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Comparison of Fe-Ni based alloys prepared by ball milling and rapid solidification

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Mechanical alloying (MA) and rapid solidification (RS) are two important routes to obtain amorphous alloys. An Fe-Ni based metal-metalloid alloy ($Fe_{50}Ni_{30}P_{14}Si_6$) prepared by these two different processing routes was studied by differential scanning calorimetry, scanning electron microscopy with microanalysis, inductive coupled plasma, X-ray diffraction (XRD) and transmission Mössbauer spectroscopy (TMS). The results were compared with that obtained from other Fe-Ni based alloys of similar compositions.

The structural analyses show that the materials obtained by mechanical alloying are not completely disordered after 40 h of milling whereas fully amorphous alloys were obtained by rapid solidification. TMS analyses show that, independent of the composition, after milling for 40 h, about 7% of the Fe remains unreacted.

Furthermore, the thermal stability of mechanically alloyed samples is lower than that of the analogous material prepared by rapid solidification. In the MA alloys, a broad exothermic process associated to structural relaxation begins at low temperature. XRD patterns of crystallized alloys indicate that the crystallization products are bcc(Fe,Ni), fcc(Ni,Fe), and (Fe,Ni)-phosphides and -silicides.

1. Introduction

Fe-based alloys prepared by rapid solidification (RS) have interesting magnetic properties. These alloys were widely investigated during the last decades [1, 2]. Nevertheless, they did not attain an important level of applicability in the industrial processes, as could be expected from their good magnetic properties. One reason for this is that by rapid solidification it is possible to produce thin ribbons only. In last decades, the mechanical alloying technique (MA) was introduced to produce Fe-based amorphous alloys [3, 4]. Using MA at room temperature amorphous powders have been obtained in great quantity and a very large composition range. During last years, the comparison of results obtained in materials developed by mechanical alloying or rapid solidification was performed in several metallic systems [5–7].

This work deals with analysis and comparison of powders obtained by MA in a planetary mill and by melt spinning under controlled atmosphere. Mechanical alloyed samples were prepared from elemental precursors. Rapidly solidified alloys were obtained by melt-spinning.

2. Experimental

The alloy analyzed is $Fe_{50}Ni_{30}P_{14}Si_6$. In MA, powders (particle size up to 25 μm) of elemental Fe, Ni, P and Si were loaded into the hardened steel vial together with steel balls inside an argon filled glove box. The ball millings were performed in a planetary type mill (Frisch Pulverisette 7). The ball-to-powder weight ratio was 5:1 and the milling intensity was held at an intensity setting of 7. The milling times were 10, 20 and 40 h. The melt-spun alloy, in ribbon form, was produced by quenching the molten alloy on the surface of a rapidly spinning (∼35 m/s) copper wheel under Ar atmosphere. In this case, the Fe_3P compound was used to prevent P sublimation.

The contamination was analyzed by induction coupled plasma (ICP) and with the energy dispersive X-ray microanalysis (EDX) system coupled to a Zeiss DSM960 A scanning electron microscope. The thermal stability of the metastable phases formed was tested, by studying their behavior on heating, in a differential scanning calorimeter (Mettler Toledo DSC30), under a pure Ar atmosphere. Structural analysis were performed by X-ray diffraction (XRD) analysis, in a D500 Siemens equipment using Cu K_α radiation, and transmission Mössbauer spectroscopy (TMS) measurements at room temperature, using a ^{57}Co in Rh source and calibrated with an α-Fe foil.

3. Results and discussion

Low contamination from the milling tools (<2 at.%) was found by ICP and EDX in the alloy milled for 40 h.

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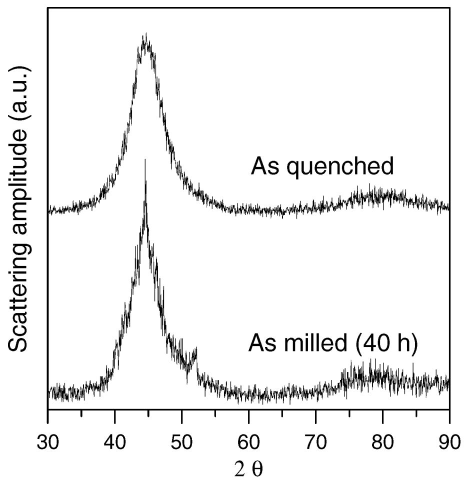

Figure 1 X-ray diffraction pattern of alloys as quenched and as milled for 40 h.

Furthermore, oxygen presence was detected probably due to the large surface area and the high reactivity of the fine particles. Likewise, the alloy obtained by melt spinning shows the same nominal composition after and before melt-spinning production. Similar results are reported in other Fe-Ni based alloys [8].

Fig. 1 shows the X-ray diffraction patterns of the alloy as quenched and as milled for 40 h. In RS alloy show the typical halos of an amorphous structure. MA alloy after 40 milling show some remains of crystalline α-Fe and Ni elemental precursors.

