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Structural evolution of the amorphous grain boundary phase during nanocrystallisation of $Fe_{72}Cu_1Nb_{4.5}Si_{13.5}B_9$

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Abstract

The structure of the amorphous grain boundary phase during progressive stages of nanocrystallisation in the $Fe_{72}Cu_1Nb_{4.5}Si_{13.5}B_9$ alloy has been followed using XRD, SAXS and Mössbauer spectroscopy. The initial compositional inhomogeneity sets-in with increasing crystallisation, as a result of the depletion in Fe of the amorphous phase, which partly homogenises for longer annealing times due to long-range diffusion.

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Keywords: Nanocrystalline alloy; Amorphous grain-boundary phase; Structural relaxation; Compositional inhomogeneity

Nanocrystalline alloys produced by a controlled partial crystallisation of FeCuNbSiB amorphous alloys are excellent soft magnetic materials. Magnetic interaction among the nanocrystalline grains via the intervening amorphous grain boundary phase results in their improved soft magnetic properties. Therefore, the structure of both nanocrystalline grains as well as the amorphous grain boundary phase is important in determining the magnetic properties of the composite structure. While the evolution of structure and composition of the nanocrystalline component has been studied extensively in the literature [1], similar studies of the amorphous grain boundary region are still lacking. In this work, we report wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS) and Mössbauer spectroscopy studies of the structural evolution of the amorphous grain boundary phase in the $Fe_{72}Cu_1Nb_{4.5}Si_{13.5}B_9$ system by increasing the degree of nanocrystallisation.

In situ SAXS and WAXS studies of nanocrystallisation were done using the beam-line 5.2L at Elettra synchrotron source, Trieste. Ribbons of $Fe_{72}Cu_1Nb_{4.5}Si_{13.5}B_9$ amorphous alloy were heated up to 600°C at a heating rate of 2.5°C/min in Ar atmosphere and data taken isochronally at the various temperatures. Mössbauer spectra were taken ex situ at room temperature after various heat treatments.

The WAXS data were fitted with two overlapping lorentzian lines: a broad hump corresponding to the amorphous phase, and a sharp peak at $q \approx 3.08\,\mathrm{nm}^{-1}$ corresponding to the (1 1 0) peak of BCC-FeSi alloy. The on-set of nanocrystallisation takes place around 500°C. The crystallite size increases with increasing the annealing temperature and reaches a saturation value of 27 nm around 550°C.

WAXS measurements also give a detailed information about the structural changes occurring in the remaining amorphous grain-boundary phase. Fig. 1 gives the

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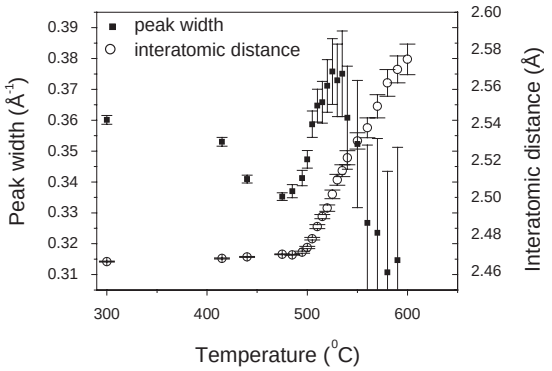

Fig. 1. Average TM–TM near neighbour distance and width of the amorphous peak.

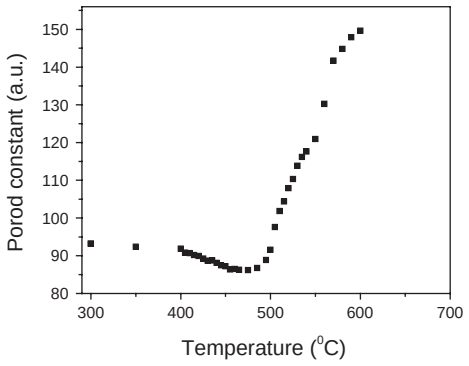

Fig. 2. Porod constant as a function of annealing temperature.

variation in the average transition metal–transition metal (TM–TM) near neighbour distance in the amorphous phase, as obtained from the position of the broad amorphous peak. A monotonous increase in the TM–TM distance may be attributed to enrichment of the amorphous phase in metalloid. Mössbauer measurements (not reported) show that after the first step of crystallisation 70% of Fe resides in the nanocrystalline phase. Moreover, the area ratios of the various hyperfine field components yield the composition of the nanocrystals as $Fe_{79}Si_{21}$ [2]. Therefore, the composition of the remaining amorphous phase comes out to be $Fe_{61}Nb_{13}B_{26}$. It is assumed that all Cu atoms precipitate out in the form of clusters before the onset of nanocrystallisation, while all Nb atoms go into the amorphous phase [3]. A simple calculation, taking into account the changes in the composition and the average TM–TM distance, shows that the density of the remaining amorphous phase decreases by $\sim$9% as compared to that of the starting amorphous phase.

The width of the amorphous peak, which is a measure of the degree of disorder in the amorphous phase, exhibits an interesting behaviour with annealing temperature, as shown in Fig. 1. This behaviour may be understood as follows. Initially, annealing in the temperature range 300–480°C causes a decrease in the disorder. This may be connected to structural relaxation in the amorphous phase, which results in an increased topological order in the system. Annealing at higher temperatures results in a sharp increase of the disorder, concurrent with the on-set of crystallisation. For still higher annealing temperature the disorder goes through a maximum and then shows a rapid decrease. Initially, with increasing crystallisation, as boron is expelled out of nanocrystalline grains, it will form a concentration gradient around the crystallites. However, boron will further diffuse with time into the amorphous phase resulting in a relatively homogeneous distribution.

The SAXS region is fitted with the Porod law [4]: $I = kq^{-4}$, yielding the Porod constant k (Fig. 2). Annealing in the temperature range 300–480°C causes a decrease of Porod constant. Occurrence of SAXS is expected in the amorphous phase because of some density fluctuations which may be associated with quenched-in stresses or some compositional inhomogeneities. Therefore, the observed decrease in Porod constant is related to relieving of internal stresses and increase in the compositional homogeneity as a result of structural relaxation. Beyond 480°C, when the nanocrystallisation sets-in, the small angle scattering increases rapidly and has contributions both from the scattering by nanocrystaline grains and from the inhomogeneity in the amorphous phase.

In conclusion, the structural evolution of the amorphous grain boundary phase during the progressive stages of nanocrystallisation in the amorphous $Fe_{72}Cu_1Nb_{4.5}Si_{13.5}B_9$ occurs in a complex way. The structural relaxation, which precedes the nanocrystallisation, results in an increase of topological short-range order as well as of chemical homogeneity. At the onset of nanocrystallisation, initial outdiffusion of boron from the crystallites causes an increase of compositional inhomogeneities in the amorphous grain boundary phase. However, for longer annealing times boron gets distributed rather uniformly throughout the amorphous phase. This redistribution will affect the magnetic properties of the amorphous phase, which in turn will modify the coupling among the nanocrystals, thus affecting the magnetic properties of the composite alloy as a whole.

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