Recent work, however, realized fast oxidation in air as compared to Bi-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. Si, S, Y as well as Mo have been chosen in order to improve the oxidation resistance. Oxidation of Zr$_2$Cu$_4$Ni$_4$Al$_2$ as a quarternary glass or alloyed with $2\text{ at.}\%$ of Si, Sn, Mo or Y as well as nanocrystalline alloys of a same composition was studied in the temperature range between 300 and 600°C by means of thermogravimetry in dry air, x-ray diffraction, SEM and TEM as well as the weight loss profiles of all glasses and alloys. The data observed to follow a parabolic law. In the quaternary glass oxidation kinetics seems to be controlled by oxygen diffusion in the scale towards the Zr$_2$O$_3$ glass interface. The scales formed contain 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 showed only minor influences. Alloying, however, not only increases oxidation resistance, but also changes the crystallization behavior. For example, Si, Sn, and Mo additions increase thermal stability. Whereas Si leads to the formation of tetragonal Zr$_2$Ni and Mo to the formation of quartzcrystals. 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 A MORPHOUS Zr$_6$Ni$_2$Al$_3$. Daniela Zander, Uwe Koester, Dept. of Chemical Engineering, University of Dortmund, Dortmund, GERMANY.

Zr$_6$Ni$_2$Cu$_4$Al$_2$ 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 absorbed phase of Zr$_6$Ni$_2$Al$_3$ amorphous alloys has been studied in detail by Inoue et al. [1]. Glassy Zr$_6$Ni$_2$Al$_3$ was prepared by melt-spinning. It exhibits a very remarkable thermal stability as observed by DSC. Around 450°C nanocrystallization was observed leading to an extremely microstructure with mean grain sizes below 5 nm. Coarsening and transformation into the stable crystalline phase proceeded during further annealing. Kinetics of crystallization was studied by DSC, its microstructure by microscopic TEM as well as its X-ray diffraction statistics. The crystalline phases formed were analyzed by means of X-ray and neutron 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 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 500°C. Results on the crystallization, hydrogenation, elements which play on the influence of hydrogen on the crystallization will be compared in detail with the behavior of the quaternary Zr$_6$Ni$_2$Cu$_4$Al$_2$ glasses. [1] X.G. Li, T. Otsuruma, S. Takahashi, T. Sugi, H.M. Kimura, A. Inoue, J. Alloys Compounds 297 (2000), 305-311.

SESSION L6/K10: JOINT SESSION QUASICRYSTAL
Chair: Uwe Koester
Wednesday Morning, November 29, 2000 Room 200 (Hyena)

8:30 AM L6.1/K10.1 FORMATION OF NANO ICSHEDRAL QUASICRYSTALLINE PHASE IN Zr-BASED BINARY AND TERNARY GLASS ALLOY. K. Junji Saida, Mitsuhiro Sato, and Shuji Iwasaki, Japan Science and Technology Corporation (JST), Sendai, JAPAN, Akihiko Iwasa, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Since the reproducible formation of an icosahedral quasicrystallic phase as a primary precipitation phase from an amorphous state has been discovered in the Zr-Al-Ni-Co-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$_x$Ni$_{20-x}$Al$_{30}$ (M=Pt, Au or Pt) and Zr$_x$Ti$_{20}$Pd$_{30}$ (M=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 the icosahedral phase exists in the Zr-Pd and Pd-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 Pd-Pt alloys. In this paper, we intend to present, which strongly supports the fact that local atomic structure is similar for the two solid states.

9:15 AM *LE3/K01.3

**NANOQUASICRYSTALLIZATION OF Zr-BASE METALLIC GLASSES**

B.S. Myers, D.H. Ping and K. Hone, National Research Institute for Metals, Tsukuba, JAPAN.

Recent investigations revealed that nanocrystallization 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 with the purpose of understanding the essential conditions for nanocrystallization. Icosahedral phase is formed in the first stage of crystallization reaction of the Zr$_{70}$-Al$_{10}$-Ni$_{5}$-Cr$_{5}$ alloy, amorphous alloys beyond a critical oxygen level, suggesting that oxygen is a factor to stabilize icosahedral phase formation in Zr-Al-Ni-Co 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$_{70}$Pd$_{30}$ (x=30 and 35) alloys show nanocrystallization in the course of amorphous to crystal transformation. Based on 3DAP and TEM observation results together with computational simulation results, the trigonal distortion and the processes 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 201 (Hynes)

10:15 AM *L7.1

**CORE LOSSES AND SOFT MAGNETIC PROPERTIES OF NANOCRYSTALLINE Fe-Zr-Nb-B ALLOYS WITH ZERO-MAGNETOSTRICTION**

Akioho Makino$^1$, Akioho Inoue$^2$, and Toshiaki Makamoto$^3$

$^1$ Department of Machine Intelligence and System Engineering, Faculty of Systems Science and Technology, Akiha Prefectural University, Honjo, JAPAN; $^2$ Institute for Materials Research, Tohoku University, Sendai, JAPAN; $^3$ Research Institute of Electrical and Magnetic Materials, Sendai, JAPAN.

