Synchrotron X-ray Diffraction Study of the Crystallization Process in the As-Prepared Amorphous Fe–Mo–Cu–B System

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Abstract. *The crystallization of amorphous $Fe_{79}Mo_8Cu_1B_{12}$ alloy was studied in situ using X-ray diffraction of synchrotron radiation. Both sides of the ribbon shaped samples were investigated. The onset temperature of crystallization, the volume fraction of primary crystalline phase, and the speed of the development of structural transformation were determined from analysis of the shape of diffraction maximum located at the position of the main bcc-Fe reflection. The surfaces of the ribbon showed the differences in these parameters.*

Keywords: Synchrotron, X-ray Diffraction, In Situ, Crystallization, Amorphous Alloy

1. Introduction

Today, there is an opportunity to study structural transformations *in situ* using intense beams of synchrotron radiation. Ideal materials for such studies are amorphous Fe–*M*–B alloys, where *M* denotes a transition metal. They are produced by rapid solidification from the melt and serve as precursors for the production of nanocrystalline alloys commercially known as NANOPERM [1]. Nanocrystalline state is achieved by annealing the amorphous precursors at optimal temperature. The temperature must be higher than the onset temperature of the first stage of crystallization so that the formation of nanocrystallites in amorphous matrix may occur. The temperature should not reach the second stage of crystallization which is accompanied by formation of borides and larger grains which deteriorate soft magnetic properties. In the optimal structural state the alloy consists of nanocrystalline *bcc*-Fe phase with grain size about 20 nm and residual amorphous matrix.

The aim of this work was to study quantitatively the evolution of primary crystalline phase at each side of the ribbon during crystallization of amorphous $Fe_{79}Mo_8Cu_1B_{12}$ alloy. To achieve this goal highly intense beams of synchrotron radiation were employed. The diffraction patterns were recorded by a two-dimensional detector.

2. Subject and Methods

Amorphous $Fe_{79}Mo_8Cu_1B_{12}$ alloy was prepared by planar flow casting technique. The casting operation was carried out in air. The result of this process is a metallic glass in the form of ribbon. The ribbon is 20-22 μm thick and 10 mm wide. The chemical composition of the glassy alloy was checked by emission spectrometry with inductively coupled plasma. To prepare samples for experiments the ribbon was cut into approximately 2 cm long pieces using ceramic scissors.

Structural transformations during heating with a rate of 10°C/min were recorded by diffraction of synchrotron radiation with the energy of 7 keV (λ = 0.177 nm) at the KMC-2 beamline at the BESSY synchrotron radiation facility in Berlin (Germany). Radiation diffracted into the region around the main (110) reflection of *bcc*-Fe phase was registered by

two-dimensional area detector HI-STAR (Bruker AXS, USA). Acquisition of the data was performed every 10 seconds. The position of detector was fixed during temperature run. Angular resolution in diffraction patterns is 0.03° 2θ. For quantitative analysis of X-ray diffraction patterns the PeakFit 3.0 (Jandel Scientific, CA) software was used.

Arrangement of the diffraction experiment was as follows: The sample in the original amorphous state was fixed by hold down clamps to tantalum plate which was firmly screwed to the Boralectric® heater (Tectra GmbH, Germany). The whole system was covered with a hemispherical beryllium window (the so-called dome) which allowed vacuum annealing of the investigated sample and also an undisturbed passage of synchrotron radiation. The pressure inside the furnace was lower than 10^{-3} Pa. There were three type K thermocouples used to monitor the temperature inside the furnace. One was connected to the heated plate, the second one to the Ta plate, and the last was in direct contact with the sample. We have used one of the clamps to secure the thermocouple and maintain a good contact with the sample.

An evacuated cone, which minimized scattering of radiation in the air, was attached in front of the detector. It was covered with a polymer foil and extended up to the proximity of the beryllium dome.

The sample was continuously heated up to the temperature of 800°C. The temperature increase was linear with a ramp of 10°C/min. After reaching 800°C, the sample was annealed for 2.7 minutes. After that time the heating was turned off and the temperature inside the furnace started to drop spontaneously. The time-to-temperature profile was set using a programmable Eurotherm 2604 (Eurotherm Limited, UK) temperature controller.

