Fabrication and investigation of intermetallic compound-glassy phase composites having tensile ductility

The purpose

The purpose of the proposed study was to produce in-situ ductile crystalline intermetallic compound-glassy composite materials with high strength, good elasticity and high wear resistance by casting and ex-situ composites by partial crystallization of the glassy phase.

The tentative compositions at which B2 crystal-glassy composites can be formed are Cu-Y (starting from the deep eutectic point of $Cu_{58}Y_{42}$ towards CuY phase), Y-Cu-Ag, Cu-Y-Ag, Mg-Cu-Y (by analogy with Mg-Y-Cu BGA, MgY phase also has a cP2 B2 structure), Mg-Y-Ag (AgMg phase also has a cP2 B2 structure and is ductile) and Y-Cu-Zn and some other systems in which Y is substituted with other RE metals like Ce and Nd. Another important group are Ni-Cu-Ti-Zr alloys in which promising preliminary result were obtained is connected with cP2 TiNi phase which demonstrates martensitic transformations.

Choice of alloys and sample preparation

1. The tentative compositions at which bulk glassy phase formation and possible formation of cP2 crystal-glassy composites are Cu-Y (starting from the eutectic points of Cu-Y and Y-Cu alloys), Y-Cu-Ag, Y-Cu-Al, Cu-Y-Ag. The compositions are based on glassy phase and ductile cP2 CuY or AgY phases. These alloys were successfully prepared. Chemical compositions and phase composition of the studied alloys are listed in Table. 1.

Table. 1. Glassy-crystal composites of Cu-Y-based alloys prepared by melt spinning.

Base System	Chemical composition	Structure
$Cu_{58}Y_{42}$(Ag)	$Cu_{54.15}Y_{40.85}Ag_5$	C+A
	$Cu_{51.3}Y_{38.7}Ag_{10}$	A+mC
	$Cu_{48.5}Y_{36.5}Ag_{15}$	A+mC
$Y_{60}Cu_{40}$(Al)	$Y_{54}Cu_{36}Al_{10}$	A+mC
	$Y_{51}Cu_{34}Al_{15}$	A+mC
	$Y_{48}Cu_{32}Al_{20}$	A+C
$Y_{60}Cu_{40}$(Ag)	$Y_{54}Cu_{36}Ag_{10}$	C
	$Y_{48}Cu_{32}Ag_{20}$	C
$Cu_{58}Y_{42}$(Al)Ag,Pd	$Cu_{44.8}Y_{35.2}Al_{10}Ag_{10}$	A+mC
	$Cu_{44.8}Y_{35.2}Al_{10}Pd_{10}$	A+mC

A-amorphous, C-crystalline, mC- minor fraction of crystalline phases.

2. Mg-Cu-Y (MgY phase also has a cP2 structure), Mg-Y-Ag (AgMg phase also has a cP2 B2 structure and is ductile) and Y-Cu-Zn alloys were planned to prepare. However, there were difficulties with alloys preparation owing to large density difference between Mg on one hand and Cu and Y on another one which did not allow to make high quality samples.

3. Ni-Cu-Ti-Zr alloys containing austenitic cP2 TiNi-type phase which demonstrates martensitic transformations. The following alloys were successfully prepared: $Ni_{35}Cu_{15}Ti_{33}Zr_{17}$, $Ni_{40}Cu_{10}Ti_{35}Zr_{15}$, $Ni_{25}Cu_{25}Ti_{33}Zr_{17}$ and $Ni_{40}Cu_{10}Ti_{40}Zr_{10}$.