The nanocrystalline Fe-rich Fe$_{50}$-Zr$_{30}$-Nb$_{5}$-B$_{5}$ (M = Zr, Hf, Nb) alloys produced by crystallization 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 Fe-rich Fe$_3$Zr$_7$B$_4$ grains about 10-15 nm in size embedded in a residual amorphous matrix containing a large amount of Zr and Nb elements and B. Owing to strong ferromagnetic exchange interaction between the grains, the net crystal anisotropy is canceled. This is a reason why the nanocrystalline Fe$_{50}$-Zr$_{30}$-Nb$_{5}$-B$_{5}$ alloys exhibit the good soft magnetic properties. The Fe$_{90}$Zr$_{10}$B$_3$ (Bs = 1.7 T, permeability = 50,000 at 1 kHz, core loss = 0.21 W/kg at 1.4 T and 50 Hz) and Fe$_{84}$Nb$_{5}$B$_{5}$ (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-MB alloys.

The nanocrystalline ternary Fe-MB alloys exhibit small but non-zero magnetostriiction. Therefore, it is expected that the soft magnetic properties of the nanocrystalline Fe$_{50}$-Zr$_{30}$-Nb$_{5}$-B$_{5}$ alloys can be improved further by achieving zero-magnetostriiction. Since the magnetostriiction is negative for the Fe-Zr-B alloys and positive for the Fe-Nb-B alloys, it is expected that zero-magnetostriiction 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$_{50}$-Zr$_{30}$-Nb$_{5}$-B$_{5}$ alloys has been studied. The magnetostriiction and grain size of the Fe$_{50}$-Zr$_{30}$-Nb$_{5}$-B$_{5}$ 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 Fe$_{90}$Zr$_{20}$B$_3$ and Fe$_{84}$Nb$_{5}$B$_{5}$ alloys.

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 with nominal composition Fe$_{80}$Ni$_{20}$B$_{6}$Fe$_{80}$Ni$_{20}$B$_{6}$ ribbons. Fe$_{80}$Ni$_{20}$B$_{6}$ Fe$_{80}$Ni$_{20}$B$_{6}$ ribbons with the same ribbon melting temperature of 1313±5 K and demonstrates a good coercive field, 8 mm wide and 15-25 micrometer thick amorphous ribbons were prepared by melt-spinning onto a copper roller. As-supplied ribbons have superior soft magnetic properties compared with those of Fe$_{80}$Ni$_{20}$B$_{6}$ Fe$_{80}$Ni$_{20}$B$_{6}$ coercive field is found to be almost the same, whereas the saturated magnetization 4M$_S$ = 142±0.3 K and maximum permeability is about 1.7 and 3 times higher. Co alloying exhibits substantial enhance thermal stability of amorphous steels. The crystallization temperature of the Fe-Co based melt-spun ribbons under continuous heating was found to be as low as 60 K higher than that of the FeNi counterpart and the activation energy for crystallization estimated by Kissinger technique was as high as 478 K. The investigated metallic glass crystallizes by the reaction: $\gamma$-Fe$_{55}$Co$_{45}$ + Fe$_{55}$Co$_{45}$ (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 has established that the improved thermal stability of the Fe-Co-based metallic glasses in comparison with that of Fe$_{80}$Ni$_{20}$B$_{6}$ Fe$_{80}$Ni$_{20}$B$_{6}$ is due to both lowered diffusion coefficient and increased value of the specific free energy of the nucleation, it is supported in part by Swiss Royal Academy of Sciences.
eutectic mode had high stability and amorphous forming ability, and thus electrons of boron atom in the amorphous PbZn did not move to 3d shell of iron but may remain electrons of Nb to move to iron. The mechanisms lead to these results.

11:15 AM 17,4
DOMAIN STRUCTURE AND THERMAL DEPENDENCE OF THE COERCIVE FIELD IN NANOCRystALLINE Fe2ZrCu.
Antonio. Hernando, Juan Arcas, Instituto de Magnetismo Aplicado [UCM, RENFE].

Nanocrystalline Fe2ZrCuZr samples have been obtained by annealing melt-spun ribbons during 1 h at temperatures ranging between 713 K and 823 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 Faraday balance 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 are 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 738 K, corresponding to the beginning of the crystallization process, undergoes a dramatic magnetic hardening, showing a coercive field of 150 A/m and a duff 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 18: HARD MAGNETISM
Chair: Antonio Hernando
Wednesday Afternoon, November 29, 2000
Room 200 (Hynes)

1:30 PM 18.1
CRITICAL BEHAVIOUR OF THE Fe-Ni CLUSTER-GRAIN PHASE IN BULK GLASSY Nd2Fe14B-HARD MAGNETIC R.J. Ortega-Martos, K.V. Rao, Dept. of Materials Science
-Imfy-MSOE, Royal Institute of Technology, Stockholm, SWEDEN; and A. Incze, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

