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The report summarizes the results of the university Structural Amorphous Metals Program sponsored by ARO/DARPA. It discusses laboratory and theoretical developments in discovery and understanding of Bulk Metallic Glasses, and experiments conducted to characterize the resulting alloys.

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Caltech Center for Structural Amorphous Metals

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II Program Summary

The DARPA SAM project was a comprehensive program to develop bulk amorphous alloys. The program was very successful, and, in addition to developing new glass forming alloys and new theories of liquids, produced 119 papers in peer review journals, 177 conference presentations, one patent, and graduated seven students with Ph.D. degrees, and one M.S. degree.

The program may be divided into several components: alloy development, mechanical characterization, and theory. The alloy development segment included modeling of phase diagrams to predict glass forming compositions, computer simulation of flow to develop advanced forming methods, rheology measurement, and thorough characterization of the all program alloys through high-energy x-ray analysis. The mechanical characterization program consisted of studies of fracture, fatigue and determination of the appropriate flow laws (e.g., Mohr-Coulomb vs. von Mises), development of constitutive laws, and shear band formation. The third focus, computer simulation, covered length scales from molecular dynamics and first principle quantum mechanics through finite element analysis to describe shear band formation under high strain rate loading.

Several new glass-forming alloy systems were developed, including *new* Cu-based, Ni-based, and Ti-Zr-based Alloy Classes with "cm" casting thickness and a monolithic Ni-Pt-base bmg with K_{IC} = 85 MPa-$m^{1/2}$. These systems include Ni-Nb-Ta-Sn glasses with 3mm critical casting thickness, Ni-Ti-Zr-Al *ductile* glasses with 6mm critical casting thickness, new *ductile* Cu-based alloys with 15mm critical casting thickness, and new Hf-Zr-Co-Al glasses with 12mm critical casting thickness and density of 11 grams/cm^3. Lightweight amorphous alloys consisted of new Ti-based composites with densities of 4.5-5 g/cm^3, strength exceeding 2 GPa, 2-cm casting thickness, high toughness and excellent ductility, and ductile magnesium alloys with 2-mm casting thickness. We also synthesized lightweight BMG foams and cellular structures with novel properties.

Fundamental theory and computational models for rheological and mechanical behavior were established and validated. We have characterized the flow vs. temperature, strain rate, and

loading conditions, and developed empirical flow laws which accurately describe flow and deformation. These flow laws were incorporated into process models (Flow 3D, Femlab and Moldflow) and mechanical FEA models were developed to describe deformation of foams, plates in bending, and high strain-rate deformation. The theory is presently being used to predict, model and design practical materials for engineering performance.

Major effort has focused on developing first thermodynamic descriptions of the 5 constituent quaternaries and then the quinary Al-Cu-Ni-Ti-Zr system. Preliminary results show alloys predicted by the model do indeed form bulk glasses. Thermodynamic descriptions of the constituent quaternaries of the six-component Al-Cu-Ni-Ti-Zr-Si system and then the description of this six-component system are being developed.

A new microscopic theory of glasses and liquids was developed based on models of the potential energy landscape of a glass. This theory is based on empirical data, results of MD simulations, and analytic methods. The theory can predict thermal properties, liquid rheology, and mechanical properties such as strength, toughness and ductility. This is a fundamental contribution to the broader science of glasses.

A technical foundation for thermoplastic processing and manufacturing of bulk metallic glasses has been established. This includes an engineering database for thermal, physical, rheological and mechanical properties of bulk metallic glass materials.

Two techniques for fabricating metallic glass foams have been developed, suitable for production of amorphous foams with both open- and closed-cell architectures. Fully amorphous closed-cell foams utilizing microsphere infiltration have been made, with glass volume fractions approaching 50% and densities of approximately 3.4 g/cm^3. In the second and more recent method, the molten alloy is infiltrated into a pattern of sintered salt particles, which are afterwards dissolved away, leaving an open-celled metallic foam network (very different from the closed-cell foam of the first method). These methods are uniquely adapted to commercially-viable amorphous metals like Vit106, giving very different structures with potentially widely-varying applications.

The properties of amorphous matrix composites have been examined, and effects fatigue, impact and environment has been characterized. The key parameters controlling toughness and ductility have been identified, and ductility enhancement and toughening strategies have been developed. The mechanical behavior of BMG matrix composites reinforced with dendritic precipitates that form *in situ* during processing has been studied extensively, using neutron diffraction and mechanical methods. A new self-consistent model to describe the *in-situ* deformation of the composite has been developed.

Mechanical characterization of BMG includes high strain-rate properties, fatigue and fracture, and deformation mechanisms. Ravichandran research group developed novel techniques for investigation of mechanical behavior including the dynamic indentation technique, establishing a systematic methodology for extracting rate sensitivity and pressure sensitivity of materials including structural amorphous alloys over a wide range of strain rates, developing a technique for studying the response of structural amorphous alloys and composites under predominantly

shear conditions using a shear compression specimen and developing analytical model for optimal size and volume fraction of ductile phase for maximizing toughening in ductile amorphous alloy composites.

Theroretical estimates of void nucleation in shear bands has been modeled. The excess free volume in a shear band results in excess free energy relative to a relaxed glass with less free volume. This excess free energy can be correlated with a free volume chemical potential that provides a driving force for void nucleation. The results indicate that any free volume generated in the shear band during deformation is unstable, with the consequence that voids are predicted to form spontaneously from the coalescence of free volume. These voids are then expected to coarsen. This may explain the common observation that failure under uniaxial tension occurs as the result of the propagation of a single shear band, whereas multiple shear bands can form under uniaxial compression without causing failure.

Recent reports have indicated that shear bands can be activated during nanoindentation. The hardness is almost independent of strain rate over this range of strain rates. However, the discrete displacement bursts evident on the loading curves are more prominent at the lowest strain rate and are suppressed at the highest strain rate. The suppression of discrete displacement bursts at the highest strain rates is thought to be caused by the overlapping of shear band events in the fast indentation process. Our results also indicate that strain bursts are suppressed by hydrogen charging, suggesting that hydrogen may be removing some of the free volume from the glass.

The thickness dependence of yielding and fracture of metallic glass plates subjected to bending in terms of the shear band processes responsible for these properties has been studied. Shear band spacing (and length) scales with the thickness of the plate deformed in bending because of strain relaxation in the vicinity of the shear band at the surface. The shear displacements in the shear band also scale with the shear band length and plate thickness, thus causing cracks to be initiated in thicker plates at smaller bending strains. This leads to fracture bending strains that decrease markedly with increasing plate thickness, consistent with recent experiments

Effects of atomic-scale open-volume regions on the flow and fracture behavior of a Zr-Ti-Ni-Cu-Be bulk metallic glass were examined. Relaxation time scales for viscous flow, plane strain fracture toughness and fatigue crack-growth rates were all significantly affected by changes of the open-volume regions brought about by annealing.

We have been studying the effects of sub-T_g temperature below the glass transition temperature (Tg) on the fatigue propagation behavior of a Zr-based bulk metallic glass. An unexpected finding of the study was the formation of elongated ridges perpendicular to the crack front that were produced in the near-threshold regime during elevated temperature testing. Such features have not been previously reported for BMGs. A new mechanism has been proposed to explain this, associated with the out-of-plane stability of a planar crack. The model was used to predict ridge shapes, as well as the trends in ridge wavelength as a function of both applied stress intensity and temperature.

We have characterized and modeled the effects of a number of environments on deformation, fracture resistance and subcritical-crack growth behavior in BMG's and their composites. We have shown that hydrogen significantly increases the glass transition and crystallization temperatures of monolithic BMG's. Fracture toughness is degraded; however, fatigue crack-growth rates were significantly retarded with hydrogen charging.

The work at CWRU has focused on determining the flow, fracture, and fatigue behavior of BMG and composites using novel experimental and processing techniques. The flow behavior is being determined by using novel high pressure testing equipment whereby specimens may be tested in either tension or compression in the presence of a constant confining pressure. Initial work with Vitreloy 1 revealed only a small pressure dependence to the flow/fracture, but fracture angles divergent from 45 degrees. Subsequent work has been performed on a variety of other Zr-based and Hf-based bulk glasses to determine the generality of these observations. Similar behavior has been exhibited in four different bulk glasses and the results have been analyzed using a Mohr-Couloumb flow/fracture criterion. The magnitude of the friction coefficient has been found to be very small (i.e. ~0.03 - 0.04), well below that exhibited by granular solids, geologic materials, and amorphous polymers.

Fracture tests were conducted in loading conditions to determine the sensitivity of bmg alloys The Mode I, and Mixed Mode I/II fracture tests were done to determine, under a variety of different loading modes, the effects of such changes to the magnitude of the fracture toughness. In the Mode I experiments, changes to the notch radius from fatigue precracked to bluntly notched produced tremendous increases to the toughness, well beyond that exhibited by typical structural materials tested under identical conditions. Complementary experiments conducted on Mixed Mode I/II have revealed that small amounts of mixed mode loading produce very large increases to the toughness, well beyond that typically exhibited by conventional structural materials. Mode II fracture toughness of bulk metallic glasses examined crack tip shear banding behavior and fracture mechanisms associated with mode II loading. The heat generated in a shear band during Mode II fracture has been modeled and the results account for the extent of heat generation and its possible effects on local glass viscosity.

One of the key components of DARPA SAM project is to develop and apply first principles based predictive modeling and simulation approaches to design amorphous metals with desired properties. A multiscale hierarchical approach which start from quantum mechanics level and based on these results develop successively coarser models with increasing length and time scales of the models studied.

We have performed extensive quantum mechanical studies on pure metals and ordered inter-metallic alloys in order to determine the correct interaction force fields for metals: Al, Zr, Ti, Cu, Ni. Using these first principles data we have derived Sutton-Chen (power law) and RGL (exponentials) for many body force fields for metals and alloys. Using these potentials we have studied: glass forming ability, the size ratio effect in binary and ternary alloys, binding strength effect on glass forming ability, phase transformation and melting behavior of binary, ternary and quaternary systems and their phase behavior, the structure and thermodynamics of binary and ternary systems, non equilibrium molecular dynamics studies on pressure dependence of

viscosity of metals and alloys, and glass formation in VITRELOY class alloys and the structure of VIT1, VIT101, VIT106 from molecular dynamics.

Simulations of theoretical strength of several binary metallic glass systems, CuZr, NiZr, and FeB, has been completed. Amorphous metals yield with varying yield strengths, depending on the loading condition, sample geometry and mostly whether or not there are surface flaws. These results indicate that plastic deformation in metallic glass is strongly influenced by surface and boundary conditions and by size

A FEA shearband model has been developed and validatged. We can now match all constitutive data and obtain strong localization in agreement with experimental observation. An important new feature of the strain-localization elements is the variational optimization of the thickness, previously assumed to be constant. The metallic glass model and the strain-localization element have been integrated into the ARES finite element dynamic code to evaluate the performance of BMG penetrators through simulation.

III Publications

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Patents

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IV Attachments – Detailed Reports for Tasks and Subtasks

Task A: Materials Discovery, Synthesis, Processing, and Characterization

A1: Centrifugal Processing of Glass Forming Melts (Prof. W.L. Johnson, *Caltech, Prof. J. Loeffler, U.C. Davis*)

Participants

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Mr. Lianfeng Fu, B.S., Tsinghua University, Graduate Student (2002)

Statement of the problem studied

To identify the microstructures that segregate from a melt in order to identify promising glass forming compositions. Centrifugal processing allows the investigator to examine the microstructures that segregate from a melt as a result of applied acceleration of up to 60,000 *g* and slow cooling, resulting in a stratification of the crystalline phases.

Patents, Presentations and Publications

Patents

None

Presentations

None Reported

Publications

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J. F. Löffler, S. Bossuyt, A. Peker, W. L. Johnson, *Eutectic isolation in Mg-Al-Cu-Li(-Y) alloys by centrifugal processing*, Phil Mag, **83** (24):2797-2813 (2003)

Summary

Centrifugal processing allows the investigator to examine the microstructures that segregate from a melt as a result of applied acceleration of up to 60,000 *g* and slow cooling, resulting in a stratification of the crystalline phases. Light primary crystals are found at the top of the crucible, and heavy primary crystals are found at the bottom. In the middle part of the sample, binary and ternary eutectic microstructures are observed with the ternary eutectic solidifying last on cooling.

The stratified layers are examined for structure and composition, which facilitates the determination of eutectic compositions and promising bulk metallic glass forming alloys.

We thoroughly evaluated samples processed during the first round of high-temperature centrifugal experiments, including Mg-Al, Al-, Cu-, and La-based alloys. The ternary eutectics found in $Mg_{56}Al_{30}Li_7Cu_7$ and $Mg_{50}Al_{30}Y_6Li_7Cu_7$ were the same (within error), which shows that the method of high-temperature centrifugation can *identify deep eutectic features*, independent of the starting composition, a prerequisite for the discovery of new BMG compositions. Furthermore, information extracted from the *sequence of crystallization* shows that with progressive cooling that for example Y-rich primary crystals nucleate very early in the present case. Thus, the addition of Y to a Mg-Al based alloy does not significantly improve glass formation. Similarly, Cu-rich crystals are found at one sample end, which shows that these crystals also nucleated early, leaving only 2-3% Cu incorporated in the ternary eutectic. Consequently, only an amount of 3% Cu lowers the eutectic temperature. Important information gained regarding which elements do (or do not) decrease the eutectic temperature are useful for an improvement of glass forming ability.

Promising compositions have also been identified in the Cu-Mn based alloy system. The eutectic compositions obtained were prepared using a variety of methods, including arc melting, water quenching and splat cooling. Alloys were examined using high-resolution SEM. Results show that in both systems the maximum thickness for glass formation is less than 0.5mm.

A2/A3: Moving Melt Zone Processing and Development of Injection Casting System for Fabrication of Samples for Mechanical Testing, Prototyping, etc. (Prof. W.L. Johnson, *Caltech*)

Participants

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Dr. Marios Demetriou, Post-Doctoral Scholar, *Caltech*

Statement of the problem studied

Numerical simulation and experimental validation of rheological and flow laws to identify major factors in processing BMG

Patents, Presentations and Publications

Patents

None

Presentations

"Steady Non-Newtonian Flow of Vitreloy-1 in Continuous Extrusion", RQ11 Conference, 25-30 August, 2002, Oxford, England

Publications

Demetriou, M. D., and Johnson, W. L., 2004, "Rheology of Undercooled $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ Liquid", Accepted in *Scripta Mater.*

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Summary

Rheology and Flow Characterization.

Over the past two years, our group at Caltech developed constitutive flow laws governing the rheology of the undercooled Zr-based liquid. In the developed laws, deformation-induced structural disorder was taken to occur as a consequence of creation and annihilation of flow defects, which were quantified respectively by production and relaxation of liquid free volume. The developed flow laws were calibrated to flow experiments in a self-consistent manner [3, 4]. Figure 1 shows a single-parameter fitting of the model to experimental flow data reported recently by Lu et al. [5]. The flow law can be taken to apply over the entire range of temperatures and shear rates of interest, and hence enable the rheological characterization of this liquid. It appears that the developed rheology governing such "visco-plastic" flow can be very well approximated by the Johnson-Segalman formulation [6], which is a rheological law developed to govern "visco-elastic" flow behavior. This rheological analogy is striking evidence that metallic glass forming liquids behave as "complex" liquid solutions, a classification that includes solutions such as polymers, wormlike micelles, and emulsions.

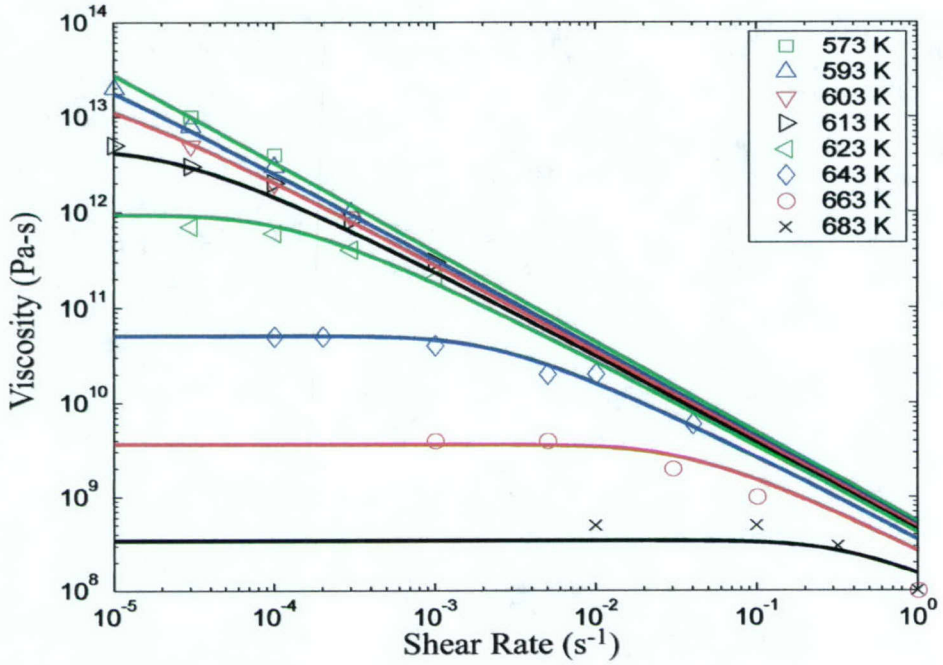

Figure 1
Fitting of the flow law to the experimental data reported in [5].

Recently, our group at Caltech has embarked on a major analytic study in an attempt to characterize these materials from a fundamental energetic level by employing statistical mechanics. In such analysis, the energy states of the system in the undercooled liquid region were sampled from the already known thermodynamic functions, and were utilized to essentially produce the entire phenomenology characterizing such complex liquids. The statistical mechanics theory yields a master equation governing the energetic evolution of microstates. The master equation, which is expected to be fluctuational, can be solved numerically by employing stiff numerical algorithms for coupled ODE's.

Simulation of Hydrodynamics and Kinetics.
In the experiment of Lu et al. [5], the deformed undercooled liquid was found to undergo three distinct flow modes: Newtonian, non-Newtonian, and localization into shear bands. We

developed a computational fluid dynamics model based on the rheological flow law to study transient flow evolutions of the undercooled liquid under specified deformation conditions. The coupled governing equations of motion (Navier Stokes), energy, and of the order parameter characterizing the structural state of the system were solved simultaneously to obtain the kinematic, thermal, and structural evolution of the system during deformation [12]. Figure 2 shows the computed 1-D transient flow evolution during Poiseuille flow of a deeply undercooled liquid. The evolution clearly shows transition into shear localization, as flow departs from its Newtonian profile and appears to localize near the wall while it accelerates unconstrained. Shear localization is a consequence of thermal and structural non-equilibration induced by deformation. Such flow evolution, which is termed "spurt", is very common in polymer flows [13]. A large-scale 3-D simulation of the evolution of the system during deformation would be of great interest, as it would enable to evaluate the role of microstructural disordering and energy dissipation in the initiation and propagation of shear bands in such liquids. Such practice would require developing a suitable adaptive-mesh numerical code, which would be capable of adequately capturing the temporal and spatial evolution of the shear instability.

Deformation-induced nanocrystallization in bulk metallic glasses has been widely reported in several recent studies [7, 8]. In all these studies, nanocrystal precipitation was observed within shear bands that were generated by shear deformation. This effect appears to be a consequence of two possible kinetic mechanisms. The first mechanism is related to the effect of deformation on the mobility of the system. The induced disorder decreases viscosity and hence enhances atomic diffusion, which ultimately facilitates crystal nucleation. This effect was recently accounted for in simplified manner in a flow simulation [9]. The other mechanism is related to the effect of shearing on the thermodynamics of the system. The induced flow stresses appear to contribute to an apparent non-equilibrium shift of the liquid spinodal. Consequently the system under flow spinodally decomposes into compositions of lower viscosity than the nominal composition. The decrease in local viscosity would in turn cause flow localization and further exacerbate fluctuational decomposition. Ultimately a strong coupling between flow and thermodynamics ensues that would result in concurrent crystallization and shear banding. This phenomenon is widely reported in polymers [10], and has been successfully interpreted by means of fluctuational hydrodynamics [11]. It would be of great interest to pursue a study in metallic glass-forming liquids in order to investigate the effects of the flow field on the kinetics of crystallization. The study could utilize experimental data, which could be fitted to a coupled hydrodynamic and kinetic model whose results could possibly interpret this phenomenon.

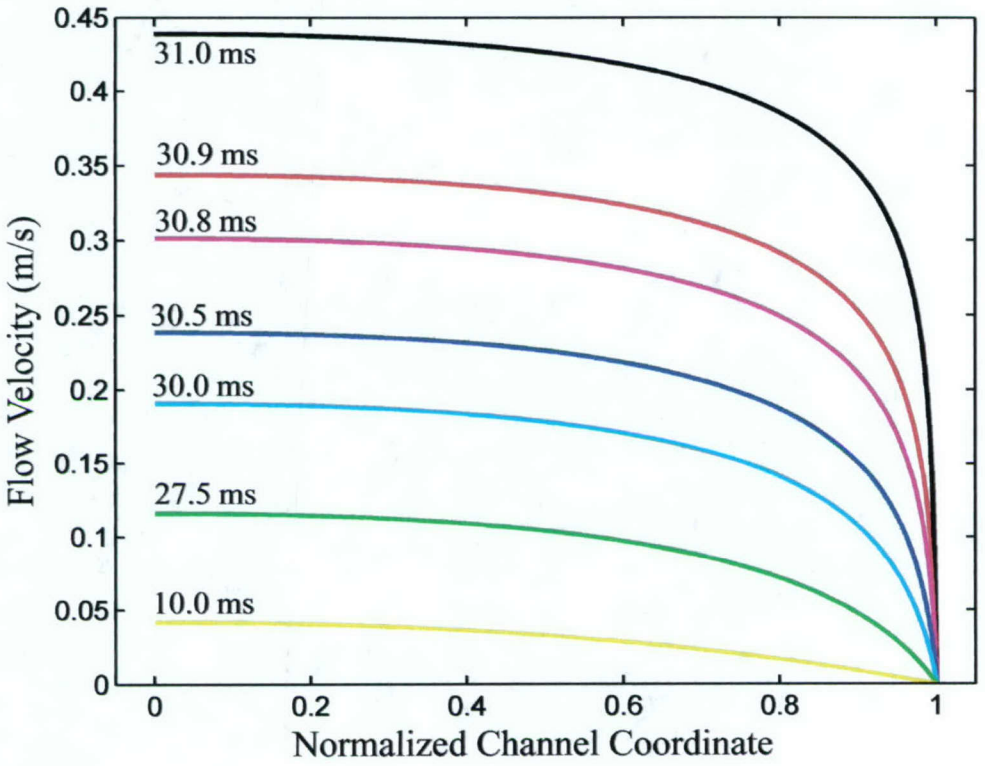

Figure 2
Computed 1-D transient flow evolution of deeply undercooled liquid during Poiseuille flow conditions [7].

