Cu-based amorphous alloys deformed by high pressure torsion

Summary of the doctoral thesis

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Introduction

Nowadays the metastable systems became one of the most widely researched fields in material science. The main reason for it is that the more and more unique needs of the applications require materials with more and more extreme properties. Those special properties are usually owned by metastable alloys far from their thermodynamic equilibrium. This demand from the applications determines basic research as well, and provides interesting and typically challenging task for the researchers.

Metallic glasses, namely metastable, amorphous, metal based alloys without long-range order, were discovered by Duwez and co-workers approximately five decades ago. Due to their special structure – that is usually prepared by freezing the structure of the melt alloy – they behave significantly different, in comparison with their crystalline counterparts of similar composition. Even the first experiments showed the special mechanical properties of metallic glasses, e. g. large hardness, high yield stress, good corrosion resistance and largely varying deformability in a tight temperature interval.

The first metallic glasses were binary, Au-Si alloys, and it was only possible to cast them into glassy state with extremely high cooling speed, that basically limited the achievable sample size. The first bulk metallic glasses were prepared in the 80s, the smallest dimension of those Pd-based alloys already exceeded one millimetre. From the mid-90s the developing of the cheaper Cu- and Zr-based metallic glasses with high yield stress and with potential to become structural material, placed the metallic glasses in the scientific spotlight.

However, possible applications of these glasses are considerably limited by their inhomogeneous room temperature deformation, i.e. the formation of the so-called shear bands. Therefore instead of work hardening, common for crystalline alloys, metallic glasses show work softening. What is more, in the regions ambient to the shear bands nucleation of nanocrystals can be observed in the metastable amorphous structure, yielding to the change of the properties of the original system.

The exact mechanism of the deformation of metallic glasses and the related phenomenon were intensively investigated in the last years with experimental and numerical methods as well. One of the most widely-used model materials are the binary Cu-Zr and ternary Cu-Zr-Ti systems that were investigated in my doctoral work as well.

The aim of the doctoral work

During my doctoral work, deformation of different Cu-based metallic glasses has been performed by high pressure torsion (HPT) that enables large plastic deformation even for rigid alloys. This deformation method is generally considered as a room temperature deformation technique in the literature. This assumption is usually true for pure crystalline metals; however because of the high yield stress it is not always accurate regarding metallic glasses. Noteworthy that the temperature rise, especially in case of amorphous metals, due to the drastic changes at the glass transition temperature might be dominantly important.

The aim of my doctoral work was to investigate in details the temperature conditions during high pressure torsion, and the effect of plastic strain and the subsidiary temperature rise on the microstructure of the metallic glass samples as well. Therefore, a quasi-three dimensional model based on the heat conduction equation has been proposed, that enables the estimation of the temperature evolution in the sample, generated by the plastic work converted into thermoplastic heating. Furthermore I have investigated experimentally the changes of the microstructure and thermal properties of different ternary Cu-Zr-Ti metallic glasses due to high pressure torsion. The observed nucleation of nanocrystals was well interpretable based on the numerical calculations. Besides, to validate the results of the model series of samples prepared by different deformational parameters were also investigated.

Applied experimental techniques

The investigated $Cu_{60}Zr_{20}Ti_{20}$ and $Cu_{60}Zr_{30}Ti_{10}$ metallic glass alloys were prepared by melt spinning technique. The amorphous ribbons were cut into small pieces that were deformed by high pressure torsion, yielding to dense disk-shaped samples. The microstructure of these metallic glass disks were investigated by scanning and transmission electron microscope together with X-ray diffraction. One part of the diffraction measurements were carried out by a traditional diffractometer the other part at the European Syncrotron Radiation Facility (ESRF), with focused high-intensity X-ray beam.

For the thermal characterization of the samples and for isotherm annealing a dynamic calorimeter was used. For the numerical calculations the program called Mathematica was used.