The magnetic properties of novel bulk glassy Nd2Fe14BAlx magnets around the transition to the paramagnetic state have been studied by magnetization measurements at constant d-fields in the range 24 - 44 kA/m, at temperatures in the range 440-570 K, and by magnetic thermogravimetry at fields ±80 A/m. Analysis of our data in the Curie-Weiss regime (effective moment and paramagnetic Curie temperature), as well as analysis of the critical behaviour of the isothermal susceptibility and magnetic isotherms suggest a transition from a low field state to a ferromagnetic-like superparamagnetic 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 α = 1.51(1), β = 0.65(5), and Tc = 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 18.2
MICROSTRUCTURE CONTROLLED MAGNETIC PROPERTIES OF THE HARD MAGNETIC BULK GLASS Nd2Fe14B-Alx.
S. Schneider, K. Samwer, I. Phys. Institut, U Göttingen,
GERMANY; M. Seibt, IV. Phys. Institut, U Göttingen, GERMANY; A. Incze, 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 Nd2Fe14B alloy can have coercivities as high as a few hundred kA/m 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 mm-sized Nd2Fe14B-Alx 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 noncrystalline Fe-rich clusters. Such a microstructure can explain the observed high as well as the low temperature magnetic behavior. Convolution flow patterns in the TEM images and the small crystals 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 18.3
LOCAL MAGNETIC STRUCTURE AND MAGNETIC PROPERTIES OF Nd2Fe14B-Nb1-xAlx ALLOY GLASSY HARD MAGNETS. Horia Chiricu, Nicoleta Lupa, National Institute of Research and Development for Technical Physics, Iasi, ROMANIA; Robert Vandenberge, 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 Nd2Fe14B-Nb1-xAlx (x = 0, 10), were investigated with VSM, SQUID magnetometer, ac-susceptometer and Mössbauer 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. This 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 bulk alloy before ejection or suction. The differences obtained between zero-field cooled (ZFC) and field cooled (FC) magnetization curves and the M(T,C) curves of one sample and its displacement towards lower 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 18.4
PROCESSING AND HARD MAGNETIC PROPERTIES OF NANOCRYSTALLINE SmCo5Zr-MAGNET POWDERS. H. Tang, J. Zhou, Y. Liu, D.J. Sellmyer, Center for Materials and Analysis, University of Nebraska, Lincoln, NE.

Nanocrystalline SmCo5Zr permanent magnet powders with Tb/Cu type structure have been synthesized by mechanochemical milling Sm21.5Co8.5Zr1.5Zr2 alloys [x = 0, 1, 2, 3] and subsequently sintering and 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 SmCo5Zr 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 1.50 nm). Compared with the parent alloy [x = 0], the hard magnetic properties (coercivity Hc, remanence Mr, maximum energy-products BHmax) have been enhanced greatly in the alloys with a small amount of Zr addition. For example, Sm21.5Co8.5Zr1.5Zr2, Zr2 alloys milled for 20 hrs and subsequently annealed, have optimal values of room temperature Hc, of 13.5 kOe (x = 0), M, of 22.03 emu/g (x = 1), M, /M, of 0.71 (x = 1), BHmax of 13.0 MG ofe (x = 2), improved greatly compared with the parent alloy [x = 0] with optimal values, Hc, of 6.4 kOe, M, of 27.38 emu/g, M, /M, of 0.66, BHmax of 11.05 MG ofe. The hard magnetic properties are found to be sensitive to the mechanical milling time. The optimal value of Hc, of 18.65 kOe (M, of 66.77 emu/g) for the Sm21.5Co8.5Zr2.5Zr2 alloys milled for 10 hrs, is much higher than the value of Hc, of 13.50 kOe (M, of 75.36 emu/g) for 20 hrs. The enhancement of remanence in this series of Sm21.5Co8.5Zr1.5Zr2 alloys is owing to the effective exchange coupling between the nanosized grains. The hard magnetic properties are discussed with correlation to the structure and microstructure development in the Zr-containing nanocrystalline SmCo5Zr alloys.

SESSION 19: MECHANICAL PROPERTIES
Chair: Jurgen Eckert
Wednesday Afternoon, November 29, 2000
Room 200 (Hynes)

3:00 PM L9.1

To increase the toughness of a metallic glass with the nominal
composition Zr$_2$Nb$_3$Al$_6$Cu$_{5.4}$Ni$_{2.6}$ it was used as the matrix in continuous fiber composites reinforced with W and also in particulate composites with W, Fe, Cu, Ni, Pb. The phase and microstructure of the composites are studied by X-ray diffraction, scanning electron microscopy, and electron microscopy. The metallic glass matrix remains amorphous after adding up to 80 vol. % of wires or 50 vol. % of composite with different volume fraction of nanophases in the matrix. The results of scattering of different phases/volume fractions to the overall mechanical behavior will be critically assessed and linked to the microstructure of the matrix, focusing on the possibility of achieving a high room-temperature strength combined with good ductility. For Zr-based alloys, results for the behavior at different conditions and stress rates will be given for single-phase alloys and specimens with different volume fraction of nanophases. The quenching rates, strong liquid behavior and small driving force for crystallization as important parameters for microstructure formation upon cooling or annealing will be critically assessed. This will be illustrated for selected transition metal and rare earth-based systems.

3:15 PM L0.2  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 Eng. 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 unconstrained 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 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 is accompanied by a significant increase in the yield strength and a remarkable improvement in the creep properties of the system. The results 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 L0.3  INTERNAL STRESSES IN BULK METALLIC GLASS MATRIX COMPOSITES. C. Uttington, D. Drangi, B. Clasen, California Institute of Technology, Dept. of Materials Science, Pasadena, CA; Dorian Balch, D. C. Dunand, Northwestern University, Dept. of MSE, Evanston, IL; M. 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 higher mechanical properties compared to monolithic BMGs. However, there is a thermal expansion mismatch between the reinforcement 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 the composites.

