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Journal of Materials Processing Technology 191 (2007) 377–380

Journal of Materials Processing Technology

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Thermal de-vitrification and formation of single phase nano-crystalline structure in Fe-based metallic glass alloys

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Abstract

The crystallization temperature obtained in a thermal analyzer has become a conventional means for characterizing the thermal stability of metallic glasses and less importance has been attached to the intermediate crystalline phases until recently that nano-structured alloys can now be prepared by careful heat treatment of metallic glass precursors. This has brought attention to studying in detail, the process of de-vitrification and the formation of intermediate crystalline phases. The de-vitrification of a number of Fe-based metallic glass alloys have been followed with differential scanning calorimeter (DSC). De-vitrification is generally accompanied by two exothermic peaks that signify a two step crystallization reaction. Small additions of transition metallic elements, Cu, Cr, Ta, Nb and Mo alter this shape either leading to complete separation or merging of the two thermal events. Crystallization temperatures characterized by the primary peak temperature varied from 450 °C to 600 °C. The separation between the peaks varied from 0 (for single peak) to more than 100 °C depending on alloy composition. It is found that for alloy compositions where peak separation is less than 20 °C, it was not possible to anneal to single phase nano-structure.

Keywords: Metallic glass; De-vitrification; Nano-crystalline; Amorphous phase

1. Introduction

Glass formation in metallic alloy was first demonstrated in 1960 but interest did not grow until the advent of rapid solidification processes in the last two decades. The theory of metallic glass formation is now well understood [1] that glass formation in metallic systems have been predicted and verified amongst many metallic systems. The Fe-based systems, in particular have generated interests because of its many potential applications in engineering systems. Glass forming Fe-based alloys typically consist about 15–25 at.% of metalloid that may be any of Si, B, Zr. Though, the Fe-based glassy alloys are known to show unique combinations of soft magnetic properties, more recent developments [2] has indicated that these soft magnetic properties can be significantly improved by small additions of Nb and Cu, and by partial de-vitrification to a single phase nanocrystalline structure. It was found that these have extremely soft magnetic properties with coercivity less than 5 A/m [2]. The origin of the soft magnetic properties is related to the size of the grains of the α-Fe(Si) magnetic phase being smaller than the magnetic exchange length and as a result lead to ferro-magnetic coupling between the crystallites [3]. Many more compositions of partially de-vitrified nano-structured alloys with similar magnetic properties have since been prepared [2,4,5].

The preparation of soft magnetic nano-structured through partial annealing of metallic glass precursor introduces a new dimension into the studies of the thermal de-vitrification of metallic alloys. Hitherto, it was simply enough to know the temperature at which the Fe-based glasses crystallize into α-Fe and other intermetallic phases. It is now more important to study the mechanism of thermal de-vitrivication and explore the compositional and thermal requirements for de-vitrivication into single phase nano-crystalline structure. In this work, we have studied the thermal de-vitrivication of a range of known Fe-based metallic glass alloys in order to explore the practicality and the design of the experimental procedure for preparing single phase nano-crystalline structure from a metallic glass precursor.

2. Experimental

Fe–Si–B-based metallic glass alloys are mostly wires made by the rotating water bath process under the wire casting program at the University of Sheffield, UK. Other compositions especially the Fe–M–B (M being Zr, Ti and Nb) alloys studied here were produced by chill block melt spinning process. Both of the processing imposed similar quenching rate of about 10^5 K/s to 10^6 K/s on the as-cast products. The as-cast structures were confirmed to be fully amorphous using X-ray diffraction methods.

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doi:10.1016/j.jmatprotec.2007.03.047

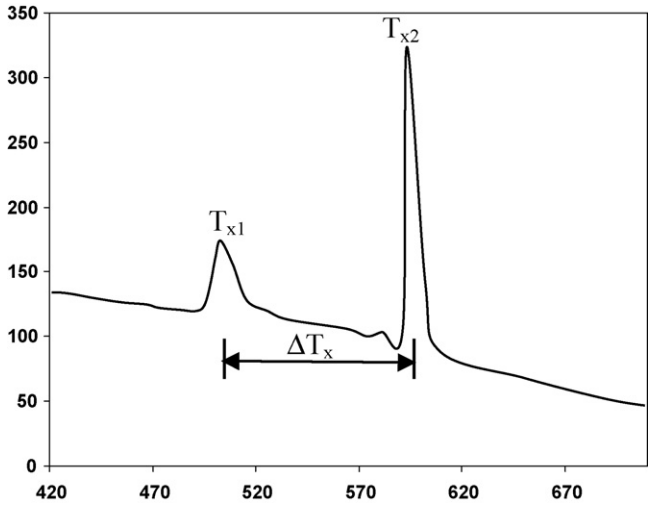

Fig. 1. DSC exothermic peaks that signifies crystallization of $Fe_{77}Mo_1Cu_{0.5}Si_{7.5}B_{12.5}$ glassy alloy.

Thermal de-vitrification was followed with a differential scanning calorimeter using a SETARAM 2000 DSC/TG thermal analyzer. About 20–40 mg of metallic glass samples were loaded into a platinum sample pan for the DSC thermal studies. Thermal scanning was done at the rate of 20 °C/min from room temperature to 750 °C using a sweeping gas of high purity argon. Phase identification for annealed samples was done with X-ray diffraction and X-ray line broadening analysis was used to estimate average crystallite sizes. Lattice parameter determined from XRD data was used to determine the extent of solid solution in α-Fe crystallites.

