OTKA K 112623

Designing novel composite materials with combination of amorphous and crystalline structure

Aims of the project

Last few years have seen a huge research activity on bulk metallic glasses. Bulk metallic glasses (BMGs) have excellent mechanical properties. Compared with crystalline alloys, BMGs exhibit outstanding mechanical properties such as larger elastic limit, higher specific strength and higher hardness. The fracture strength of typical BMGs is above 1800 MPa. Compared with conventional crystalline alloys, BMGs exhibit better corrosion resistance in different types of solutions due to the unique amorphous structure. Unfortunately, BMGs do not display sufficient ductility for industrial applications yet. When submitting our project, we were looking for answers to the following questions:

1. The initial hypothesis of the research is that the properties of the amorphous matrix can be improved by adding crystalline powder to amorphous powder, mixing and hot pressing.
2. We are looking for an answer, whether or not sufficient consolidation can be achieved in the supercooled liquid region, and to what extent the theoretical density can be approached.
3. Furthermore, how the ratio of amorphous and crystalline powders influences the mechanical properties.

Results

1. Production of Cu-Zr-based amorphous powders

In order to conduct this research, we produced amorphous powders by high-energy ball milling. In all cases, master alloy ingots were prepared by arc melting of pure metal mixtures (min. 99.9 wt. %) with a Ti-getter under purified argon atmosphere, which were naturally crystalline structures. The master alloys were grinded and fractioned to a particle size below 300 μm for ball milling. Amorphous/nanostructured powders were obtained in a Pulverisette 5 high-energy ball-mill in argon atmosphere using a stainless-steel vial and balls. The ball-to-powders ratio was 60:1 and 80:1 and milling speed was 200 rpm. The micrographs of master alloys and powders were acquired by a Hitachi S-4800 scanning electron microscope (SEM) equipped with BRUKER AXS type energy-dispersive X-ray spectrometer (EDS), FEI Technai G2 Transmission Electron Microscope (TEM) and a X-ray diffractometer (XRD). Amorphous fraction was determined by evaluation of XRD patterns. Backscattered electron micrographs were recorded in order to get information about the microstructure of the samples. The particle size distribution was determined as a function of milling time. The change of hardness change was observed.

The master alloys were Cu-Zr-Al alloys. In the first experimental series the $(Cu_{49}Zr_{45}Al_6)_{100-x-y}Ni_xTi_y$ (x = 0, 5, 10; y = 0, 5, 10) were selected in order to investigate the amorphization progress caused by milling. $Cu_{49}Zr_{45}Al_6$ near eutectic composition was selected as the basic alloy. The effect of Ni and Ti alloys on the glass-forming ability was studied. The monoclinic