3:45 PM L0.4  BULK AMORPHOUS AND NANOSCALE STRUCTURES IN TRANSITION METAL BASED ALLOYS. J. Eckert, U. Kühn, G. J. Fan, W. Lüser, 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, (nanocrystalline/macrocrystalline) or nanocrystalline/melt quenched alloys with different grain size and volume fraction of nano-phases can be obtained. For several different alloys, uniaxial phase mixture phases 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 quenching in short-range/mesoscale order clusters produced at different

4:15 PM L0.5  FRACTURE AND FATIGUE CRACK GROWTH OF BULK METALLIC GLASS ALLOYS AND THEIR COMPOSITES. Katherin M. Flores, Reinhold H. Dauskardt, Department of MSE, 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-Cu-Nb 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.m$^{1/2}$ with remarkably little plastic deformation. Intense shear bands, associated with localized straining in five volume percent nanophase 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.m$^{1/2}$. 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.m$^{1/2}$ 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, 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 L0.6  Abstract Withdrawn.

4:45 PM L0.7  SYNTHESIS AND CHARACTERIZATION OF IN-SITU BULK METALLIC GLASS MATRIX COMPOSITES. C.P. Kim, W.L. Johnson, California Institute of Technology, Dept. 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-Co-Ni-Be system. The formula for such a mixture is given by BMG(100-X) M(X), where M is Ti, Nb, V, or Mo. Upon cooling from high temperature of melt, the mixture undergoes partial crystallization by nucleation and subsequent dendritic growth of nearly pure M dendrites, with phase symmetry in the remaining liquid. The remaining liquid subsequently freezes to the glassy state producing a two-phase microstructure containing rich M 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

Chair: Robert O. Ritchie and A. Lindsay Greer

Thursday Morning, November 30, 2000 Room 209 (Hynes)
8:30 AM *L10.1
COMPARISON OF THE MECHANICAL BEHAVIOR AND QUALITY OF TITANIUM GLASSES IN RIBBON AND BULK SHAPES. M. Calvo-Dávila, Laboratoire de Science et Génie des Matériaux Métalliques [LSGM], CNRS UMR7684, Ecole des Mines, Nancy, FRANCE.

A short history on the appearance of metallic glasses of large dimensions, so-called “bulk”, is recalled. The quality and mechanical behavior of metallic glasses in the shape of ribbons is reviewed. The problems of their technological application 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. Work was expected with the “bulk” 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-Dinary, B.P. Vinci, Lehigh University, Department of Materials Science and Engineering, Bethlehem, PA; T.C. Hafner, 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 Zr75Fe15Cu10NiAl1 bulk metallic glass during deformation. It is well known that low temperature plastic deformation is accommodated 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 strain-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
EFFECT OF HYDROGEN ON THE CRYSTALLIZATION AND MECHANICAL BEHAVIOR OF A Zr-Ti-Nb-Cu-Be BULK METALLIC GLASS. Dae-woong Suh and Reinhold H. Dauskardt, Department of Materials Science and Engineering, Stanford University, Stanford, CA.

Hydrogen is a well-known embrittlement 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. For amorphous metals, studies with 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 effect of hydrogen on the deformation and fracture behavior of a Zr-Ti-Nb-Cu-Be bulk metallic glass, specifically hardness and crack propagation behavior induced by hydrogen gas and cyclic loading. Microstructure, glass transition and crystallization kinetics of the hydrogen-charged metallic glass were examined using high-resolution electron microscopy, 3D X-ray diffraction, X-ray photoelectron spectroscopy and 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, retardation of the 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-metals and non-magnetic materials, for which 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 metallic glasses (BMGs) which 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.

10:00 AM L10.5
NEWTONIAN FLOW IN BULK METALLIC GLASSES. T.G. Nieh, Lawrence Livermore National Lab, Livermore, CA; C.T. Le, 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 non-viscoplastic viscous flow (mism) where m in 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: Zr53Al15Fe15Cu10Ni8 and Zr55Al15Fe15Cu10Ni8, both in wt %) 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 AND STRESS TRANSITION REGION AND INFLUENCE OF CRYSTALLIZATION. Bertrand Van de Moortele, Jean-Marc Polletier, GEMMP, INSIA, Villeurbanne, FRANCE, Jean-Louis Soubyreux, 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: Zr55Ti15Cu10Ni8Al7 and Zr65Ti8Ni20Cu8. In DSC we were able to measure different heating rates to determine the beginning and the end of glass transition (T_g) and relaxation (T_r), respectively, and the onset of crystallization (T_x). The complex shear modulus G"(w) = G"(w) + iG"'(w) was measured versus temperature (between 28 °C and 610 °C) and frequency ω = 2πf, 10^4 < f < 1 Hz (G": storage modulus, G": loss modulus).

In the Zr-based alloy, it is generally admitted that the SLR spreads over about 30-50 K, however this value refers to the difference between T_g and T_r. While, considering the effective onset of this region (T_g), 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 Pb-based alloy, a wide effective SLR is observed. The influence 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 minimum of the loss modulus (G"").
Crystallization leads to a very important increase of the shear modulus. Finally, a physical analysis of this phenomenon is presented.

11:15 AM L10.7
ON THE HIGH TEMPERATURE CREEP AND RELAXATION BEHAVIOR OF Zr-BASED BULK METALLIC GLASSES.
M. Heinemann, R.S. Daniel, A. Bregel, J. Ecker, and L. Schultz, 1FW Dresden, Institut für Metallische Werkstoffe, Dresden, GERMANY.