Experimental procedure

Ingots of the studied alloys were prepared by arc melting (induction melting in case of Mg-based alloys) of high purity (99.9 wt% purity) component mixtures under argon atmosphere. From these ingots, ribbon samples of approximately 20 µm thick and 1 mm width were prepared by melt spinning onto a single copper roller (Fig. 1). Tangential roller velocity was approximately 40 m/s. Bulk cylindrical samples of 1 and 2 mm in diameter were prepared by Cu-mould casting by which samples up to 5 mm in diameter can be cast. The structure of the ribbon samples was examined by x-ray

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14. ABSTRACT
The purpose of this research was to produce in-situ ductile crystalline intermetallic compound-glassy composite materials with high strength and good plasticity. A range of composite specimens was prepared (Cu-Y, Y-Cu-Ag, Y-Cu-Al, Cu-Y-Ag, Mg-Cu-Y, Mg-Y-Ag, Mg-Y-Zn, Ni-Cu-Ti-Zr) using casting and melt spinning techniques. Structure was examined by x-ray diffraction; phase transformations were studied by differential scanning and isothermal calorimetry. Crystal-glassy composites formed in Y-Cu-Ag, Y-Cu-Al and Cu-Y-Ag and Ni-Cu-Ti-Zr alloys whereas Mg-based alloys did not smelt well. Ribbon samples of Y-Cu-Ag, Y-Cu-Al and Cu-Y-Ag alloys showed good bending ductility while bulk Ni-Cu-Ti-Zr alloy samples of 2 mm in diameter demonstrated large plasticity owing to martensitic transformation in B2 crystalline phase and TRIP effect. Large deformations up to about 20% were achieved in Ni-Cu-Ti-Zr alloys.

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diffraction (Bruker D8 Advance with Cu Kα radiation). Phase transformations were studied by differential scanning and isothermal calorimetry (Seiko Instruments Inc. DSC 6300 Exstar).

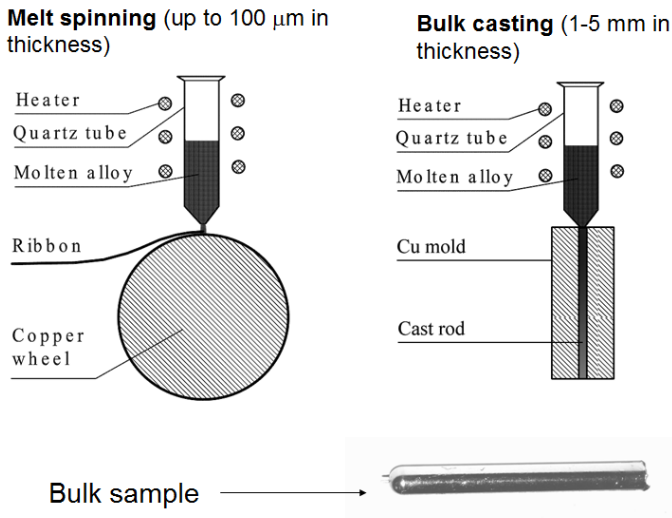

Fig. 1. Casting technique for ribbon and bulk sample preparation.

Experimental results

XRD analysis revealed that the structure of all ribbon samples prepared, except for $Cu_{54.15}Y_{40.85}Ag_5$, $Y_{54}Cu_{36}Al_{10}$ and $Y_{48}Cu_{32}Ag_{20}$ alloy was mostly amorphous but contained a fraction of a crystalline phase(s) (Fig. 2). The XRD patterns of the samples $Cu_{54.15}Y_{40.85}Ag_5$, $Cu_{51.3}Y_{38.7}Ag_{10}$, $Cu_{48.5}Y_{36.5}Ag_{15}$, $Y_{54}Cu_{36}Al_{10}$, $Y_{51}Cu_{34}Al_{15}$, $Y_{48}Cu_{32}Al_{20}$, $Cu_{44.8}Y_{35.2}Al_{10}Ag_{10}$, $Cu_{44.8}Y_{35.2}Al_{10}Pd_{10}$ clearly showed crystalline peaks and the broad peaks of amorphous phase.