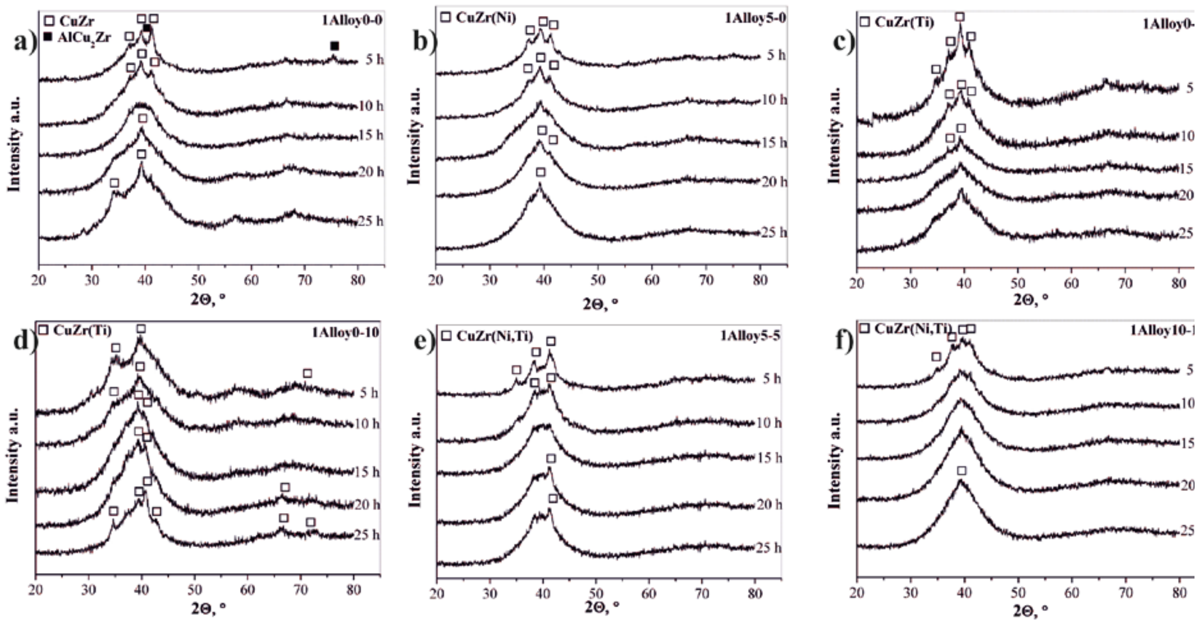

Fig. 1: XRD patterns of as-milled powders:
a) $Cu_{49}Zr_{45}Al_6$; b) $(Cu_{49}Zr_{45}Al_6)_{95}Ni_5$; c) $(Cu_{49}Zr_{45}Al_6)_{95}Ti_5$; d) $(Cu_{49}Zr_{45}Al_6)_{90}Ni_{10}$; e) $(Cu_{49}Zr_{45}Al_6)_{90}Ni_5Ti_5$; f) $Cu_{49}Zr_{45}Al_6)_{80}Ni_{10}Ti_{10}$

CuZr phase was identified in each sample. Furthermore, in the compositions alloyed with 5 at. % of Ni and 5 at. % of Ti, CuZr phase containing dissolved alloying elements can be observed. According to phase identification based on X-ray measurements, this phase is transformed into the latest amorphous structure, and the peaks belonging to this phase appear first in the X-ray diffractogram to the effect of energy input due to further milling (Fig. 1.). The crystalline-amorphous-crystalline process occurs.
Based on the X-ray diffractogram, the initial $Cu_{49}Zr_{45}Al_6$ alloy and the compositions alloyed with 5 at. % of Ni and 5 at. % of Ti demonstrate a broad diffuse halo in the amorphous structure. The transmission electron microscopy studies confirmed that there is a CuZr nanosized crystalline particle in the $Cu_{49}Zr_{45}Al_6$ and amorphous matrix (Fig. 2). TEM examination of the $Cu_{49}Zr_{45}Al_6$ sample showed only diffuse rings after 15 h of milling which implies the structure was amorphous.

In the next experimental series, six compositions in the $((Cu_{49}Zr_{45-x}Al_{6+x})_{100-y-z}Ni_yTi_z$ (x = 1, y, z = 0; 5; 10) system were selected in order to investigate the amorphization progress caused by milling. The initial phases of the powders were different behavior during the high-energy ball milling process.

$AlCu_2Zr$ and an unknown phase with $Al_{13}Cu_{37}Zr_{50}$ at. % have become an amorphous structure after 5 hours of milling. On the other hand, CuZr and Cu_2ZrTi are phases that have not been transformed by the input energy. In all cases, the structure of the alloys changed very much after the first 5 hours of milling, most of the phases disappeared and a broad diffuse halo appeared in the amorphous structure.

