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NANOSTRUCTURED Zr-BASED ALLOYS-PHASE FORMATION AND MECHANICAL PROPERTIES

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Newly developed nanostructured Zr/Ti-Al-TM multiphase alloys can provide a large bandwidth of interesting properties, such as mechanical properties. Bulk materials with nanocrystalline/ amorphous and (nano)quasicrystalline/ amorphous microstructure with different volume fractions of nanophases and with different grain sizes can be obtained by slowly cooling the melt as well as by solid state reactions. Multiphase structures are realized either by partial devitrification of bulk glass-forming alloys or by defined addition of inert compounds upon alloying. Special preparation techniques e.g. copper mould casting and subsequent controlled annealing and mechanical alloying combined with hot consolidation of powders are described. The phase formation and transformation processes and the thermal stability of such materials in dependence on alloy composition and processing parameters are discussed in detail. Currently, the exploration of properties with respect to potential applications of these nanostructured alloys is still at the beginning. First investigations on the contributions of different phases/ volume fractions to the overall mechanical behaviour will be shown. At room temperature, the deformation behaviour of amorphous/crystalline bulk samples is governed by contributions of all existing phases yielding a high strength of the material.

Keywords: metallic glasses, nanoscale systems fabrication, mechanical properties, mechanical alloying
PACC: 8120Q, 8130D, 6220, 8140L

I. INTRODUCTION

Our research work is focused on the preparation of materials with multiphase microstructures in the nanoscale or – with other words – on the preparation of microstructures where preferentially nano-sized quasicrystalline or crystalline phases occur that are embedded in an amorphous matrix. From those composite structures, interesting new properties are expected as for example improved mechanical properties or increased catalytic or electrocatalytic activity. Those structurally complex materials can be produced relatively simply using newly developed bulk glass-forming alloy systems[1] as precursors which are prepared by slowly cooling a melt as well as on the basis of solid state reactions.[2] Composite structures are obtained upon partial crystallization of amorphous cast alloys or by addition of inert crystalline particles upon mechanical alloying. In this paper we present examples that are related to the preparation and property characterization of those Zr-base materials.

II. EXPERIMENTAL

Amorphous alloys have been known for several decades and have attracted great interest because their atomic configuration yields interesting physical, mechanical and chemical properties. However, firstly discovered multicomponent metal-metalloid systems or binary metallic alloys exhibited only a relatively low glass-forming ability (GFA) which is expressed in very high critical cooling rates necessary for amorphization from the melt and in only small sample thickness. In the last years, new multicomponent metallic alloys also on Zr-base[3] have been developed with critical cooling rates in the range of only 1–100K/s, which are almost comparable with those for oxide glasses. Thus, now it is possible to prepare amorphous alloys in bulk shape with up to several micrometers of thickness. Additionally, a direct correlation between a high GFA and the existence of a wide under-cooled liquid region prior to crystallization was detected. The basic principle for the development of bulk metallic glasses (BMG) is illustrated in Figure 1 in terms of a schematic time-temperature-transformation diagram (TTT) for the crystallization of undercooled liquids.[4] To increase the GFA one has to modify the alloy composition in a way, that leads among others to a frustration of the crystallization process. In the TTT-diagram this is expressed in a shift of the crystal nucleation curve ("nose") to longer times corre-

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sponding to a change in the applicable cooling process from quenching to slow cooling. On the other hand, this elongated time scale can be used after bulk glass formation for a subsequent controlled partial crystallization upon annealing at defined temperatures and times above the glass-transition.

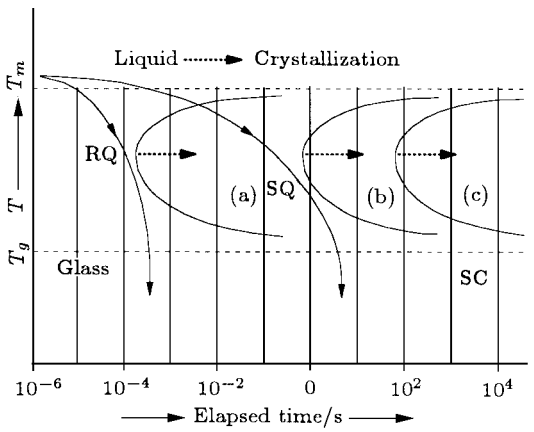


Fig.1. Schematic time-temperature-transformation diagram comparing the crystallization kinetics of rapidly quenched (RQ), slower quenched (SQ) and slowly cooled (SC) alloys[4]