TMS analyses show that, independent of the composition [8], the material obtained by RS is fully amorphous. After milling for 40 h, less than 5% of the Fe remains unreacted. Fig. 2 shows the hyperfine magnetic field (BHF) distribution for both materials. The BHF distribution of the amorphous phase shows the typical shape of amorphous P-bearing phases. Similar shapes of the BHF distribution are obtained for MA and RS samples in other Fe-Ni based alloys, although the presence of unreacted iron is clearly detected in the spectra of MA samples [9, 10].

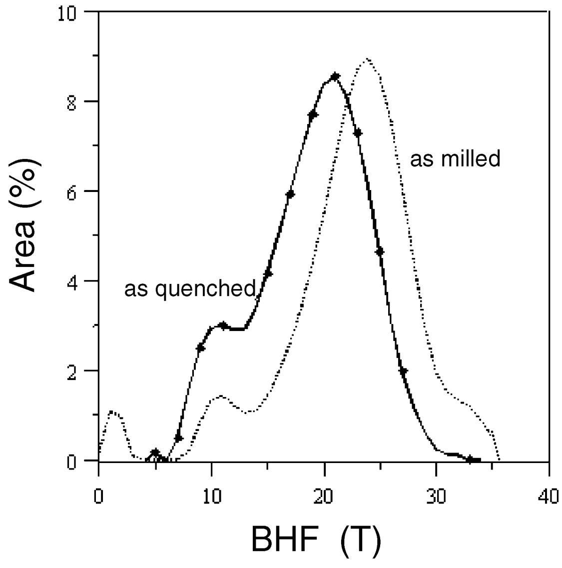

Figure 2 Hyperfine field distribution of alloys as quenched and as milled for 40 h.

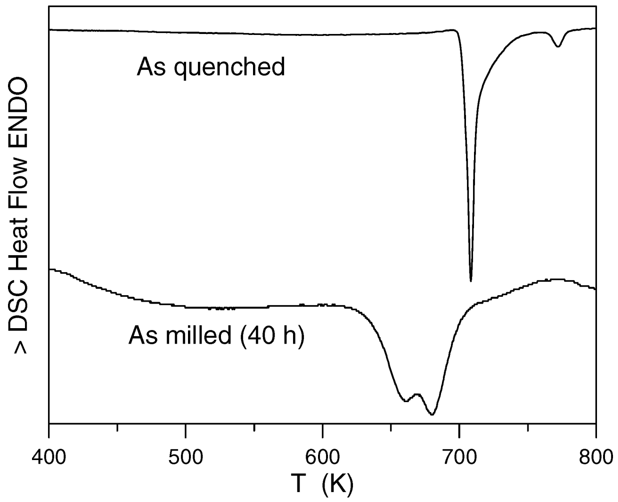

Figure 3 DSC scans at a heating rate of 10 K min^{-1} of quenched and mechanically alloyed samples.

Furthermore, preliminary work by XRD and TMS on the progress of alloying revealed a reduction of the grain size to the nanometer range, an increase in atomic-level strain and stored enthalpy as well as a change of the lattice parameter of the constituents upon milling [9]. The same effect was detected in other metallic alloys [11].

DSC measurements performed support the existence of an amorphous phase deduced from XRD and TMS. Fig. 3 shows DSC scans performed at a heating rate of 10 K/min, for quenched and milled samples. In all heating experiments several exothermic processes were detected that are related to the crystallization of the amorphous-like alloy. There are at least three processes for samples MA. The first one is shallow and broad. It is typical for a relaxation process and starts at about 410 K. A crystallization peak starts at about 620 K and overlaps with a second crystallization peak. The crystallization process in the rapidly solidified samples produces a very sharp main exothermic peak and at least one flat high temperature second peak. Both, the onset temperature of the main peak and the crystallization enthalpy are comparatively higher for rapidly solidified samples than for sample MA, as expected since the last ones are powders with some remains of crystallinity. The apparent activation energies of exothermic processes observed on continuous heating experiments were calculated by the Ozawa's shift peak method [12]. For it, the samples were heated at different rates: $\beta = 2.5, 5, 10, 20, 40\ \mathrm{K\ min}^{-1}$.

The value of the apparent activation energy, E, of the two crystallization process are 2.8 and 3.6 eV respectively in MA sample and between 5.3 and 4.6 in RS sample. The values obtained in other alloys were between 2.4 and 3.8 in MA samples, and between 3.1 and 6.9 in RS samples [13, 14]. The apparent activation energy of the MA alloyed powders seems reasonable to be associated with a grain growth process.

