Nucleation and growth of crystalline phases in FeBZrMoTiTa glass forming melt during superheating

T A M Aboki

Groupe de Métallurgie Strucurale (GMS) UMR 7045, ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05
tiburce-aboki@enscp.fr

Abstract. Development of multicomponent Fe-B-based bulk glass is very important for industrial applications requiring the best mechanical properties. To improve the glass forming ability (GFA) of Fe-B based alloys, Mo, Zr, Ti and Ta have been added. During the melting of different alloying elements of FeBMoZrTiTa alloy, a growth of crystalline phases in the melt was observed mainly when it was superheated for homogenization. The melt was then separated into homogenous and inhomogeneous parts. They were injected into two ingots which microstructures were studied by scanning electron microscopy and X ray diffraction. Microstructure of the inhomogeneous melt ingot contains additional Zr phases that are characterized as Fe$_3$Zr, Zr alpha and ZrB$_2$. Some other unknown crystalline phases can likely exist within the characterized crystalline phases. Thin specimens from outer areas of the two ingots show glassy state only for the inhomogeneous melt ingot.

1. Introduction

Fe-B based glassy alloys are more difficult to process than Zr-Cu based glass. However they exhibited better mechanical and magnetic properties. Additions of elements like Y [1] and Zr [2] to Fe-B based alloys enhance greatly their glass forming ability (GFA). In the case of Zr addition the good GFA is obtained for Zr < 10 at.% [2]. The glassy Fe-B-Zr alloys are mostly multicomponent systems containing other elements like Mo, Nb, Ni, Ti, and Ta. These melts are sensitive to superheating and annealing and can undergo melt separation [3] and heterogeneous crystal nucleation [4].

In order to verify the empirical rule stating that GFA is enhanced by additions of minor element in a glass composition, we have incorporated Ti and Ta to Fe-B-Zr-Mo alloys. During the melting of the master ingot, we observed the appearance of insoluble solid in the melt when it was superheated in order to gain more homogeneity. This crystalline solid was dissolved when the temperature reached again the melting point. After the appearance of the insoluble solid, we have separated the melt into two parts: the homogeneous and the inhomogeneous melt that contains this solid. Two separated ingots were then processed and their microstructures and thermal behaviors were investigated.

2. Experimental

Fe$_{70}$Mo$_{2}$B$_{18}$Zr$_{8}$Ti$_{1}$Ta$_{1}$ master ingot was prepared by melting of high purity elements: Fe (zone melting), Mo (99.95), B (99.95), Zr (99.96%), Ti (99.99%), Ta (99.99%) in a copper water-cooled boat by high frequency (HF) electromagnetic induction under argon atmosphere. The melting temperature was about
1300 K. The alloying elements contents were selected in order to have a composition close to the eutectic. During superheating at about 100-200 K above the melting temperature, visible crystalline solid growth was observed. Therefore, the starting melt was separated into two parts, the right-hand part that contains the visible crystalline and left-hand part that is more homogeneous without visible crystalline phases. Two master ingots were obtained that re-melted and injected into a watercooled copper mold to obtain ingots of 8 mm of diameter and 40 mm in length under 0.3 MPa of argon pressure. The cooling rate of the casting technique was estimated to about 100 K/s. Discs for investigations were cut from cylindrical ingots.

3. Results and discussions
3.1. Homogeneous melt ingot
Figure 1 shows the SEM microstructure of the ingot obtained from the homogenous melt (H). Three main contrasted phases can be observed. A white contrasted phase (W) that is located at the grain boundary (figure 1a) of a dark green phase (D). In the centre of the specimen (figure 1b), the (W) phase is distributed as needles or plates of about 1-2 μm of width (figure 1c). The (G) phase is in fact a multiphase containing some white contrasted dots. It looks like twinned grains of about 2-3 μm. It is not observed in the border of the sample. It is there probably embedded in the grain of about 5-10 μm (see figure 1a).

![Figure 1. SEM microstructure of the border (a) and central (b and c) areas of the homogeneous melt ingot.](image)

The (W) phase is a Fe-Zr-rich phase, while (D) is a Fe-rich phase and (G) is a Zr-rich phase demonstrated by qualitative EDS spectra. SEM and X-ray mappings of detailed area of the specimen shown in figure 2 indicate clearly (see the dots) the Zr-rich and the Fe-rich phases locations.