Bulk metallic glasses processed at very low cooling rates of 1-10 K/s were vitrified without crystallization have attracted much interest regarding their atomic structure and the ensuing properties. These multi-component systems also exhibit a wide supercooled liquid region which provides excellent stability against crystallization, enabling fabrication of components with the smallest dimension of 10 mm using conventional casting techniques. In the present study, 50 mm long ingots with diameters ranging from 3 to 5 mm of Zr_{x}Cu_{y}Al_{z}Ni_{w} 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 Tg 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 ε-log σ relation over a wide ε-range (10^{-4} to 10^{-1}) was established for different temperatures. Both the amorphous and crystalline state and homogenous and heterogeneous strain behavior and true 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 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.
Yoshitoyo Kawamura, Akihiko Inoue, IMR, Tohoku Univ., Sendai, JAPAN.

Deformation Behavior in Bulk Metallic Glasses was investigated by constant strain-rate stretching in Zr-Al-Ni-Co, Pd-Ni-P, Li-2Al-Ni, and Pd-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 the stress-relaxation rate 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 characteristics even the wide temperature interval ranging from the glass transition regime to the melting regime. On the contrary, Coben-Greath 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
Thurs., 12:30-2:30 November 30, 2000
Room 200 (Hynes)

1:30 PM L11.1
LOCAL ATOMIC STRUCTURES AND PLASTIC DEFORMATION MECHANISMS IN THE SUPERCOOLED LIQUID STATE OF Lm_{x}Al_{y}Ni_{z}. Tadahito Ohsaku, Yoshihiro Horiuchi, Osaka Univ., Inst. of Sci. & Ind. Res., Osaka, JAPAN; Akishin Inoue, Tohoku Univ., Inst. Mater. Res., Sendai, JAPAN.

Amorphous Lm_{x}Al_{y}Ni_{z} alloy has an excellent superplasticity in the stable supercooled liquid state between temperatures from about 470 to 515 K. These temperatures, 470 and 515 K, correspond to those of the glass transition (Tg) and the crystallization (Tc), respectively. We have recently performed an in-situ electron diffraction and HREM study of this alloy by annealing up to Tc using specimen-heating stage in TEM. Diffraction intensity changes were recorded on imaging plates. In order to avoid mechanical scattering, energy-filtered was used. Any appreciable change was observed by HREM on heating across the temperature Tg. However, atomic radial distribution function analysis revealed that a clear structural change proceeds in the temperature range between Tg and Tc on 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 Tg and Tc 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 related to relation of diffusion rates of constituent atoms. A larger elongation was obtained for the structure near Tg, but for the structure near Tc the elongation was relatively smaller, due to the local phase separation. A good agreement between the experiment and simulation behaviors in superplastic deformation that the elongation is enhanced near Tg but suppressed as the temperature is increased towards Tc.

2:00 PM L11.2
STRAIN SOFTENING IN BULK METALLIC GLASSES.
On 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-Co-Ni-P bulk glasses at temperatures 80 to 400K below the glass transition temperature. Constant strain-rate compression and creep tests revealed a strain-softening phenomenon. The strain-rate curve measured at 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-annulated 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 A MODIFIED Mg-Ni-Y ALLOYS.
Sovvak Saifer, Nikolai Kobelev, Inst of Solid State Physics, Chernogolovka, Moscow Region, RUSSIA; Eli Keren, Leonid Saifer, Dmitrii Mogilyanski, Aronm Bedellum, Dept of Chemical Engineering, Ben-Gurion Univ of Negev, ISRAEL.

Mechanical spectroscopy techniques have been applied to investigate of structural relaxation and crystallization of Mg-Ni-Y alloys. The composition of the alloys was varied due to change of yttrium concentration from 0 to 9 at. % corresponding magnesium decrease. The internal friction and Young’s modulus of amorphous Mg-Ni-Y alloys obtained by the wet spinning technique have been measured by a vibrating reed at frequency of 250Hz, heating and cooling runs in the temperature range from 268K to 650K. The structural relaxation and different stages of crystallization can
A MORPHOUS ALLOY. Liqian Xing, Todd C. Huflgael, Dept. of MSE, 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 "activated plastic flow" which occurs in these alloys is composed of regressed sections of elastic deformation followed by abrupt load drop. By compressing the specimens to various strain short of failure in the plastic region and examining the sample surface microscopically, we observed the development of the shear bands and 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 bursts may be due to the crack propagation. Microscopic analysis shows that bursts 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 failures 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 \( \eta \) of the form

\[
\eta(T) = \frac{A}{(T - T_0)^{\beta}}
\]

describes some of the most characteristic features of supercooled liquids. Using the Interstability Theory of Condensed Matter (Phys. Rev. Lett. 88, 974 (1992)) and the Dyre, et al (Phys. Rev. vol B53, 2717 (1996)) Shoving Model for diffusion, we derive this relation and obtain \( T_0, T_0, T_0 \) as \( \gamma/\theta, 1, \) \( \bar{U} = \text{const} \), where \( \theta \) is a softening parameter and \( \bar{U} = U(T_0)/T_0 \) is the interstitial migration energy at the glass temperature \( T_g \) related to the normalized frequency parameter by \( \gamma = \frac{A}{\theta} \).