Modeling of Thermoplastic Fabrication.
We have employed scientific software packages such as FEMLAB, ANSYS, and FLOW-3D into which we have incorporated the physical, thermal, mechanical, and rheological properties characterizing the undercooled liquid and glass and hence developed metallic-glass material databases in these packages. The packages were then employed to simulate fabrication processes such as casting and extrusion of bulk amorphous plates [9,14]. Moreover we employed the industrial software package MOLDFLOW, which was originally developed to simulate injection molding of plastics, to simulate injection molding and thermoplastic forming for the production of parts conventionally made out of plastic, such as electronic-component casings. Figure 3 shows some modeling results obtained by implementing the rheology into software packages for processes such as continuous extrusion of plates, thermoplastic forming of honeycomb structures, injection molding of electronic casing, and die casting of machining probes. Our group at Caltech possesses a laboratory-scale injection-casting machine, and we are planning on purchasing a laboratory-scale injection-molding machine. Comparing the modeling of part fabrication to actual parts produced by those machines would be a great research study. Moreover, calibration of the thermoplastic-process modeling to the actual machines would enable accurate prediction of part fabrication, and could potentially solve issues related to part quality.

Another interesting application that utilizes the thermoplastic-forming ability of metallic glass-forming liquids is the development of bulk amorphous foam. Figure 4 shows a Pd-based amorphous foam product developed by Schroers et al. [15]. A synthesis method is developed which exploits the supercooled-liquid region such that amorphous foam dimensions are no longer constrained by the critical casting thickness. Within this synthesis method, bulk amorphous foams of up to 80% bubble volume fractions were successfully produced [16]. Such application finds interest in space technologies, as small light miniature structures can easily be transported to space where they could be foamed-up to actual size. We recently developed a model to simulate the foaming kinetics in such liquids, and work is underway to compare the results to experiments. Detail characterization of the foaming process however would require modeling of the prefoaming kinetics. Such modeling would be much more sophisticated, as it would involve stochastic modeling of the evolution of bubble distribution dictated by the detailed balance between bubble generation, merging, sedimentation, and collapse.

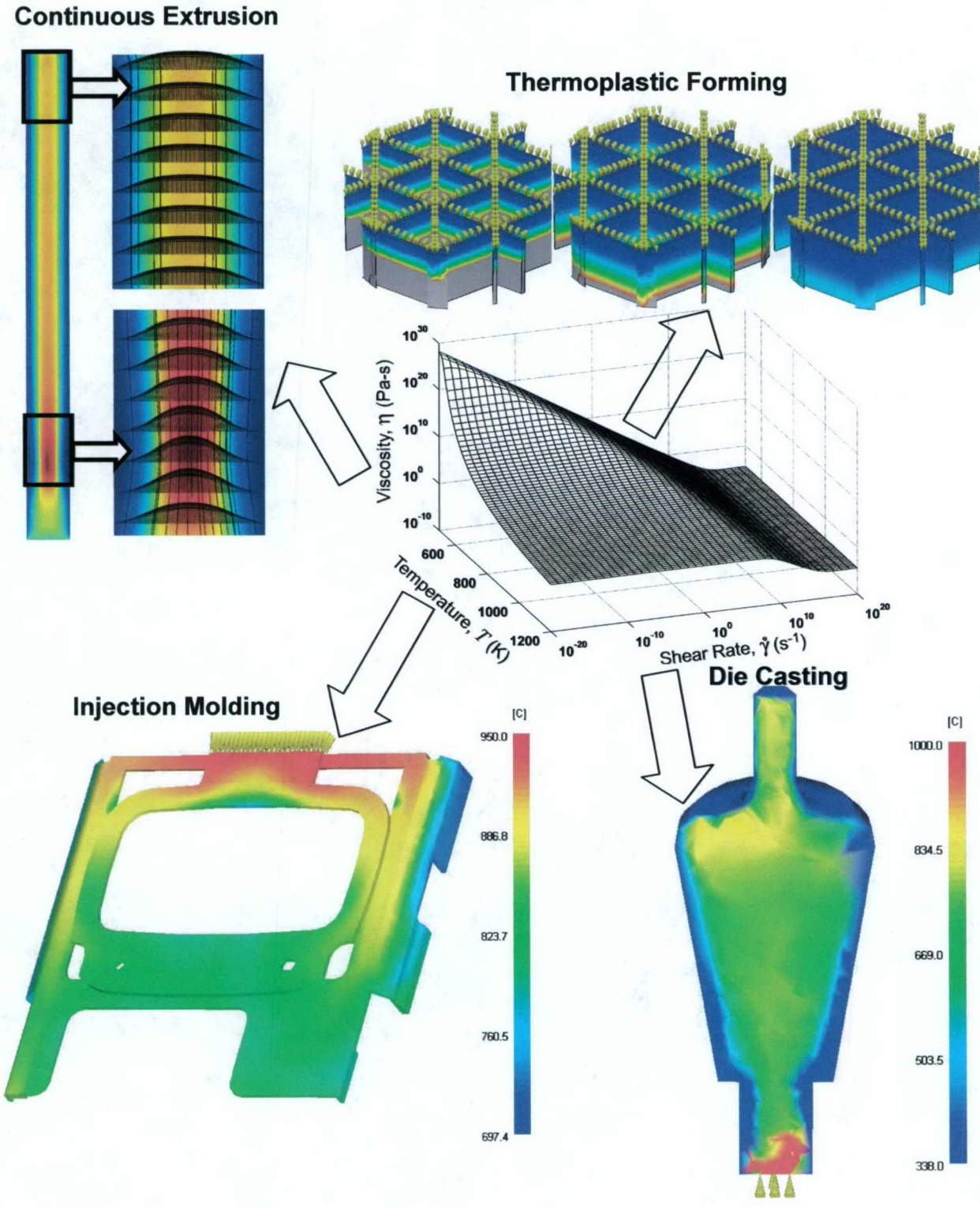

Figure 3
Modeling results for various thermoplastic processes.

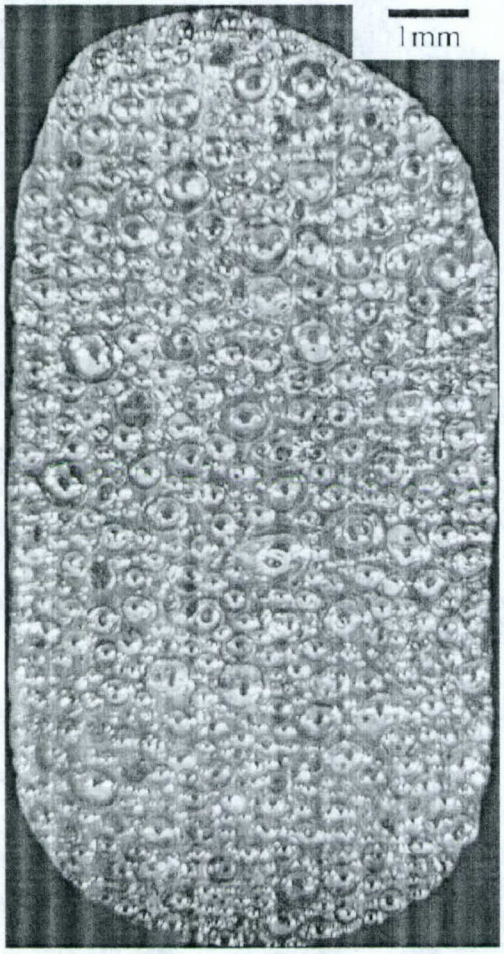

Figure 4

A Pd-based amorphous foam product developed by Schroers et al. [11].

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A4: Development of New Alloys (Prof. W.L. Johnson, *Caltech*)

Participants

Dr. Haein Choi-Yim, Staff Research Scientist, *Caltech*
Dr. Jason Kang, Sr. Post-Doctoral Scholar, *Caltech*
Mr. Donghua Xu, Graduate Research Assistant, *Caltech*

Mr. Boonrat Lohwangwatana, Graduate Research Assistant, *Caltech*

Statement of the problem studied

To identify and develop new bulk glass forming systems based on refractory metals (e.g., Zr, Ni, Hf, Cu) and lightweight amorphous alloys based on Al and Mg.

Patents, Presentations and Publications

Patents

Patent Disclosure "Bulk Amorphous Refractory Glasses based on the Ni-Nb-Sn Ternary Alloy System" H. Choi-Yim, D. Xu, and W.L. Johnson, applied for July 5, 2002

Presentations

None Reported

Publication

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D.H. Xu, B. Lohwongwatana, G. Duan, W.L. Johnson, C. Garland, "Bulk metallic glass formation in binary Cu-rich alloy series - Cu100-xZrx (x=34,36,38.2,40 at.%) and mechanical properties of bulk Cu64Zr36 glass", Acta Materialia, **52**, 2621 (2004).

Summary

Ni-based Alloys

Extremely stable in-situ bulk metallic glass matrix composites were successfully synthesized by arc melting $Ni_{50-x}Cu_xTi_{33}Zr_{16}Si_1$ alloys with x=0-20. We found that there is no size limit to form the in situ composite in this system confirmed by X-ray diffraction. X-ray diffraction patterns of 1mm cast strip, 12g arc melted button, 36g arc melted button, and 72g arc melted buttons are compared. Figure 1 shows X-ray diffraction patterns of 1mm thick cast strip and arc melted buttons of composition $Ni_{40}Cu_{10}Ti_{33}Zr_{16}Si_1$. The buttons have weights of 12 g, 36 g, and 72 g, respectively. All four samples exhibit bcc crystalline phases from the dendrite with broad peaks from the amorphous phase. 1mm cast strip shows the strong ordered peak (100) with lower glass volume fraction. Arc melted buttons has small intensity of ordered peak with higher glass volume fraction. X-ray diffraction patterns of 12g arc melted buttons of the composition $Ni_{50-x}Cu_xTi_{33}Zr_{16}Si_1$ alloys with x=0, 20 and $Ni_{40}Cu_{10}Ti_{37}Zr_{12}Si_1$ shows the same diffraction pattern as the $Ni_{40}Cu_{10}Ti_{33}Zr_{16}Si_1$ alloy. This indicates that the composition range of in situ composite

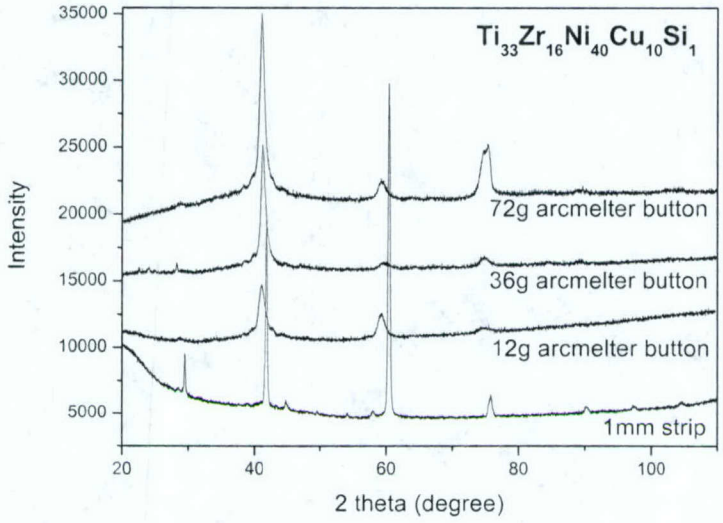
formation with bcc crystalline phase and the glass is large. The glass transition and the crystallization behaviors of samples cut from the same buttons were investigated using DSC at a heating rate of 20 K/min (not shown in the figure). The glass transition occurs around 673-693K. However, no crystallization events occur upon heating.

The microstructure of the composites was investigated with scanning electron microscopy and transmission electron microscopy. The in situ formed composite contains dendritic Ni solid solution with bcc structure in a glassy matrix. Figure 2 (a) shows the composite microstructure on sections of the arc melted button for the Ni-based alloy. A microstructure with a dendritic phase (white) is dispersed in the matrix (black). The dendritic phase is estimated to be about 60 vol% and the dendritic branches to be about 3-5 microns. Figure 2 (b) is the bright field TEM image of the same microstructure. The image includes glassy and crystalline phases. The selected area diffraction pattern taken from the glassy phase is shown in the Fig. 2 (c). Figure 2 (d) shows the selected area diffraction pattern taken from the dendrite, which confirms the bcc structure of the dendritic phase. SEM electron microprobe analysis reveals the average composition for the dendritic phase to be $Ni_{42.1}Cu_8Ti_{36.7}Zr_{13.2}$ and for matrix phase to be $Ni_{35.69}Cu_{12.86}Ti_{28.72}Zr_{19.23}Si_{3.48}$.

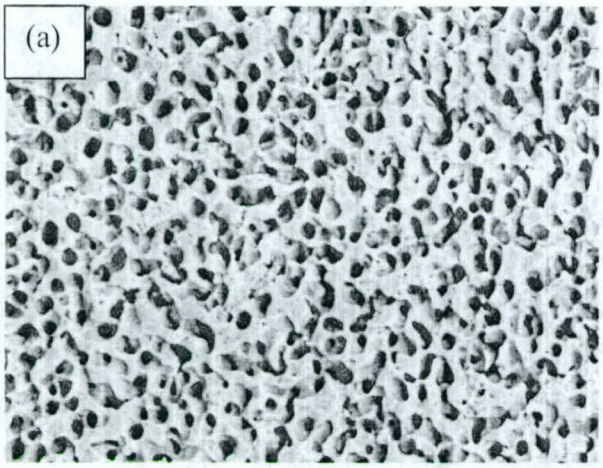
Compression tests were carried out for this alloy. The 3mm diameter cylinders were machined from 36g arc melted button. Figure 3 shows the compressive stress-strain curves for two cylinders of same composition. The stress-strain curves present work hardening and plasticity of about 3.4% plastic strain. Yielding occurs at 1 GPa and the ultimate stress is 1.9 GPa. The compressive fracture takes place along the maximum shear plane, which is declined by about 45 degrees to the direction of compressive load.

Young's modulus and shear modulus were obtained by measuring the sound propagation velocities of plane waves in the samples. The calculated modulus data for different alloys are presented in Table 1. The alloy of the composition $Ni_{50}Ti_{33}Zr_{16}Si_1$ shows shear modulus of 39 for 1mm cast strip and 25 for 12g arc melted button. Shear modulus of typical metallic glass is 30GPa, which implies softening of dendritic phase of 12g arc melted button. The Young's modulus is 106 GPa for 1mm cast strip and 72 GPa for 12g arc melted button. The alloy of the composition $Ni_{40}Cu_{10}Ti_{33}Zr_{16}Si_1$ shows similar behavior i.e. higher elastic modulus or 1mm cast strip than that of arc melted buttons.

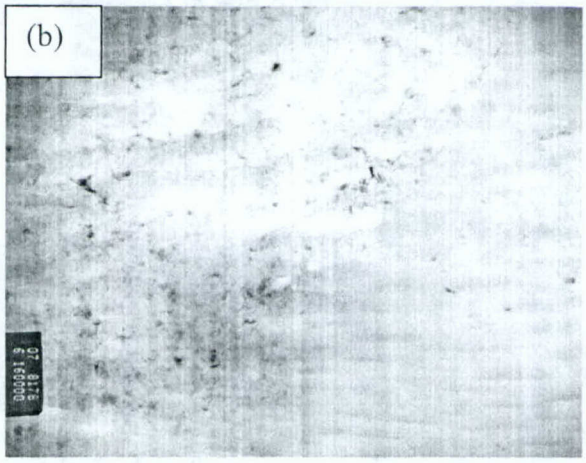
We observed some unusual phenomena on this alloy system. At first, fast cooled 1mm strip has an order peak in X-ray diffraction and contains less glass phase compared to the slowly cooled arc melted buttons (without size limit). Secondly, there was no crystallization event on DSC measurement even though we observed the glass transition. Third, elastic modulus and Poisson's ratio differ depending on the cooling rates of samples which indicates that the sound propagation velocities of plane waves (longitudinal and transverse) in the samples are significantly different depending on the different cooling rate during processing.

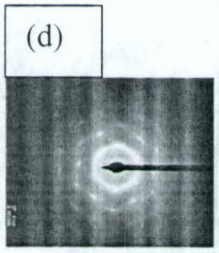


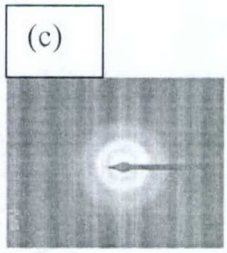
	$Ni_{50}Ti_{33}Zr_{16}Si_1$ 1mm strip	$Ni_{50}Ti_{33}Zr_{16}Si_1$ 12g button	$Ni_{40}Cu_{10}Ti_{33}Zr_{16}Si_1$ 1mm strip	$Ni_{40}Cu_{10}Ti_{33}Zr_{16}Si_1$ 12g button	$Ni_{40}Cu_{10}Ti_{33}Zr_{16}Si_1$ 24g button
G (Shear modulus, GPa)	39	25	47	23	28
E (Young's Modulus, GPa)	106	72	127	66	78
ν (Poisson's Ratio)	0.37	0.41	0.36	0.42	0.41

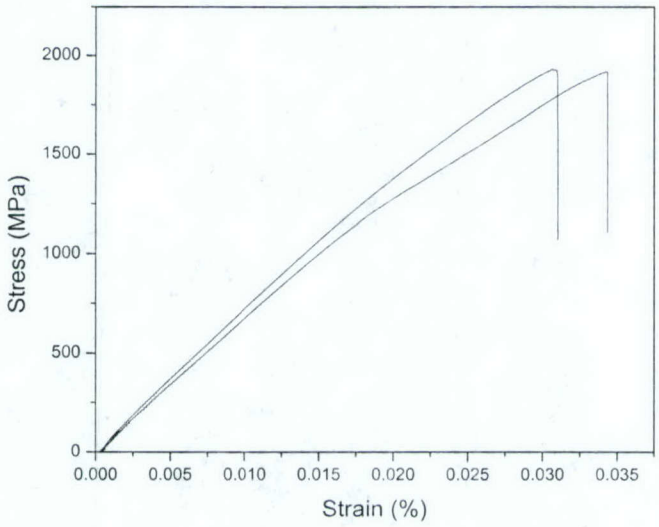

(a)

10 μm


(b)


(d)


(c)


2000
1500
1000
500
0
Stress (MPa)
0.000
0.005
0.010
0.015
0.020
0.025
0.030
0.035
Strain (%)

Binary BMG Alloys

It has been proposed as an empirical rule that in order to form a bulk amorphous structure a metallic system must comprise at least three elements [1]. Nevertheless, in an attempt to establish a good starting point for new multi-component bulk metallic glasses, several binary alloys were found to form bulk amorphous structures by themselves using the regular copper mold casting method, although they only consist of two elements. These include: $Cu_{46}Zr_{54}$, $Cu_{64}Zr_{36}$ and $Cu_{66}Hf_{34}$. The critical casting thickness of these three alloys is all 2mm. X-ray and electron diffraction methods were used to identify the glassy structures of the 2mm thick bulk samples. The results are presented in Fig. 1 and Fig. 2, respectively. Thermal and mechanical properties of the binary bulk metallic glasses were measured. The measurement data are listed in Table 1 and Table 2, respectively. Fig. 3 presents the stress vs. strain curves of these alloys obtained in compression tests. These binary BMGs have quite high strength and very good toughness. The 0.5mm thick strips of these amorphous alloys can be plastically bent to certain angles without cracking. Particularly, the $Cu_{46}Zr_{54}$ glass shows ~1.1% plastic deformation upon compression (Fig. 3). It is speculated that these binary alloys are tightly related to several reported Cu- *(2)* and Zr- *(3,4)* based multi-component BMGs and that even better glass forming abilities or glass forming systems might be obtained by adding more alloying elements to these binary BMGs. Since they are extremely simple alloys, these binary BMGs also provide a good chance to investigate the physics underlying the fundamental problem of glass formation the knowledge of which may be applied to guide the engineering development in turn.

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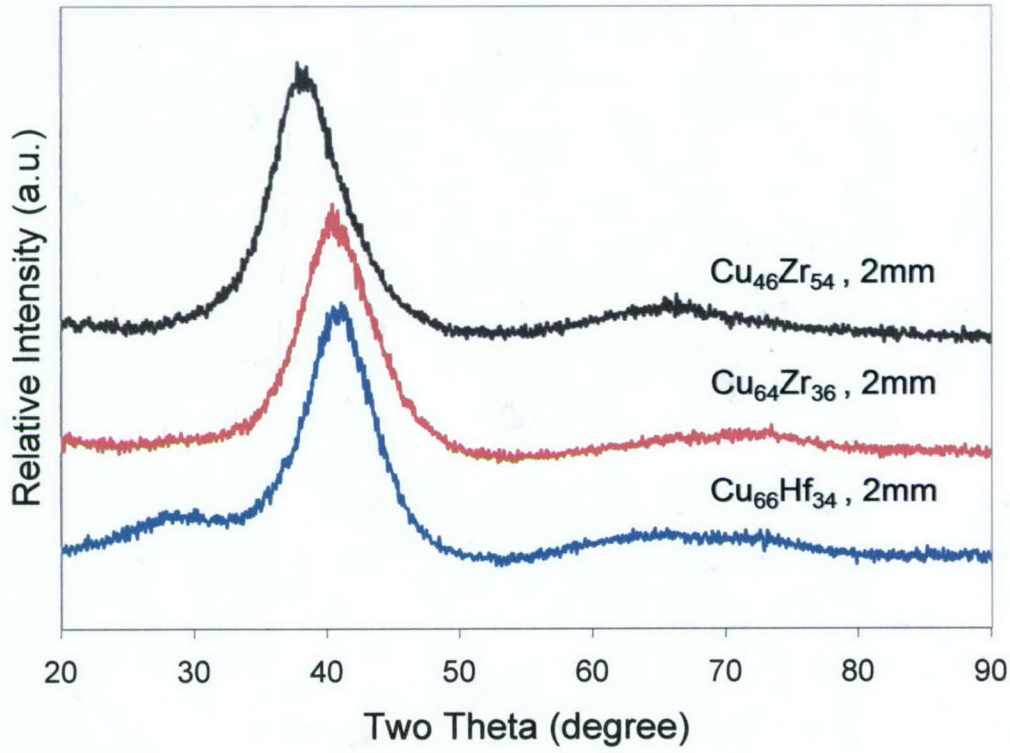
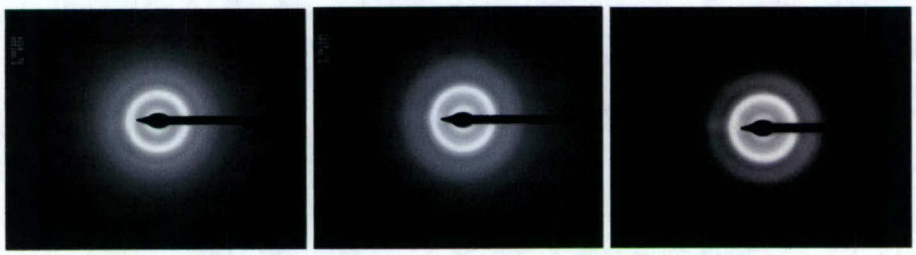


Figure 1. XRD patterns of newly discovered Cu-Zr, Cu-Hf binary bulk metallic glasses (2-mm thick strips), taken with a Cu-Kα radiation.



