Advanced Engineering Forum
ISSN: 2234-991X, Vol. 13, pp 54-58
doi:10.4028/www.scientific.net/AEF.13.54

Submitted: 2014-10-07
Revised: 2015-01-06
Accepted: 2015-02-16
Online: 2015-06-22

Synthesis of $Fe_{75}Si_{20-x}B_5M_x$ (M=Ti, Ta or Zr) powders by wet mechanical milling

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Keywords: amorphous, wet mechanical alloying, thermal analysis, Ti, Ta and Zr substitutions

Abstract. Amorphous $Fe_{75}Si_{20-x}B_5M_x$ powders with M= Ti, Ta or Zr and x = 0 and 5 were synthesized by wet mechanical alloying, using benzene as a surfactant. The thermal stability of the Fe-Si-B alloy increases by introducing transition metals. The replacement of 5% Si with Ti, Ta or Zr leads to an increase of the crystallization temperature. It was found that the replacement of 5% Si with Zr increases the crystallization temperature with 115 °C, and also reveals a glass transition temperature around 580 °C.

1. Introduction

Amorphous alloys usually have unique mechanical and physical properties due to their disorder in the atomic structure [1]. In order to obtain amorphous alloys several techniques have been developed in the last decades, such as rapid quenching, mechanical alloying (MA). Mechanical alloying techniques involve the synthesis of materials by high-energy ball milling, in which elemental blends (or prealloyed powders, oxides, nitrides, etc.) are milled to achieve alloys or composite materials. Due to the material transfer and solid state reactions homogeneous alloys are obtained[3]. The addition of process control agent (PCA) to the mixture during milling inhibits agglomeration of the particles and also shortens the milling times. Amorphous alloys based on Fe, Ti, Zr, Cu and Ni are produced by mechanical alloying in the past years [4-7]. In the last decades, a great deal of amorphous alloy systems, such as Ti-based, Zr-based, Cu-based, Ni-based and Fe-based alloys, have been developed through mechanical alloying [8-10]. The main difficulty to obtain the amorphous alloys is represented by their low glass forming ability (GFA). To improve the GFA of the Fe-based alloys several metalloids are added (B, C, Si and P) [11]. Also, addition of other transition metals such as Ti, Zr, Nb and Ta, inhibits the precipitation of the primary phase [12]. The goal of the present research is to develop new amorphous powders, $Fe_{75}Si_{20-x}B_5M_x$ (M=Ti, Ta or Zr, x=0, 5 at. %) in order to increase the thermal stability of the classical $Fe_{75}Si_{20}B_5$ alloy. A higher crystallization temperature increases the chances of obtaining compacts with high density, preserving in the same time the amorphous state [13].

2. Experimental procedures

The starting mixtures ($Fe_{75}Si_{20-x}B_5M_x$, M=Ti, Ta or Zr, x=0, 5 at. %) contained high purity elemental powders: iron powder - NC 100.24 - (Höganäs), silicon powder 99.9% (Alfa Aesar), boron amorphous powder 99.9% (Alfa Aesar), titanium powder 99.5% (Alfa Aesar), tantalum powder 99.6% (Alfa Aesar) and zirconium powder 99.2% (Alfa Aesar). All of the mixtures were

homogenized in a Turbula-type apparatus for 30 min, to ensure an uniform distribution of the elemental powders. The homogenized powder mixture was then processed in a tempered steel vial, together with stainless steel balls. The ball to powder ratio (BPR) of 16:1 was chosen, leading to the filling factor of 60%. Wet MA was performed on a high-energy planetary ball mill (Fritsch Pulverisette 6) in Ar atmosphere for 60 hours. Several milling times were used ranging from 2 h up to 60 h.. The chosen PCA was benzene - C_6H_6. The rotation speed was set to 350 rpm. To avoid powder oxidation, the samples handling was done under Ar atmosphere in a glove-box (Iteco engineering SGS 30). The evolution of the powders structure at different milling times was investigated by X-ray diffraction (XRD) using Co Kα radiation (Inel Equinox 3000). Thermal stability of the alloys was studied by differential scanning calorimetry technique (DSC) using a Setaram Labsis TG-DSC apparatus under argon atmosphere using a heating/cooling rate of 20 °C/min.

3. Results and discussions

In figure 1 are presented the X-ray diffraction (XRD) patterns of the quaternary alloys $Fe_{75}Si_{20-x}B_5M_x$ obtained by MA, milled for 60 h using benzene as surfactant. The XRD patterns revealed a broadened peak around 52 degrees, for all the investigated samples ($Fe_{75}Si_{20}B_5$, $Fe_{75}Si_{15}B_5Ti_5$, $Fe_{75}Si_{15}B_5Ta_5$, $Fe_{75}Si_{15}B_5Zr_5$), typical for the Fe-based amorphous powders, as can be observed in figure 1.