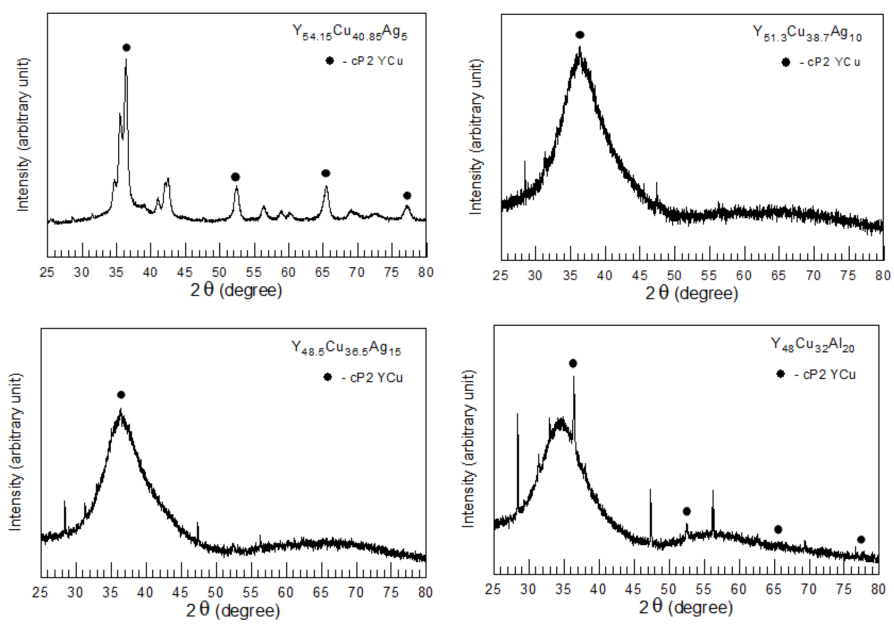

Fig. 2. XRD patterns of the glassy-crystal composites of Cu-Y-based alloy samples after melt spinning. cP2 phase peaks are marked.

DSC trace of the $Y_{51}Cu_{34}Al_{15}$ alloy is shown in Fig. 3. It is very interesting to note that even partially crystalline samples of $Y_{54}Cu_{36}Al_{10}$ and $Y_{51}Cu_{34}Al_{15}$ alloys containing glassy phase still demonstrate the glass-transition behavior and formation of a supercooled liquid prior to its crystallization.

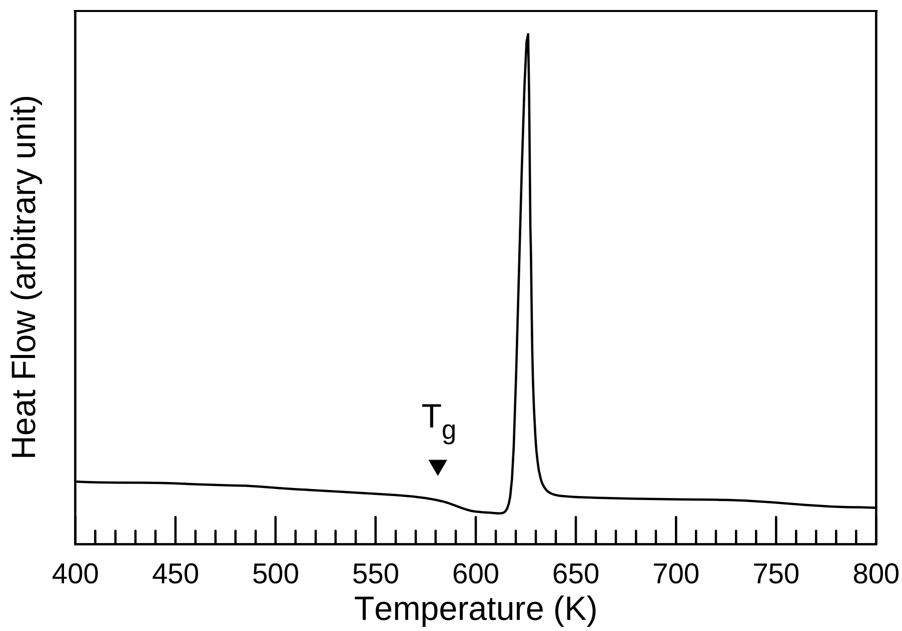

Fig. 3. DSC trace of $Y_{51}Cu_{34}Al_{15}$ alloy. Glass-transition temperature, T_g is 580 K.