(a) (b) (c)

Figure 2 Electron diffraction patterns of binary Cu-Zr and Cu-Hf alloys: (a)$Cu_{46}Zr_{54}$; (b) $Cu_{64}Zr_{36}$; (c) $Cu_{66}Hf_{34}$

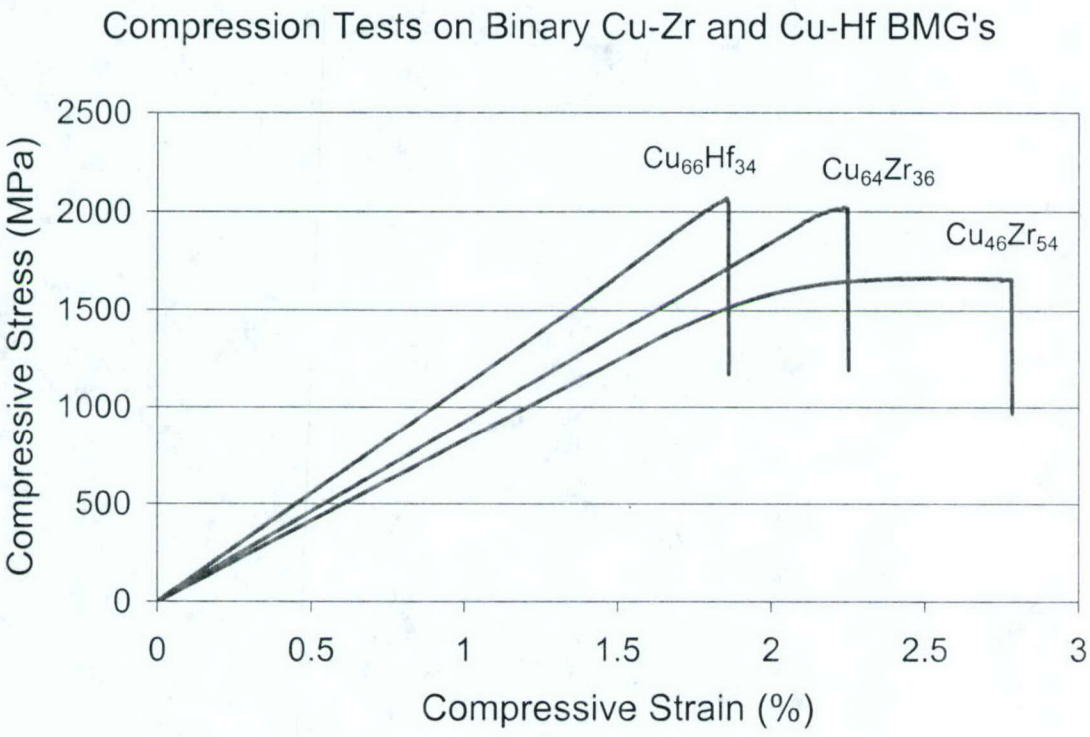


Figure 3. Compressive stress vs. strain curves of the three binary bulk metallic glasses obtained at a strain rate of ~$4x10^{-4}$ s^{-1}.

Table 1. Thermal properties of binary Cu-Zr and Cu-Hf BMG's

Alloy	T_g (K)	T_{x1} (K)	T_l (K)	$\Delta T = T_{x1} - T_g$ (K)	$T_{rg} = T_g/T_l$	Critical casting thickness (mm)
$Cu_{46}Zr_{54}$	696	746	1201	50	0.58	2
$Cu_{64}Zr_{36}$	787	833	1233	46	0.64	2
$Cu_{66}Hf_{34}$	787	841	1263	54	0.62	2

Table 2. Mechanical properties of binary Cu-Zr and Cu-Hf BMG's

Alloy	Density (g/cc)	Vicker's Hardness (Kg/mm^2)	Young's Mod. (GPa)	Shear Mod. (GPa)	Poisson Ratio	Yielding Strength (GPa)	Fracture Strength (GPa)	Yielding Strain (%)	Plastic Strain (%)
$Cu_{46}Zr_{54}$	7.3	698	83	31	0.35	1.4	1.7	1.7	1.1
$Cu_{64}Zr_{36}$	7.9	742	92.3	34	0.34	2	2	2.2	~0
$Cu_{66}Hf_{34}$	11.4	779	111	40	0.37	2.1	2.1	1.86	~0

Lightweight BMG Alloys

Boonrat Lohwangwatana is currently working on the design of light weight structural amorphous alloys. Primarily titanium based compositions alloys containing have Zr,Hf, Nb, Co, V, Cu, Ni, Al have been made. Ingots were made in the arcmelter, and promising candidates were cast into 1-2 mm thick strips using miniarcmelter's suction casting apparatus. As of now (Feb 2004) none were found to be fully amorphous. The published Ti-based alloy has only 37% Ti. The goal is to maximize the Ti content in order to achieve the desired density.

Until recently, many alloys are found to have beta-Ti dendrites which can be a good candidate for strengthening the amorphous matrix. XRD analysis does not show any significant amorphous content, but high-energy synchrotron analysis show diffused areas similar to those of diffused amorphous bands. Unlike fully amorphous sample that has diffused ring in all 360 degrees, the diffused areas are spotty and spread out in different directions. We are currently trying to figure out the cause of such diffused areas, and whether or not they are indeed the sign of amorphous content which is directional (similar to that of smecticcrystal).

A5: Novel Computational Approach to Predict Multicomponent Alloy Compositions for Bulk Metallic Glass Formation (Prof. Y.A. Chang, *Univ. of Wisconsin*)

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Hongbo Cao, Graduate Student, Materials Science & Engineering, UW-Madison; began summer 2003

Statement of the problem studied

A thermodynamic approach has been used to predict the compositions of Zr–Ti–Cu–Ni-Al alloys exhibiting low-lying-liquidus surfaces, which tend to favor the formation of bulk metallic glasses. The idea is to build on all thermodynamic information from the lower order constituent binaries and ternaries to obtain the thermodynamic properties of the higher order alloys. These thermodynamic properties enable us to predict the compositions of liquid alloys involved in the 6-phase invariant reactions. The predicted alloy compositions agree well with those reported in the literature. Furthermore, using these calculations as a guide we have successfully discovered a series of new alloys, which can readily form amorphous rods of up to12 mm in diameter. All these findings demonstrate that our thermodynamic approach is robust in developing new bulk metallic glasses.

Patents, Presentations and Publications

Patents

None

Presentations

K. C. Hsieh, D. Ling, Y. Pan, G.-X. Sun and Y. A. Chang, "Thermodynamic Prediction of Potential Multicomponent Alloys to form Metallic Glasses", presented at the Symposium on Intermetallic and Advanced Metallic Materials: C. T. Liu Symposium", Annual TMS Meeting, San Diego, CA., 03/04/03.

Y. A. Chang, "Phase diagram Calculation in Teaching, Research and Industry", presented at the October 2003 ASM International Annual Meeting, Pittsburgh, PA as part of the Society's Annual Edward DeMille Campbell Lecture.

Y. A. Chang, "Phase Diagram Calculation: A Tool to Accelerate Insertion of Materials and processes", presented at the Symposium on the Accelerated Implementation of Materials and Processes, the 2003 Fall TMS Meeting, Chicago, IL, 11/11/03.

D.Ma, H.Cao, K. C. Hsieh, L. Ding and Y. A. Chang, "Role of Ti Replacement for Zr in the formation of ZrTiCuNiAl Bulk Glasses", to be presented at the Symposium on the Bulk Metallic Glasses: Processing and Fabrication I, the 2005 Spring TMS Meeting, San Francisco, CA, 02/14/05.

H.Cao, D.Ma, K. C. Hsieh, L. Ding and Y. A. Chang, "A Calphad Approach for Predicting the Bulk Glass-Forming Tendency of Zr-Ti-Ni-Cu-Al Alloys", to be presented at the Symposium on the Bulk Metallic Glasses: Processing and Fabrication II, the 2005 Spring TMS Meeting, San Francisco, CA, 02/14/05.

Publications

D. Ma, H. Cao, K. C. Hsieh, L. Ding and Y. A. Chang, "Bulkier Glass Formation towards a Deeper Eutectic", a first draft is available, 2005.

H. Cao, D. Ma, K. C. Hsieh, L. Ding and Y. A. Chang, "A Thermodynamics Approach for Predicting the Zr-rich Bulk Metallic Glass", a first draft is available, 2005.

Z.P. Lu, D. Ma, C.T. Liu and Y. A. Chang, "Where are the best glass formers?", submitted for publication,.2004.

Summary

Introduction

The ability to make novel non-crystalline metallic materials such as bulk metallic glasses at cooling rates approaching that of conventional casting conditions affords opportunities not only for investigating the fundamental behavior of deeply undercooled metallic melts but also for manufacturing potential metallic glass components for practical applications. Since most of these metallic glass alloys have been developed purely by experimentation using empirical rules in terms of atomic sizes of the component elements and highly exothermic enthalpy of formation of the liquid alloys [e.g. 00Ino], which are inadequate in most cases due to their qualitative nature, it is desirable to have an alternative approach to first predict the compositions of multicomponent alloys that can potentially yield glasses. And then, the calculated compositions (or compositional ranges) could be used to guide the experimental search for, and eventually locate, the optimum glass formers within the multicomponent system. This would save time and money to develop novel bulk metallic glasses.

In 2001 Yan et al. [01Yan] used a thermodynamic approach to predict the compositions of alloys exhibiting low-lying-liquidus surfaces that would favor glass formation using phenomenological thermodynamic models. They then applied this approach to the quaternary Zr-Ti-Cu-Ni alloy system and demonstrate that the calculated compositions of these quaternary alloys which possess a low-lying-liquidus surface are in accord with those found experimentally for bulk metallic glass formation by Lin and Johnson [95Lin]. The results are shown in Figure 1. The solid circles represent the compositions of the liquid alloys at the five phase invariant reactions in this quaternary system. The open squares represent the alloys found by Lin and Johnson to form bulk metallic glasses. These results demonstrate that this approach can be used as a valuable tool for predicting alloy compositions of multicomponent systems as potential materials for glass formation. The primary objective of this sub-program of the DARPA program is (1) to develop thermodynamic databases of two alloy systems, one is Al-Cu-Ni-Ti-Zr and the other Al-B-Co-Cr-Ni-Ti and (2) to carry out experiments to make bulk metallic glasses based on the calculated low-lying liquidus surfaces using the developed databases for the first system. We chose to focus on one system because lack of resources to investigate both alloys systems.

In the following we first present the approach used and then the great utility of the calculated low lying-liquidus surfaces to identify bulk metallic glasses.

Development of the Thermodynamic Descriptions or Databases

Methodology used to develop thermodynamic databases:

Figure 2 shows the phenomenological route in calculating phase diagrams of a multicomponent alloy system. In essence, thermodynamic descriptions of the constituent lower order systems, normally binaries and ternaries, are obtained based on experimental and "first principles" total energy information and phase equilibrium data. The term "thermodynamic description" means that a set of thermodynamic models with parameters for phases in a system are obtained so that not only thermodynamic properties of the phases but also phase diagrams of the system can be calculated. However, once descriptions for the lower order systems are known, it is possible in many cases to obtain thermodynamic descriptions of the higher order systems by using an extrapolation method so that phase diagrams of the multicomponent system can be calculated. Although there are a number of such geometrical methods to make these extrapolations [89Cho], the most often used one is that due to Muggianu et al. [75Mug]. It is obvious that the calculated multicomponent phase diagrams must be verified by key experiments, but the amount of experimental efforts involved is insignificant comparing to the traditional approach using exclusively experimental determination. For the rare cases when quaternary phases do exist in systems such as some of the quaternary aluminum alloys [e.g. 98Lia, 01Yan], optimization of model parameters for the quaternary phases in question is necessary. However, the amount of effort involved is minimum normally. For the two five-component systems studied under this program, their thermodynamic descriptions or thermodynamic databases are obtained from extrapolations since phase diagram data are not available for the constituent quaternary systems.

Database developed:

Let us first use the quinary Al-Cu-Ni-Ti-Zr system as an example. In order to develop a database for this 5-component system, we must first obtain descriptions for the 10 constituent binaries: Al-Cu, Al-Ni, Al-Ti, Al-Zr, Cu-Ni, Cu-Ti, Cu-Zr, Ni-Ti, Ni-Zr and Ti-Zr. Based on the descriptions of these binaries, we proceed to develop descriptions of the 10 constituent ternaries: Al-Cu-Ni, Al-Cu-Ti, Al-Cu-Zr, Al-Ni-Ti, Al-Ni-Zr, Al-Ti-Zr, Cu-Ni-Ti, Cu-Ni-Zr, Cu-Ti-Zr and Ni-Ti-Zr. Based on the descriptions of the lower order systems, i.e. 10 binaries and 10 ternaries, thermodynamic descriptions for the 5 quaternaries and the quinary Al-Cu-Ni-Ti-Zr system are obtained by extrapolation [75Mug, 89Cho]. Experience has shown that such approach is quite acceptable except for cases when higher ordered intermetallic phases appear or one of ternary or quaternary intermetallic phases extend into space! For the quaternary and quinary systems studied here, new phases were not found in the literature. Thermodynamic descriptions for the 10 binaries are available in the literature [85Sau, 90Mey, 91Sau, 91Sau1, 92Sau, 93Zen, 96Bel, 96Bel1, 96Kun, 98Hua, 04Lia]. Minor modifications for some binary descriptions are necessary. Thermodynamic descriptions of the 4 constituent ternaries of Cu-Ni-Ti-Zr are taken from Yan et al. [01Yan]. Descriptions for the other 6 ternaries, Al-Cu-Ni, Al-Cu-Ti, Al-Cu-Zr, Al-Ni-Ti, Al-Ni-Zr, and Al-Ti-Zr systems were developed by us using experimental data available in the literature. Reasonable agreements between calculations and experimentations are obtained. As an

example, a comparison of the calculated invariants with one of the phase being liquid is shown in Table 1.

In a similar manner we also developed descriptions of the quinary Al-B-Co-Cr-Ti and quaternaries Al-Cr-Fe-Ti and Al-Cr-Ni-Ti. There are a total of 21 constituent binaries and 16 constituent ternaries. All binary descriptions are available in the literature [02Zha]. We developed descriptions for all 16 ternaries using data obtained from the literature [88Eff]. Agreement between the calculations and experimental data is as good as those for the Al-Cu-Ni-Ti-Zr quinary system.

Experimental procedures and Results

In this section, we report the experimental approach used to identify alloy compositions focusing only on the quinary Al-Cu-Ni-Ti-Zr system. Alloys were prepared first by arc melting mixtures of high purity Zr, Ti, Cu, Ni and Al (Zr: 99.95%; the rest: 99.99+%) pieces in an argon atmosphere deoxidized with titanium sponge. Each alloy was arc-melted several times to assure homogeneity and then drop cast (or suction-cast) into a copper mold with an internal cylindrical cavity of a diameter up to 12 mm, under a purified Ar (or He) atmosphere. Each of the castings was characterized primarily by XRD and DSC as well as microhardness measurement. The amorphous nature of the as-cast rods was examined by analyzing the central part of their cross-sections using x-ray diffractometry (XRD) with a Cu-Kα source, and Scanning Electron Microscopy (SEM) in Backscattered Electron Imaging (BEI) mode. The glass transition and crystallization behaviors of these alloys upon reheating were characterized using a Perkin-Elmer DSC7 (Differential Scanning Calorimeter) at a heating rate of 20K/min.

Figure 3 shows the calculated compositions of liquid alloys at 6-phase invariant equilibria, with the reaction temperatures lying between 675 and 800°C. Also shown in this figure are the BMG-forming compositions reported in the literature ([96Xin], [98Zha], [03Wen], [01Eck], [00Pel], [97Lin]), which fall into the glass-forming region defined by our calculations. The blue stars in Figure 3 represent the new BMG-forming compositions discovered experimentally in the present study (as illustrated in Table 2), which can yield bulk metallic glasses ranging from 2 mm up to 12 mm in diameter, or even larger. Thus, Figure 3 provides a validation of our thermodynamic approach.

Figure 4 shows the typical X-ray diffraction patterns obtained from the cast rods for three representative compositions, i.e., BMG1 ($Zr_{51.1}Ti_{6.4}Ni_{3.5}Cu_{30.7}Al_{8.3}$), BMG2 ($Zr_{51.3}Ti_{4.9}Ni_{4.0}Cu_{31.3}Al_{8.5}$) and BMG3 ($Zr_{45.2}Ti_{2.6}Ni_{8.7}Cu_{32.8}Al_{10.7}$), with diameters of 9, 12 and 9 mm, respectively. For these three samples, the smoothness of the first and second diffuse diffraction bands is observed, indicative of a monolithic amorphous structure. Our SEM studies on these alloys are also consistent with the XRD results: the fully amorphous samples exhibit a featureless structure without any discernible crystallite. Based on XRD and SEM, it is noted that for both BMG1 and BMG3 further attempts to cast fully amorphous rods larger than d = 10 mm were not successful. However, for BMG2, it can readily cast into 12-mm fully amorphous rod. Thus, we have not as yet established an upper bound on the critical casting size for BMG2.

Figure 5 shows the DSC traces taken for BMG1, BMG2 and BMG3, respectively, which exhibit a clear endothermic event characteristic of the glass transition (Tg), followed by characteristic exothermic event indicative of single or multiple crystallization events (Tx). Table 2 summarizes the glass transition temperature (T_g), the temperature of the onset crystallization (T_x) and the supercooled liquid region ($\Delta T_x=T_x-T_g$), which were measured/calculated from the DSC traces. One can see that the largest supercooled liquid region (~61K), which is observed in BMG3, is not associated with the best glass-forming alloy, i.e., BMG2. Vickers hardness measurements on these three representative amorphous alloys have been carried out as well. Using the scaling relation $\sigma_y = 3VH$, we estimated the yield strength of these amorphous alloy around 1.65 to 1.68Gpa, comparable with those of ZrCu-based BMGs reported earlier [99Ino].

Summary

A thermodynamic approach has been used to predict the compositions of Zr–Ti–Cu–Ni-Al alloys exhibiting low-lying-liquidus surfaces, which tend to favor the formation of bulk metallic glasses. The idea is to build on all thermodynamic information from the lower order constituent binaries and ternaries to obtain the thermodynamic properties of the higher order alloys. These thermodynamic properties enable us to predict the compositions of liquid alloys involved in the 6-phase invariant reactions. The predicted alloy compositions agree well with those reported in the literature. Furthermore, using these calculations as a guide we have successfully discovered a series of new alloys, which can readily form amorphous rods of up to12 mm in diameter. All these findings demonstrate that our thermodynamic approach is robust in developing new bulk metallic glasses.

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Table 1. Invariant Liquidus Reactions in the Al-Cu-Ni System

Reaction	Type	Temperature. (°C)		Composition (wt%)
L==(Al)+θ+Al_6Cu_3Ni	E	546.6	[91Pri]	32.9%Cu0.7%Ni
		540	[23Bin]	
		540	[28Nis]	
		547.5	[61Phi]	32.9%Cu0.6%Ni
		540	[48Kos]	32.5%Cu0.9%Ni
		547.1	Calculation	33.1%Cu0.3%Ni
L+Ni_2Al_3==(Al)+Al_6Cu_3Ni	U8	~590	[91Pri]	22.6%1.6%Ni
			[61Phi]	27.4%Cu4.7%Ni
		590	[48Kos]	22%Cu2%Ni
		585±5	[23Bin]	
			[28Nis]	23%Cu2.5%Ni
		583.5	Calculation	21.4%Cu3.7%Ni
L+Al_3Ni==FCC+Al_3Ni_2	U6		[91Pri]	16.9%Cu3.6%Ni
		600	[28Nis]	23%Cu4%Ni
		630	[48Kos]	16%Cu4%Ni
		598.8	[61Phi]	14.1%Cu4.7%Ni
		602.8	Calculation	15%Cu5.3%Ni
L+$AlNi_3$==FCC+B2	U1		[48Kos]	10%Al43%Cu
		1250	[38Ale]	
			[91Pri]	10.1%Al46.9%Cu
		1250.2	Calculation	8.6%Al35.6%Cu

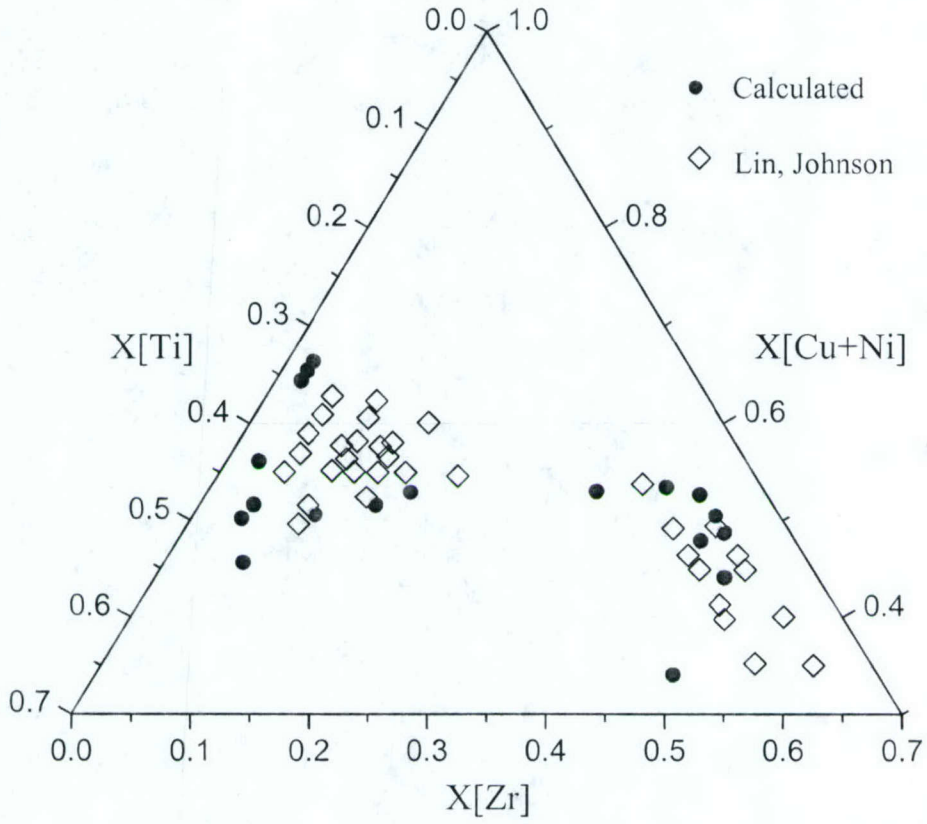

Figure 1. Comparison of the thermodynamically predicted compositions of quaternary Zr-Ti-Cu-Ni liquid alloys at the five-phase invariant equilibria with those determined experimentally for bulk glass formation by Lin and Johnson [95Lin].