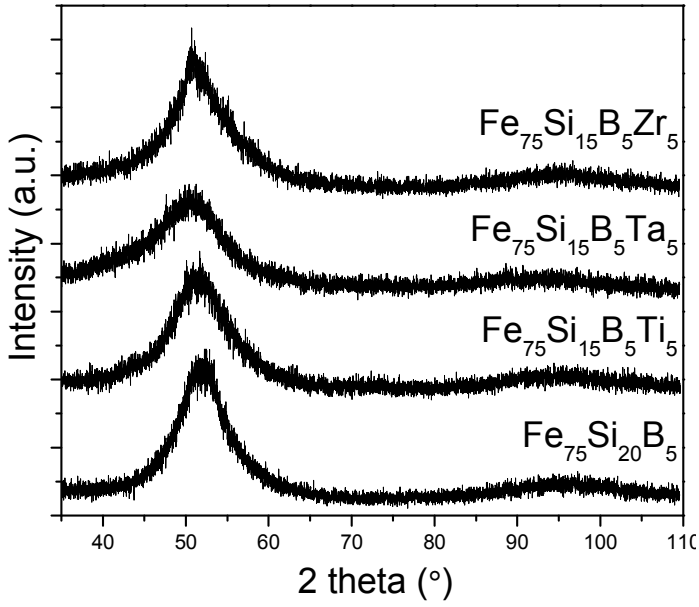

Fig. 1. XRD patterns corresponding to the Zr, Ta and Ti substitution (x=5) for the $Fe_{75}Si_{20-x}B_5M_x$ samples wet milled 60 hours. For clarity, the X-ray patterns have been vertically shifted.

The XRD patterns show no sharp peaks in any of the four cases, revealing the fact that the Ti, Ta and Zr for Si substitution did not lead to crystallization of the material for this milling time. The broad peak indicates the lack of long-range atomic ordering, proving that 60 hours of wet milling using benzene are enough to induce powder amorphisation [13]. The fact that the X-ray patterns of all the samples are nearly the same after the partial replacement of Si with Ti, Ta or Zr suggest that the substitutions do not change structure of the material, preserving the amorphous state.

In order to determine the thermal stability of the quaternary $Fe_{75}Si_{20-x}B_5M_x$ alloys obtained by MA and to compare them to the classical ternary $Fe_{75}Si_{20}B_5$ alloy, DSC measurements were performed. The DSC heating and cooling curves are presented in figure 2.a.

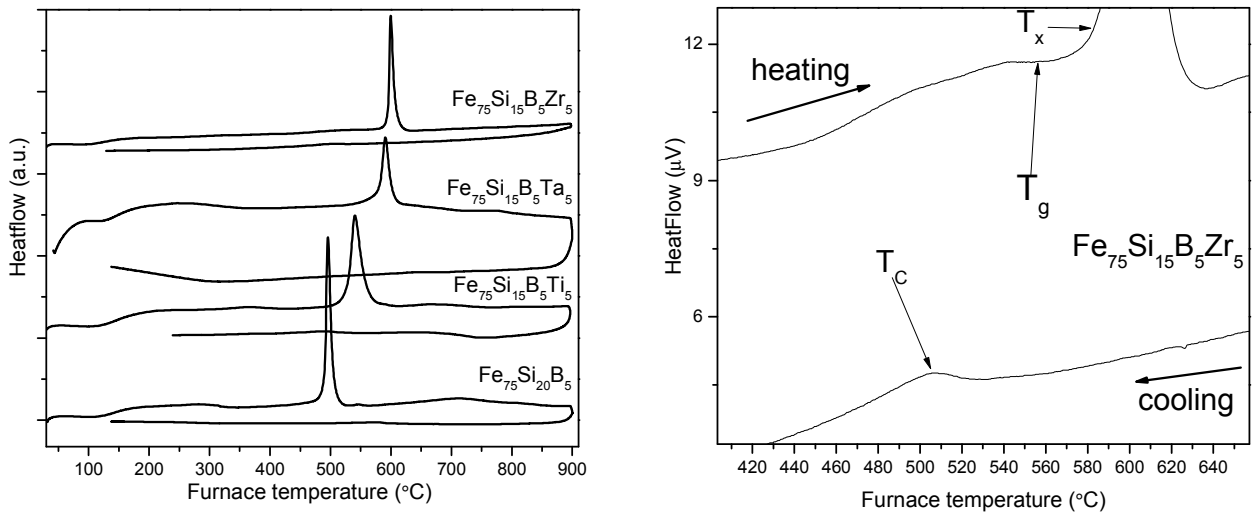

Fig. 2.a. Heating/cooling DSC curves of $Fe_{75}Si_{15}B_5M_5$ (M=Si, Ti, Ta, Zr) powders wet milled up to 60 hours;2.b A zoom of the DSC heating curve between 455-680 °C of $Fe_{75}Si_{15}B_5Zr_5$ powders wet milled up to 60 hours. The used heating rate was 20°C/min in Ar atmosphere