Points of the thesis

1. The microstructural changes and relevant temperature conditions during large plastic deformation of melt-spinned metallic glasses were investigated. We have estimated the temperature evolution in the sample, generated by the plastic work converted into thermoplastic heating during high pressure torsion in case of one of the most widely used metallic glasses (Vitreloy) as a model material. With one dimensional simulations based on the heat conduction equation we have calculated the temperature profiles both throughout the diameter of the samples and perpendicular to their surfaces. The simulations with typical parameters for sample preparation showed, that significant temperature rise may happen in the disks. Consequently the temperature of the metallic glass samples may reach the glass transition temperature in a period of time shorter than the total processing time. Based on these results a semi-analytic form, taking into account the remarkable heat dissipation as well, was determined to calculate this critical time. [S4, S5]

2. To improve the one dimensional simulations, a quasi-three dimensional model was developed for calculating realistically the temperature evolution during high pressure torsion. Based on this model we have found, that a certain region of parameters (regarding the thickness of the sample and the revolution time), applied in experiments, does exist, where the temperature of the metallic glass samples reaches the glass transition temperature during the process. On the grounds of a series of numerical calculations it was found, that the degree of the temperature rise is fundamentally determined by these deformation parameters, on contrary the exact composition or material parameters of the metallic glass are not so important. In case of thin samples and short revolution times it was found that the glass transition temperature is reached in the sample As a result the deformation mode of the system is changed to homogenous viscous flow. On contrary, in case of thick samples or slow rotation the glass transition temperature is not reached. The results of the numerical simulations have been summarized in a parameter-map. [S6, S8]

3. Using X-ray diffraction measurements, both in-situ at synchrotron and traditional, it was shown that the microstructural processes during high pressure torsion of amorphous $Cu_{60}Zr_{20}Ti_{20}$ metallic glass are significantly different from the observable processes throughout pure annealing. On one hand, during linear annealing $Cu_{51}Zr_{14}$ nucleates first followed by Cu_2ZrTi phase on higher temperatures, on the other hand, in the samples deformed by high pressure torsion only the Cu_2ZrTi is observable. The reason for it is the following: during pure annealing the necessary atomic movements for the growth of the nanocrystals are provided by the thermally activated diffusion. In this case the depleted zone surrounding the nuclei controls the size of the nanocrystals of a given composition. On contrary in case of the high temperature phase of high pressure torsion the metallic glass is in the state of a viscous fluid under external shear stress that together extends the atomic diffusion length, yielding to a different crystallization sequence. [S1, S2, S3, S4]

4. In order to experimentally validate the thermoplastic model, the microstructure of series of samples of $Cu_{60}Zr_{30}Ti_{10}$ metallic glass produced by high pressure torsion with varying deformation parameters were investigated by synchrotron and traditional X-ray diffraction together with scanning and transmission electron microscopy.

A) It was found, that even after a half rotation dense, compact, homogenous disks were produced from the small pieces of the ribbons. After further shearing the morphology of the disks changes drastically, and characterized by strong radial dependence. Close to the rotation axis large, approximately twenty times larger than observed for pure annealing, heavily deformed, crystalline Cu_2ZrTi blocks were located. After further deformation these blocks became more robust and showed devitrified and decomposed morphology (Ti-rich and almost Ti-free regions). In the more heavily deformed outer regions the size of these blocks decreased, close to the perimeter the morphology was almost homogenous on a milimeter length-scale. However it was shown using transmission electron microscopy, that these heavily deformed regions contain several nanocrystals.

Based on the simulations we may assume that in these experiments the shearing even after one rotation happened above the glass transition temperature, so the system was severely deformed in a viscous state. Therefore two competing processes co-exist: on one hand, the diffusion length of the atoms grows significantly compared to the plain annealing, supporting the nucleation and growth of nuclei, on the other hand heavy, radial dependent shearing limits growth of the nanocrystals considerably. This made possible the formation of the robust crystalline blocks close to the rotation axis, and later on their devitrification, and simultaneously the severe shearing blocked the growth of nuclei, and supported the evolving of a more homogenous microstructure at the perimeter. [S9]

B) With changing the revolution time of high pressure torsion in the simulations, we determined the values, where the temperature of the samples does not reach the glass transition temperature. The microstructure of the samples prepared with parameters from this interval was found to be significantly different than in the previous case, namely: bunches of elongated crystalline bands were observed in small volume fraction in the amorphous matrix. These crystalline bands refer to the formation of locally heated deformation zones during the plastic deformation of the glass under the glass transition temperature, presumably the bands were formed along those shear bands.

Based on the above detailed results, we may pronounce, that the microstructure and thermal properties of metallic glasses deformed by high pressure torsion with different total shearing or different revolution times can be well interpreted using the results of the thermoplastic model. [S7]

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