Structure Formation in Metallic Glasses

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**Abstract.** Experimental investigations on the structural behavior of metallic glasses confirm the close relationship to the structure of the corresponding under-cooled melts. In the case of bulk metallic glasses a continuous transition from the glass to the liquid is observed starting at the glass transition temperature. In the ternary system Ni-Nb-Y decomposition of the alloy occurs already in the melt due to the immiscibility gap in the liquid state. Consequently, a heterogeneous two-phase amorphous structure can be obtained by quenching from the melt.

**Introduction**

Metallic glasses first discovered by quenching of an Au$_{80}$Si$_{20}$ melt in 1960 [1] are meanwhile industrially used e.g. as soft magnetic materials in electronics. In the last decade new bulk glasses forming metallic alloys were developed [2]. These multi-component metallic alloys can be obtained in an amorphous state at relatively low cooling rates. Furthermore, bulk metallic glasses show a glass transition at the temperature $T_g$ up to 120 K lower than the crystallization temperature $T_x$ enabling hot deformation and shaping in the deep under-cooled liquid state. The most significant property of bulk metallic glasses is their outstanding mechanical behavior, such as large elastic strain up to 2 % and high strength up to 2 GPa. Significantly improved plasticity was achieved by coupling the glassy phase with an *in-situ* formed ductile dendrite bcc phase [3, 4]. The knowledge of the microstructure is the basis for understanding the structure formation as well as the physical properties. We review our recent results on the formation and the structural properties of bulk metallic glasses.

**Structure of liquid and amorphous metallic alloys**

Metallic glasses are usually produced by rapid quenching techniques from the melt. The glassy structure is formed by freezing in the under-cooled liquid at the glass transition temperature $T_g$ as shown in Fig. 1 by the schematic temperature-time-transition diagram. In order to prevent transition from a liquid to a crystalline phase a critical cooling rate has to be exceeded. The nucleation of crystals is suppressed due to the combination of a low driving force for nucleation and a low mobility in the under-cooled melt. Good metallic glass formers have usually compositions, which are close to the deep eutectics in multi-component systems that are composed of elements with high negative heats of mixing for all possible combinations. Consequently, the elements mix homogeneously with dense packing configurations in a deep eutectic. For bulk glass forming alloys the super-cooled liquid state is stabilized which enables to investigate relationships between the liquid state and the formed glass.
Fig. 1: Schematic presentation of temperature - time - transition diagram

Fig. 2: Structure factor $S_T(q)$ of bulk metallic glass at elevated temperatures

Fig. 2 shows the thermal behavior of Zr$_{52}$Ti$_{5}$Cu$_{18}$Ni$_{15}$Al$_{10}$ bulk metallic glass by the structure factor $S_T(q)$ obtained from in situ high-temperature X-ray diffraction patterns. Due to the lack of long-range order only diffuse maxima are present in the scattering curves of the amorphous and the liquid states. The amorphous structure is preserved up to 733 K. At a temperature of $T = 753$ K the sample is partially crystallized. Above the liquidus temperature the sample melts as indicated by the diffuse diffraction patterns at high temperatures. The behavior of the height of the first maximum of the structure factor is also shown in Fig. 2. The height decreases with increasing temperature. At the caloric glass transition temperature $T_g$, the slope is altered. Extrapolating the temperature dependence of the super-cooled liquid state to higher temperatures one obtains the experimental values for the equilibrium melt. Up to the glass transition temperature the changes of the structure factor are determined by the Debye-Waller temperature factor. Above $T_g$ structural changes start to develop continuously in the liquid state with temperature. The behavior of the structure factor and the corresponding atomic pair correlation functions give evidence for melting the glass at $T_g$. [5,6].

Amorphous metallic alloys composite

Composite materials can be prepared by partly crystallization of the glass. Nanostructured states can be obtained with unique properties like the nanocrystalline soft magnets. Partly crystallization during casting of Zr- or Ti- based bulk metallic glasses were recently developed to improve mechanical properties [7]. A quite different approach is a composite material with heterogeneous amorphous structure, which is generally difficult or even not possible to obtain. Phase separation from a homogeneous amorphous state by spinodal decomposition reported in previous studies was not confirmed by recent investigations. The requirements for the formation of a two-phase amorphous alloy from the melt are high glass-forming ability of the alloy and a demixing tendency of components, which are contrary conditions to prepare a non-crystalline solid. Bulk metallic glass can be formed in the binary
Ni-Nb system by deep under-cooling of the eutectic composition. Nickel forms also an eutectic with yttrium at a similar composition. Furthermore, yttrium is immiscible with niobium. Thus, the Ni-Nb-Y system is a good candidate for a phase-separated glass. Fig. 3 shows the quasi-binary section of the calculated ternary phase diagram. The tendency of phase separation of the binary Nb-Y liquid is transmitted in the ternary Ni-Nb-Y system.

Ribbons of a Ni-Nb-Y alloys 3 mm in width and about 30 μm in thickness were prepared by means of rapid quenching from the melt using a single-roller melt-spinner under argon atmosphere. Fig. 4 shows the microstructure of the as-quenched ribbon. The TEM bright field image exhibits composition heterogeneities ranges down to the nanometer scale. The chemical composition was locally determined by EDX. A mean composition of Ni$_{53}$Nb$_{42}$Y$_{5}$ (at%) is obtained for the dark regions, and Ni$_{60}$Nb$_{10}$Y$_{30}$ for the gray matrix respectively. Electron diffraction patterns included in Fig. 4 exhibit diffuse diffraction rings confirming the amorphous structure for both regions. High-resolution TEM images also show an amorphous structure of the two different regions. The microstructure confirms that the two-phase metallic glass corresponds to the frozen in structure of the decomposed melt.

References