3.2. Inhomogeneous melt ingot
Figure 3 shows the SEM microstructure of the ingots obtained from the inhomogeneous melt (I). A smooth (S) and porous (P) areas can be observed in the microstructure. The size of the latter is greater in the border area than at the center of the specimen. Their size is also variable and their proportion is lower in the center than in the border area. The phases distribution seems to be different within the (P) than in the (S) one. The latter presents the microstructural trends like that of the H specimen. The compositions of the two ingots are obviously different and that is mainly manifested by the presence of
the porous area in the (I) specimen. EDS analysis on a broad (P) area indicates a higher proportion of Zr and that of minor alloying elements Mo, Ta, Ti than in the (S) area (figure 4). It is likely due to the white contrasted phases in the porous area. In the smooth area, the (W), (D) and (G) phase were observed again. The (G) phase is more homogeneous with a cloudy aspect.

![Figure 2. SEM and X-ray mappings of detail area of the (H) ingot.](image)

![Figure 3. SEM microstructure of the border (a) and central (b and c) areas of the inhomogeneous melt ingot.](image)

3.3. Crystalline phases characterization and thermal behaviour

Figure 4 represents the XRD spectra of the (H) and (I) specimens. It is shown that most of the lines are common to the two specimens and belongs to cubic (C) Fe\(_3\), Fe\(_2\)Zr, (Fe,Mo)B and Zr\(_2\), tetragonal (Fe,Mo)\(_3\)B. The main difference appeared in the presence of the lines of orthorhombic (O) Fe\(_3\)Zr and hexagonal (H) ZrB\(_2\) crystalline phases with probably more Zr\(_2\) and some unknown phases that could be Mo-rich phases. The Fe\(_3\)Zr and ZrB\(_2\) phases are intermediate high temperature phases located between the two eutectic valleys of the Zr-Fe and the Zr-B binary diagrams. This would explain their formation within the melt during superheating. The observations confirm also the tendency of multicomponent melt to form multieutectic systems when the proportions of the alloying elements are chosen in the
eutectic range of the binary systems. If we consider that the additional crystalline phases are located in the (P) areas in the (I) specimen, they are certainly evolved from a liquid-liquid separation from the original melt.

DSC results of specimens from the two ingots show that a glass transition and onset crystallization temperatures are about 829 and 890 K respectively for the (I) only. The undercooled liquid region value ΔT of 62 K is quite appreciable. It seems that the presence of pores and additional crystalline phases have favored the GFA of the FeMoBZrTaTi (I) composition. This would be to one hand in agreement with the clusters nature of the amorphous structure [5]. To the other hand, this sheds a light on the necessity of glass forming melts to create defects to dissipate thermal energy so as to reach the room temperature rapidly without any crystal growth. Formation of chemically different clusters is probably a way to share energy in order to minimize the internal energy of the final solid material.

From the results, the (I) alloy seems to have a better GFA than the (H) part. However a border area of about 0.5 mm shows glassy aspect that means that (H) has also a glassy composition. The samples were analyzed by X-rays diffraction (XRD) using Cu-Ka radiation. An error of about ± 0.02 (2θ) is considered on the XRD lines in the characterization of the crystalline phases. Microstructural observations were performed by scanning electron microscopy (SEM) on as-cast carefully polished surfaces with a 1 μm diamond. The microstructure’s chemical compositions were analyzed by energy dispersive X-ray spectroscopy (EDS) in the SEM apparatus. An estimated error of about ± 2% is allowed on the data analysis. All SEM micrographs were obtained in the backscattered electron image mode (BEI), that enables chemical contrast maps of the microstructure.

DSC scans were preformed on thin specimens of about 40-100 μm thick from the header of each ingot in order to check the thermal behavior of the two alloys.

![Figure 4](image-url)  
**Figure 4.** XRD spectra with indexed crystalline phases in the two specimens.
The observations on the FeMoBZrTaTi alloy (I) suggest that a liquid separation exists in the multicomponent melt and that a superheating is one of a suitable way to reveal it. An eutectic melt can form the separated liquid in case of the glass forming or deep undercooling melt too.

4. Conclusions
We have investigated the formation of solid phase during superheating of FeBMoZrTaTi melt by separating the original melt into homogeneous (H) and inhomogeneous (I) parts. The latter contains the insoluble solid phase. The microstructural observations on specimens from the two ingots show the presence of porous areas in (I) in addition to common smooth areas. XRD patterns confirm the occurrence of the additional crystalline Fe$_3$Zr, Zr$_2$ and ZrB$_2$ phases in the (I) specimen. They are likely the phase constituents of an eutectic liquid separated from the smooth areas liquid. The (I) alloy seems to exhibit a better GFA than (H) since thin specimen from it is glassy. This suggests that liquid phase separation favor the formation of glassy structure in agreement with the clusters ideas of amorphous structure. Transmission electron microscopy investigations are planned characterized the crystalline phases.

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