Metals, Alloys and Intermetallics

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Structural heterogeneities in thin foils of CuZr based bulk metallic glasses

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Bulk metallic glasses (BMG) are amorphous materials 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. In order to obtain structural information transmission electron microscopy (TEM) methods as electron diffraction or fluctuation electron microscopy can be applied. In all cases thin TEM specimens are of advantage to obtain interpretable results. It is the aim of the present work to show that in very thin areas of a CuZr-based BMG structural heterogeneities compared to the bulk sample can occur.

BMG of $Cu_{36}Zr_{48}Al_8Ag_8$ were prepared by centrifugal casting. Both as-cast samples and samples deformed by rolling were prepared by grinding, dimpling and ion milling to TEM foils. In addition, samples were also thinned by electropolishing using a solution of 33% nitric acid and 66% methanol. The TEM foils were studied in a Philips CM200 operating at 200kV. Selected area electron diffraction (SAED) patterns of the BMG were acquired from areas of different thickness using a Gatan Orius CCD camera. The apertures used select areas with a diameter of 300 or 1200 nm. In addition, energy dispersive X-ray (EDX) spectra were taken to obtain information on the chemical composition.

Figure 1 shows the SAED pattern of $Cu_{36}Zr_{48}Al_8Ag_8$ BMG taken from different areas of a wedge shaped TEM foil prepared by the multiple step procedure including ion-milling. In the thinnest area next to the edge of the sample two closely spaced diffuse diffraction rings (A, B) are present in the SAED pattern (cf. Fig. 1(a)). With increasing thickness a third diffuse ring (C) emerge between A and B and becomes dominant (cf. Fig. 1(b,c)). This change of the SAED pattern is summarized in Fig. 1(d) showing the intensity profiles. The integration along rings was carried out using the PASAD software [1]. The intensity maxima of the peaks A, B and C are at about 3.6, 4.7 and 4.3 nm^{-1}, respectively. It should be mentioned that (i) EDX spectra at thinner areas reveal enhanced oxygen content compared to thicker areas and (ii) the position of peak A can be correlated to that of amorphous zirconia. In the literature, double diffraction rings at similar positions as in Fig. 1(a) were observed in a $Cu_{32}Zr_{51}Al_9Ni_8$ alloy [2]. These double rings emerge from a single very broad peak during in-situ heating and are attributed to the formation of compositional and structural heterogeneities in thin films upon annealing. Contrary, in our case local heating of the thin area during ion-milling can be excluded since double rings are also observed in SAED patterns of thin films prepared by electropolishing.

Based on our results, it is concluded that in CuZr-based BMG thin foils structural heterogeneities in the form of three different structures (dependent on the distance to the surface) are present: (i) oxidized amorphous zirconia (peak A) at the surface, (ii) amorphous CuZr structure (peak B) affected by the surface layer (less Zr content) and (iii) amorphous bulk CuZr structure (peak C). The shift of peak position B to C by a change of the Zr content is supported by experimental data of CuZr based BMG [3].

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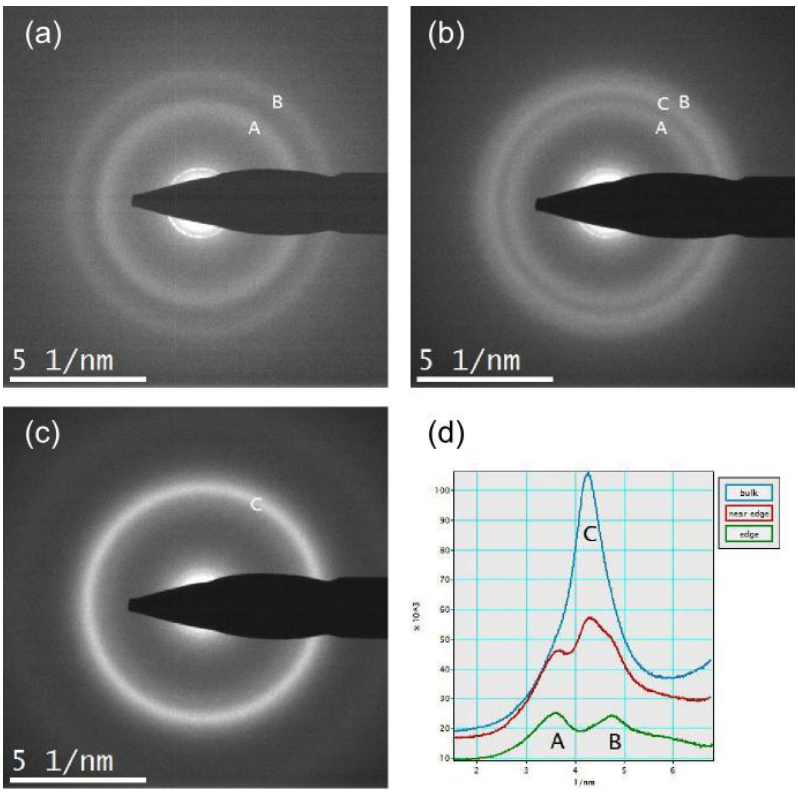

Figure 1. (a) Diffraction pattern of $Cu_{36}Zr_{48}Al_8Ag_8$ bulk metallic glass taken at the edge of the wedge shaped TEM foil shows double rings indicated A and B. (b, c) With increasing distance from the edge (increasing thickness) a strong third ring appears. (d) Intensity profiles obtained by integration along diffraction rings. Peak C lies between peak position A and B.