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 Hiramatsu, Yoshitomo Kawanisi, Akihiko Inose, TKK, Tochigi Univ, Sendai, JAPAN; Ho-Hua 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-Ti (MAT) transition metal alloy system is known to be one of the best glass formers. Although the bulk glassy alloy exhibits high glass transition temperature, the transition temperature of the glass modules and mechanical properties, using the Interstability Theory of Condensed Matter, are independent of the glass transition temperature. However, recently, we have found that an acoustic reaction between Zr metal and graphite to form Zr-C particles during preparation is effective for the mechanical properties of the disordered alloy because the acoustic reaction process is not only a good wetting and homogenized dispersion of the filler particles.

This paper is intended to demonstrate the effect of the acoustic reaction method on the synthesis of the glassy alloy and to examine the feature of its viscoelasticity in comparison with that of the Zr55Al11Nb5Cu3Si30 single glassy phase.

4:45 PM  L11.10
HYDROGEN-DOPED BULK METALLIC GLASSES AS HIGH DENSITY MATERIAL. Tetsuki Yagi, Rikio Oguno, Ryoji Tanura, Shin Takeuchi, Science University 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 hydrogen is a strong amorphous metal, as well as hydrogenized metallic crystals, exhibit a Snark-type relaxation, and hence metallic glasses containing a high density of hydrogen can have an 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 0.5 eV in Zr-based and Pd-based metallic glasses. We have shown that the fracture strength is as high as 1.5 GPa. Thus, we have shown that...
L12.1 CORRELATION BETWEEN RESISTIVITY CHARACTERISTICS AND ELECTRONIC STRUCTURE PARAMETERS OF THE Ni-Pd-P AMORPHOUS ALLOYS. Mykola Balibich, Olegyn
Nakonechnyya, Olegyn Yakovenko, Mykola Zhupaenko, Taras Shevchenko National University, Dept. of Physics, Kyiv, UKRAINE; Alain R. Yavari, LTPCM-CNRS, INPG, St. Martin-d’Heres, FRANCE.

The temperature dependences of resistivity $\rho(T)$ 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 $\rho(T)$ curves permits us to use the Fisher-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 20 % of P. The other side, TCR value is increased with P 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 to the Fermi level shift according to the change in Ni concentration and to the influence of the Mo'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/Au-Si NANO COMPOSITES. Viktor Kunatsa, Atanas Ivanov, Rodi Nicula, Eberhard Barkel, 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 atom 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 were 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 Ag80Sm15 alloy ribbons obtained by rapid-quenching. After 50 hours milling time at a milling frequency of 250 rpm only approx. 10% of the initial iron phase could be evidenced. Information about the structural coherence length of the Ag80-Sm15-Fe solid solution were obtained from the evolution of the X-ray diffraction line widths. The effect of the embedding Ag-Sm-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 in situ in 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 Bienstock*, Stanford University, Stanford Synchrotron Radiation Lab, Stanford, CA; "currently 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 20 % Ge, two phases with compositions of approximately Ge and MoGe have been observed. When alloyed with Ge, a tremendous array of metallic elements, M, nonmetallic periodic table (including Mo, W, Pd, Fe, Rh, Ir, Cu, Ag, and Au) form the so-called dimeronides as the Ge-rich equilibrium phase. The chemical bond typically dominates in amorphous systems as well. It is assumed that this 1:2 Mo-Ge stoichiometry provides the most stable phase in the amorphous state as in the crystalline state. Therefore, the 1:3 Mo-Ge stoichiometry discovered in the Mo-Ge system is unexpected. We apply anomalous x-ray scattering [AXS] to Mo-Ge, the metal-rich endpoint for phase separation in the spinodal Mo-Ge metastable alloy system. Near atomic scale examination of the individual elements in the sample, the atomic scattering factor can be changed by varying the incident x-ray energy. The resulting changes in intensity can be captured as element-specific X-ray 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 effects were directly measured, and a variable-focus graphite monochromated crystal was used to dispense scattered radiation onto a position-sensitive linear detector. The result is lower background and enough energy resolution to allow direct removal of Kα resonant Ramman 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-MoGe phase.

Department of MSE, Johns Hopkins University, Baltimore, MD; Department 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, inevitably created through extremely nonequilibrium processes, 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 (spinal) 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 or cryogenic temperatures amorphous alloys can be obtained in this highly nonequilibrium 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 in a recent Monte Carlo (MCM) 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 MCM configuration and EAM potential.

L12.5 THE GLASS TRANSITION AND LOW ENERGY EXTENSIONS IN SUPERCOOLED METALLIC LIQUIDS AND GLASSES. Hisao Kunieda, Tokyo Institute 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 to 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 of the supercooled liquids. In this study, adopting the theoretical formula (4-5) extended from the Nelson-Schulz-Settna formula (2), we 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

