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Comments on "Structure origin of a transition of classic-to-avalanche nucleation in Zr-Cu-Al bulk metallic glasses"

In the article by Lan et al. [1], the authors observe the crystallization kinetics of Zr-Cu-Al bulk metallic glasses through differential scanning calorimetry (DSC), neutron diffraction and transmission electron microscopy. They report an avalanche-type nucleation during the crystallization of these bulk glasses. Reading this article, one gets the impression that this type of crystallization occurs only for ternary Zr-based bulk metallic glasses. In fact, this unusual crystallization behaviour was first reported in melt-spun binary Zr-M (M = Fe[2], Co[3], Ni[4]) metallic glasses, which the authors, apparently, were unaware of.

In our crystallization studies of these glasses, we found that during the 1st stage of crystallization, for compositions near Zr_2M, a metastable nanocrystalline Zr_2M compound with a face-centred-cubic structure with a lattice parameter of about 12 Å was formed (this structure was later named "the big cube"). The crystals were nanocrystalline (typically about 3 nm) and upon further heating they transform into the stable tetragonal Zr_2M. This process produced two exothermal peaks in the DSC scans (also observed by Lan et al. [1]). The Avrami exponent for the 1st crystallization process is about 10, which implies rapid nucleation with very little growth. We termed this process explosive crystallization [2] as it gives a better description than "avalanche" as the crystallization originates from the formation of the big cube from multiple quenched-in nuclei throughout the material. This explosive crystallization in metallic glasses was first reported in 1984 during the crystallization of Fe-Zr metallic glasses [2]. A similar effect was also observed in the crystallization of Co-Zr metallic glasses [3]. It is important to note that this explosive crystallization is always accompanied by an increase in the electrical resistance of these glasses [2,3]. Indeed, measuring the changes in the resistivities as a function of temperature is a far more sensitive way to detect the presence of explosive crystallization. Explosive crystallization was only observed in Ni-Zr glasses at one composition ($Ni_{36.5}Zr_{63.5}$) [4] and not at all in Cu-Zr glasses [5].

A literature search revealed that oxides of the composition Zr_4M_2O exist for M = Cu, Ni, Co and Fe with the same big cube structure with a ~ 12 Å. We next investigated if impurities that could have contaminated the starting compositions during the manufacturing of these glasses were the source of this behaviour. Oxygen, silicon, boron and nitrogen (present in boron nitride and quartz crucibles) were deliberately added to the starting materials, and the effect of the temperature of the melt during the melt-spinning process was also examined. This study [6] showed that for Ni-Zr glasses, the big cube was formed when the oxygen content was >1 at.%, while for Fe and Co, the big cube formed when oxygen levels were higher than 0.3 at.%. Boron and nitrogen also played a role but to a lesser extent to that of oxygen. In all these cases, both an increase in the electrical resistance and the presence of the double peak in the DSC scans were observed. It should be noted that the observed increase in the electrical resistance is not due to grain-boundary scattering associated with the presence of the nanoparticles, as was initially suspected, but is in fact an intrinsic property of the big cube [7], as shown by the fact that the resistivity does not decrease as the big cube crystals grow. It is interesting to note here that in addition, the resistivity of this phase *decreases* with *increasing* temperature. This was also shown to be a property of the big cube [7].

The presence of oxygen in these alloys is unavoidable. The stated purity of the commercially supplied metals, such as 99.99%, is immaterial as gases, such as oxygen, are not included in this number. Furthermore, one has to remember that Zr (Hf and Ti) are extremely efficient getters and will absorb oxygen during the alloying process no matter the quality of the vacuum. The existence of quenched-in nuclei of Zr-M-O sub-nanoparticles acts as nucleation sites for the big cube in these glasses. These particles are difficult to characterize by high-resolution electron microscopy as the thinning of the samples, from bulk down to about 10 to 20 nm may not provide a true representation of the bulk material. In a study on melt-spun $NiZr_2$ metallic glasses [8], we were also able to demonstrate that the temperature of the molten alloy plays a crucial role in the crystallization of the glass. At high melt temperatures, ≥1250 K, a two-stage crystallization is observed. This could be due to the reaction of the melt with the quartz tube in the melt-spinning process. In the same study we also showed that the speckles seen in the TEM micrographs were due to the presence of nanometer-size oxides.

A significant number of publications [9–14] (due to space limitations, we only refer to these references, which in turn, give citations to even more references) have reported on the effects of oxygen on the crystallization behavior of ternary metallic glasses of the type Zr-Cu-Al similar in composition to those studied by Lan et al. [1] who, surprisingly, do not cite any of these relevant publications.

To understand why different transition elements and certain impurities affect the crystallization process to different degrees we can use Miedema's semi-empirical model [15] for estimating the enthalpy of formation/mixing to identify a pattern. The results show that the strongest bonds with Zr, in order of decreasing strengths, are O, (N, C, B, Si), and Al, which confirm our observations of the role of the contaminants. It is interesting to note that the presence of the big cube was mentioned in ref. 32 of Lan's article [1].

In summary, the first exothermic heat release indicates the occurrence of explosive crystallization of Zr_2M (M = Fe, Co, Ni) nanocrystalline cubic structure. The heat release is accompanied by an increase of the electrical resistance. This effect is triggered by the presence of very small amounts of oxygen, boron, silicon, carbon, aluminum, etc.

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