Due to their low critical cooling rates, bulk glasses can be prepared relatively simply by conventional metallurgical casting processes. Preparation of Zr-based bulk samples, for example, is performed by die casting a pre-alloyed ingot into a copper mould under an argon atmosphere. This way, completely amorphous rods with up to 5mm diameter are obtained.[5] An alternative way for preparation of bulk amorphous alloys is the powder-metallurgical route. Elemental powders are milled in a planetary ball mill to obtain amorphous alloy powders. From DSC (DSC – Differential Scanning Calorimetry) scans the undercooled liquid region is determined which is restricted by the glass transition temperature T_g and the crystallization temperature T_x. In a next step the alloyed powder is hot pressed at temperatures above T_g by utilising the large viscous flow of the undercooled liquid. Under proper conditions compacted amorphous bulk samples with several millimeters diameter are obtained which can be also further deformed, as for example by hot extrusion.[6]

III. RESULTS AND DISCUSSION

A. Preparation of glass-matrix composites by alloying and annealing

One way to form nanocrystalline precipitates in a glassy matrix is a carefully controlled annealing process of fully glassy alloy samples in the temperature region of the undercooled liquid, i.e. above the glass transition temperature.[7] A characteristic DSC trace obtained on an as-cast amorphous $Zr_{55}Al_{10}Cu_{30}Ni_5$ alloy sample (Figure 2) shows an endothermic transition corresponding to the glass transition. Annealing at 50K below the onset of the crystallization temperature results in the formation of precipitates with up to 400nm size in a fraction of about 25 vol.% which are embedded in the amorphous matrix (Figure 3).

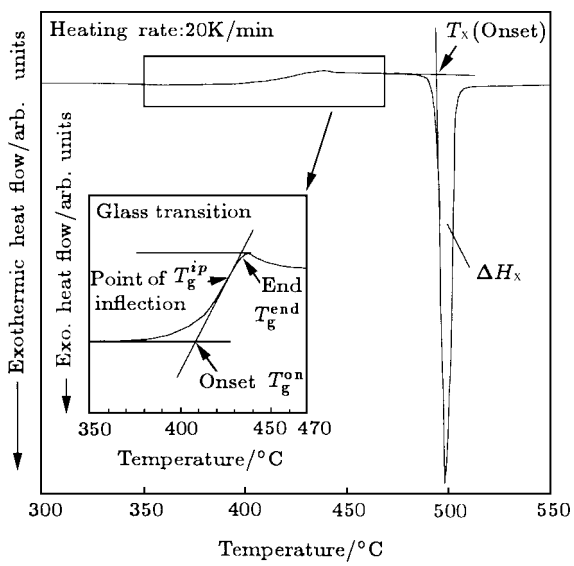


Fig.2. DSC scan of a cast bulk amorphous $Zr_{55}Al_{10}Cu_{30}Ni_5$ alloy sample

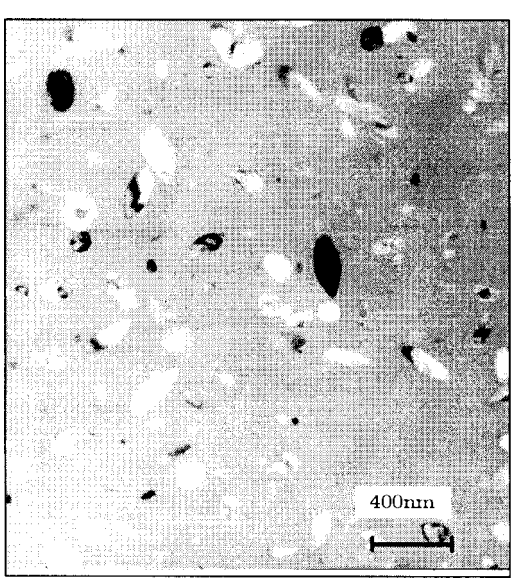


Fig.3. TEM bright field image of an annealed $Zr_{55}Al_{10}Cu_{30}Ni_5$ alloy with nano-sized precipitates