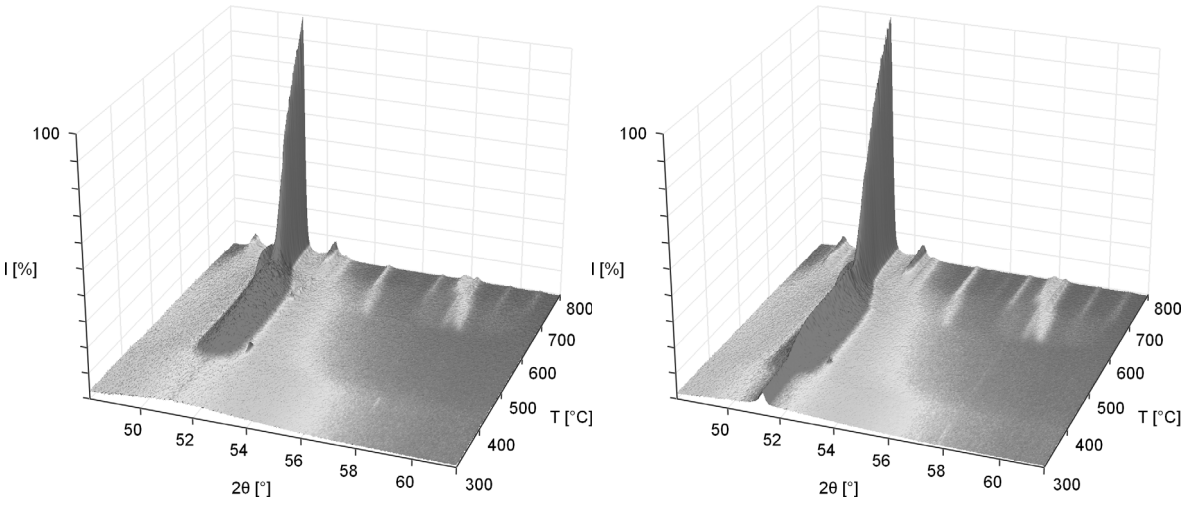
With respect to the different surfaces of the ribbon we will use the following denotation. The side of the ribbon, which was in contact with the quenching wheel during the production – optically matte, will be denoted as the wheel side. The side of the ribbon, which was exposed to the surrounding atmosphere in the production process – optically glossy, will be denoted as the air side.

3. Results

During heating 2-D diffraction patterns were acquired which were subsequently integrated over all χ angles. The obtained profiles were arranged into 3-D images depending on temperature. The obtained 3-D mappings from both sides of the ribbon are presented in Fig. 1. Both 3-D records show gradual formation of the (110) reflection which corresponds to a *bcc* phase with increasing temperature. In the second stage of crystallization, the creation of cubic $Fe_{23}B_6$ phase and subsequently the tetragonal Mo_2FeB_2 phase can be observed.

Using diffraction of synchrotron radiation we were able to trace the onset temperature of primary crystallization T_{x1} *in situ* in each specimen. Individual temperatures T_{x1} were determined to be of 410°C and 392°C for the air and the wheel side, respectively.

Relative volume fraction of crystalline *bcc*-Fe phase was determined from the reflection of the main diffraction line (110). A typical X-ray diffraction pattern of partially crystalline $Fe_{79}Mo_8Cu_1B_{12}$ sample is illustrated in Fig. 2. It also shows the decomposition of the main diffraction line into its corresponding components, i.e. relative contributions originating from crystalline phase and amorphous rest. For determination of the envelope of the narrow reflection, Lorentzian and Gaussian line profiles were used. The amorphous phase was described by Voigt line profile. The relative area of the profiles is proportional to the relative fraction of each phase.



(a) Air Side (b) Wheel Side

Fig. 1. Diffractograms of the $Fe_{79}Mo_8Cu_1B_{12}$ alloy measured *in situ* during linear heating with the rate of 10°C/min and arranged into three-dimensional record: (a) the air side of the ribbon, (b) the wheel side of the ribbon.

From the quantitative analysis of 1-D diffraction patterns of the as-quenched $Fe_{79}Mo_8Cu_1B_{12}$ alloy it was found that a considerable amount of crystalline *bcc*-Fe(Mo) phase occupying 8.2% of the total volume is located at the wheel side of the ribbon. During casting, this side of the ribbon is expected to have better conditions for solidification of the melt (mainly due to higher cooling rate). However, this phenomenon occurs at the opposite side as we have expected. Contribution of the crystalline phase at the air surface of the ribbon is as low as 0.6 vol.%. The hypothesis is proposed that heat removal was sufficient but the alloy was still located at the boundary of glass forming ability as a consequence of low concentration of boron. Therefore additional factors which can initiate the crystallization began to manifest. These include defects or impurities at the wheel side of the ribbon which can act as base of heterogeneous embryos.