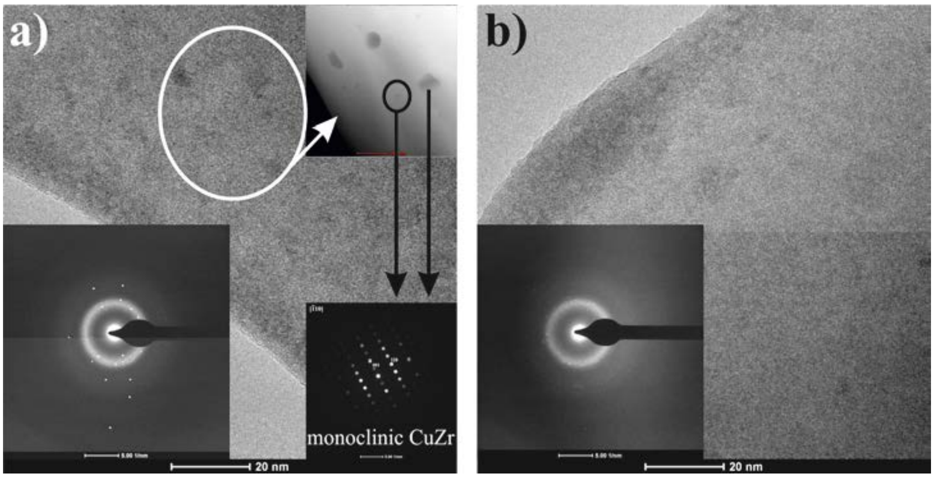

Fig. 2: Bright field images and corresponding SAED pattern for alloys of different compositions after 15 h of milling, a) $Cu_{49}Zr_{45}Al_6$, b) $Cu_{49}Zr_{45}Al_6)_{80}Ni_{10}Ti_{10}$

The largest amorphous content was measured after 15 hours of milling alloy powders not containing Ni and Ti and after 10 hours of milling compositions alloyed with 5 at. % of Ni and 5 at. % of Ti. After further milling, the amorphous structure over crystalline phases appeared due to the energy input of milling.

TEM analysis demonstrated the formation of a fully amorphous structure after 12 h of milling the compositions alloyed with 10 at. % of Ti and 10 at. % of Ni ($Cu_{49}Zr_{45}Al_6$ and $Cu_{49}Zr_{44}Al_7$ samples).

