Electron microscopy analysis of flash-annealed CuZr based bulk metallic glass

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Bulk metallic glass (BMG) is an amorphous material with no long-range order. Still, topological and chemical short-range or medium-range order is expected to occur. The unique atomic structures of BMG lead to interesting physical and mechanical properties that make them useful for potential applications. To circumvent the limited ductility of BMG, the concept of heterogeneous microstructure by forming composites has recently been used [1]. One route to achieve a composite structure is thermal treatment of the BMG. Here we present the structure of flash-annealed CuZr based BMG studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods including electron diffraction and fluctuation electron microscopy (FEM).

During the flash-annealing process the structure of BMG samples is modified by heating to different target temperatures above glass transition temperature and subsequent rapid cooling in a water bath leading to changes in the atomic structure. $Cu_{44}Zr_{44}Al_8Hf_2Co_2$ samples heated to 898 K and 916 K with a mean rate of 67 K/s were studied in a Zeiss Supra 55VP SEM at 20 kV as well as a Philips CM200 TEM operating at 200 kV.

SEM observation of the 916 K sample using back-scattered electrons reveals both an amorphous and a crystalline part each taking up about 50 percent of the sample with a transition area of amorphous material containing crystallites of different size in between (Figure 1). Figure 2 results from the TEM study of a FIB lamella prepared from a single crystallite as shown in Figure 1. The associated diffraction pattern (DP) with superlattice reflections indicates the presence of the B2 ordered structure. It is interesting to note that in crystalline CuZr based materials, devitrified from the amorphous structure, $Cu_{10}Zr_7$ and $CuZr_2$ structures are expected to occur.

To obtain structural information of the samples flash-annealed to 898 K, fluctuation electron microscopy was applied since no indication of crystallization was found. Figure 3a illustrates a corresponding DP with integrated intensity using the software PASAD [2] indicating a fully amorphous structure. Tilted dark field (DF) images show intensity variations in form of speckles as a result of local structural correlations (Figure 3b). Statistical analysis of a series of DF images acquired at different scattering vectors k and angles φ yields mean intensity and normalized variance as a function of k. The normalized variance is defined as $V(k) = (\langle I(k,r)^2\rangle / \langle I(k,r)\rangle^2) - 1$, with I being the image intensity and <> meaning the average over sample position r. Figure 4 shows intensity and variance curves for the 898 K sample using an objective aperture of 10 µm. While the maximum of mean intensity is located at about 4.0 nm^{-1} the normalized variance shows a significant shift to larger k values. Similar curves were obtained using different spatial resolution by varying the objective aperture size.

Based on our results flash-annealing of CuZr based BMGs facilitates the formation of the B2 ordered crystalline structure as a metastable phase. In the amorphous phase of all samples the presence of a significant medium range order can be concluded from peaks in the normalized variance curve of DF FEM analysis. The maxima position of the normalized variance (~ 5 nm^{-1}) is different to that found in $Zr_{50}Cu_{45}Al_5$ BMG at about 4.0 nm^{-1} reported in literature [3].

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References

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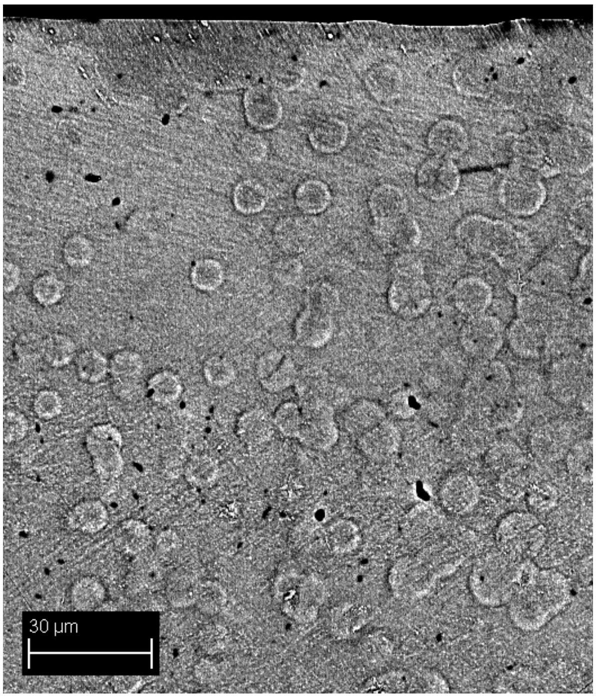

Figure 1: Back-scattered electron image of spherical crystallites embedded in the amorphous structure of the CuZr based bulk metallic glass flash-annealed to 916 K.