Mixed components with atomic size ratios larger than 1.3 rare lead to the formation of metallic glasses even at high cooling rate [1]. Efficient atomic packing, based on atom packing in the first coordination shell of solute-centered clusters, is a fundamental consideration in the formation of metallic glasses. According to the concepts of the efficient cluster packing (ECP) model [2] specific radius ratios, defined as the radius of the solute atom divided by the radius of the solvent atom, are preferred in the constitution of metallic glasses which emphasizes the influence of topology on the formation of metallic glasses.

The glass-forming ability of several alloys in Y-Cu-Ag and Y-Cu-Al system was investigated. Despite on the large difference in atomic radii between the components in the investigated system none of the alloys was made amorphous even by melt spinning. As one can notice the difference in atomic radii between the components is very large R_Y/R_{Ag} =1.24, R_Y/R_{Al} =1.27, R_Y/R_{Cu} = 1.39 which is essential for alloys with high GFA but the studied alloys are not so stable against crystallization. Thus, for obtaining an alloy with high glass-forming ability a large difference in atomic radii between the components of the alloy is essential but not enough. This difference must have an optimal value to be able to lead to the formation of a low-temperature eutectic.

Moreover, good bending plasticity of ribbon samples was obtained. For example, one can see the lateral surface of the $Y_{54}Cu_{36}Al_{10}$ sample after deformation over 180 degrees without fracture (Fig. 4). The samples demonstrate formation of multiple shear bands on the surface as marked in Fig. 4.

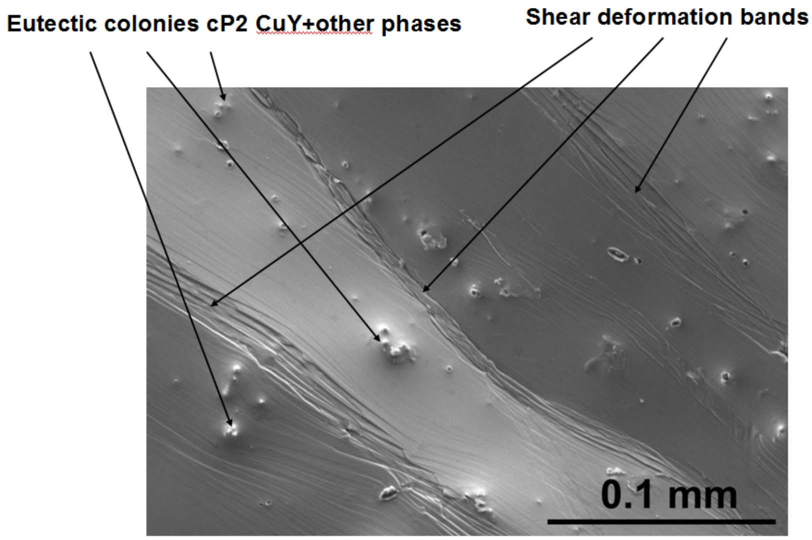

Fig. 4. Lateral surface of the $Y_{54}Cu_{36}Al_{10}$ sample after deformation over 180 degrees.

Ni-Cu-Ti-Zr alloys contain austenitic cP2 TiNi-type phase which demonstrates martensitic transformation. XRD patterns of as-cast Ni-Cu-Ti-Zr glassy-crystal composite cylindrical samples of 2 mm in diameter (cP2+glassy phase) are shown in Fig. 5.