3. Results and discussion

3.1. De-vitrification of metallic glass alloys and the importance of ΔT_x

Typically the thermal de-vitrification of Fe–Si–B or Fe–M–B metallic glass alloys follows a two stage crystallization process and is typified by two exothermic peaks when monitored on a thermal analyzer. Fig. 1 shows the DSC de-vitrification profile obtained for $Fe_{77}Si_9B_{12.5}Mo_1Cu_{0.5}$ metallic glass wire. This is characterized by two crystallization peaks T_{x1}, T_{x2} and the peak separation ΔT_x. Annealing of an Fe-based glass at a temperature around T_{x1} often lead to the transformation of the amorphous phase into α-Fe type phase and intermetallic phases of the type Fe_xB_y, for which Fe_2B, Fe_3B and $Fe_{23}B_6$ have all been identified [6]. Fig. 2 shows the XRD for glassy and annealed $Fe_{75}Si_{10}B_{15}$.

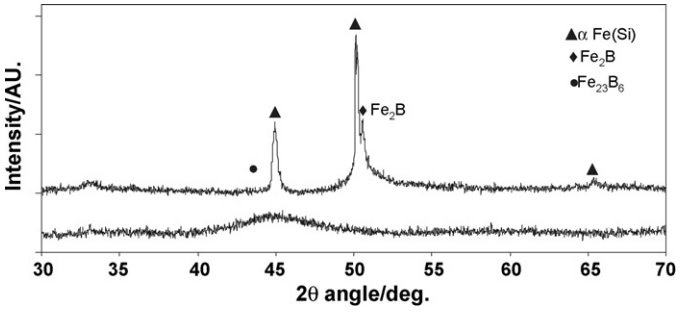

Fig. 2. XRD pattern for $Fe_{75}Si_{10}B_{15}$: (a) as-cast indicating amorphous phase and (b) annealed at 550 °C.

Table 1
Some glass forming alloys and DSC crystallization peaks

Composition	Form	First DSC peak, T_{x1} (°C)	Peak separation, ΔT_x (°C)
$Fe_{77.5}Si_{7.5}B_{15}$	Wire	538	8
$Fe_{75}Si_{10}B_{15}$	Wire	551	18
$Fe_{67.5}Cr_{10}Si_{7.5}B_{15}$	Wire	551	0
$Fe_{67}Cr_8Si_{10}B_{10}$	Wire	572	0
$Fe_{73.5}Nb_3Si_{13.5}B_{15}$	Wire	600	0
$Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$	Wire	560	160
$Fe_{77}Mo_1Cu_{0.5}Si_{7.5}B_{12.5}$	Wire	490	100
$Fe_{85}Zr_7B_8$	Ribbon	535	–
$Fe_{84}Cu_1Zr_7B_8$	Ribbon	524	165
$Fe_{82}Cu_1Ti_7B_{10}$	Ribbon	439	258
$Fe_{84}Cu_1Nb_7B_8$	Ribbon	467	143

The Sharp peaks from the annealed sample have been indexed to α-Fe(∼12 at.% Si) and Iron borides mostly Fe_2B and Fe_3B.

Many systematic thermal studies (e.g. [3]) have revealed that the de-vitrification of these types of glasses follows a two stage process that is accompany by the formation of supersaturated α-Fe(Si, Zr) followed by the transformation of the residual amorphous into intermetallic phases. It is apparent therefore, that a large thermal lag separating these two events would provide practical advantage for partial de-vitrification into the initial crystalline phase. Table 1 gives a list of some compositions studied with the DSC exothermic crystallization peaks. Two groups are presented consisting of glass forming compositions around Fe–Si–B and Fe–M–B (M = Zr, Ti, Nb). For both groups their basic compositions are characterized by two peaks as indicated by the ΔT_x values given. The peak separation is affected by minor modifications from the original glass forming compositions as indicated by the values of ΔT_x. The basic Fe–Si–B alloys showed peak separation (ΔT_x) of less than 20 °C. The substitution of Fe with similar transition element (Cr) actually leads to single peak. The combined effect of transition metals (Cr, Ta, Nb and Nb) and Cu widens the gap between T_{x1} and T_{x2} to give a larger ΔT_x. All the Fe–M–B-based alloys listed have T_{x1} around 500 °C and exhibited very large ΔT_x (>100 °C). The practical implication of a large ΔT_x value is that such alloys could be partially devitrified into the first crystalline phase, which in this case is α-Fe type. Fig. 3 shows the TEM microstructure and selected area diffraction pattern (SADP) obtained for $Fe_{77}Si_9B_{12.5}Mo_1Cu_{0.5}$ metallic alloy annealed for 1 h at 480 °C. Analysis of the rings of the SADP showed that the grains are nanocrystalline bcc iron. X-ray line broadening analysis confirmed that the average crystallite size was 10 nm and the lattice parameter measurements also indicated that the α-Fe phase was supersaturated Fe-Si with Si content of about 12 at.%. A cursory examination of the thermal de-vitrification properties of alloys listed in Table 1 showed that those with ΔT_x greater than 100 °C are those that have been reportedly [2,4,5,7] prepared as single phase nano-structured alloys. The key to the practicality of such partial de-vitrification into nano-structured body appear to lie with the effects of minor modifications to the chemical compositions of the traditional glass forming alloys and how these affect the de-vitrification kinetics as indicated