Furthermore, selective crystalline phase formation can be induced due to the presence of special additives introduced as alloying elements or as impurities upon casting or milling. As an example, for special bulk glass-forming Zr-Al-Cu-Ni alloys, oxygen was found to trigger the preferential formation of nano- and quasicrystalline metastable phases.[8] For the $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy only for cast bulk samples with oxygen contents below 0.28 at.% a fully amorphous state is obtained, whereas with rising oxygen content the formation of an increased fraction of a metastable fcc-NiZr-type phase was detected, which typically consists of single crystals of about 10 nm size. Upon casting, these fcc-nanocrystals can act as heterogeneous nuclei for further crystallization processes.[9] In turn, small traces of oxygen in the amorphous alloy can strongly affect its thermal behaviour. For the $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy a change in the crystallization sequence from a one-step to a two-step process is observed with increasing oxygen content corresponding to the primary oxygen-triggered formation of fcc-nanocrystals or quasicrystals and their subsequent transformation at elevated temperatures (Figure 4). Additionally, this results in a strong reduction of the undercooled liquid region mainly due to the decrease of the crystallization temperature.

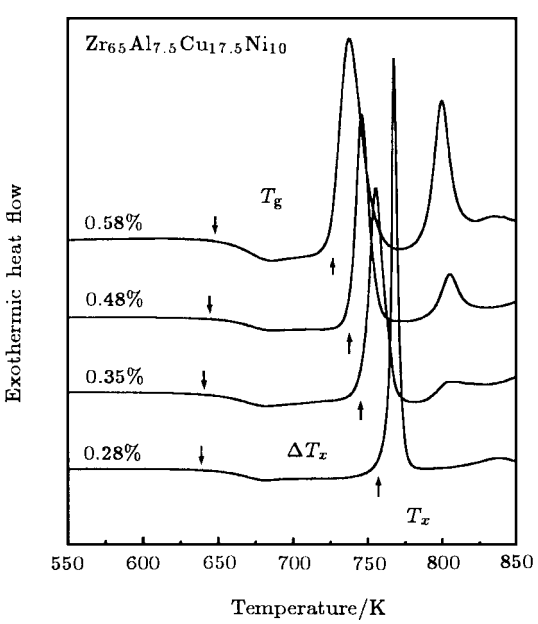


Fig.4. DSC scans of cast $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy samples with different oxygen content

Another component favouring the precipitation of nano-sized quasicrystals in a primary transformation process upon annealing of fully amorphous Zr-based alloys is titanium. Adding Ti to the quaternary Zr-Al-Cu-Ni alloy was found to improve the glass-forming ability making the casting step to get fully amorphous precursors easier. In subsequent heating experiments a change from a one-step to a two-step crystallization process with increasing titanium content is observed. It was found that the alloy with 3 at.% titanium forms in the first crystallization step up 70 vol.% of icosahedral quasicrystals with sizes of 50–70nm which are embedded in the residual amorphous matrix. Increasing the titanium content to 5 at.% leads to the formation of higher volume fraction of much smaller quasicrystals with sizes of only a few nanometers.[10]

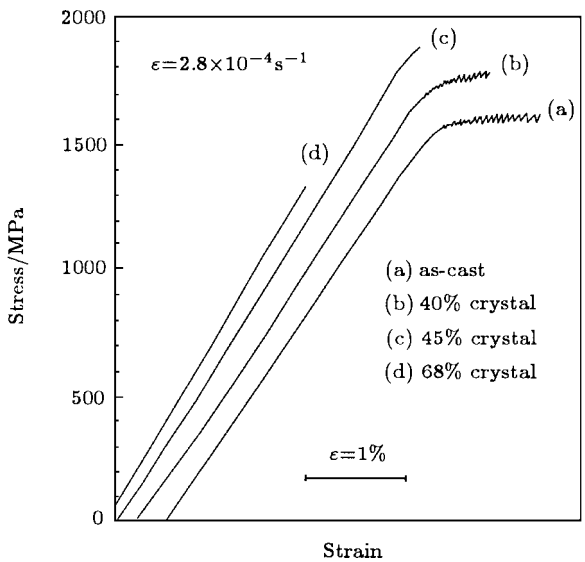


Fig.5. Room temperature deformation behaviour of as-cast bulk amorphous and partially crystallised $Zr_{57}Ti_5Al_{10}Cu_{20}Ni_8$ samples