CALCULATION APPROACH

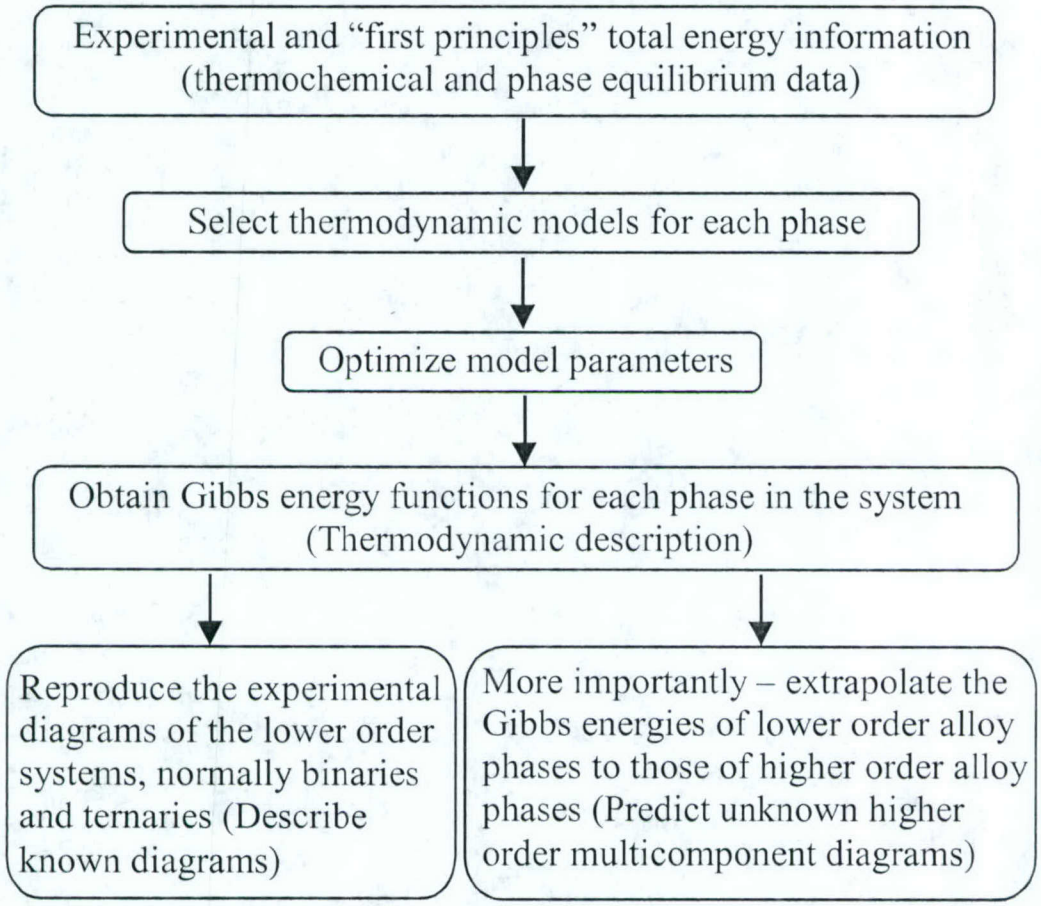

Figure 2. The Calphad or phenomenological approach used to obtain a thermodynamic description of a multicomponent system.

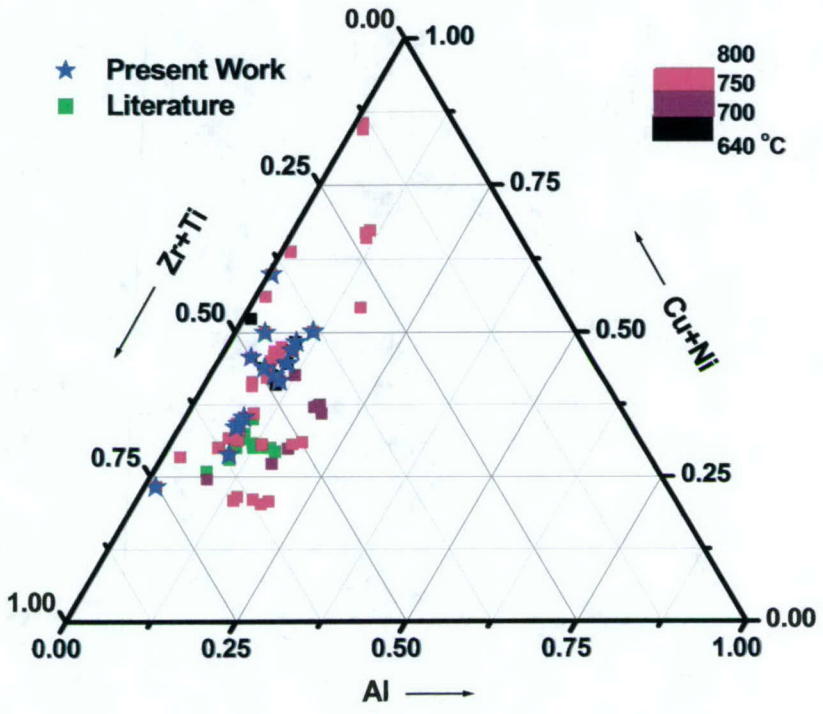

Figure 3. Comparison of the predicted compositions of the liquid alloys at the six-phase invariant equilibria with those found experimentally for bulk glass formation.

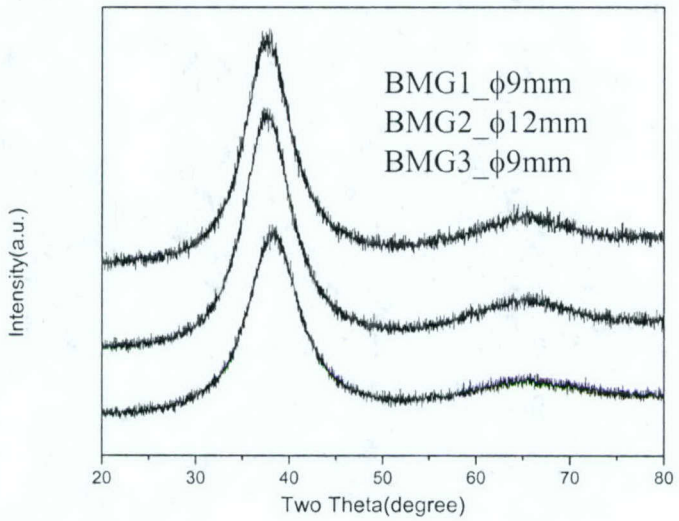

Figure 4. X-ray diffraction patterns (Cu-Kα radiation) taken from cast samples of three representative BMG-forming alloys.

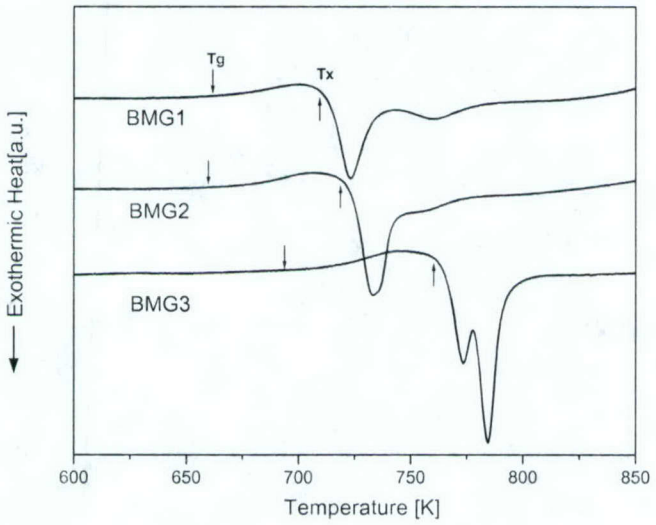

Figure 5. DSC curves of representative amorphous alloys obtained at a heating rate of 20 K/min to show the glass transition and crystallization behavior.

A6: Metallic Glass Foams

Participants

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Statement of the problem studied

Professor Dunand's research focused on new and novel methods to produce open- and closed-cell metallic glass foams from bulk metallic glasses.

Patents, Presentations and Publications

Patents

None

Presentations

AH Brothers, DC Dunand. "Ductile Bulk Metallic Glass Foams." *2004 Fall Meeting of the Materials Research Society* (Boston, MA) **2004**.

AH Brothers, DC Dunand. "Liquid State Processing of Foams Using Zr-Based Bulk Metallic Glass Forming Alloys." *2003 Fall Meeting of the Minerals, Metals, and Materials Society* (Chicago, IL) **2003**.

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D Balch, E Ustundag, DC Dunand. "Synchrotron X-Ray Diffraction Measurements of Stress Relaxation in Bulk Metallic Glass Composites." *2002 Fall Meeting of the Minerals, Metals, and Materials Society* (Seattle, WA) 2002.

Publications

AH Brothers, DC Dunand. "Mechanical Properties of Bulk Metallic Glass Foams." *Acta Materialia* 2005, in preparation.

AH Brothers, DC Dunand. "Micromechanics of Cellular Bulk Metallic Glasses" *Acta Materialia* 2005, in preparation.

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AH Brothers, R Scheunemann, JD DeFouw, DC Dunand. "Processing and Structure of Open-Celled Amorphous Metal Foams." *Scripta Materialia* 52(4) 335 2005.

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D Balch, E Ustundag, DC Dunand. "Diffraction Strain Measurements in a Partially Crystallized Bulk Metallic Glass Composite Containing Ductile Particles." *Journal of Non-Crystalline Solids* 317(1-2) 176 2003.

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Summary

Overview

The stated goal of this subproject was to develop methods for processing Zr-based bulk metallic glass foams and to investigate their structure and mechanical behavior. At the inception of the project, no such methods had been discovered and consequently nothing was known regarding the potential of bulk metallic glass foams as structural materials. Over the course of the project period, seven potential methods were studied, from which the two most successful were identified for further study. More detailed investigation revealed that despite the critical absence of ductility in monolithic alloys, low-density Zr-based bulk metallic glass foams have ductility on par with conventional aluminum foams, motivating their investigation as structural materials.

All of the methods investigated during the project made use of the commercial BMG alloy Vit106 ($Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$), selected based on: (1) high glass-forming ability/low critical cooling rate; (2) robustness against crystallization in the presence of externally-introduced phases, as demonstrated through prior composites processing work; and (3) commercial relevance, as evidenced by lack of precious metal components and toxic beryllium. With one exception, all methods are melt-based, as these methods make use of the high formability of the melt and the relatively low glass transition and liquidus temperatures of Vit106. In the following section, the methods investigated are reviewed and suggestions for future work are made. In Section 3, current understanding of the mechanical properties of Vit106 foams is discussed. In Section 4, the scope and impact of the work is summarized. Figures are provided in Section 5, presentations and publications resulting from project work are listed in Section 6, and related references are listed in Section 7.

Processing Methods

The ideal method of introducing porosity into a reactive melt is incorporation of an inert gas (i.e., gas entrapment or 'bubbling'), as this method does not require the use of potentially contaminating pore-forming agents. Ordinarily, the low viscosity of metallic melts still necessitates the use of stabilizing additives designed to delay pore coarsening and collapse by increasing viscosity and altering melt surface tension; the high inherent viscosity of glass-forming melts, however, suggests that truly additive-free foaming could be accomplished using this method.

Early investigations in gas entrapment showed that introduction of purified argon gas into the Zr-based BMG via a porous quartz crucible wall led to bubble diameters in the range of 1–3 mm, though smaller (0.5–1 mm) bubbles were on occasion produced. Given cooling rate limitations, and the consequent sample diameter limitations, such pore sizes are unacceptably high. In addition, rapid introduction of argon bubbles required melt temperatures sufficiently high that the bubbles were also prone to coarsening, and the volume fraction of pores was therefore limited to low values (< 50%) by the relative rates in which bubbles were introduced and lost at the melt surface. No combination of melt temperature, argon pressure, and crucible pore size was found to address these limitations, and work on this method was suspended. A representative sample is shown in Fig. 1, though this sample was not amorphous. Further work should investigate alternative methods for gas injection (i.e. impellers, nozzles, or entrainment through rapid melt stirring), or use of different crucible materials, whose surface energies with the molten alloy are known to affect bubble size and formation rate.

The second foaming method involved replication of polymer foams using investment casting techniques. In this method, a mold was built around polyurethane foam by gradual accumulation of refractory powders deposited from aqueous slurries, and the sacrificial foam was then removed by pyrolysis in air. The resulting mold was then infiltrated by the glass-forming melt, giving a replica of the original plastic foam. Several mold materials were investigated, including zirconia, graphite, and yttria, with varying degrees of success, but it was soon determined that no viable mold material would give sufficiently high conductivity to allow vitrification of the alloy. Once again, foam structures were produced (Fig. 2), but full vitrification was never achieved and work was discontinued. Though this method could be further investigated for other alloys with extremely high glass-forming ability (e.g., Pd-based alloys), it is not recommended for further study using reactive alloys and those with higher critical cooling rates.

The third foaming method involved infiltration of the open space inside a bed of low-density pellets made from agglomerated graphite. These pellets were made by tumbling mixtures of fine graphite powder, sodium fluoride (a soluble binder), and water, followed by screening to a desired size range (*ca.* 1–5 mm). Though low-density structures could be made in this way (Fig. 3), it was found that the pellets themselves became partially infiltrated by the melt, preventing use of pellets with sufficiently small size to allow a statistically-significant number of pores in the sample cross-section. In addition, samples made using this method could only be partially vitrified. It is not known whether this resulted from poor purity in the initial alloys or from reaction between the melt and the salt binder. Further work using this method is conceivable but not highly recommended, as better methods have been developed.

The fourth method involved infiltration of the space within a packed array of thin-walled tubes (in this case, titanium) filled with a temporary place-holder (in this case, yttria). This method potentially gives interesting structures with high anisotropy and high porosity (limited by the ideal two-dimensional packing of fibers, *ca.* 90%, mitigated by the density of the tubes as defined through wall thickness and material). However for the sample sizes accessible using glass-forming alloys, the availability of thin-walled tubes was limited. Low-density structures (Fig. 4) were produced using titanium tubes, but preventing dissolution of these tubes into the Zr-based melt (and subsequent crystallization during solidification) required pack-carburizing the tubes, a process which could not be done with sufficient uniformity to fully prevent attack of the tube walls, so that a fully amorphous structure was never produced. Future work using this method may be advisable if the extreme anisotropy of the structure is desirable, since conventional foaming methods (with the exception of melt-hydrogen eutectic decompositions) do not permit this.

The fifth method differed from earlier methods through the use of amorphous powders in place of glass-forming melts. In this method, blended powders consisting of varying ratios of BMG powder and soluble placeholder (NaCl was used) with varying particle sizes were subjected to equal-channel angular extrusion (ECAE) in the laboratory of Prof. K.T. Hartwick (Texas A&M University) in an attempt to produce a compact in which both phases were interpenetrating, allowing subsequent dissolution of the placeholder. It was found that powder blends could be coextruded without inducing crystallization of the alloy powders, but that the final distributions of the two phases became highly nonuniform, such that the compacts did not achieve full consolidation. During removal of the placeholder, samples were therefore found to lose mechanical integrity. Continued work on this method was rendered impossible by extrusion equipment failures, and successful melt-based approaches were subsequently discovered, but the coextrusion method in general is considered worthy of further investigation.

The sixth method investigated was the first fully successful one, and the first reported method by which foam was produced from a commercially-viable BMG alloy.[1] This method is an improvement on the method of pellet infiltration described above, wherein the pellets are replaced by hollow carbon spheres (i.e., 'cenospheres'). This approach solves the problems associated with that method; namely, the pore size is determined by the cenosphere diameter, which is much smaller (on the order of 25–50 μm) than the sample diameter, the use of fully-intact cenospheres prevents loss of porosity during infiltration, and no potentially contaminating palletizing binder is required. It was found that samples of 5 mm diameter could be fully vitrified, though redistribution of the cenospheres in the melt during the infiltration process led to structures which were nonuniform in the direction of infiltration, limiting the overall size of the sample. The presence of the carbon cenospheres inside the alloy caused an additional exothermic event during heating of the foam (presumably due to the highly-exothermic formation of ZrC), but did not lead to loss of thermal stability relative to the unprocessed alloy. Further details are provided in the references, but images of the foam structure are reproduced in Fig. 5 for convenience.[1] Further work on this process is considered very promising, but has been limited by time constraints and the discovery of the second successful process, described below.

The seventh method, and the second successful method, involves infiltration of the melt into a pattern of sintered refractory salt, in this case BaF_2, followed by removal of the pattern in a bath

of strong acid. Using this method, highly regular foam structures have been produced with pore sizes (determined by salt particle size) between 150 μm and 350 μm, relative densities as low as 15% and as high as 24%, and fully amorphous diameters as large as 7 mm, though none of these limits has been fully established. Details of the processing and structure of foams produced by this method are provided in the references,[2,3] but images of the foam structure are reproduced in Fig. 6 for convenience. To date, this method and the previous one are still the only methods reported for foaming of commercial BMG alloys. The salt replication method has also provided the first mechanical behavior for Zr-based BMG foams, as discussed in the next section. The method has been under active investigation for several months, and is considered highly promising as a basis for future work after expiration of the project.

Mechanical Properties

Foams produced using the salt replication method have been tested in uniaxial compression.[2] The major purpose of gathering compression data is to determine whether foam architectures impart anomalously high ductility to the BMG, which is prone to catastrophic failure in monolithic form. The reason for expecting such ductility arises from the high observed bending ductility of amorphous metal wires and foils, and originates from changes in the density and scale of shear bands within these structures, as discussed elsewhere.[4] Due to the similarity between wires, foils, and the struts within a typical foam, the same effect is expected to provide ductility to BMG foams.

A typical quasistatic compression curve for Vit106 foam is shown in Fig. 7, for foam with relative density 22% (bulk density 1.5 g/cm^3), pore size *ca.* 200-250 μm, and sample diameter 4.5 mm. The behavior is characterized by a quasielastic loading region terminated by yield at around 21 MPa, followed by a 'plateau' region wherein the flow stress increases gradually to about 100 MPa at an engineering strain of 50%. This region was terminated by unloading of the sample, with no evidence of macroscopic failure. Throughout the plateau region, load drops (i.e., serrations) are seen, presumably corresponding to failure of individual struts, or small clusters of struts, but macroscopically the behavior very much resembles that of aluminum foams made using a similar process involving NaCl placeholders.[5] Further details are provided in the references.[2,3] By contrast, the behavior of Pd-based BMG foam (made using an NaCl placeholder) recently reported elsewhere[6] shows severe stress drops (up to 80% loss in flow stress over the curve), more characteristic of brittle ceramic foams, such that only in these lower-density Zr-based BMG foams has ductility comparable to conventional metal foams been established.

Current work has focused on a full exploration of the mechanical behavior of Vit106 foams made by the replication process. The final results of this work, expected to be submitted for publication early in 2005[7], will thoroughly explore variations in yield strength, stiffness, and damage evolution with respect to relative density and pore size, along with fitting equations allowing prediction of these properties for materials selection purposes. In addition, a model will be published[8] to relate the unique structure of these foams to the observed scaling relationships, in an effort to understand the origins of the observed mechanical properties.

Seven distinct foaming methods for the commercial bulk metallic glass alloy Vit106 were studied during the project period. Of these, four are considered worthy of future study, and two

have already been proven successful for the production of fully amorphous Vit106 foams, which have now been processed with pore sizes ranging from *ca.* 25 μm to 350 μm, relative densities between 15% and 50% of the bulk, and in diameters as high as 7 mm. To date, these methods are the only known methods for producing Zr-based BMG foams. In addition, work done at the completion of the project demonstrated for the first time that BMG foams can achieve ductility on par with that of foams made from conventional ductile metal foams, potentially allowing the production of BMG foams exploiting the high strength and corrosion resistance of BMG alloys without suffering from either the poor toughness of monolithic BMG or the poor compressive properties of ceramic foams.

The investigators thank DARPA for their financial support of this project and make themselves available for any future comments, questions, or correspondence.

Figures

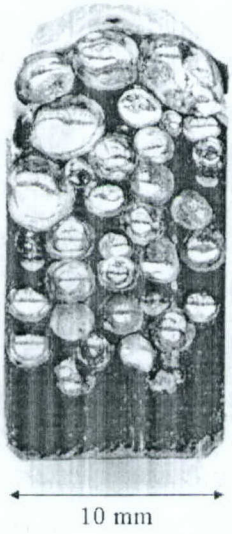

Fig. 1 Axial section of Vit106 foam made by entrapment of argon gas in a rapidly solidified melt. This sample demonstrates the complications of large pore size, relatively low volume fraction, and bubble coarsening typical of this process. The Vit106 surface has been blackened to enhance contrast with the gas bubbles.

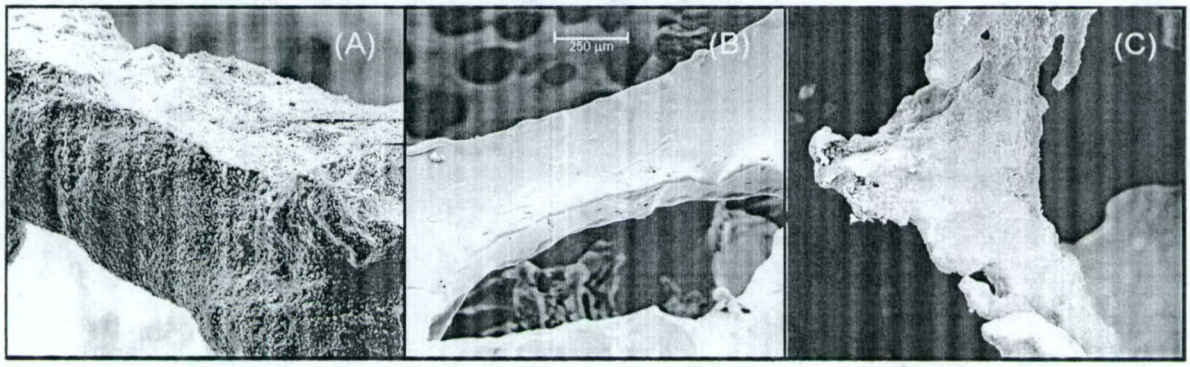

Fig. 2 SEM micrographs comparing strut morphologies in polyurethane foam (B) to those of Vit106 foam (A, C) made by infiltrating the alloy into an Y_2O_3 mold built around the polyurethane foam. Some Vit106 struts, such as the one shown in (A), are similar to those of the original foam; others, such as the one in (C), are highly defective. The foam shown in (A) and (C) was quenched but is still fully crystalline, on account of the low conductivity of the Y_2O_3 mold, a major reason why this process was discontinued. The scale bars on all three figures are the same.

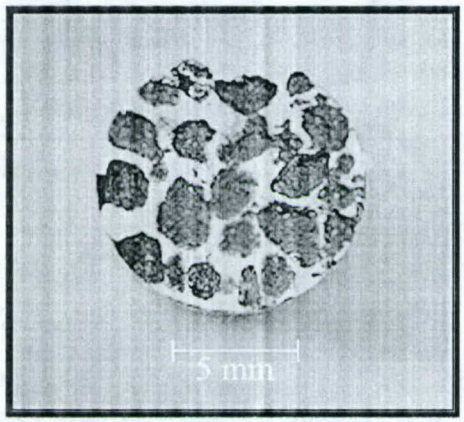

Fig. 3 Cross-sectional image of Vit106 foam made by infiltrating the interstices of a bed of pellets fabricated by tumbling graphite and NaF powders in the presence of water. Pellets made in this way were not small enough to permit amorphous samples with statistically significant numbers of pores across their diameter.

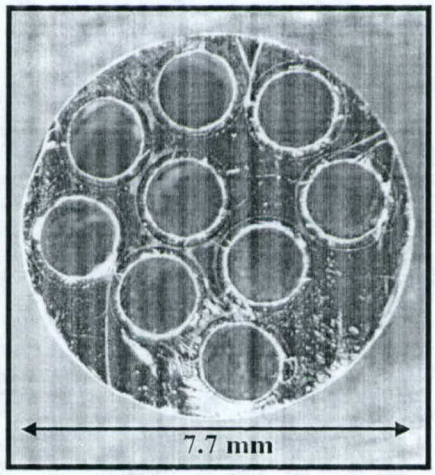

Fig. 4: Cross-sectional image of a Vit106 foam produced by infiltrating the interstices of a pattern made from thin-walled Ti tubes. The tubes were pack-carburized to protect them from the reactive Vit106 melt, and packed with Y_2O_3 powder to prevent the alloy from infiltrating the tube interiors (Y_2O_3 packs have been mechanically removed for clarity). This sample crystallized upon cooling, likely due to incomplete protection from the carbide case.