L12.6 KINETIC STABILITY OF FAR FROM EQUILIBRIUM BULK AND SURFACE STRUCTURES OF CHAOS AND QUASICRYSTAL PHASES. Diego Segovia, D. Jacobs. Grupo de Fisica de Materiales, Dep. Fisica, Univ. Autonoma de Barcelona, Bellaterra, SPAIN, and Chugueva, 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 indicate kinetic evaluation of FCC-Al nanocrystal 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 the isothermal ordinate data of the Al corner of the quasimatrix system by the CALPHAD method. Derived quantities are a critical supercooled liquid and mirror diffusion coefficients. In this paper all the previous growth and nucleation quantities are used to complete 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 crystallization of the FCC-Al and/or the stoquiomometric 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 \( Pd_{43}Ni_{57}Cu_{27} \) P20 METALLIC GLASS. Evgenia Pekarskaya, Jan Schoons, 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 lie at \( 0.1-0.3 \) K/s at the edge of the time-temperature-transformation diagram, which indicates the onset of crystallization in an isothermal experiment, is located at \( 200 \) K for the Pd-Ni-Cu-P samples in equilibrium with \( PdO \). The reason for 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 \( Pd_{43}Ni_{57}Cu_{27}P20 \) alloy are studied in the present paper. 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 mechanism is what kind of phase mixture develops. The study of the different 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 using heating from the as-quenched phase. The microstructure of the alloys were then analyzed and compared.


The recently developed multicomponent Zr-Ti-Co-Ni-Al and Zr-Ni-Co-Ni-Al systems exhibit bulk glass forming ability for a variety of compositions [2]. 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 inert gas. The cast and ingots samples were 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 region is limited to the formation of intermetallic or quasicrystalline phases. Special emphasis is placed on the nature and size of the competing crystalline phases formed upon cooling and annealing. For some of the alloys almost single-phase quasicrystalline material is formed directly upon cooling from the melt. In contrast, nanocrystalline grains with sizes on the order of \( 5-10 \) nm were observed upon precipitation of the magnetic phase and amorphous specimens. At higher temperatures, the metastable nano-quasicrystalline turn into intermetallic alloys. Besides the difference in quasicrystal grain size for the differently prepared samples there are some differences in the composition of the non-quasicrystalline phases between quasicrystals nucleated from the melt upon cooling and the nano-quasicrystals produced upon 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. Lüser and L. Schultz, Appl. Phys. Lett. 74, 664 (1999).

L12.9 NANO-CRYSTALLINE STATES AND STABILITY OF MELT SPUN \( Ag_{78}Cu_{22} \) ALLOYS. P.M. Julia, L.G. Schröter, 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; D.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 thermal stability 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 difference 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 \( Ti-Al \) AND \( Zr-Ni-Al \) ALLOYS. Rosario Nicola, Adrien Jiran, Viktor Koneker, Gerd Holzheuer, Eberhard Barkel, Rostock Univ, Dept of Physics, Rostock, GERMANY.

Ti/Zr-based metallic glasses and crystalline intermetallic compounds with improved mechanical properties are present in 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-heating-rate 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 microstructural 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 nanocrystalline intermetallics in Ti/Zr-based alloys.

L12.11 SIMULATION OF CRYSTALLIZATION AND STRESS RELAXATION IN METALLIC GLASSES. Yoshiaki Kogure and Mineo Deyama, Tokyo 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 nanoparticle materials. Fundamental mechanism of crystallization of metallic glasses [3] and formation of stable metal soot [Cu, Ag, Au] are investigated by means of molecular dynamics.
The effect of alternative preparation methods on glass formation and properties of Ni$_2$Fe$_2$Al$_3$Al$_4$ and Ni$_2$Fe$_2$Co$_2$Al$_3$Co$_2$ 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 Ni$_2$Fe$_2$Co$_2$Al$_3$Co$_2$ alloys which may give rise to nickel-like Ni$_2$Fe$_2$Al$_3$ crystall in as-cast Ni$_2$Fe$_2$Co$_2$Al$_3$Co$_2$ nanocrystalline rods. Samples containing 55 at% Fe exhibit different phase transformation behaviour in DSC runs. The cast Ni$_2$Fe$_2$Al$_3$Co$_2$B$_4$ rod exhibits crystallization at 790 K, preceded 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 pre-alloys display two exothermic peaks at roughly the same temperatures. The J - H hysteresis loops of materials were studied by different techniques. The under 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 Ni$_2$Fe$_2$Co$_2$Al$_3$Co$_2$ B$_4$ rods, whereas the $M$($T$) plots of Ni$_2$Fe$_2$Al$_3$Co$_3$Co$_3$Co$_3$Co$_3$ samples exhibit a two-phase behaviour with $T_C = 476$ K for the glassy matrix and $T_C = 576$ K similar to Ni$_2$Fe$_2$B$_4$. The investigation has proved that amorphous samples with different local order can be prepared by different processing routes.


We report the temperature variation of the hyperfine field in a crystallized sample of Metglass 2655 SC, from 673 K up to 833 K, where the system becomes paramagnetic (Curie temperature), as measured by Mainauer Spectroscopy (MS). The hyperfine fields of the different phases, identified as Fe$_7$Co$_3$B and Fe$_5$Si by X-ray diffraction, vary as predicted by the molecular field theory of Weiss with a total spin moment of 3/2 (Fe$_7$Co$_3$B) and 5/2 (Fe$_5$Si) B$_4$Si$_4$. The majority phase in the crystallized Metglas corresponds to Fe$_7$Co$_3$B, and the 3/2 value of the total spin is in contrast with the 9/2 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. Xudong Gu, Liping Xing, Todd G. Hufnagel, Johns Hopkins Univ, Dept of M&SE, Baltimore, MD. We have prepared bulk metallic glasses of composition [Hf$_{52.3}$Zr$_{25.9}$Al$_{17.8}$Ni$_{4.8}$]$_{1.0}$Ti$_{0.1}$ [with x=0.1] by an arc melting/moisture 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 quasi-static strain rates also increases with Hf content, reaching ~2.2 GPa for Hf$_{52.3}$Zr$_{25.9}$Al$_{17.8}$Ni$_{4.8}$Ti$_{0.1}$.