The DSC curves display a series of transformations that occur during heating up to 900°C. Independent on the type of the element that was used for Si substitution, for all the samples a broad exothermic peak is noticed in the temperature range 100-250 °C. This peak is assigned to the internal stresses release. This is a typical thermal event that is encountered during heating of mechanically milled samples [13]. Also, it can be noticed a sharp and large exothermic peak in the temperature range of 485-600 °C. For the $Fe_{75}Si_{20}B_5$ sample, the peak is found at 485 °C. The position of the peak depends on the element that was used for Si substitution. The sample containing Ti, has a peak at 540 °C, the one containing Ta, has a peak at 590 °C and for the one with Zr the peak is observed at 600 °C. This sharp exothermic peak is attributed to the primary crystallization phase of the amorphous powder, α-Fe(Si) with traces of B and M [13]. It is worth to be noticed that, the crystallization phenomena is shifted to the higher temperatures for the samples in which 5 % of silicon was substituted with Ti, Ta or Zr, compared to the $Fe_{75}Si_{20}B_5$ alloy, resulting in an increase of the thermal stability [12], as can be seen in table 1. Also, the Ta or Zr for Si substitution leads to higher crystallization temperatures as compared to the Si rich Finemet alloys [10, 14, 15]. The thermal stability of the amorphous alloys is linked to the geometric and electronic effects. These effects increase the difficulty of atomic rearrangement, and the degree of dense random-packed structures. One of the geometric effects is the fact that one empirical rule for increasing the stability of the amorphous alloy is increasing the number of constituents [16]. Another geometric effect represents the atomic radius ratio of the elements in the mixture ($\Delta r/r \geq 0.12$). Higher atomic radius ratio and more constituents in the alloy determine a larger degree of dense random-packed structure. The sample containing 5% of Zr presents the highest crystallization temperature because Zr has the largest atomic radius, as compared to other used substitution elements. The sample contains small atoms (Si, B), intermediate atoms (Fe) and large atoms (Zr). The smaller atoms occupy the interstices between the larger atoms, requiring higher energies for long-range atomic ordering through geometric means. This atoms size distribution decreases the tendency for the formation of crystalline phases. The atoms rearrange more difficult by increasing the degree of dense random-packed structure. Despite the fact that Ti and Ta are intermediate atoms, and they have approximately similar atomic radius, as can be seen in table 1, the sample containing Ta, presents a higher crystallization temperature. This difference is due to the fact that the thermal stability of the alloy is also linked to the bond valence and the electronic configuration (electronic effects) [16]. Higher bond valence determines a higher energy required for atomic rearrangement. It was generally observed that substitution with elements with 5d configuration (Ta) determine a higher bond valence and will have a higher crystallization temperature, T_x, than elements with 4d

(Zr) and 3d configuration (Ti) [16]. The fact that the sample containing Zr, has the highest crystallization temperature reveals that the atomic radius ratio has a larger influence than the bond valence, in the case of this type of amorphous alloy.

Table 1. Chemical and thermal properties of substitution element [17]

Type of substitution			
$Fe_{75}Si_{15}B_5M_5$	Ti	Ta	Zr
Crystallization temperature [°C]	540	590	600
Glass transition [°C]	-	-	580
Atomic radius [10^{-12} m]	143	145	155
Bond valence	2.9	4.6	3.4

The sample containing 5% of Zr also reveals a glass transition temperature, T_g, around 580 °C which can be observed in the detail presented in figure 2.b. Due to the fact that the crystallization temperature is increased as compared to the other alloys, it is possible to observe the glass transition temperature and determine the supercooled liquid region, ΔT_x. For the quaternary alloy containing Zr, the ΔT_x is about 20 °C. For the other alloys, $Fe_{75}Si_{20}B_5$, $Fe_{75}Si_{15}B_5Ti_5$ and $Fe_{75}Si_{15}B_5Ta_5$ this phenomenon it is not noticeable on the heating curves due to their lower crystallisation temperature which is very close to the glass transition temperature. On the DSC cooling curve of $Fe_{75}Si_{15}B_5Zr_5$, around 510 °C, change of slope of the DSC signal can be observed. This slope change can be easily remarked in the figure 2b, where is presented DSC heating curve between 455-680 °C of $Fe_{75}Si_{15}B_5Zr_5$ powders wet milled up to 60 hours. This thermal event is assigned to the Curie temperature of the α-Fe(Si) phase [13]. The presence of the other elements, B and Zr, leads to a lower Curie temperature as compared to $Fe_{75}Si_{20}B_5$ alloy [13].

4. Conclusion

It was noticed that 60 hours of wet mechanical milling leads to powder amorphisation, for all the samples investigated. Increasing the difficulty of atomic rearrangement through geometric and electronic effects leads to higher thermal stability of the alloys. The replacement of 5% Si with Ti leads to an increase of the T_x with about 55 °C, while the replacement of the same amount of Si with Ta or Zr leads to an increase of the T_x with about 105 °C for Ta, and 115 °C for the substitution with Zr. Due to the higher crystallization temperature of the alloy containing Zr, in its DSC curve a glass transition temperature, around 580 °C can be observed. The higher values of T_g, T_x and the difference between them (ΔT_x) lead to increase of the amorphous phase stability. Further researches are needed in order to increase the interval between crystallization and glass transition temperatures of the powder, ΔT_x, in order to achieve high density compacts by spark plasma sintering at relatively low temperature and pressure.

ACKNOWLEDGEMENT

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2012-3-367.

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