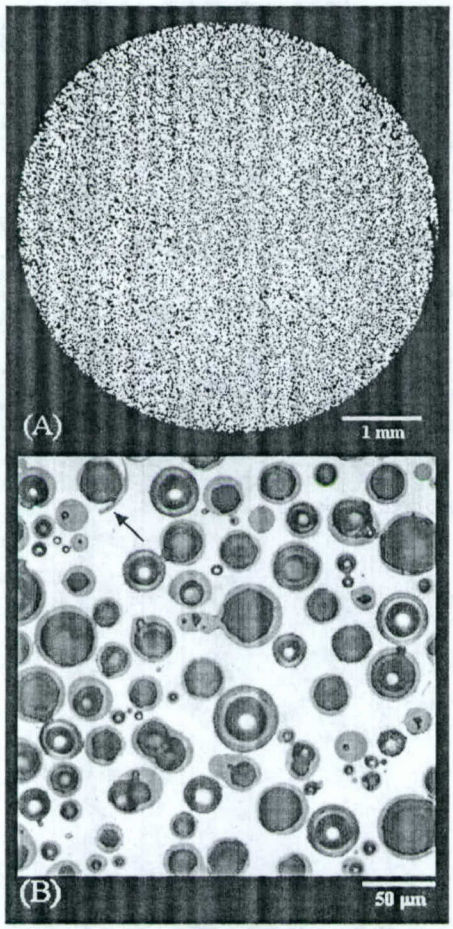

Fig. 5 Cross-sectional images of Vit106 foam made by infiltration of a bed of hollow carbon microspheres, showing: (A) macroscopic foam uniformity; and (B) microstructure of the foam. This was the first reported Zr-based BMG foam, and is described in more detail in the references.

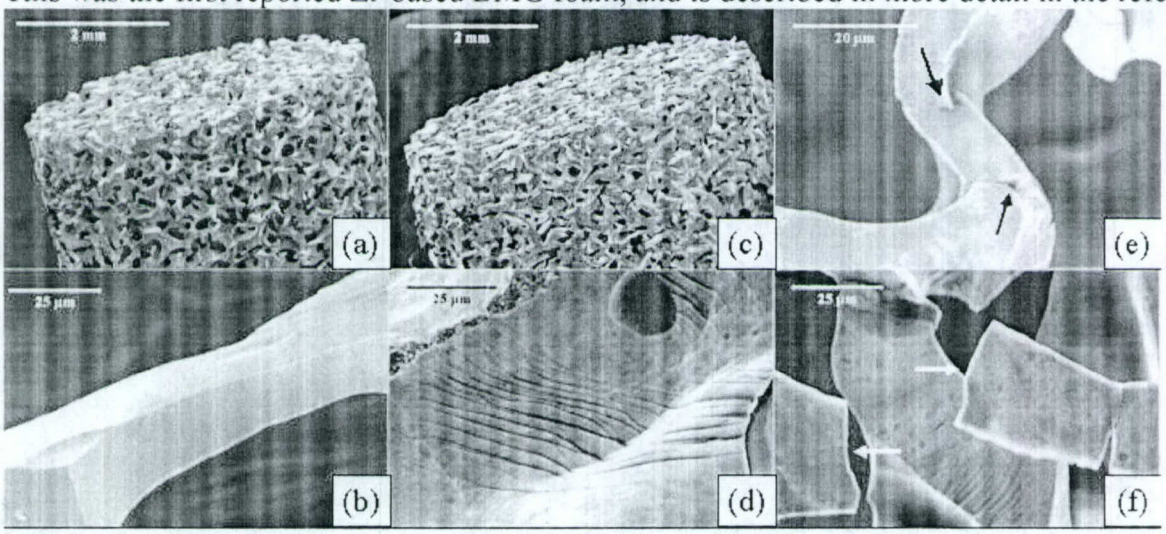

Fig. 6 SEM micrographs of amorphous Vit106 foam with 22% relative density. (A) Macrostructure of the foam prior to compression. (B) Individual strut within the undeformed foam. (C) Macrostructure of the foam after 50% compression. (D) Deformed strut in the compressed foam, showing evidence of ductility in the form of shear lips, caused by intersection

of shear bands with free surfaces. (E) Buckled strut in the compressed foam, showing evidence of shear bands as well as incipient cracks (indicated by arrows). (F) Fractured strut in the deformed compressed foam, exhibiting fracture with no shear bands. Mating fractured surfaces are indicated by arrows.

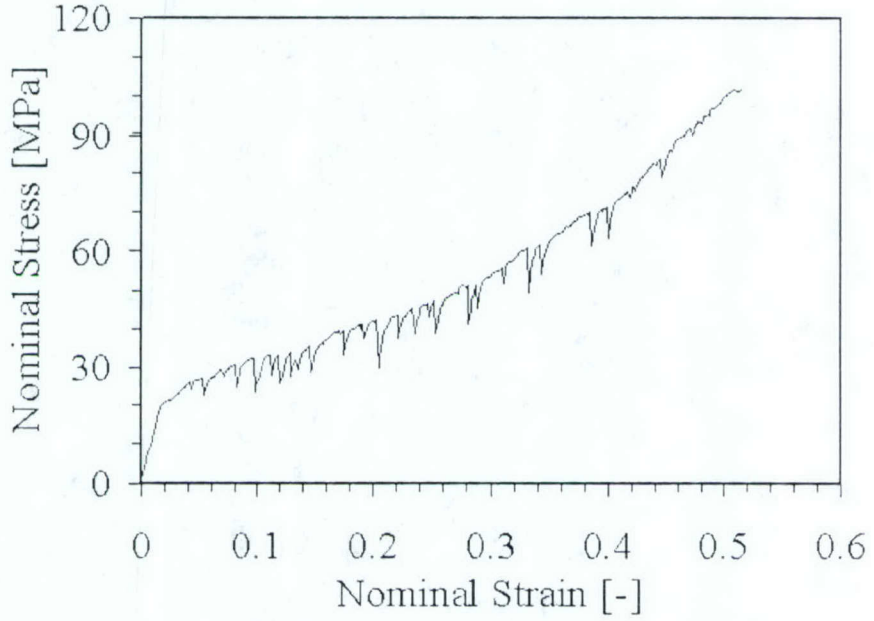

Fig. 7 Compressive stress-strain behavior of the 22% dense Vit106 foam shown in Fig. 6A. The foam was unloaded from 50% engineering strain without macroscopic failure (Fig. 6C), demonstrating high ductility. The behavior shown here, except for the low-amplitude stress drops associated with individual strut failures, is characteristic of ductile metallic foams.

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7. AH Brothers, DC Dunand. "Mechanical Properties of Bulk Metallic Glass Foams," *Acta Mater.* (2005), in preparation

8. AH Brothers, DC Dunand. "Micromechanics of Cellular Bulk Metallic Glasses," *Acta Mater.* (2005), in preparation

A7: Internal Stress Distributions in BMG and Composites (Prof. E. Ustundag, *Caltech*)

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Dr. Bjørn Clausen: Post-Doctoral fellow (diffraction stress analysis, modeling, composites studies). Currently a technical staff member, Los Alamos Neutron Science Center.
Dr. C. Can Aydiner: graduate student (thermal tempering of BMGs) (defended Ph.D., 2003)
Mr. Seung-Yub Lee: graduate student (processing and characterization of BMG composites)
Mr. Gregory S. Welsh: graduate student (processing and characterization of BMG composites)
Ms. Kathryn Hsu: undergraduate student (thermal tempering of BMGs)
Ms. Tracy Janov: undergraduate student (*in-situ* BMG composites)

Statement of the problem studied

Internal stresses and deformation mechanisms in bulk metallic glass, metallic glass composites and foams.

Patents, Presentations and Publications

Patents

None

Presentations

C. C. Aydiner and E. Üstündag, "Thermal Tempering of Bulk Metallic Glasses," T. Egami, A. L. Greer, A. Inoue and S. Ranganathan (eds.), *MRS Symposium Proceedings,* **754**, Materials Research Society, Warrendale, Pennsylvania, pp. 185-190, 2003

Publications

C. C. Aydiner, E. Üstündag, M. B. Prime and A. Peker, "Modeling and Measurement of Residual Stresses in a Bulk Metallic Glass Plate," *J. Non-Cryst. Solids*, **316**[1], 82-95, 2003

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C. C. Aydiner, "Investigation of Thermal_Tempering in Bulk Metallic Glasses", *Ph.D. thesis*, California Institute of Technology, 2003

C. C. Aydiner, E. Üstündag, B. Clausen, J. C. Hanan, R. A. Winholtz, M. A. M. Bourke and A. Peker, "Residual Stresses in a Bulk Metallic Glass - Stainless Steel Composite," in press: *Mater. Sci. and Eng. A*, 2004

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B. Clausen, S. Y. Lee, E. Üstündag, C. P. Kim, D. W. Brown and M. A. M. Bourke, "Deformation of *In-Situ*-Reinforced Bulk Metallic Glass Matrix Composites," *Mater. Sci. Forum,* **404-407**, 553-560, 2002

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I. Halevy, E. Üstündag, S. Salhov, A.F. Yue, A. Broide and J. Hu, "High Pressure Study of a Zr-based Bulk Metallic Glass and its Composite," in press: *Z. Krist.*, 2004

Summary

Thermal Tempering of Bulk Metallic Glasses

Our previous work using the instant freezing model [1] had suggested the existence of significant residual stresses in BMGs due to the thermal tempering phenomenon. To determine the exact

values of stresses found in cast specimens we initiated a comprehensive effort to measure them using mechanical relaxation techniques. After trying several of these techniques (layer removal, hole drilling and crack compliance) the last one was determined to be the most accurate. This technique employs several strategically placed strain gages to monitor strain relaxation when a fine cut is extended across a specimen. The residual stresses are then back calculated. We used this method, first on a thick cast plate from Liquidmetal Technologies. The results showed that the residual stresses in cast BMGs are extremely dependent on processing conditions which some time involve insufficient heat transfer during quenching and eventually low thermal tempering [**2,3**]. The second sample geometry was cylindrical and was designed to assure thermal contact (and hence better heat transfer) during casting and quenching [**2-6**]. The residual stress data obtained from the second sample geometry showed that BMGs can be tempered with surface compression values exceeding 400 MPa.

In a parallel study, we have developed a more realistic tempering model [2] that takes into account the viscoelastic properties of BMGs. To this end, we have used viscosity data collected by W. L. Johnson and co-workers. These data were implemented in a finite element model that simulates the exact conditions during the casting of BMGs. The comparison of the model predictions with experimental data showed that the model is accurate within 15% [4,5] and is therefore a powerful tool to estimate thermal tempering in BMGs.

There are two additional issues to address before the thermal tempering study of BMGs can be fully completed. First, to estimate processing history dependence and to evaluate transient stresses during quenching, the viscoelastic model has to be improved to allow structural relaxation. We have already started preliminary studies [7] on this aspect and have observed drastic differences between the nature of thermal tempering of BMGs and silicate glasses. The second important issue to resolve before concluding the thermal tempering study is the effect of tempering stresses on the mechanical properties of BMGs. We are currently preparing bending specimens to study this topic.

After obtaining a complete understanding of thermal tempering in BMGs, we intend to collaborate with Johnson and co-workers to develop a sophisticated finite element model that can simulate the complete casting and quenching of a BMG. The model will incorporate fluid dynamics aspects of casting (as recently studied by Demetriou and Johnson) and stress development during quenching. As such, it can be used as a powerful tool to model BMG processing of various components.

Deformation Mechanisms of Bulk Metallic Glass Matrix Composites and Foams

During the initial period of the DARPA program we studied the mechanical behavior of BMG matrix composites reinforced with dendritic precipitates that form *in situ* during processing. The "β phase"/BMG composites exhibit significantly improved ductility compared to monolithic BMGs. To determine how the "β phase" precipitates behave *in situ* while incorporated in a BMG matrix and to help elucidate their toughening mechanism, we performed neutron diffraction (ND) and high energy XRD experiments on both "β phase"/BMG composites as well as monolithic "β phase" samples. We applied compressive/tensile stress on these specimens while monitoring the internal strains in the "β phase" with ND and XRD. The results can be summarized as follows [2,3]:

- No stress-induced martensitic phase transformations or twinning were observed in the "β phase" in both monolithic and composite forms. These were mechanisms initially suspected to be responsible for the toughening of the composites. Instead, the dendrites experience large plastic deformation by slip.
- The mechanical properties of the monolithic "β phase" are very sensitive to the annealing conditions during processing. For example, one specimen showed significant plasticity with a yield stress of about 560 MPa (typical behavior), while another failed in a brittle manner at 1425 MPa. The reason for this behavior is ordering and phase transformation in the "β phase" during annealing. Both samples had the same chemical composition and were prepared under identical conditions, but second sample had subsequently been annealed at 350°C for about 20 min.
- Additional high temperature XRD experiments were performed to study phase evolution in monolithic "β phase" as well as the composite. These experiments showed that the dendrites are quite stable in the composite and melt after the matrix.
- Single-crystal elastic constants of the "β phase" were determined for the first time using ND data by employing a new self-consistent analysis [8]. These results were again very sensitive to annealing conditions. This approach was then used to develop a new self-consistent model to describe the *in-situ* deformation of the composite. It was shown that the "β phase" yields first and then transfers load to the amorphous matrix.

The "β phase" composites were also studied to quantify their microstructure. We showed that most composites contain about 40 vol.% dendrites, much higher than the 25% originally measured In addition, the dendrite size and spacing was seen to vary tremendously within a specimen reflecting large variations in cooling rates.

Following our parallel work on particulate [2,3] and wire reinforced BMG composites [2-4], a generic pattern is now emerging about the deformation mechanisms in ductile phase reinforced BMG composites. We have shown that it is always the reinforcement that yields first and then induces multiple shear bands in the matrix. The extent of the shear banding (and hence the "ductility" of the BMG matrix) is governed by the elastic and plastic properties of each phase, the strength of the interface and the morphology of the reinforcement. However, the exact micromechanics of deformation are still unknown. For this reason, we have recently initiated a systematic study of model BMG composites with "sandwich" and concentric cylinder geometries. These model composites offer simple, well defined boundary conditions and controlled deformation (e.g., quasistatic shear banding in BMG) allowing a deeper insight into the micromechanics of BMG composites. We are employing X-ray microdiffraction and optical methods (e.g., laser speckle interferometry) to measure local strains and displacement fields in composites (both model and dendritic). We then intend to collaborate with modelers such as M. Ortiz to develop a comprehensive model of BMG composite deformation.

In a related study, we showed for the first time that one can employ the amorphous diffraction patterns of a BMG to measure its elastic strain. This is important in composite studies where the strain data from the crystalline reinforcements (obtained by diffraction) can be complemented with strain information from the BMG matrix allowing a more rigorous analysis of composite deformation.

We have also initiated a related study on the deformation mechanisms of BMG foams. These materials can be considered an extreme version of a composite and by understanding their deformation one can also obtain insight about other composites. In addition to traditional

mechanical loading experiments, we will soon perform the first *in-situ* X-ray microtomography experiment on a BMG foam at the European Synchrotron Radiation Facility in France. We will apply compression while collecting three-dimensional images of deformation with a sub-μm resolution. There is speculation that thin cell walls in BMG foams may deform plastically without breaking by forming multiple shear bands. To optimize the structure and properties of BMG foams one needs to understand how they deform. The ability to see the elastic deformation of cell walls *in situ* with microtomography is a significant advantage to postmortem observations where these deformations are lost. This is particularly important for BMG foams due to their high elastic strain limit. Critical dimensions for obtaining plasticity within cell walls can also be determined from microtomographs.

In conclusion, we envision a fruitful endeavor to understand the micromechanics of BMG composites and foams by following an integrated approach that combines advanced characterization techniques and sophisticated modeling.

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A8: Melt Rheology and Processing at Oregon State University (Prof. R. Busch, *OSU*)

Participants

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Christopher Way, Graduate Student, OSU
Tyler Shaw, Graduate Student, OSU
Ludi Shadowspeaker, Graduate Student OSU

Statement of the problem studied

To study the melt rheology of bulk metallic glasses, including fragility, melt relaxation, non-Newtonian flow, and viscoelasticity. To apply knowledge of these properties to bulk glass processing, including molding and surface replication.

Patents, Presentations and Publications

Patents

None

Presentations

T. Shaw, C. Way, and, R. Busch, "Shear thinning of bulk metallic glass forming alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ close to the melting point." Mat. Res. Soc. Symp.Proc. **806**, 215 (2004).

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M. Shah, I Gallino and R. Busch, "Thermodynamics and kinetics of the $Zr_{58.5}$ $Nb_{2.8}$ $Cu_{15.6}Ni_{12.8}$ $Al_{10.3}$ bulk metallic glass forming liquid". Journal of Applied Physics, pending (2003).

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P. Wadwa, J. Heinrich, and R. Busch, "Processing of Cu wires embedded in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass" in preparation.

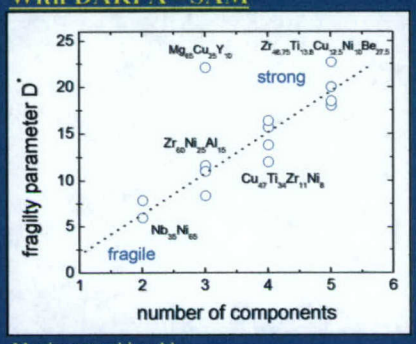
Summary

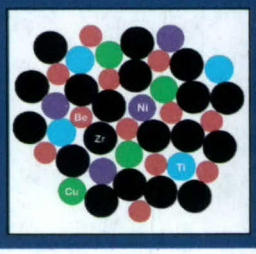
Fragility

Before DARPA - SAM

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vitreloy1) and other SAM are relatively strong liquids (at slow shear rates)
No systematic studies on alloy complexity and composition, yet

With DARPA - SAM





Maximum achievable fragility parameter increases linearly with number of components N

$D^*_{max} \cong 5N - 3$

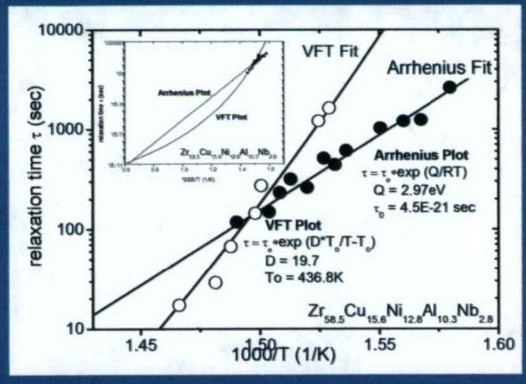
More components of different size lead to more effective packing, smaller free volume and higher viscosity sluggish kinetics and slow crystallization

Enthalpy relaxation

Before DARPA - SAM

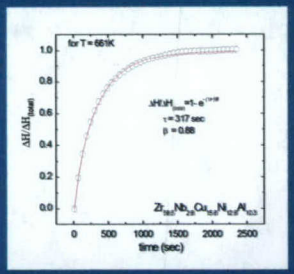
No data on temperature dependence of enthalpy relaxation time

With DARPA - SAM



Enthalpy relaxes faster than expected from VFT fit

Activation energy similar to activation energy for diffusion of mid-size atoms



New method to measure enthalpy relaxation

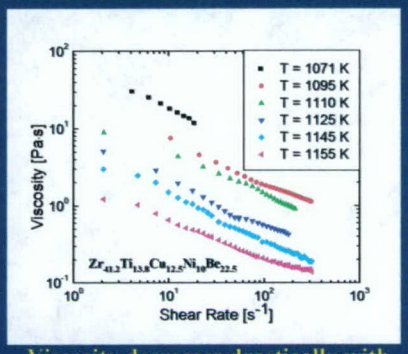
Shear thinning above $T_{liquidus}$ (non-Newtonian flow)

Before DARPA - SAM

Paradigm:

Metallic liquids are Newtonian fluids above the melting point

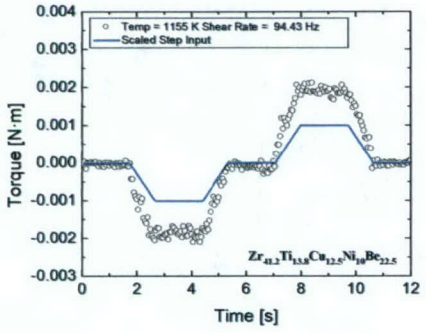
With DARPA - SAM



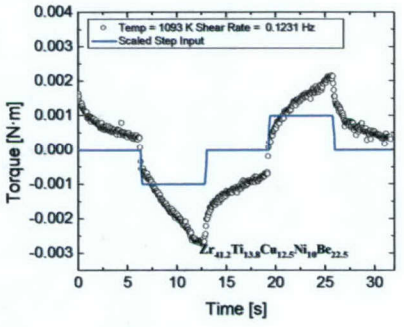
Viscosity decreases drastically with increasing shear rate (power law with n=-0.5)

Vitreloy and other alloys show shear thinning like polymer blends and other emulsions, suggesting that they consist of mixtures of liquid clusters with different short range orders even above T_m

Visco-elastic behavior in the melt

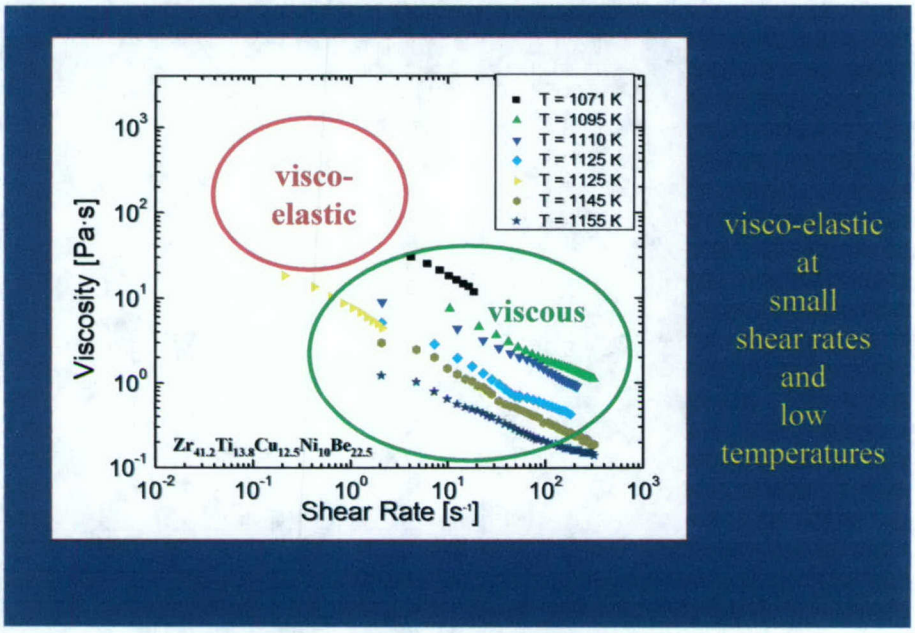


Non Newtonian
but steady state viscosity
(at high shear rates)



Relaxation
Visco-elastic (at low shear rates)

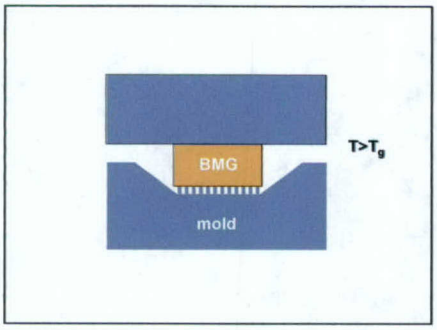
Visco-elastic behavior in the melt

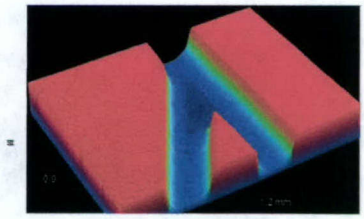


visco-elastic at small shear rates and low temperatures

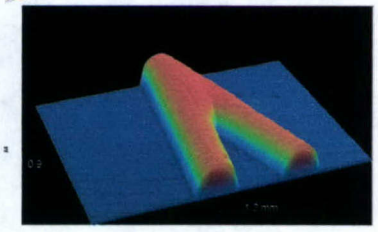
Replication of surfaces

a) from the glassy state



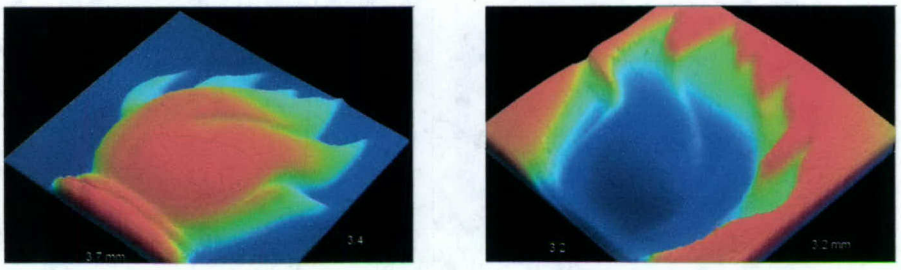


Steel micro channels



Vitreloy 4 replica

Replication of surfaces



Coin **Vitreloy 4 replica**

Torch on a dime

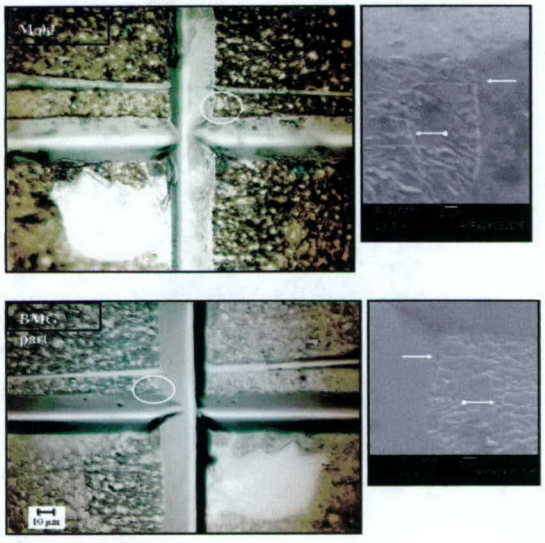
Replication of sub micron surfaces features

b) from the melt

Die casting into steel mold

T_{melt}=1223K

T_{mold}=548K



I. McCracken and R. Busch, to be published

A9: Real Time *in situ* Characterization of the Structure of Amorphous Metallic Glass Alloys

Participants

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Statement of the problem studied

Significant contributions to the understanding of the structure of refractory metallic glasses have been made with the use of synchrotron radiation and other complementary characterization techniques.