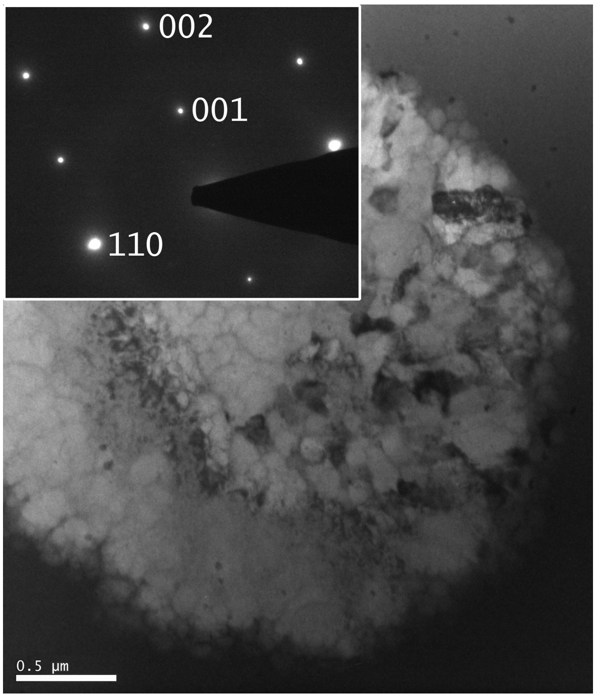

Figure 2: TEM image of a single crystallite embedded in the amorphous structure. The DP containing superlattice reflections indicates the formation of the B2 structure by flash-annealing up to 916 K.

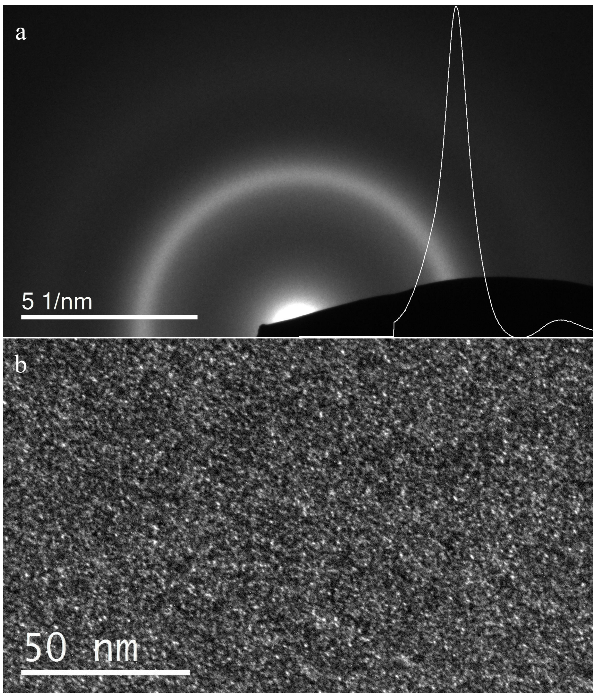

Figure 3: a) DP of sample flash-annealed to 898 K implying fully amorphous structure. b) Tilted DF image taken with a given scattering vector shows intensity speckles due to structural correlations.

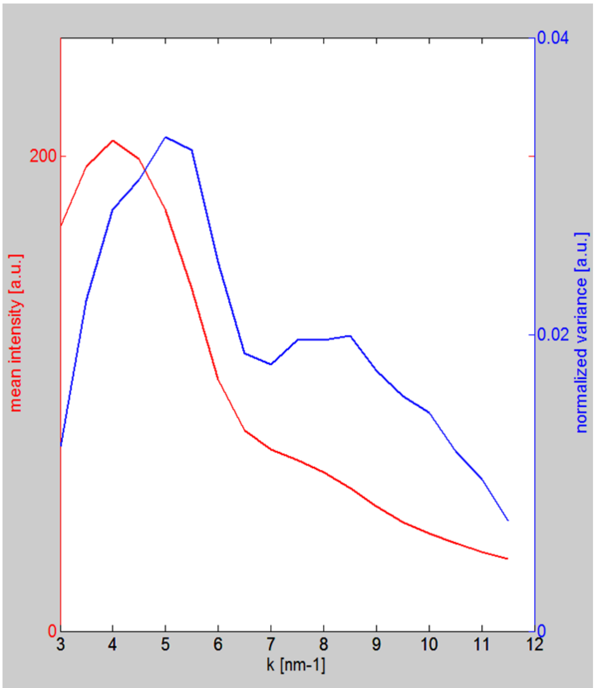

Figure 4: Mean intensity and normalized variance calculated from 320 images of a DF series of the sample heated to 898 K. The first maximum of the normalized variance is shifted to higher k-values compared to the peak of the mean.