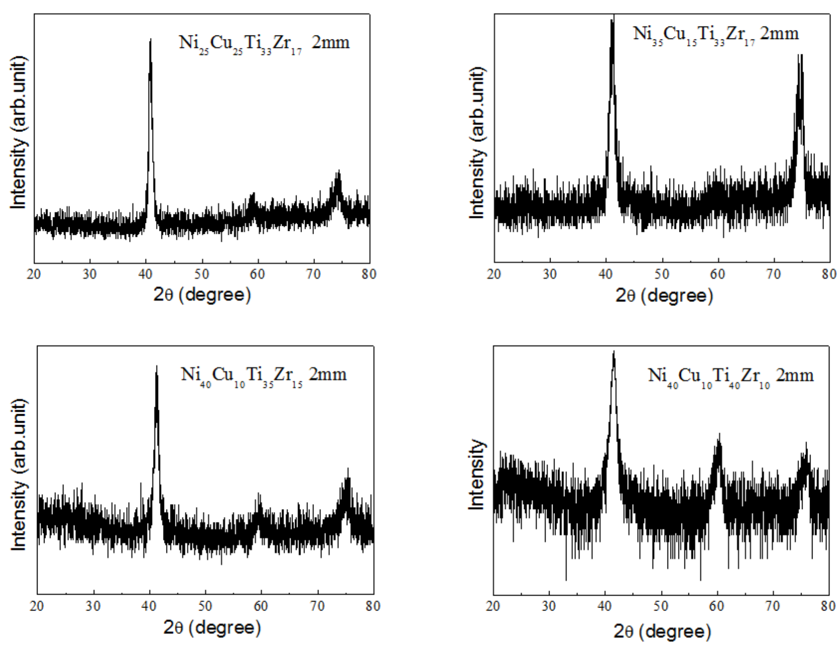

Fig. 5. XRD patterns of Ni-Cu-Ti-Zr glassy-crystal composites containing cP2 and glassy phase.

These samples exhibit transformation-induced plasticity (TRIP effect) as shown in Fig. 6. The initial elastic deformation is followed by a distinct irreversible deformation stage associated with phase-transformation-induced plasticity resulting in a sigmoidal shape of the stress-strain diagram. After plastic deformation of the samples except for $Ni_{25}Cu_{25}Ti_{33}Zr_{17}$ to about 5% the phase composition of the sample was found to be altered significantly. The mechanical behavior resembles a pseudoelastic effect, which is regularly observed in crystalline TiNi alloys. However, the sigmoidal stress-strain diagram with a plateau-like deformation strain is irreversible. Hence, the observed plateau region shortly after yielding should be attributed to transformation aided plasticity similar to TRIP effect. The apparent Young's modulus of the alloys is rather low and the yield stress (below 700 MPa) is low too, while the ultimate compressive strength is high and the total strain to break is quite considerable (~20 %). The low magnitude of the Yield stress value may correspond to the critical stress required to induce a phase transformation [3] in the metastable parent cP2 phase and the glassy matrix. Compared with many bulk glassy alloys, no serrated flow [4,5] is observed in the present material exhibiting a rather homogeneous accommodation plastic flow in the glassy phase.