Patents, Presentations and Publications

Patents

None

Presentations

M. L. Tokarz, M. Daniels, J. C. Bilello and Z. Rek, "Characterization of the Structure of a Novel Refractory Alloy Glass – $Ni_{60}Nb_{37}Sn_3$", *Materials Research Society Symposium Proceedings*, **Vol 754,** (2003) CC2.30, p. 141-146

M. L. Tokarz and J. C. Bilello . "On the Structural Characterization of a Series of Novel Ni-Nb-Sn Refractory Alloy Glasses." *Materials Research Society Symposium Proceedings*, **754,** (2004) MM9.5

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Michelle L. Tokarz and John C. Bilello, "Nanoscale Structural Characterization of NiNbSn Based Bulk Metallic Glasses", presented in the Symposium "Frontiers of X-Ray Micro and NanoBeam Diffraction - TMS – Materials Science and Technology Conference, Chicago, IL, November 10, 2003.

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M. L. Tokarz, S. Speakman, W. Porter, J. C. Bilello "Stability of Ni-Based Bulk Metallic Glasses" *TMS* - accepted for publication in *Intermetalics* (March 2004).

M. L. Tokarz and J. C. Bilello "Structural Characterization of Ni-based Refractory Glassy Metals" *Journal of Non-crystalline Solids.* **Vol 334**, (2004), p. 110-118.

M. L. Tokarz and J. C. Bilello "Investigation of Species-specific Atomic Order in Ni-based Metallic Glasses via Anomalous Scattering Techniques" submitted to *Journal of Applied Physics*

M. L. Tokarz and J. C. Bilello "Characterization and Properties of $Ni_{60}(Nb_{1-x}Ta_x)_{34}Sn_6$ Metallic Composites" submitted to *Journal of Non-crystalline Solids*

Summary

Structure of Refractory Alloy Glasses

Figure 1 shows a specific example of laboratory x-ray scattering results with (1a) indicating an apparently fully amorphous structure for a RAG1 ($Ni_{60}Nb_{37}Sn_3$) alloy.

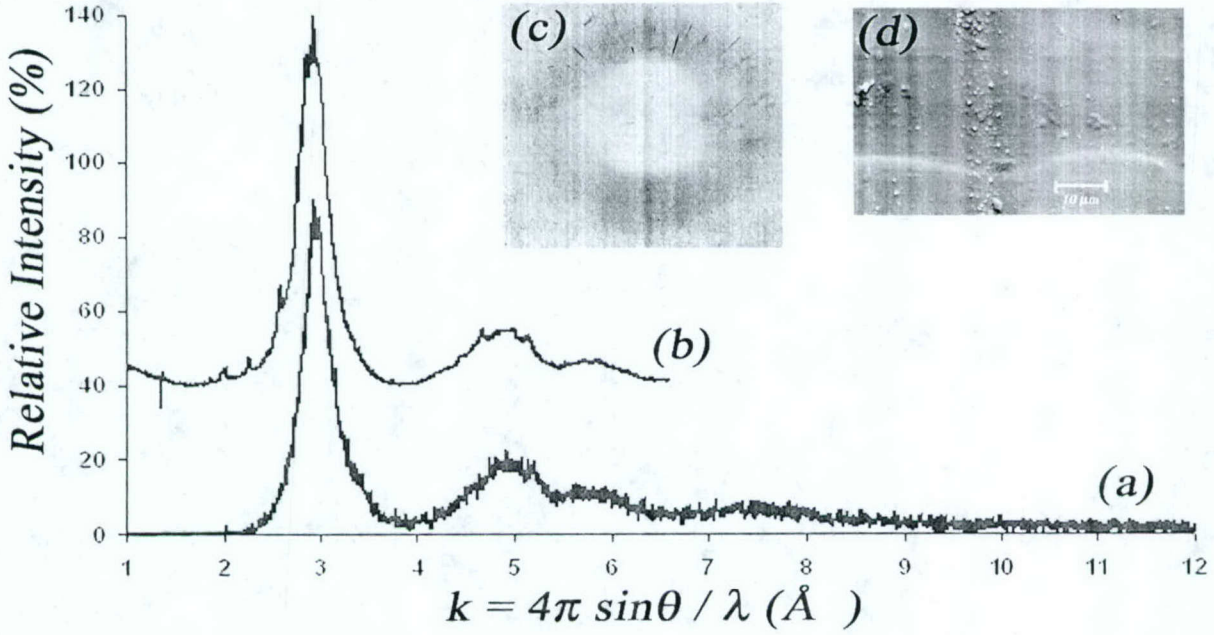

Figure 1: Comparison of Several Characterization Results for RAG1 ($Ni_{60}Nb_{37}Sn_3$). a) Laboratory X-ray Reflection Scattering Pattern, b) Synchrotron X-ray Reflection Scattering Pattern, c) Laue White-beam Synchrotron Transmission Synchrotron Amorphous scattering ring with streaking from highly strained nanocrystallites inclusions, d), Scanning Electron Microscopy Image of Cross Sectioned Sample showing crystallite phase (most SEM pictures showed nothing).

Comparisons to synchrotron x-ray scattering patterns however (1b), (Obtained from Beamline 2-1 at Stanford Synchrotron Radiation Laboratory) reveal the presence of nanocrystallites within an amorphous matrix. This is directly attributable to the low source divergence and high intensity of a synchrotron source as compared to even the best lab x-ray source. Comparisons for other RAG (Refractory Alloy Glass) samples showed similar results and are detailed elsewhere.[1] Insets (1c) and (1d) directly confirm the nanocrystalline results found in high resolution scattering experiments (1b).

Utilizing a LaB_6 (Lanthanum Hexaboride) NIST powder diffraction standard, an estimate of instrumental line-broadening could be made for both x-ray sources, and consequently, deconvolution and Scherrer line-broadening analyses were performed to determine both *sizes* and *amounts* of crystalline portions in each of four different RAG compositions. The results are given in Table 1. Overall, this analysis revealed ~1 % crystallites by volume with individual grain sizes ranging from 15 to 140 nm.

Table 1: Residual Grain Sizes for the Ternary Ni-Nb-Sn RAG alloys

RAG designation	Average grain dimension (nm)	Range of grain dimensions (nm)
RAG1 ($Ni_{60}Nb_{37}Sn_3$) *[10 peaks]*	40	15 - 74
RAG4 ($Ni_{59.35}Nb_{34.45}Sn_{6.2}$) *[4 peaks]*	124	101 – 148
RAG5 ($Ni_{59.5}Nb_{33.6}Sn_{6.9}$) *[1 peak]*	102	NA

Note: RAG 3 was completely amorphous and therefore there were no residual grains and RAG 5 almost entirely amorphous and hence only one distinct diffraction peak could be analyzed.

X-ray attenuation depths for these RAG materials are on the order of 10 μm. Therefore reflection mode experiments only give information about the structure of the top layer of the bulk (2mm thickness) sample. In contrast, the high energies of the Beamline 2-2 synchrotron white-beam x-ray source (2-40 KeV), allow penetration of these samples and confirm the presence of a small amount of nanocrystallites through the entire thickness. This is shown in (c) of Figure 1 for RAG1.

Scattering Electron Microscopy (SEM) techniques allow for direct phase imaging of materials, as compared to x-ray techniques, which give global average information. Hundreds of these images were obtained from various as-cast and fracture surfaces, with most showing no contrast. Figure 1(d) is a specific example of one of the few images that confirmed the presence of second phase crystallites and indicated a great degree of non-homogeneity in the distribution of these particles.

Similar characterization methods were employed for a quaternary Ni-Nb-Ta-Sn series that were fabricated in an attempt to form materials with higher glass transition temperatures, Tg's, due to the higher melting point of Ta (3020 °C) as compared to that of Nb (2477 °C). These materials do indeed show Tg's up to 647 °C as compared to the ternary Ni-Nb-Sn series with Tg's ~ 600 °C. However, they show up to 33% crystalline fractions, as revealed by synchrotron x-ray scattering.

Thermal Stability

Figure 2 is one example of several *in-situ* heating x-ray experiments that was performed on all ternary Ni-Nb-Sn samples in collaboration with the High Temperature Materials Laboratory at Oak Ridge National Labs.[2]

Differential Scanning Calorimetry (DSC) scans of these materials revealed Tg ~600 °C, followed by a complex crystallization and melting sequence, as is indicated by the inset in Figure 2. However, the sensitivity of x-ray scattering experiments allowed one to observe local crystallization occurring at temperatures well below the Tg. Indeed, RAG samples began crystallization at a reduced temperature, T/Tg, of 0.84 compared to 0.91 for Vitreloy-106 ($Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$), a well-characterized bulk metallic glass.

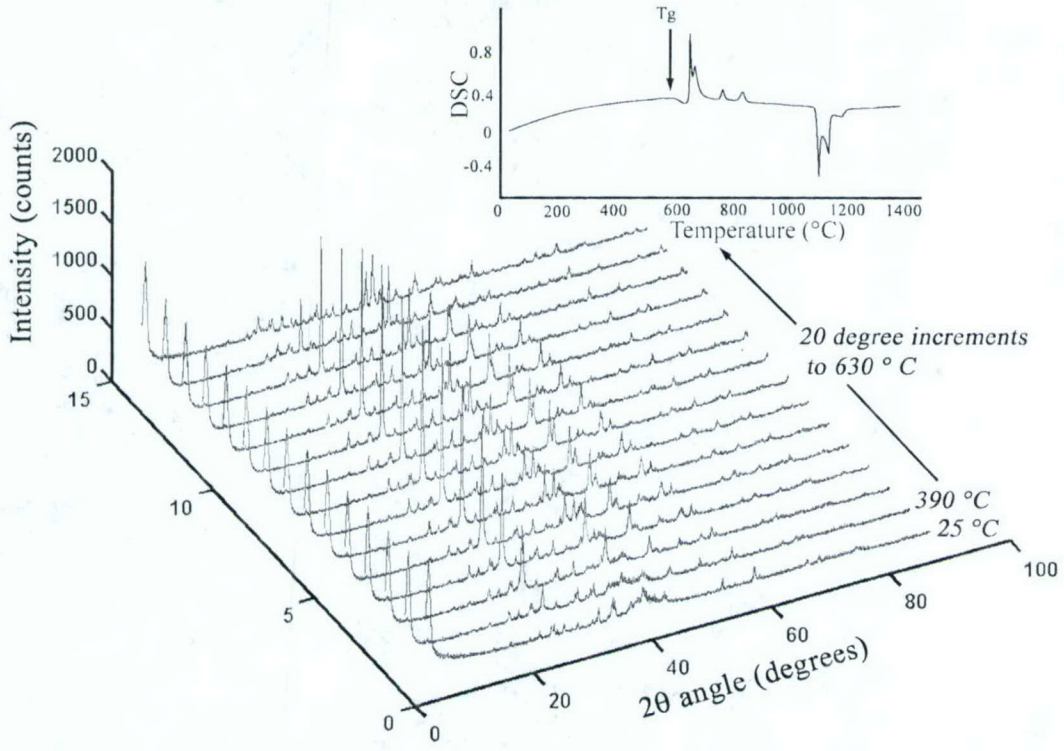

Figure 2: X-ray Scattering Patterns from *in-situ* Heating Experiments on RAG1. 90 minute scans from 390 °C to 630 °C in 20 ° increments. Inset on upper right corner is DSC scan showing Tg ~ 600 °C. Comparison of x-ray scans and DSC indicates local crystallization as low as 390 °C, well below the Tg.

Additionally, because of the direct relationship between peak area and number of scattering centers, the peak area could be correlated to a phase concentration. Thus, the growth (or reduction) of any particular diffraction peak could be plotted and compared to a reciprocal temperature to produce an Arrhenius plot. This analysis revealed a diffusion limited growth (or dissolution) process for the formation of Ni_3Sn and Nb_2O_5 phases, with activation energies of 1.6 and 1.2 eV/atom, respectively.

Investigation of Non-Random Order

Early investigations of short-range order of these Ni based RAGs indicated a divergence from a random hard-sphere model.[3] This is indicated in Table 2 in terms of the nearest neighbor distances and numbers of atoms in the first three nearest neighbor shells. These results were obtained from Radial Distribution Functions (RDFs), which give overall average short-range order information. In an attempt to discern species-specific data, anomalous x-ray scattering was pursued.

Table 2: Radial Distribution Function Results (Nearest neighbor distances and # atoms in first three shells) Compared to Random Hard-sphere Model.

	Shell 1		Shell 2		Shell 3	
RAG1 ($Ni_{60}Nb_{37}Sn_3$)	**# atoms**	**r (Å)**	**# atoms**	**r (Å)**	**# atoms**	**r (Å)**
Synchrotron source	10.6 ± 0.5	2.8 ± 0.2	27.4 ± 1.4	4.7 ± 0.2	48.8 ± 2.5	6.9 ± 0.2
Labsource	10.2 ± 0.5	2.7 ± 0.3	26.5 ± 1.3	4.6 ± 0.5	44.2 ± 2.3	6.8 ± 0.7
Random model	11.5 ± 1.2	2.7 ± 0.3	33.9 ± 1.2	5.4 ± 0.3	62.4 ± 1.2	8.0 ± 0.3
RAG3 ($Ni_{60}Nb_{35}Sn_5$)						
Synchrotron source	11.0 ± 0.6	2.8 ± 0.2	27.8 ± 1.4	4.7 ± 0.2	49.0 ± 2.4	6.8 ± 0.2
Labsource	10.4 ± 0.5	2.7 ± 0.3	26.7 ± 1.4	4.7 ± 0.5	46.3 ± 2.3	6.8 ± 0.7
Random model	11.6 ± 1.2	2.7 ± 0.3	33.6 ± 1.2	5.5 ± 0.3	63.6 ± 1.2	8.2 ± 0.3
RAG4 ($Ni_{59.35}Nb_{34.45}Sn_{6.2}$)						
Synchrotron source	10.6 ± 0.6	2.8 ± 0.2	27.3 ± 1.4	4.7 ± 0.2	48.2 ± 2.4	6.9 ± 0.2
Labsource	11.7 ± 0.6	2.8 ± 0.3	31.3 ± 1.6	5.0 ± 0.5	53.4 ± 2.7	7.1 ± 0.7
Random model	11.9 ± 1.2	2.7 ± 0.3	32.9 ± 1.2	5.4 ± 0.3	61.7 ± 1.2	8.1 ± 0.3
RAG5 ($Ni_{59.5}Nb_{33.6}Sn_{6.9}$)						
Synchrotron source	10.8 ± 0.5	2.8 ± 0.2	25.9 ± 1.3	4.7 ± 0.2	48.0 ± 2.4	6.9 ± 0.2
Labsource	10.6 ± 0.5	2.8 ± 0.3	37.1 ± 1.9	4.8 ± 0.5	55.5 ± 2.8	7.0 ± 0.7
Random model	11.8 ± 1.2	2.7 ± 0.3	31.7 ± 1.2	5.4 ± 0.3	63.1 ± 1.2	8.1 ± 0.3
Vit-106 ($Zr_{57}Nb_5Cu_{15.4}Ni_{12.8}Al_{10}$)						
Labsource	9.4 ± 0.5	2.9 ± 0.3	26.0 ± 1.3	4.9 ± 0.5	50.2 ± 2.5	7.2 ± 0.7
Random model	10.7 ± 1.2	3.0 ± 0.3	32.7 ± 1.2	6.0 ± 0.3	56.0 ± 1.2	9.0 ± 0.3

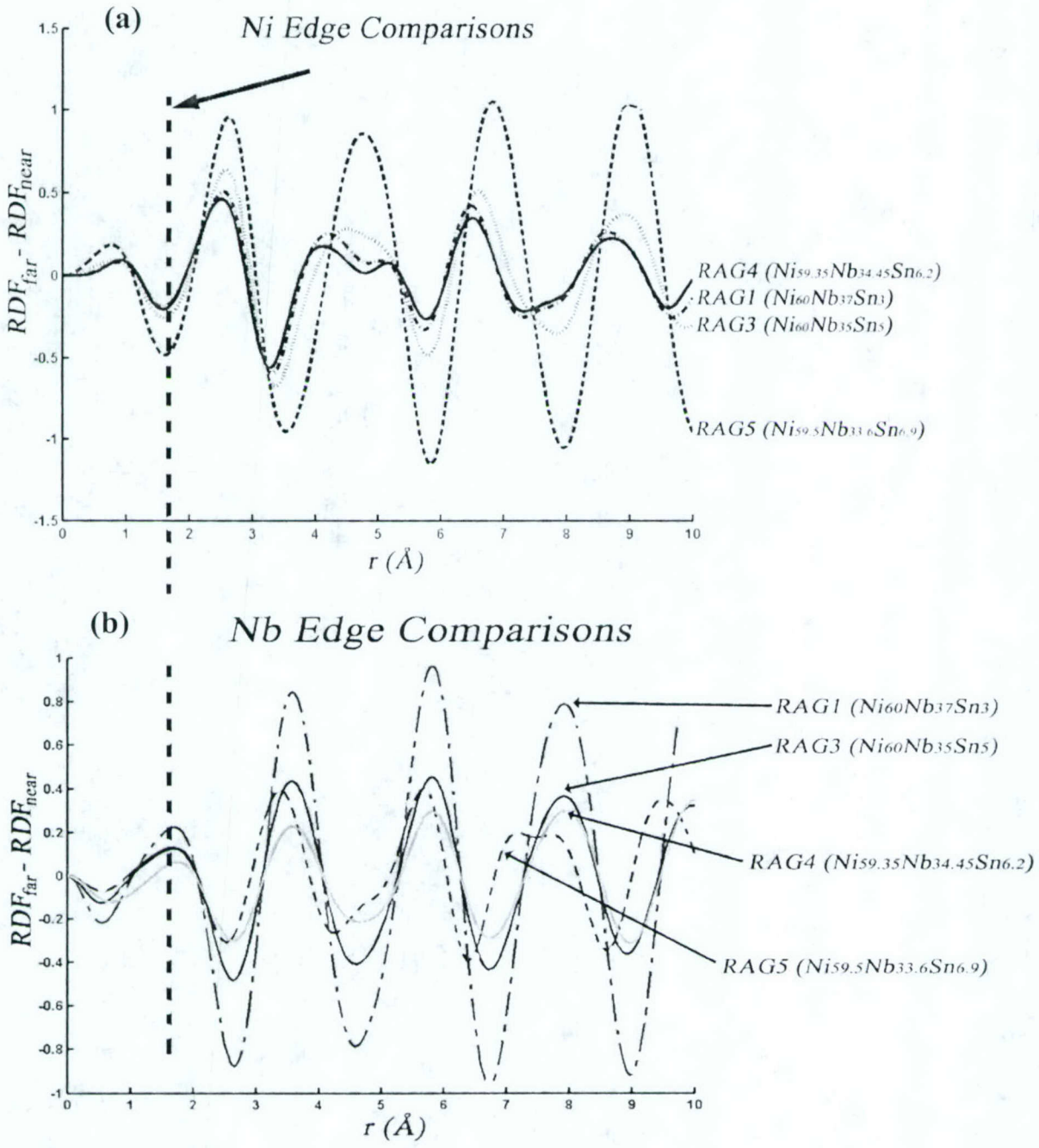

Figure 3: RDF Differences (defined as RDF_{far}-RDF_{near}) at Ni edge and Nb Edge for All RAG Compositions. Dotted line illustrates a qualitative increase in Nb bonding with a decrease in Ni bonding.

Utilization of the tunability of the energy of a synchrotron source allows one to choose wavelengths near edge energy of a component, such that a difference in scattering intensity related specifically to that component is maximized. This is possible because of the sharp slope of the f' and f'' anomalous dispersion corrections to the atomic scattering factor at an absorption

edge, and is reflected as a difference in the RDFs at energies 5eV and 100eV from the edge. Figure 3 shows these results for both Ni (a) and Nb (b) for all RAG compositions.[4]

The non-zero data in these figures indicate a definite Ni-based and Nb-based non-random order associated with these materials. Further, the tendency to form Ni_3Sn (as was described in the Thermal Stability section) is confirmed in the Ni-edge results by the increase in "non-randomness" as the Sn content is increased from RAG1 to RAG5, due to the increase in availability of Sn to form this intermetallic. This is concurrently confirmed by a similar *decrease* in "non-randomness" with Sn content in the Nb-edge results. Additionally, one notes the qualitative increase in Ni-associated bonding with a decrease in Nb-associated bonding, and vice-versa.

The use of Anomalous Scattering for this particular study is significant in that it is the first to uniquely describe > 90 % of the local structure of a *bulk* material. (Ni and Nb components make up 93-97% of the composition of the samples studied.) In-depth knowledge of the short and intermediate-range order of these materials can give clues as how to best create fully randomly oriented bulk glasses.