Further information on thermal behavior was obtained by the help of isothermal scans, as shown in Fig. 4. The MA sample exhibits a monotonically decreasing heat evolution. This is due to grain growth of some quantities of nanocrystalline phases already

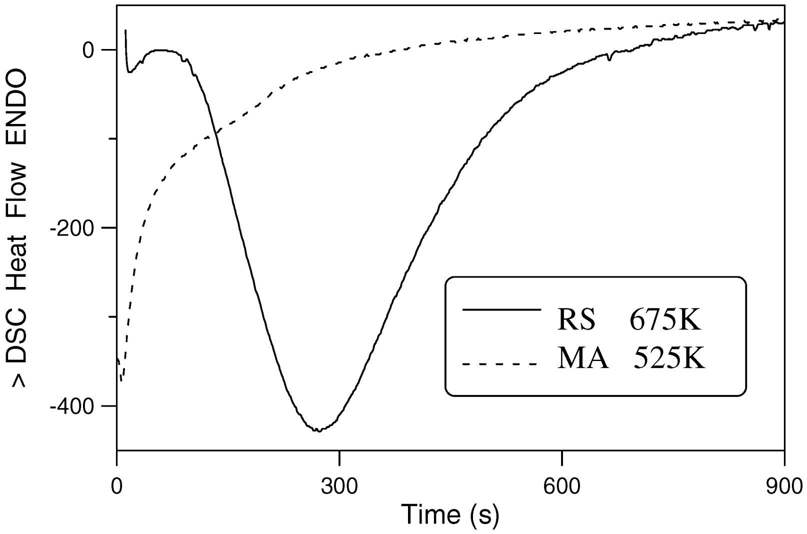

Figure 4 Isothermal DSC scans of quenched and mechanically alloyed samples.

present in the powder [15]. The RS sample shows an accentuated peak due to the nucleation and growth process.

Fig. 5 shows the XRD patterns of fully crystallized alloys. Crystallization was thermally induced by isothermal treatment during 1 h at a temperature of 850 K. The results indicate that the crystallization products are bcc(Fe,Ni), fcc(Ni,Fe), and (Fe,Ni)-phosphides and -silicides. Nevertheless, the relative amount of each phase changes. Similar behavior was found in different Fe-Ni based alloys [9, 10].

It is reasonable to expect that both amorphization behavior and properties could be different when using MA or RS as preparation methods [15]. This is due to the completely different mechanisms of glass formation for the different techniques. In MA an amorphous structure is formed by solid state reaction starting from crystalline phases and the whole process is controlled by both thermodynamic and kinetic parameters [16, 17]. Differently from RS methods, where the amorphous phase is obtained through kinetic constraints on the system during the cooling from its liquid or vapour phase [18]. It should be pointed out that the final products of the milling process strongly depend on the milling conditions. Using different ball mills—or different conditions for the same mill—results in markedly different reaction pathways. Changing the milling conditions will strongly affect the way by which energy is transferred to the milled powder and, hence, the nature of final products. As an example, using other milling device, and milling alloys of similar composition a nanocrystalline phase was found as the main phase [19].

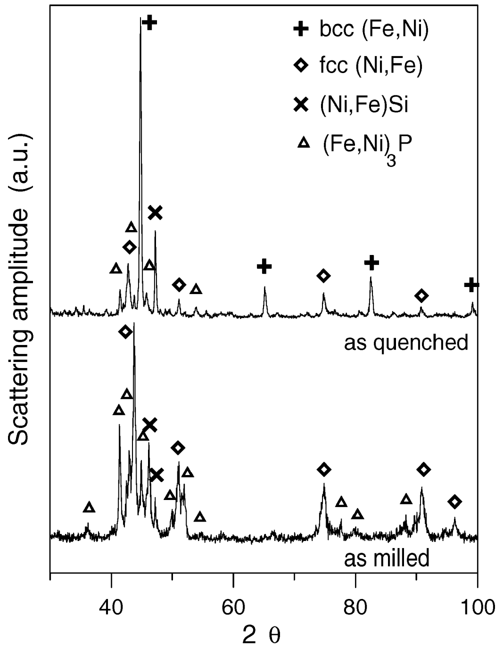

Figure 5 XRD diffraction patterns of alloy as milled (40 h) or as quenched after a isothermal treatment (1 h) at 850 K.

At present, new analysis is performed in materials developed by the MA of bulk amorphous metallic glasses as a two-step procedure prior to the consolidation or compacting of complicated shape materials in the powder metallurgy industry [20].

4. Conclusions

The $Fe_{50}Ni_{30}P_{14}Si_6$ alloy was produced by mechanical alloying (40 h) and melt spinning. In both cases, the alloy was obtained in a disordered state. X-ray diffraction and Mössbauer spectroscopy analyses show that the material obtained by RS is fully amorphous. Nevertheless, MA alloys shows some remains of crystalline α-Fe and Ni elemental precursors. Less than 7% of the Fe remains unreacted after milling for 40 h. As expected, contamination from the milling tools and surface oxidation were found in MA alloy.

From calorimetry analysis, values of crystallization enthalpy, as well as transformation temperatures, lower for MA sample, confirms the presence of nanocrystalline phases in the milled alloy. The apparent activation energy of the MA alloyed powders, between 2.4 and 3.3 eV, seem reasonable to be associated with a grain growth process.

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