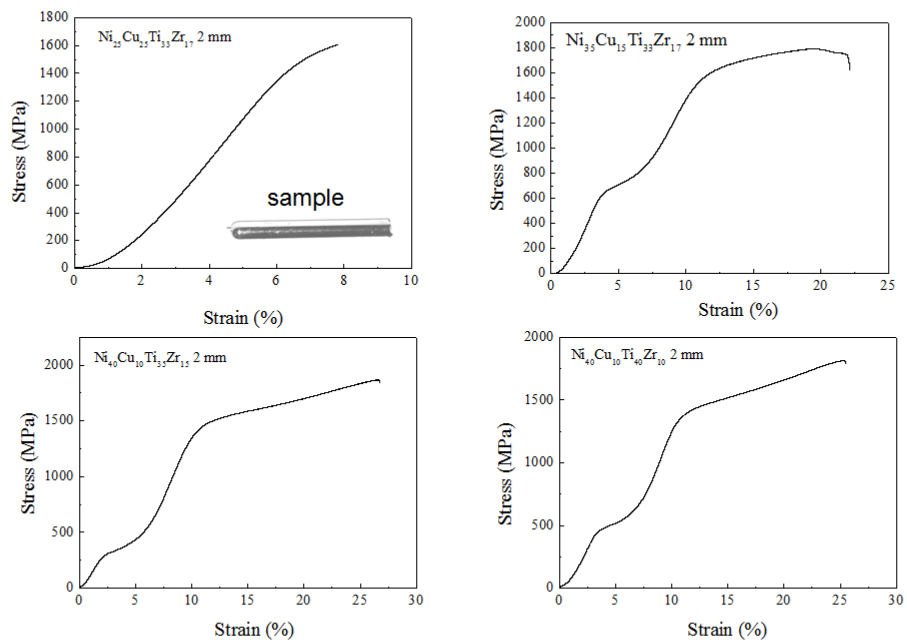

Fig. 6. Compressive mechanical properties of Ni-Cu-Ti-Zr bulk glassy-crystal composites. Modification of Yield stress takes place depending upon volume fraction of cP2 phase.

The fracture surface is shown in Fig. 7. The formation of cleavage and vein fracture patterns was found. Fracture occurred along the maximum shear stress plane inclined at about 45° to the loading axis. The vein-type fracture surface is characteristic of metallic glasses. Fine slip lines and coarse shear deformation bands are readily seen on the lateral surface of the sample deformed to fracture. One can suppose that the crystals also act as strong barriers to shear band propagation within the glassy phase, enabling multiple shear deformation and preventing the sudden brittle fracture of the sample.

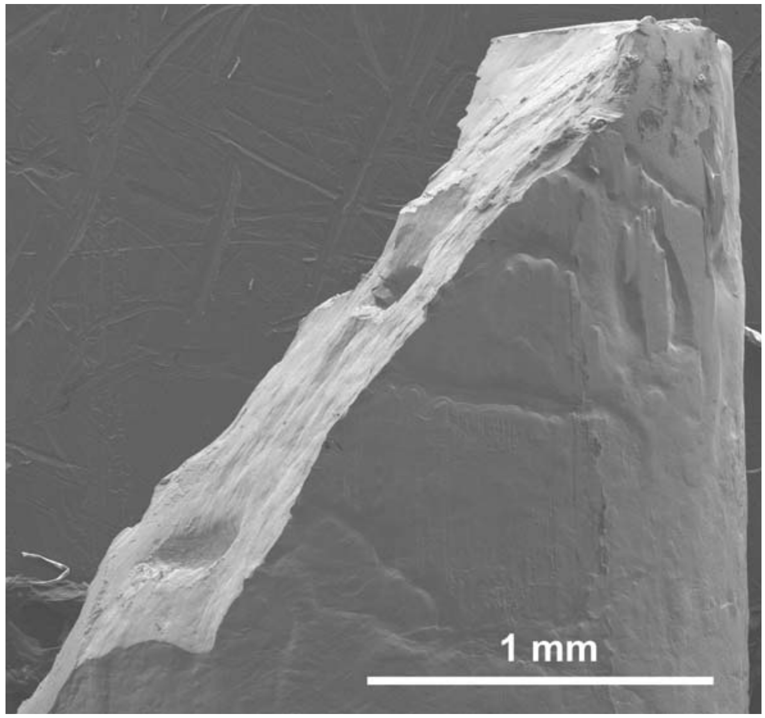

Fig. 7. Fracture and lateral surfaces of the $Ni_{40}Cu_{10}Ti_{35}Zr_{15}$ alloy.

Thus, the crystal-glassy composites were formed in Y-Cu-Ag, Y-Cu-Al and Cu-Y-Ag and Ni-Cu-Ti-Zr alloys. Mg-based alloys were did not smelt well. Y-Cu-Ag, Y-Cu-Al and Cu-Y-Ag alloys showed good bending ductility while Ni-Cu-Ti-Zr alloys demonstrate martensitic transformations and TRIP behavior. Large deformations up to about 20 % were achieved in Ni-Cu-Ti-Zr alloys.

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