Conclusions

Several different characterization methods have confirmed a heterogeneous dispersion of 1-2% nanocrystallites within a mostly amorphous matrix for Ni-Nb-Sn ternary RAG samples. Conversely, the addition of a fourth component, Ta, resulted in samples with up to 40% crystallinity, thus limiting the quaternary Ni-Nb-Ta-Sn quaternary series for use as fully amorphous alloys.

Additionally, while these ternary RAG samples showed a higher Tg as compared to a well-characterized Vitreloy-106, (600 °C for Ni-Nb-Sn ternaries vs. 400 °C for Vitreloy-106), the crystallization and melting sequence above Tg was much more complex. A further complication was the propensity for *local* crystallization of these materials at reduced temperatures (T/Tg) of 0.84.

The quantitative nature of the *in-situ* x-ray scans allowed an Arrhenius analysis that proved the diffusion-related growth (or reduction) in Ni_3Sn and Nb_2O_5 phases, with activation energies of ~ 1.6 and 1.2 ± 0.2 eV/atom, respectively.

Finally, the inadequacy of the hard-sphere model to describe the average atomic structures of these materials is explained by the anomalous scattering results. It is apparent that some Ni and/or Nb associated clustering defines an intermediate range order that is inconsistent with an assumption of random distribution of component pairs (Ni-Ni, Ni-Nb, Ni-Sn, Nb-Nb, Nb-Sn, and Sn-Sn). This further explains the tendency to form Ni_3Sn as a residual in the bulk samples, and the local instabilities at temperatures below the Tg even in RAG 3, an alloy with no apparent residual nanocrystallite phase in the as-received form.

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Appendixes
None

Task B: Mechanical Testing and Evaluation

B1: Studies of Dynamic Deformation, and Constitutive Laws
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Dr. J. Lu (Graduate Student; PhD, 2002)
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Statement of the problem studied
Our task was to develop novel techniques for investigation of mechanical behavior, and to develop an analytical model to optimize bmg composite properties with respect to reinforcement volume fraction and geometry. Mechanical behaviors include dynamic indentation, strain rate and pressure sensitivity, and response of amorphous alloys and composites under pure shear loading.

Patents, Presentations and Publications
Patents
None

Presentations
None reported

Publications
S. Zhuang, J. Lu and G. Ravichandran, "Shock Wave Response of a Zirconium-Based Bulk Metallic Glass and its Composite", Applied Physics Letters,Vol.80(24), 4522-4524, (2002).

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J. Lu, G. Ravichandran and W. L. Johnson "Deformation Behavior of the $Zr_{41.2}$ $Ti_{13.8}Cu_{12.5}$ $Ni_{10}Be_{22.5}$ Bulk Metallic Glass over a Wide Range of Strain-rates and Temperatures,", *Acta Materialia*, in review (2002).

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J. Lu, S. Suresh and G. Ravichandran "Dynamic indentation for determining the strain Rate sensitivity of metals,", *Journal of the Mechanics and Physics of Solids*, 51, 1923-1938 (2003)

Summary

Developed novel techniques for investigation of mechanical behavior including the dynamic indentation technique;

Established systematic methodology for extracting rate sensitivity and pressure sensitivity of materials including structural amorphous alloys over a wide range of strain rates;

Developed a technique for studying the response of structural amorphous alloys and composites under predominantly shear conditions using a shear compression specimen;

Developing analytical model for optimal size and volume fraction of ductile phase for maximizing toughening in ductile amorphous alloy composites.

B3: Fatigue, Environmental Effects, Nano-indentation, Serrated Flow, and Deformation

Participants

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Ms. Wendelin J. Wright, Graduate Research Assistant, Ph.D. Candidate (with primary support from the DARPA contract) Graduated 2003
Mr. Feng Gang, Graduate Research Assistant, Ph.D. Candidate
(with primary support from a Stanford Graduate Fellowship)

Statement of the problem studied

The Nix research group at Stanford studied mechanics of bulk metallic glasses, focusing on four topics: plasticity of metallic glass rods subjected to combined tension-torsion, theroretical estimates of void nucleation in shear bands, nanoindentation of bulk metallic glasses, shear bands and cracking of metallic glass plates in bending

Patents, Presentations and Publications

Patents

None

Presentations

None Reported

Publications

W.J. Wright, "Shear Band Processes in Bulk Metallic Glasses," *Ph.D. Dissertation*, Stanford University (2003).

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Summary

Theroretical Estimates of Void Nucleation in Shear Bands

We have investigated the possibility of void nucleation from the coalescence of excess free volume generated in shear bands during deformation of the $Zr_{41.2}$ $Ti_{13.8}$ $Cu_{12.5}$ $Ni_{10.0}$ $Be_{22.5}$ bulk metallic glass. This is an important question as it may help to explain why shear band activity in tension leads immediately to fracture while shear band activity in compression does not cause immediate failure. We have argued that excess free volume in a shear band results in excess free energy relative to a relaxed glass with less free volume. To calculate the free energy of the material in a shear band with excess free volume, we model it as having the same structure as a glass solidified at an elevated glass transition temperature, which we call the fictive temperature. This excess free energy can be correlated with a free volume chemical potential that provides a driving force for void nucleation. The results of this modeling indicate that any free volume generated in the shear band during deformation is unstable, with the consequence that voids are predicted to form spontaneously from the coalescence of free volume. These voids are then expected to coarsen. Under tension, void growth and linkage would be facilitated by a tensile stress state, perhaps leading to premature fracture, whereas a compressive stress state would hinder void growth. This may explain the common observation that failure under uniaxial tension occurs as the result of the propagation of a single shear band, whereas multiple shear bands can form under uniaxial compression without causing failure.

The analysis we have done indicates that the material within the shear band is extremely unstable with respect to the formation of voids. Indeed, the shear band, like the glass matrix itself is unstable with respect to a denser state. Given the large thermodynamic driving force for densification, or free volume elimination, it is reasonable to ask why the material in the shear band does not simply densify uniformly rather than form voids. We believe the answer lies in the kinetics of the void nucleation and in the mechanical constraint on the shear band by the surrounding matrix. We know from our previous studies that the material in the shear band is heated during its operation. We believe that the shear band heating increases the kinetics of densification and causes voids to form. Because the shear band is bonded on either side by the rigid glass matrix, the thin layer of material within the shear band is not free to densify in an isotropic manner. The in-plane tension stresses that develop as the shear band starts to densify restrains isotropic densification and forces void nucleation to occur.

Nanoindentation of Bulk Metallic Glasses

Recent reports have indicated that shear bands can be activated during nanoindentation. This is suggested by discrete displacement bursts in the course of nanoindentation and, to a lesser degree, by shear offsets in the field of the indentation. We have recently conducted constant strain rate indentation experiments on the Zr-based glass, with strain rates ranging over four orders of magnitude, from 0.002 to 20 s^{-1}. These experiments are conducted by holding the ratio of the indentation loading rate to the indentation load constant with increasing depth of indentation. This causes the characteristic strain rate for indentation to be constant. We find that the hardness is almost independent of strain rate over this range of strain rates. However, the discrete displacement bursts evident on the loading curves are much more prominent at the lowest strain rate and are suppressed at the highest strain rate. Fast data acquisition experiments permits a direct measurement of the time duration of each displacement burst, presumably the time needed for one shear band to operate. The suppression of discrete displacement bursts at

the highest strain rates is thought to be caused by the overlapping of shear band events in the fast indentation process. Our results also indicate that strain bursts are suppressed by hydrogen charging, suggesting that hydrogen may be removing some of the free volume from the glass.

Shear Bands and Cracking of Metallic Glass Plates in Bending

It is commonly observed that thin ribbons or wires of amorphous metals can be bent plastically without breaking, while thick plates of the same materials fracture almost immediately on bending. By contrast, thick plates fail on bending even though their surfaces appear to be initially crack-free. These results show that plasticity of metallic glasses, when deformed in bending, depends on sample size. Indeed, Conner and Johnson have shown that the plastic strain to fracture for metallic glass wires increases with decreasing wire diameter. By bending wires of different diameters around mandrels of different radii and noting the surface strain at which failure occurs, they showed that the strain to fracture increases markedly as the wire diameter drops below about 1 mm.

The observation that thin wires of metallic glasses can be bent plastically while thick plates, without surface cracks, cannot, is not expected for elastic, perfectly-plastic materials subjected to bending, as this mode of deformation, unlike tension, is inherently stable. Thus, metallic glasses, with compressive deformation properties showing elastic, perfectly-plastic behavior, might be expected to deform stably in bending, regardless of the plate thickness. Yet thick plates of metallic glasses invariably fracture in bending while thin ribbons deform extensively. Conner and Johnson also noted that the shear band spacing on the surface of the bent wires scales linearly with the wire diameter. This, too, is an important sample size effect which, we believe, leads to the strong effect of sample size on bend ductility.

We have studied the thickness dependence of yielding and fracture of metallic glass plates subjected to bending in terms of the shear band processes responsible for these properties. We argue that the shear band spacing (and length) scales with the thickness of the plate deformed in bending because of strain relaxation in the vicinity of the shear band at the surface. This is consistent with recent measurement of shear band spacing vs. sample size. We also argue that the shear displacements in the shear band also scale with the shear band length and plate thickness, thus causing cracks to be initiated in thicker plates at smaller bending strains. This leads to fracture bending strains that decrease markedly with increasing plate thickness, consistent with recent experiments. These results suggest that amorphous metals in the form of foams might have superior ductility and toughness.

Plasticity of Metallic Glass Rods Subjected to Combined Tension-Torsion

The major mechanical shortcoming of metallic glasses is their limited ductility at room temperature. Monolithic metallic glasses sustain only a few percent plastic strain when subjected to uniaxial compression and essentially no plastic strain under tension. Here we describe a room temperature deformation process that may have the potential to overcome the limited ductility of monolithic metallic glasses and achieve large plastic strains. By subjecting a metallic glass sample to cyclic torsion, the glass is brought to the yield surface; the superposition of a small uniaxial stress (much smaller than the yield stress) should then produce increments in plastic strain along the tensile axis. This accumulation of strain during cyclic loading, commonly known

as ratcheting, has been extensively investigated in stainless and carbon steel alloys, but has not been previously studied in metallic glasses. We have successfully demonstrated the application of this ratcheting technique of cyclic torsion with superimposed tension for polycrystalline Ti–6Al–4V. Our stability analyses indicate that the plastic deformation of materials exhibiting elastic–perfectly plastic constitutive behavior such as metallic glasses should be stable under cyclic torsion, however, results obtained thus far are inconclusive.

Participants

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Statement of the problem studied

Fatigue and fracture behavior of bulk metallic glass alloys and their composites.

Patents, Presentations and Publications

Patents

None

Presentations

K. M. Flores, D. Suh, R. Howell, P. Asoka-Kumar, P.A. Sterne, and R. H. Dauskardt, "Flow and Fracture of Bulk Metallic Glass Alloys and Their Composites," in Supercooled Liquid, Bulk Glassy, and Nanocrystalline States of Alloys, Proceedings of the Fall MRS Meeting, Boston, v. 644, pp. L.9.5.1 – L.9.5.6, 2000.

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Summary

Not Provided

B4: Multi-axial Loading Effects, Yield Criteria, and Crack Propagation

Participants

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Statement of the problem studied

1. Determine Effects of Systematic Changes in Stress State on Flow and Fracture of BMG/BMG Composites
   - Utilize High Pressure Testing Facilities to Determine Pressure Sensitivity of Flow and Fracture
   - Conduct Mixed Mode Fracture Experiments
   - Model the Flow and Fracture Behavior

2. Determine Mechanisms Controlling Fracture Toughness in BMG/BMG Composites
   - Investigate Effects of Changes in Notch Radius on Toughness
   - Investigate Effects of Mixed Mode Loading on Toughness
   - Investigate Effects of Changes in Free Volume/Annealing on Flow/Fracture

3. Evaluate Fatigue Crack Growth Behavior of BMG/BMG Composites

Patents, Presentations and Publications

Patents
None

Presentations
**"Fracture of Bulk Metallic Glass", J.J. Lewandowski, WPAFB, Dayton, OH, July 15, 1998.

"Effects of Annealing Treatment on the Mechanical Behavior of Bulk Zr-Ti-Ni-Cu-Be", P. Lowhaphandu, L. Ludrosky, and J.J. Lewandowski, TMS-ASM Fall Meeting, Rosemont, IL October 12, 1998.

** "Fracture and Fatigue of Bulk Metallic Glass", J.J. Lewandowski, Howmet Technical Center, Whitehall, MI, March 31, 1999.

** "Fracture and Fatigue of Bulk Metallic Glass", P. Lowhaphandu and J.J. Lewandowski, IUMRS-ICAM '99, Beijing, China, June 17, 1999.

** "Fracture and Fatigue of Bulk Metallic Glass", J.J. Lewandowski and P. Lowhaphandu, Workshop on Bulk Metallic Glass, Beijing, China, June 18, 1999.

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"Effects of Stress Triaxiality on Flow and Fracture of a Zr-Ti-Ni-Cu-Be Bulk Amorphous Alloy", P. Lowhaphandu, L.A. Ludrosky, and J.J. Lewandowski, TMS-AIME Fall Meeting,

Cincinnati, OH, November 3, 1999.

** "High Pressure Effects on Flow and Fracture", J.J. Lewandowski, NASA Glenn Research Center, Cleveland, OH, November 8, 1999.

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**"Pressure and Stress State Effects on Flow and Fracture of Inorganic Materials", J.J. Lewandowski, International Conference on the Fundamentals of Fracture 6 – ICFF-6, Cirencester, UK, March 29, 2001.

**"Pressure and Stress State Effects on Flow and Fracture of Inorganic Materials", J.J. Lewandowski, Dept. of Chemical and Materials Engineering, Arizona State University, Tempe, AZ, April 6, 2001.

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**"Processing of Bulk Metallic Glass", J.J. Lewandowski, WPAFB Workshop on Amorphous Metals, Dayton, OH, December 11, 2001.

**"Effects of Multiaxial Stresses on Flow and Fracture of Bulk Metallic Glass", J.J. Lewandowski, DARPA/California Institute of Technology Workshop on Structural Amorphous Metals, Pasadena, CA, January 10, 2002.

"Effects of Stress State on Shear Banding", J.J. Lewandowski and P. Lowhaphandu, TMS Annual Meeting, Seattle, WA, February 19, 2002.

"Fracture and Fatigue of Bulk Metalllic Glass Composite Materials", J.J. Lewandowski, S. Solv'yev, and P. Lowhaphandu, TMS Annual Meeting, Seattle, WA, February 21, 2002.

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**" Stress State and Temperature Effects on Flow/Fracture of Amorphous Metals – Relevance to Deformation Processing", J.J. Lewandowski, Engineering Foundation Conference on Bulk Metallic Glasses II, Keelung, Taiwan, March 25, 2002.

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**"Flow and Fracture of Bulk Metallic Glasses", J.J. Lewandowski, National Taiwan University – Dept. Materials Science and Engineering, Taipei, Taiwan, March 28, 2002.

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**"Fracture and Fatigue of Bulk Glasses", JJ Lewandowski, California Institute of Technology, Pasadena, CA, January 9, 2003.

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**Effects of Interfaces on Systems Containing Amorphous Metals", JJ Lewandowski, ONR Steels Review, St. Michael, MD, April 11, 2003.

**'Amorphous Metals-Properties and Performance", JJ Lewandowski, Lawrence Livermore Nat'l Lab, Livermore, CA, April 30, 2003.

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"Mechanical Behavior of BMG/BCC Metal Composites", P Wesseling, AK Thurston, P Lowhaphandu, and JJ Lewandowski, TMS Fall Meeting, New Orleans, LA, September 28, 2004.

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Task C: Computation and Modeling

C1: Molecular Dynamics Simulations

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Dr. Hyon-Jee Lee, Graduate Research Assistant, *Caltech* (Graduated 2003)
Mr. Peng Xu, Graduate Research Assistant, *Caltech*

Statement of the problem studied

To develop and apply first principles based predictive modeling and simulation approaches to design amorphous metals with desired properties. We use a multiscale hierarchical approach which start from quantum mechanics level and based on these results develop successively coarser models with increasing length and time scales of the models studied.

Patents, Presentations and Publications

Patents

None

Presentations

None provided

Publications

H-J. Lee, T.Cagin, W. A. Goddard, III, and W. L. Johnson, "Molecular Dynamics Simulations of Glass Formation and Crystallization in Binary liquid Metals, *J. Metastable and Nanocrystalline Materials,* **15-16**, 181-186 (2003)

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H-J Lee, A Strachan, T Cagin, W. A. Goddard III and W. L. Johnson, Crack propagation in metallic nano-slabs: Molecular dynamics study (Mod. Sim. Mat. Sci. Eng. to be submitted.)

Peng Xu, T. Cagin, W. A. Goddard, III, Pressure dependence of viscosity of Liquid metals from NEMD, to be submitted

Summary

One of the principal tasks of the DARPA SAM program is to develop and apply first principles based predictive modeling and simulation approaches to design amorphous metals with desired properties. We use a multiscale hierarchical approach which start from quantum mechanics level and based on these results develop successively coarser models with increasing length and time scales of the models studied.

1. In order to determine the correct interaction force fields for metals: Al, Zr, Ti, Cu, Ni, etc.. We have performed extensive quantum mechanical studies on pure metals and ordered inter-metallic alloys.
2. Using these first principles data we have derived Sutton-Chen (power law) and RGL (exponentials) for many body force fields for metals and alloys. The unlike interactions are explicitly determined and no combination rules are used.
3. Using these potentials we have studied the
    a. Glass forming ability
        i. Size ratio effect in binary and ternary alloys
        ii. Binding strength effect on glass forming ability
    b. Phase transformation and melting behavior of binary, ternary and quaternary systems and their phase behavior

c. We have studied structure and thermodynamics of binary and ternary systems. Here we have employed two-phase model for eenntropy contribution (S.T. Lin, M. Blanco, W. A. Goddard, III, J. Chem. Phys. 2003)

4. Non equilibrium molecular dynamics studies on pressure dependence of viscosity of metals and alloys
5. Glass Formation in VITRELOY class alloys and the structure of VIT1, VIT101, VIT106 from molecular dynamics

First Principles Many Body Force Fields For Al, Cu, Ni, Ti, Zr Alloys

The Quantum Mechanics Calculations are carried out using SeqQuest Program which is a program implements modern Density Functional Theory using gaussian basis functions. To carry out accurate QM-DFT calculations, we first developed pseudopotentials and basis sets for Al, Ni, Cu, Ti, Zr for Generalized Gradient Approximation (GGA) level of the theory.

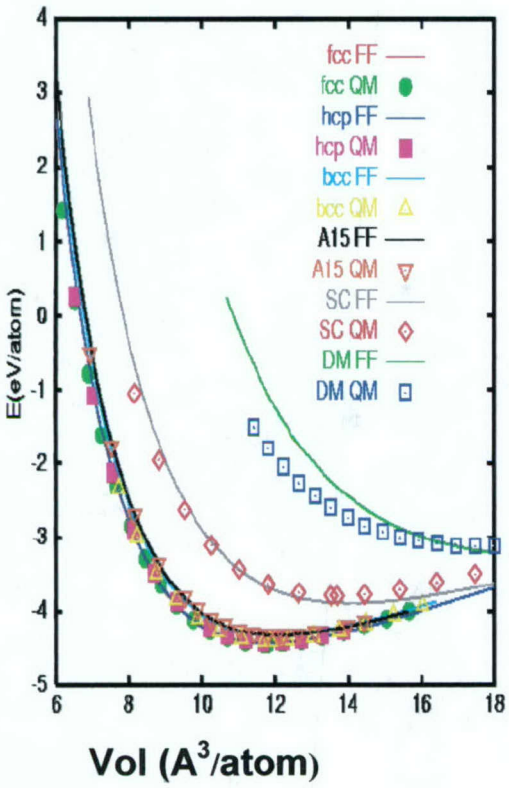
We obtained equations of states for Al, Cu, Ni, Ti and Zr, in various phases (FCC, BCC, HCP, SC, A15, Diamond) and showed good agreement with experimental results. We also studied the A1B1, A1B2, A1B3, A2B, A3B inter-metallic ordered compounds. Using the following Energy expression we have fitted the parameters to reproduce quantum results with the many body force fields.

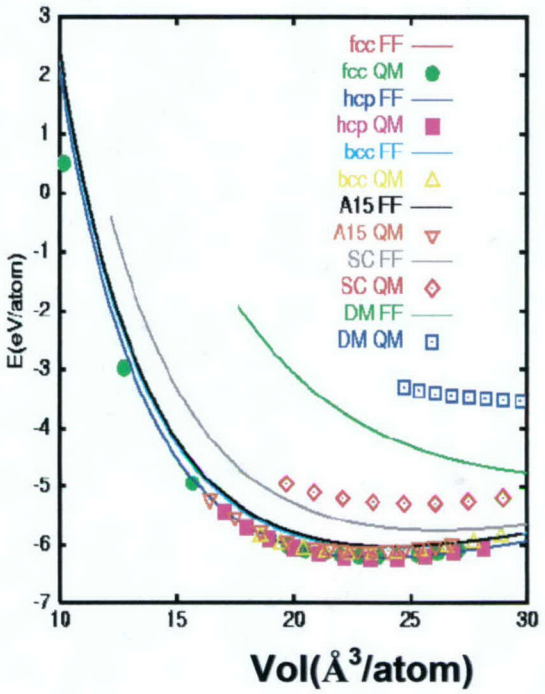
$$E = \sum_i \left\{ \sum_{j \neq i} A_{\alpha\beta} \exp\left[- p_{\alpha\beta} \left(\frac{r_{ij}}{d_{\alpha\beta}} - 1 \right) \right] - \sqrt{\sum_{j \neq i} \xi_{\alpha\beta}^2 \exp[-2q_{\alpha\beta} \left(\frac{r_{ij}}{d_{\alpha\beta}} - 1 \right)} \right\}$$

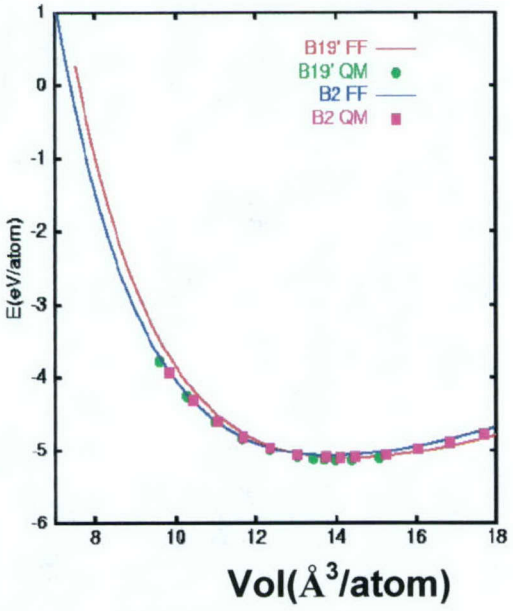
Table 1: Interaction parameters for Ni, Zr, Ti

	d(Å)	A(eV)	ξ(eV)	p	q
Ni-Ni[a]	2.5534	0.104	1.591	11.198	2.413
Ti-Ti	2.9364	0.156	1.879	9.253	2.513
Zr-Zr	3.21	0.1844	2.3365	7.9273	2.025
Ni-Ti	2.607	0.361	2.693	8.1	3.298
Ni-Zr	2.817	0.3435	2.291	8.358	1.846
Ti-Zr	3.0702	0.261	1.915	8.05	1.833

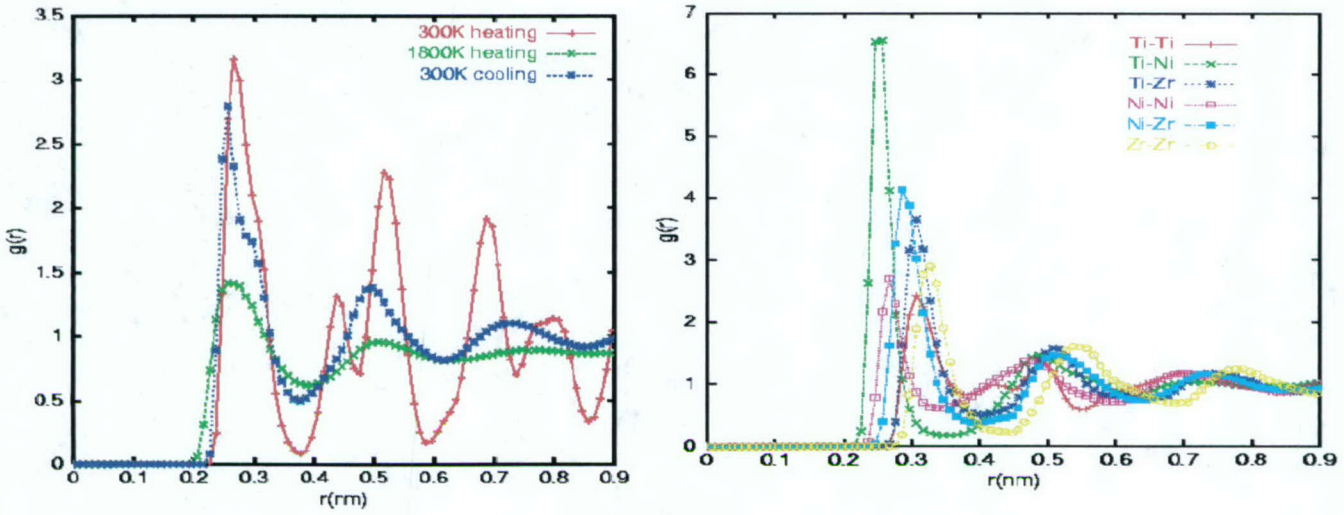
Figure 1: Equations of state for Ni, Zr and NiZr alloy.