L12.17 MOLECULAR DYNAMICS SIMULATIONS OF FRACTURE IN AMORPHOUS Ni. Diana Farkas, Dept. of M&SE, 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 obtained using the same interatomic potential in a technique that allows the calculation of fracture toughness. The results showed ductility even at very low temperatures. The typical behavior of the crack 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$_4$, Ti$_{(1-x)}$, Ce$_x$, N$_{10}$, S$_{50}$, Fe$_{52}$-5 bulk amorphous metal fractured under impact and fatigue loading conditions. Topographs of conjugate fracture surfaces were just produced 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 roughness data to obtain a parameter (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 μm before rupturing. This finding suggests a contributory mechanism for the high values of measured toughness and implies that rapid growth 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 perturbations of ΔK may be obtained from roughness measurements. This relationship and the insight regarding activity within the crack tip process zone provide the basis for fracture model development.

L12.10 MICROSTRUCTURAL CHARACTERIZATION OF SHEAR BANDS IN Zr-BASED METALLIC GLASSES. Jing Li, Xinong Gu, Luqian Xing, Todd C. Hufnagel, Johns Hopkins University, Department of MSciE, 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 unusually 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 foil of both binary and bulk Zr-based glasses. We have also examined shear bands formed during mechanical testing. For example, across 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 synchrontron x-ray diffraction techniques in transmission geometry.


The thermal expansion coefficients of glass-forming Zr-based alloys were measured in the undercooled liquid and the glassy/crystalline state. Due to the high reactivity of the liquid material the experiments were performed contractless 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 TEMPOUS performed under microgravity conditions in the mission MSL-1 [1] and ground based DMA tests [2]. The thermal expansion data can be interpreted in terms of the free volume model.


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L12.22 BULK METALLIC GLASSES AND AMORPHOUS NANOCRYSTALLINE COATINGS. Tetiana Shymyeva, Praxair-TAPA, 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 set on amorphous-nanocrystalline phase transformation temperature and kinetics, and can improve the hardness up to 20%.

L12.23 CONSOLIDATION OF AMORPHOUS GAS ATMORIZED Ti-Cu-Zr-Ni POWDERS BY WARM EXTRUSION. Daniel Stredolet, 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. Results based on differential scanning calorimetry, X-ray diffraction and transmission 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 temperature of the starting powders (~415° 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 x-ray microscopy did not detect any O within the nanocrystalline all phase. The microhardness values of extruded samples (~8.0 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, Akhiam House, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

It is shown that large shape changes (high deformations) can be achieved without crystallization. For example, coining 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 synchrontron x-ray diffraction techniques in transmission geometry.

D. A. Shockey, Poulter Fracture Mechanics Center, SRI International, Menlo Park, CA.
Rotating disk continuous casting as a new method of producing amorphous alloy wire has been developed. The rotating disk, which is made of copper, has a semi-circular groove on its upper 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 the melt-spun amorphous alloy ribbon and copper mold cast cylinder with the same composition. Therefore, the present success of forming amorphous wires with 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 Qian, Inoue 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 meltspun 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 Zr50Cu40Pd10 bulk nanocrystalline alloy prepared by annealing the glassy alloy. The compressive strength increases with increasing volume fraction of nanocrystals, from 1760 MPa at Vp = 10% to 2060 MPa at Vp = 70%. The plastic strain increases significantly and the maximum value of about 4.5%, which is much larger than that of melt-spun glassy alloys (such as Zr55Ni45Al15 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.

L12.30 ULTRASONIC INVESTIGATION OF BULK METALLIC GLASSES. Wei Hua Wang, X.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-Co-Ni-Fe, Zr-Ti-Nb-Co-Ni-Al-Zr-Al-Ni-Co-Y, Nd-Al-Fe-Co, and Pd-Ni-Co-P bulk metallic glasses (BMGs) were formed using a quenching method. 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 characteristic 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 characteristic upon pressure and temperature of the BMGs are found. The microstructure, and elastic and thermal 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 metallic glasses. A strong softening of longitudinal and 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, 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. Gies, T. Glatzner, S. Sartinch, M.D. Ibarra, Universitat Autonoma de Barcelona, Departament de Fisica, Bellaterra, SPAIN.

Al-Ti-Mn-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 particulate structure consisting of a random distribution of α-Al nanoparticles in an amorphous matrix. 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 Al44Ni30Sm6 than for Al44Ni30Sm6. 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 EQUILIBRIUMS DETERMINING THE CRYSTALLIZATION OF supercooled LIQUID Al-NiNd ALLOYS. Reinald Lack, Tijs Godecke, Wen Shen Sun, Max-Planck-Institut für 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]AlNiAl3Nd3, whereas the stable diagram is characterized by the ternary eutectic reaction L = [Al]Al15Ni3Al13Nd3 and the transition reaction L = [Al]Al15Ni3Al13Nd3 → [Al]Al15Ni3Al13Nd3. Supercritical liquid samples produced by melt-spinning 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 partly 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.