2. Production of Ti-based amorphous powders

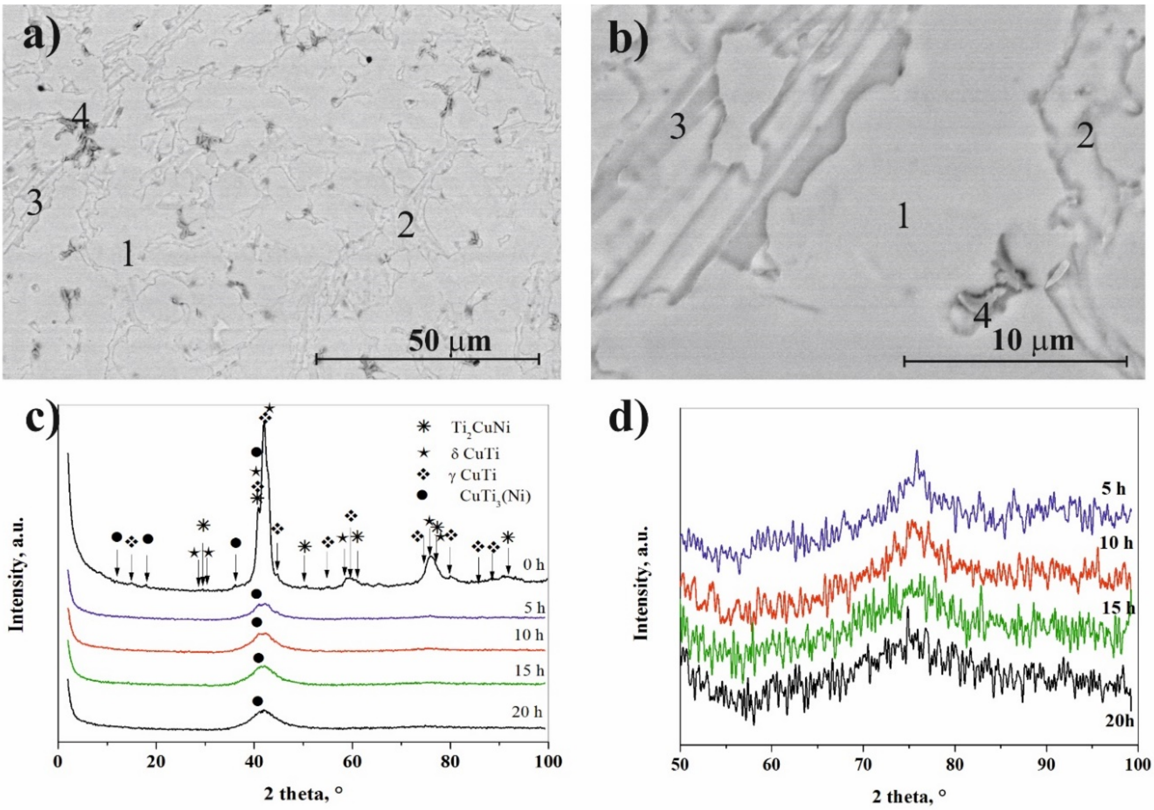

Fig. 3: Backscattered SEM (BSEM) images (a, b) and XRD patterns of powders with different milling time (c, d) of $Ti_{48}Cu_{39.5}Ni_{10}Co_{2.5}$ alloy

The production of Ti-based amorphous/nanostructured alloys along with fully amorphous alloys is studied quite actively because titanium is biocompatible. Currently, the maximum diameter of Ti-based amorphous bulk alloys 50-60 mm; however, these alloys contain beryllium, which is toxic for the human organism. The maximum thickness of Ti-based amorphous bulk alloys containing palladium of the Ti-Zr-Cu-Pd-Sn alloy family is 10 mm per moment. Beryllium is toxic, while palladium is quite expensive. For this reason, the new alloy family chosen by us is Ti-based, for powder metallurgy is promising.
The high-energy milling of master alloys of $Ti_{48}Cu_{39.5}Ni_{10}Co_{2.5}$ and $Ti_{48}Cu_{39.5}Zr_{10}Co_{2.5}$ composition (at. %) was studied. The effect of Ni and Zr on both alloys was investigated. In the $Ti_{48}Cu_{39.5}Ni_{10}Co_{2.5}$ alloy, 5 vol. % of the tetragonal $CuTi_3$ phase containing 6 at. % of Ni in dissolved state was also found.

The ball-to-powder ratio varied. For pre-experiments, a 60:1 ball-to-powder ratio was applied. After 15 hours of milling the fraction of amorphous structure was 87 wt. %. Using an 80:1 ball-to-powder ratio, more energy was put in the system; despite this, the fraction of amorphous structure was 88 wt. % only. This is explained by the fact that – according to XRD – after 5 hours of milling the fraction of amorphous structure is 97 wt. %. Further milling leads to decrease in the amorphous fraction, while the fraction of the tetragonal $CuTi_3$(Ni) phase increases (Table 1). That is, the $CuTi_3$(Ni) phase crystallizes from the amorphous structure. After 15 hours of milling the mass fraction of the amorphous phase increases, while the fraction of the $CuTi_3$(Ni) phase decreases again. In the case of nanostructured $CuTi_3$(Ni) phase the amorphization/crystallization process is reversible. There is inhomogeneity in the amorphous structure because two peaks are visible in the amorphous halo (Fig. 3). The first one suggests that there is amorphous content rich in Ti because this element is of the largest atomic radius in the system, while the second one characterizes the Cu-Ni enrichment in the amorphous structure.

Table 1: Features of crystallites based on the XRD of amorphous structure in the case of $Ti_{48}Cu_{39.5}Ni_{10}Co_{2.5}$ alloy

milling time, h	ball/powder ratio	amorphous fraction, m/m%	amorphous halo				crystallite size of $CuTi_3$(Ni), nm	crystallite size of Ti_2CuNi, nm
			first peak		second peak			
			position, nm	size, nm	position, nm	size, nm		
15	60/1	87	0.2212	1.5	0.1341	0.8	17.00-30.00	15.00-20.00
5	80/1	97	0.2152	1.9	0.1258	2.5	1.8-2.9	-
10		91	0.2152	1.8	0.1263	1.9	1.8-2.9	-
15		88	0.2148	1.8	0.1274	1.2	1.7-3.0	-
20		90	0.2145	1.6	0.1274	1.4	1.6-2.9	-