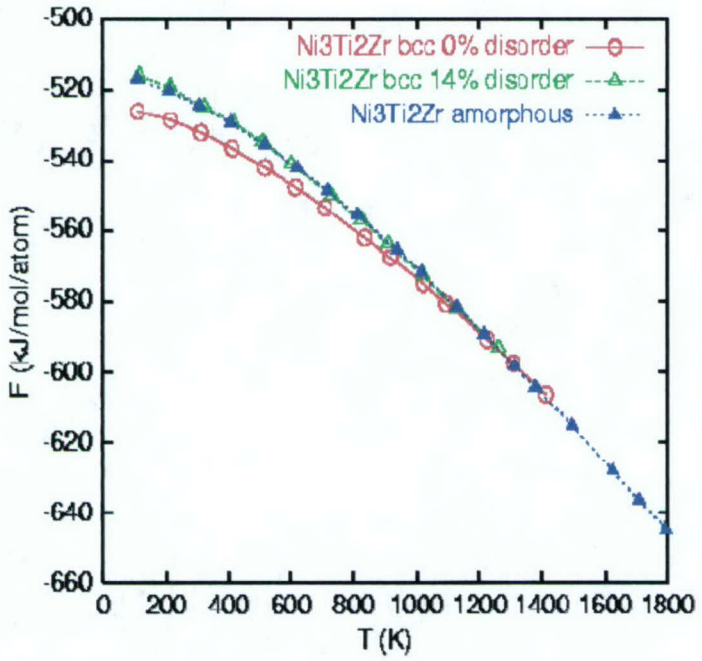




Radial Distribution Functions for Ni3Ti2Zr and Partial Pair Distribution Functions for Ni3Ti2Zr

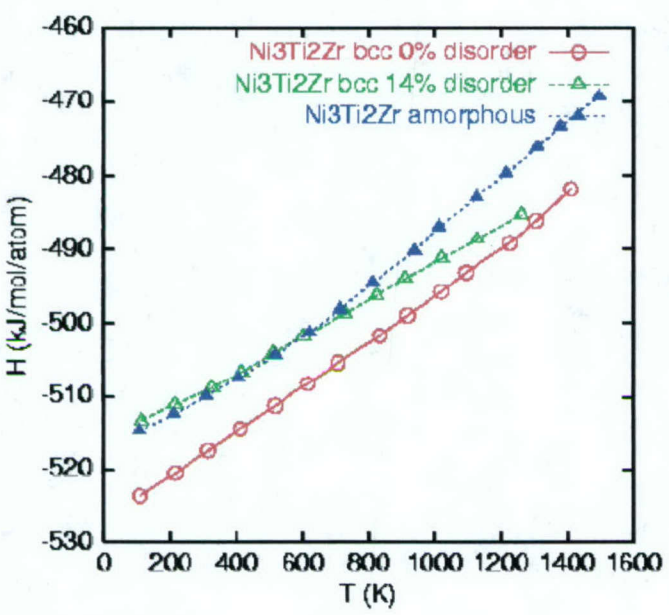


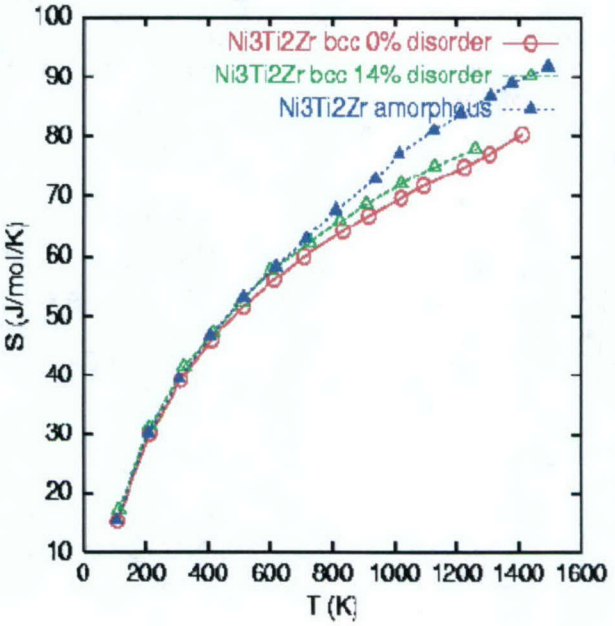
Determination of Reentrant melting point from Free Energy Calculations



For Ni_3Ti_2Zr bcc structure: the melting temperature is about 1300K; With 14% disorder in bcc structure, there are two melting points: one is the normal melting point at about 1100K, another is reentrant melting point at about 600K

Enthalpy and entropy for the Ni3Ti2Zr system





The necessary conditions for inverse melting to take place: $Gl<Gc$ since $G=H-TS$, for Gl has another crossing point with Gc, $Sl< Sc$, So $Hl<Hc$. In conclusion, only the meta-stable crystalline structure can have reentrant melting behavior.

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C2: Atomic and Mesoscopic Modeling of Shear Localization in Metallic Glasses

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Statement of the problem studied

Molecular dynamics of metallic glass alloys to simulate shear band formation, propagation and surface effects.

Patents, Presentations and Publications

Patents

None

Presentations

Mo Li, "In Search of the Nature of the Glass Transition", SE Regional APS Meeting, Charlottesville, VA, Nov. 2001

Mo Li, "Ginzburg-Landau Theory and Phase Field Modeling of Deformation and Shear Localization in Non-Crystalline Materials", 2nd United Engineering Foundation Conference in Bulk Metallic Glass, Taiwan, March 2002

Mo Li, "Mesoscopic Modeling of Fracture in Metallic Glass", TMS Annual Meeting, Seattle, WA, 2002

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G. Zheng and M. Li, "Mesoscopic Theory of Shear Localization in Metallic Glass", TMS Annual Meeting, San Francisco, Feb. 2005

Q. K. Li and M. Li, "Atomistic Modeling of Shear Band Formation in Metallic Glasses", TMS Annual Meeting, San Francisco, Feb. 2005

Publications

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X. M. Bai, *Ph.D. Thesis:* "Freezing, Melting and Nucleation: A Molecular Dynamics Study", M.S. thesis, Johns Hopkins University, 2001

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Summary

The research performed under the DARPA SAM Caltech support focuses on mechanic property modeling. Our goal is to seek the underlying atomic mechanisms of deformation in amorphous metals.

In the past four years, we have dealt with various technical issues facing modeling of deformation behaviors of metallic glasses; and at the same time sought the mechanisms at atomic and mesoscopic level. In the following, we summarize our efforts and highlights:

Mesoscopic Theory for Plastic Deformation in Metallic Glasses

A mesoscopic theory was developed early on (2001) as a part of Ph.D. thesis by G. P. Zheng (T1, and P2, P3, P16, P22). The assumptions for the theory are (a) deformation process under static and quasi-static loading conditions can be described as a non-equilibrium thermodynamic process, (2) free volume can be used as a (dis-)order parameter to determine system free energy, (3) local variation of free volumes exist and lead to different local free energy.

With those assumptions, we set up a Landau-Ginzburg theory which has the system free energy contributed from applied stress, free volume and interfacial regions between deformed and undeformed regions:

$$F[\rho,\varepsilon,T] = F_0 + F_{FreeVolume}(\rho) + F_{AppliedStress}(\varepsilon) + F_{Interface}(\nabla\rho) + F_{Coupling}(\rho,\varepsilon),$$

where ρ, ε and T are local free volume density, strain and temperature, respectively.

This formulation allows us to test the hypothesis of deformation mechanisms (yet to be discovered from or confirmed by atomistic simulations and experiments). The preliminary test was performed using phase field modeling. The results are very encouraging (Fig. 1). As more atomistic modeling results are coming out and allow us for comparison (Fig. 2). We continue to refine and check this theory. However, as shown below (Fig. 2), we believe that the theory gives an accurate description for the deformation process in amorphous metals.

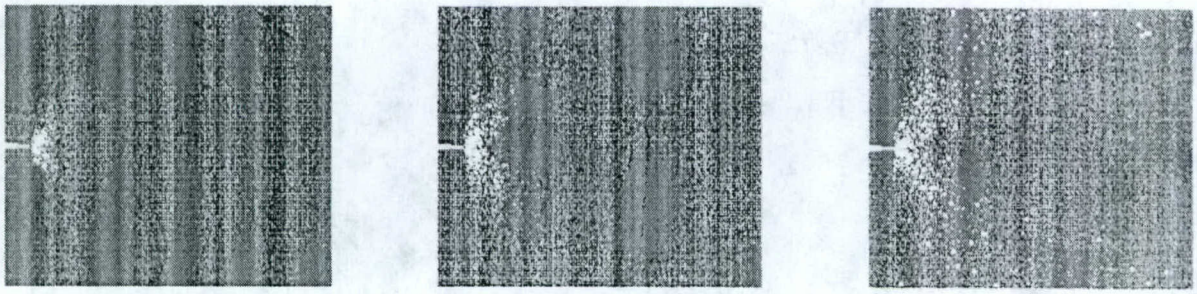
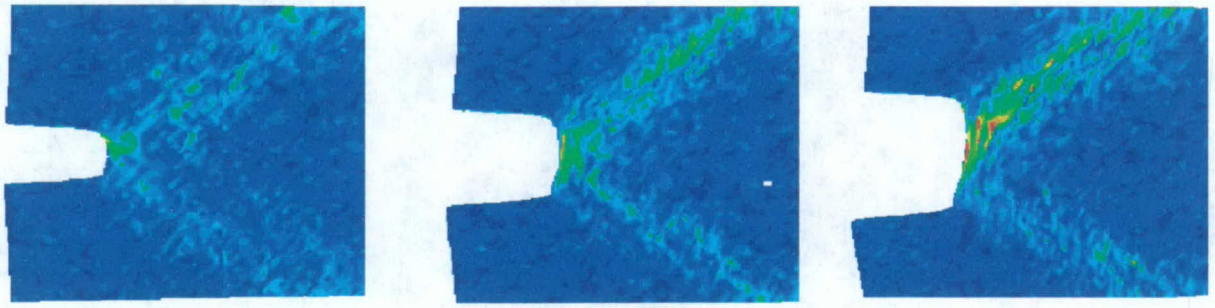


Figure 1. Local deformation and shear band formation from a sharp notch. The white areas are where free volumes form. The images are obtained using phase field modeling.



(a) *(b)* *(c)*

Figure 2. Shear band formation in front of a notch. The highlighted regions (green and read) are regions with high local strain. The dimensions along the horizontal direction is about 60 nm. The images are obtained from molecular dynamics simulation of NiZr binary alloy. (a) 10%, (b) 20% and (c) 30% overall sample strain.

Tensile Test of Metallic Glasses

Tensile tests are conducted to determine whether metallic glass is intrinsically ductile, or how the brittleness occurs. For this purpose, we conducted extensive tensile tests on various samples. In particular, we tested strain rate and surface morphology and their effects on deformation. As shown below (Fig. 3), the samples without surface notch, the amorphous metals show a remarkable elongation, a sign of incredible ductility. For samples with surface notch, the ductility disappears entirely. We also observed strain rate effects. Increasing strain rate does increase the strength of the sample, but the strain rate sensitivity is well within the known limit for metals (0.002-0.05), rather than 1 as for Newtonian liquid.

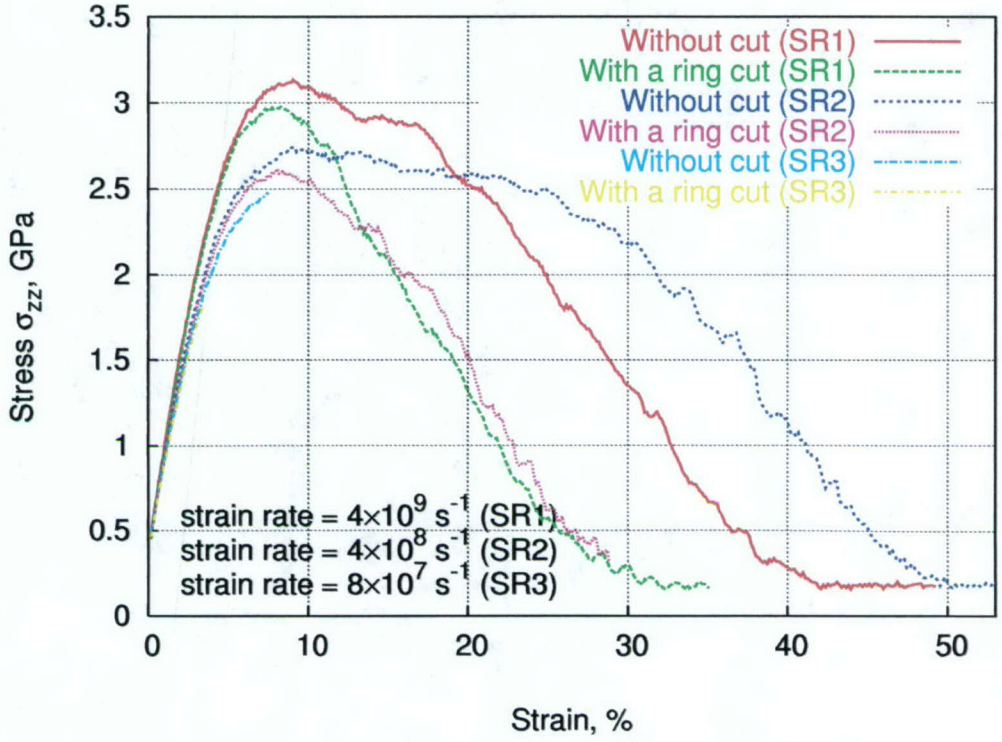


Figure 3. Stress-strain relation for a metallic glass wire made of $Ni_{40}Zr_{60}$. It is 13 nm in diameter and 43 nm in length. The sample is under tensile stress. The samples are under different strain rates. For each set of loading conditions (stress and strain rate), two types of samples are tested: one with surface notch and the other without surface notch.

Surface Effects on Deformation and Fracture

The results presented above motivated us to look into the surface properties of metallic glass (it turned out that there is almost no investigation of surfaces of metallic glasses in the past 40 years!). Using both molecular static and molecular dynamics simulations, we carried out various calculations for surface energy of ZrNi and ZrCu systems.

Our results are summarized below (Fig. 4):

(1) The surfaces of metallic glass in general have significantly low surface energy, as compared with corresponding crystalline materials.
(2) The surface energy varies slowly with overall chemical composition change (for example, Zr in ZiNi alloy from 20-60 at. %)
(3) The surface energy is affected by temperature (decrease by 10-20% at T_g)
(4) Cooling rate has a strong effect on surface energy also.
(5) Glass surface does not relax significantly. Only about the thickness of 1-2 atomic spacing expands outward and form a loosely packed amorphous surface layer.

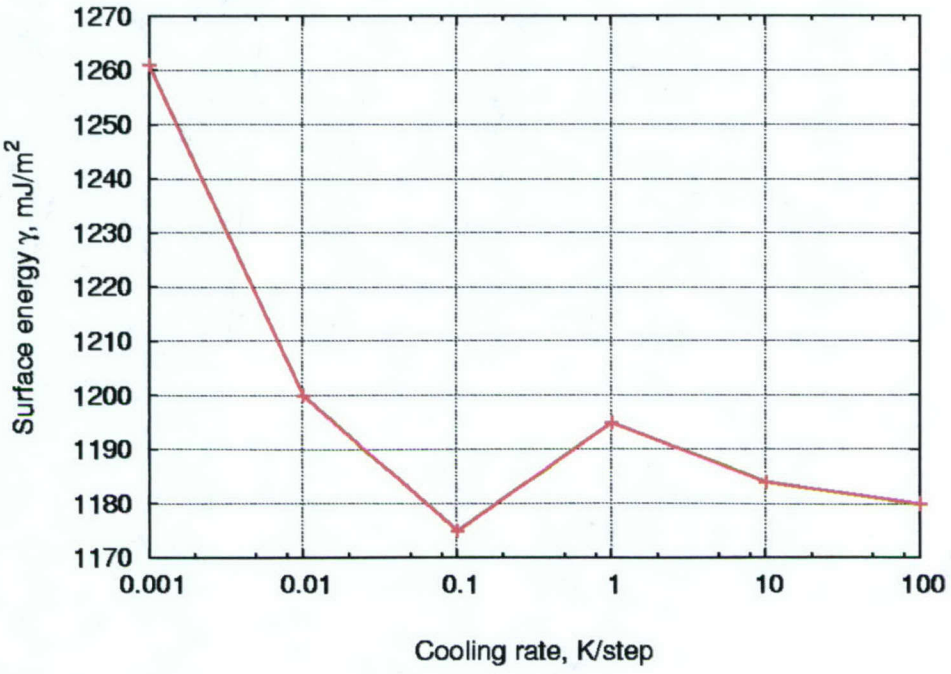


Figure 4a. Cooling rate dependence of the surface energy for $Zr_{60}Ni_{40}$ at T=300K. Surface energy for pure Ni is ~1940 mJ/m^2 and for Zr is ~ 1850 mJ/m^2.

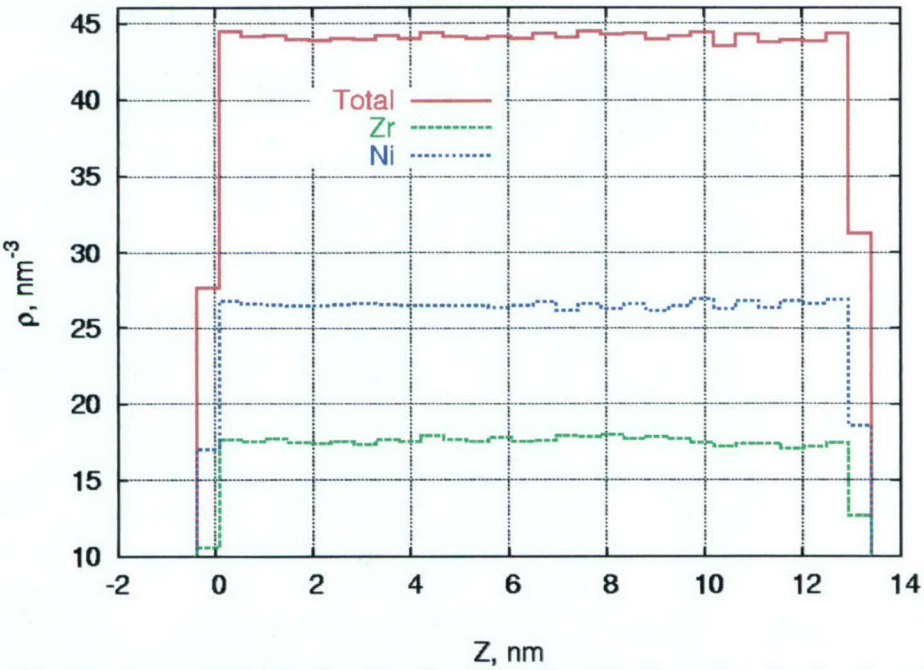


Figure 4b. Surface and bulk density for $Zr_{60}Ni_{40}$. Surface density is about 50% lower (in 2 atomic spacing). The sample is obtained with cooling rate ~0.1K/s and at T=300K

Suggestions to Experiments for Improving Surface Properties

Our results suggest that mechanical properties can be improved if surface of metallic glasses are properly treated. However, there are a series of questions need to be answered in order to have a quantitative estimate of the surface effects. One of these questions is how big the critical surface imperfection is that can initiate failure. Our preliminary results show that the critical length scale is about 1 nm.

C3: Variable Length Scale Finite Element Modeling (Prof. M. Ortiz, *Caltech*)

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Qiang Yang defended his Ph.D. dissertation on May 2004, with the title *Thermodynamical variational principles for dissipative materials with application to strain localization in bulk metallic glasses.*

Statement of the problem studied

We are concerned with the development and implementation of a continnum, finite-deformation constitutive model to describe the mechanical behavior of bulk metallic glasses for a wide range of temperatures and strain rates. One of the main objectives is that the model be suitable for finite-element computer simulation, in particular when the material is subjected to high-velocity loads, impact, strain localization, fracture and fragmentation.

Patents, Presentations and Publications

Patents

None

Presentations

Q. Yang, A. Mota, K. Weinberg and M. Ortiz. Finite-deformation Shear Band Elements for Three-dimensional Shear Band Propagation Analysis. *7th US National Congress on Computational Mechanics.* Albuquerque, NM, 2003

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Publications

Q. Yang, A. Mota and M. Ortiz. A class of variational strain-localization finite elements. *International Journal for Numerical Methods in Engineering.* In print. 2005

Q. Yang, A. Mota and M. Ortiz. A Finite-Deformation Constitutive Model for Bulk Metallic Glasses. *Computational Mechanics.* Submitted for publication, 2004

Summary

We have successfully completed the development of the constitutive model mentioned above. We can now match all experimental data and obtain strong localization in agreement with experimental observations [1]. We have also developed specialized strain-localization finite elements that match experimental data on dynamic shear band propagation [2-4]. We have integrated the metallic glass model and the strain-localization element into our ARES finite element dynamic code and validated the performance of our models by comparison of simulation results with experimental data, such as the results of bending experiments [5].

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