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### **NANOCRYSTALLIZATION DURING INDENTATION OF BULK METALLIC GLASSES AT ROOM TEMPERATURE**

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This presentation deals with recent experimental observations of the effects of micro- and nano-indentation of Zr-based bulk metallic glasses on nanocrystallization at room temperature and the use of instrumented indentation for the extraction of mechanical properties. First, direct experimental evidence is presented to show that highly confined and controlled local contact at the ultra-fine scale in the form of quasi-static nanoindentation of a bulk glassy metal alloy at room temperature can result in nanocrystallization. Atomic force microscopy and transmission electron microscopy are conducted to demonstrate that nanocrystallites nucleate in and around shear bands produced near indents, and that these nanocrystallites are the same as those formed during annealing without deformation at 783 K. By making a comparison with recent experiments in amorphous polymers, these results are reasoned to be a consequence of flow dilatation inside the bands and the attendant, radically enhanced atomic diffusional mobility inside actively deforming shear bands. Next, the deformation characteristics of Vitreloy 1 bulk metallic glass is characterized by recourse to instrumented indentation. These experiments, in conjunction with three-dimensional finite element simulations of instrumented indentation, are used to formulate an overall constitutive response. By matching the experimentally observed continuous indentation results with the finite element predictions, a Mohr-Coulomb type constitutive description for multiaxial deformation is extracted to elucidate the role of shear stresses and normal stresses in influencing the formation of shear bands around indents. Constrained deformation of the material around the indenter results in incomplete circular patterns of shear bands whose location, shape and size are also captured by the numerical simulations.

## DEFORMATION AND FRACTURE OF Zr-BASED BULK METALLIC GLASS ALLOYS

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Plastic deformation in metallic glasses occurs by the formation of intense shear bands. Recent progress elucidating the mechanisms of shear band formation and propagation will be presented. Specifically, time scales for atomic-scale structural rearrangement, the role of free volume, and the effect of local adiabatic heating and stress state, will be reviewed. Using positron annihilation spectroscopy direct evidence of free volume changes associated with plastic deformation of a zirconium based bulk metallic glass are presented. In addition, the distribution and chemical environments of free volume sites are considered. Relaxation time scales, both below and above the glass transition temperature, were studied using dynamic and transient mechanical experiments. Annealing of the glass is shown to decrease the free volume and significantly increase relaxation time scales at higher temperatures, but have little effect on secondary relaxation processes.

During fracture, voids and veined patterns on the resulting fracture surfaces also indicate the activation of flow processes and suggest that failure occurs via shear band formation and microvoid coalescence. However, in the vicinity of a crack tip, such shear bands may form stable damage zones and increase the apparent toughness to more than 80 MPa.m<sup>1/2</sup>. This has important implications for the design of bulk metallic glass matrix composites. The fracture and fatigue crack growth behavior of composites utilizing various ductile particle reinforcement phases will be described. The second phase is shown to block the propagation of shear bands and distribute plastic deformation over a larger volume.

Finally, environment plays a central role in the ability of a material to perform in structural applications. Previous evidence from metallic glasses in ribbon form suggest that they are susceptible to the deleterious effects of hydrogen embrittlement. Accordingly, the effect of hydrogen on the flow and crystallization behavior together with associated effects on fracture will be described.

## **CONTROL OF SHEAR BAND BEHAVIOR THROUGH MICROSTRUCTURAL DESIGN**

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Plastic deformation in metallic glasses is governed by the initiation and propagation of shear bands. The successful use of bulk metallic glasses in structural applications will depend on controlling these processes to improve ductility and toughness. We describe here two ways to manipulate the structure of bulk metallic glasses, and thereby influence the shear band behavior. We have found that the composition and structure of the amorphous matrix material can have a significant effect on mechanical properties. For instance, bulk amorphous Zr59-Ta5-Cu18-Ni8-Al10 shows significantly enhanced plastic strain to failure, relative to other closely related compositions. The enhanced plastic strain to failure is associated with increased structural order on the 1-2 nm length scale, which appears to promote shear band branching, which in turn suppresses crack initiation.

Another route to controlling shear band propagation is to make a composite material consisting of second phase particles or fibers in a metallic glass matrix. We have developed a series of non-beryllium-containing bulk glass-forming alloys that develop ductile micron-scale precipitates on cooling from the melt. The size and volume fraction of the particles can be controlled by controlling the cooling rate and alloy composition. The plastic strain to failure of these materials in uniaxial compression can be as large as 15%, as compared to 1-2% for a monolithic bulk metallic glass. The ductile particles appear to play two roles: They initiate new shear bands, and impede propagation of existing shear bands.

## RESEARCH ON APPLICATION PROPERTIES OF Zr-BASED BULK AMORPHOUS ALLOYS

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New technologies were invented to prepare Zr-based amorphous alloy plates and rods. By the way of sucking casting, Zr-based bulk amorphous alloy rods of 500 mm in length and 20mm in diameter were successfully produced with low purity raw materials. It can be machined and processed by super-plastic deformation. In order to apply Zr-based bulk amorphous alloy in industry, its properties are studied. It exhibits excellent mechanical properties, high wear-resistance, high corrosion-resistance, and low thermal expansion coefficient. It was found that three different stages existed on the curve of wear loss versus operating time. At the beginning, the sample was worn out at a fast rate as an unsteady stage, then it went into a steady stage with lower wearing rate, and at last the weight loss increased abruptly. The wear resistance was directly related to the microstructure of the sample. In electro-chemical corrosion experiment, it was found that anode reaction of amorphous alloys was weaker, and the alloy had a higher self-corrosive potential and a smaller self-corrosive electric current compared with crystalline state. Furthermore, oxidation behaviors at high temperature of Zr-based bulk amorphous alloy were studied. The results showed that the material exhibits excellent oxidation-resistance under the melt point and the oxidation rate increased sharply after melting. In addition, the electro-catalytic property of the material used as electrode in NaCl solution was studied. It shows that the material has excellent catalytic property in electrolytic NaCl solution in comparison with graphite material, and is suitable to be used as a negative pole in electrolytic NaCl solution.