According to the results of XRD and SEM measurement, 5 phases are identified in the master alloy if Ni is replaced with Zr. In the course of milling, the formation of amorphous structure takes place slower in the case of Zr containing alloy than in the case of Ni containing one. There is no amorphous structure after 5 hours of milling, which proves that these phases are more

stable towards the energy input by milling. After 20 hours of intensive milling the fraction of amorphous structure is only 69 wt. %. The energy input by milling is insufficient to destabilize the Cu_2ZrTi_2 phase because the nanocrystalline particles of this phase stay until the end of milling.
Observed changes in the particle size, we can conclude that the average particle size in the case of Ni containing alloy decreases gradually as function of the milling time: from 85 µm after 5 hours of milling to 33.73 µm after 20 hours of milling. In contrast, the average particle size in the case of $Ti_{48}Cu_{39.5}Zr_{10}Co_{2.5}$ alloy does not decrease so significantly.

After 20 hours of milling, the average microhardness of particles is $HV_{0.01}$ 519 ± 40 for the $Ti_{48}Cu_{39.5}Ni_{10}Co_{2.5}$ alloy and $HV_{0.01}$ 630 ± 55 for the $Ti_{48}Cu_{39.5}Zr_{10}Co_{2.5}$ alloy, respectively.

3. Synthesis of copper-based composites reinforced by amorphous/nanostructured particles

Ductile and pure copper powder as matrix was mixed with amorphous/nanostructured hard CuZr-based powder. The amorphous powders of two compositions: $Cu_{39.2}Zr_{36}Al_{4.8}Ni_{10}Ti_{10}$ and $Cu_{39.2}Zr_{35.2}Al_{5.6}Ni_{10}Ti_{10}$ produced by ball-milling were used as reinforcement of the composites (described in section 1). Crystalline copper powder of 99.9 wt. % purity was added to the amorphous powders with a mass percentage of 30, 40 and 50. Different mixing techniques were applied to obtain homogenous mixture of powders. The mixed powders were hot-pressed at 390°C under 1 GPa pressure for 4 hours in high-purity argon atmosphere in order to obtain amorphous/crystalline composites. 390°C was chosen as pressing temperature, because this temperature is close to the glass transition temperature of cast samples (Tg) which is between 415 and 420°C. Mixing by planetary ball-milling gives the optimal result in homogenous dispersion of both phases based on the optical and image analysis. Radial distribution function (RDF) was applied for numerical characterization of the amorphous particle arrangement in cross-sections of the hot-pressed samples. The effect of ball-to powder ratio and milling time on the homogeneity was investigated. One can conclude that random arrangement of the particles can be achieved by mixing in a ball-mill with the following parameters: 15 minutes milling time and 80:1 ball-to-powder ratio. The contact surfaces between the Cu matrix and the reinforcing particles are continuous and gapless. The yield strength of copper enhanced drastically from 168 MPa to 398-414 MPa owing to the reinforcement with 50 wt. % of reinforcing particles. Ti-based amorphous-nanocrystalline powders mixed with an oxygen free high conductivity (OFHC) Cu powder in a high-energy planetary ball mill. The production process of amorphous-nanocrystalline powders was described in section 2. The average particle size of the initial copper powder was ~50 µm.

Considering the effect of two different reinforcing compositions it can be observed that the Zr (ρ = 43.3 µΩcm) containing particles reduce the electric conductivity to a larger extent than the Ni (ρ = 6.99 µΩcm) containing particles in the case of f = 10 wt. %. However, the mechanical properties are better in the case of Zr containing reinforcing particles. Based on the compressive strength-strain curves and average distance between reinforcing particles, it can be established that the percolation threshold is near 40 wt. %, namely this is the minimum reinforcing content, where the particles may form a continuous network during deformation. The 0.2% offset compressive yield strength (MPa) of the composite with f = 2 wt. % is 210 MPa and 253 MPa with Ni and Zr containing reinforcing particles. For the composite with f = 50 wt. %, it is 526 and 643 MPa, respectively (Fig. 4).