B. Mechanical properties of cast glass-matrix composites

The modification of the microstructure of cast bulk samples by partial nanocrystallization can significantly modify their mechanical properties at room temperature. An as-cast fully amorphous bulk sample with 5 at.% Ti exhibits in compression tests a favourable combination of high strength and low Young's modulus (70GPa) corresponding to a large elastic region and also some microplasticity (Figure 5). This deformation behaviour can be ascribed to inhomogeneous flow of the material since the strain is localized in very thin shear bands. The fractured surface of such a sample shows a typical vein-like pattern.[11] Partial nanocrystallization leads to an increase in strength, but in that case also to a decrease in ductility (Figure 5). However, there are other ex-

amples showing that certain constituents, such as palladium, can improve both – strength and ductility.[12] Since the amorphous as well as the crystalline phases contribute to these mechanical properties at room temperature, the deformation mechanism for those composites, especially the effect of particle size is not yet understood in detail.

C. Glass-matrix composites by mechanical alloying with inert particles

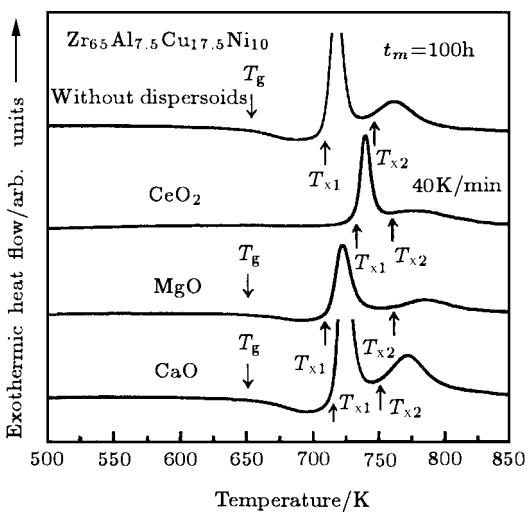


Fig.6. DSC scans of mechanically alloyed Zr-Al-Cu-Ni powders with different dispersoids (5 vol.%)

Another possibility to prepare glass-matrix composites is the defined addition of insoluble particles to the glass-forming alloy composition.[13,14] This is often restricted to the powder metallurgical route, where micrometer-sized particles, such as oxides or carbides are ball milled with the alloying powders and during the milling process the particle size is reduced to nanometer scale. In most cases, this is not applicable to casting processes where those particles can act as heterogeneous nucleation agents for crystallization during slow cooling. For certain dispersoids, such as MgO and CaO, almost no deterioration of the thermal stability was observed, whereas other compounds like CeO_2 do not act as inert particles but tend to be alloyed causing the disappearance of the supercooled liquid region (Figure 6). However, similar to partially crystallized cast bulk samples also for mechanically alloyed and compacted bulk alloy samples with nanocrystalline dispersoids a significant increase in strength was detected (Figure 7).

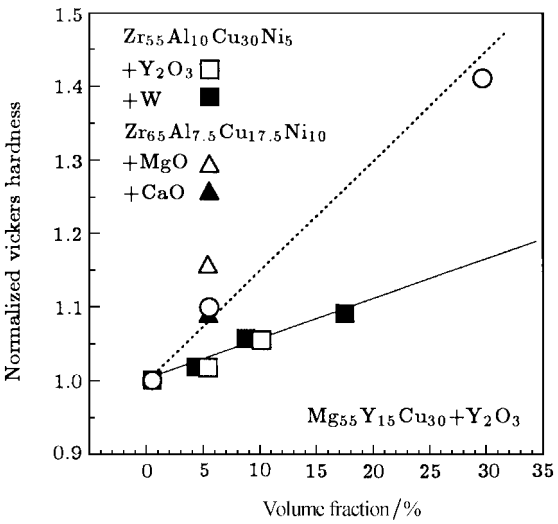


Fig.7. Vickers hardness of amorphous Zr-Al-Cu-Ni compacted powders with different dispersoids

IV. SUMMARY

Our investigations revealed that materials with a multiphase microstructure in the nanometer range prepared on the basis of bulk glass-forming alloy systems can provide a variety of new interesting mechanical properties. Currently, the complex phase formation processes to create a glass-matrix composite structure are not understood in detail, but they are of special interest also for basic research. A prospective advantage of those bulk glass-forming Zr-based alloys is the relatively simple production and further processing as compared to other ways to form bulk nanostructured metallic materials.

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