Besides *bcc*-Fe(Mo) nanocrystals, traces of tetragonal Mo_2FeB_2 phase were unveiled in the amorphous matrix of the as-quenched alloy. Indications of this phase are visible as bright spots of incomplete Debye rings in 2-D patterns. Quantification of its contribution from 1-D pattern would be difficult, but considering a high scattering factor of Mo_2FeB_2 phase we can clearly say that its contribution to the amount of other present phases (*bcc*-Fe(Mo) and mainly the amorphous rest) is at this point negligible.

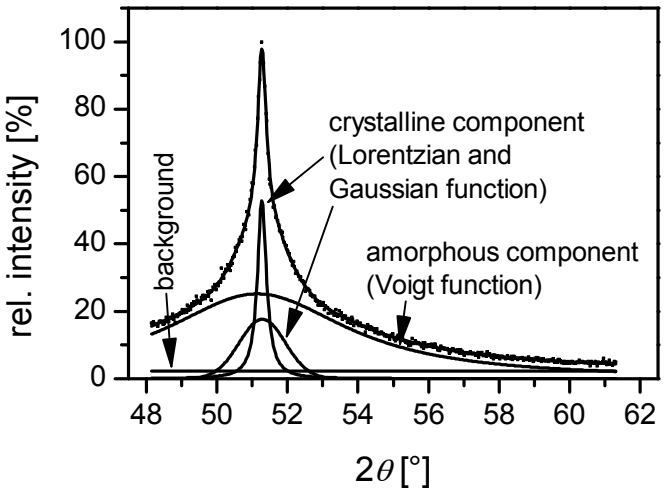


Fig. 2. X-ray diffractogram of the wheel side of the $Fe_{79}Mo_8Cu_1B_{12}$ ribbon and its decomposition into corresponding components. It was measured *in situ* at a temperature of 410°C.

Quantitative assessment of the evolution of the crystalline *bcc*-Fe(Mo) phase in the $Fe_{79}Mo_8Cu_1B_{12}$ alloy is shown in Fig. 3. After the onset of primary crystallization at 392°C, we observe a linear increase in relative volume fraction of crystalline *bcc*-Fe(Mo) phase with the slope of 0.64 vol.%/°C on the wheel surface of the $Fe_{79}Mo_8Cu_1B_{12}$ ribbon. It should be noted that this surface had already some quenched-in Fe-rich nanocrystals with *bcc* structure in initial stages of structural transformation. On the air surface, the onset temperature of crystallization is located at 410°C and evolution of the principal crystalline *bcc* phase is more rapid with the slope of 1.17 vol.%/°C. At the temperature of 590°C the alloy studied exhibit about 52% of the volume fraction of the crystalline phase.

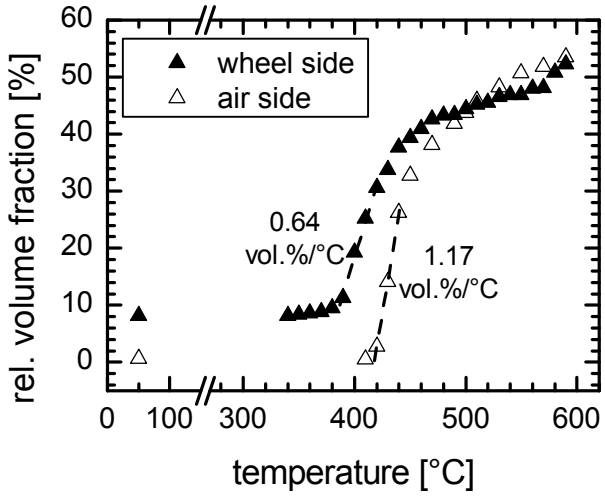


Fig. 3. Temperature evolution of the relative volume fraction of the crystalline *bcc*-Fe(Mo) phase in the $Fe_{79}Mo_8Cu_1B_{12}$ alloy.

4. Discussion

This work was focused on structural transformations which are taking place in NANOPERM-type alloy with the composition of $Fe_{79}Mo_8Cu_1B_{12}$ during thermal treatment. Attention was focused mainly on investigation of surface layers utilizing rarely used analytical technique such as *in situ* temperature scans of diffraction of synchrotron radiation.

Analysis of X-ray diffraction results obtained from $Fe_{79}Mo_8Cu_1B_{12}$ alloy in the as-quenched state has shown that significant amount of crystalline *bcc*-Fe(Mo) phase (~8 vol.%) is located at the wheel side of the ribbon. In addition, the crystallization starts earlier at this side of the studied ribbon.

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