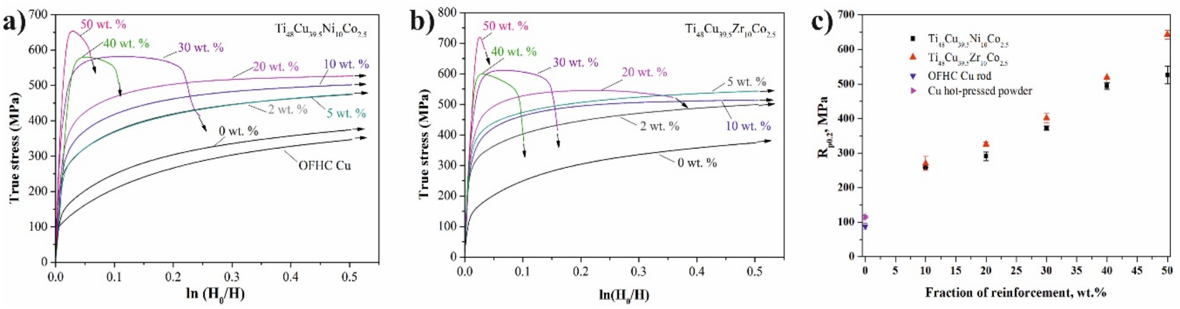

Fig. 4: Compressive stress-strain curves of the composites: (a) reinforcing particle $Ti_{48}Cu_{39.5}Ni_{10}Co_{2.5}$; (b) $Ti_{48}Cu_{39.5}Zr_{10}Co_{2.5}$; (c) 0.2% offset of compressive yield strength

Our research results have been published in 4 prestigious international journals with a total impact factor of 6.649. In addition, another article is currently under review. The results of this project served as basis for a M.Sc. and two scientific student conference (TDK) theses.

Journal papers:

1. *K. Tomolya, D. Janovszky, A. Sycheva, M. Sveda, T. Ferenczi, A. Roósz:* Studying Amorphisation Progress in Cu-Zr-Al-based Powders during Ball Milling, *Resolution and Discovery, 1: (1) pp. 9-14 (2016)*

2. *K. Tomolya, D. Janovszky, A. Sycheva, M. Sveda, T. Ferenczi, A. Roósz,* Peculiarities of ball-milling induced crystalline-amorphous transformation in Cu-Zr-Al-Ni-Ti alloys, *Intermetallics 65 (2015) 117-121*

3. *M. Sveda, A. Sycheva, T. Miko, F. Kristaly, A. Racz, T. Ferenczi, D. Janovszky*: Effect of Ni and Zr on the microstructural evolution of Ti-based alloys during ball-milling, *Journal of Non-Crystalline Solids 473 (2017) 41-46*

4. *K. Tomolya, A. Sycheva, M. Sveda, P. Arki, T. Mikó, A. Roósz, D. Janovszky:* Synthesis and characterization of copper-based composites reinforced by CuZrAlNiTi amorphous particles with enhanced mechanical properties, *Metals 7, 92 (2017) 1-11 Open access*

5. *D. Janovszky, T. Miko, F. Kristaly, M. Sveda, A. Sycheva*: Synthesis and characterisation of nanocrystalline Cu-based metal matrix composites reinforced with Ti-Cu-Co-M (M: Ni, Zr) amorphous-nanocrystalline powder, *JALCOM-under review*

Conference proceedings:

1. D. Janovszky, K Tomolya, A. Sycheva, M. Sveda, A. Roosz: Producing Ti- based amorphous/nanocrystalline powder using high-energy mechanical milling, In: Graz University of Technology 9th International conference on Processing and Manufacturing of Advanced Materials, THERMEC'2016, 29.05-03.06.2016, Graz, Austria; Book of Abstracts. p. 264.

2. K Tomolya, D. Janovszky, A. Sycheva, M. Sveda, P. Arki, A. Roosz: Producing amorphous/crystalline composites by powder metallurgy, *In: Graz University of Technology 9th International conference on Processing and Manufacturing of Advanced Materials, THERMEC'2016, 29.05-03.06.2016, Graz, Austria; Book of Abstracts. p. 559.*