NANOSTRUCTURED $Al_{90}Fe_5Nd_5$ ALLOY OBTAINED BY MECHANICAL ALLOYING

KÁTIA R. CARDOSO[1,2], ASUNCIÓN GARCÍA-ESCORIAL[1]*, WALTER J. BOTTA[3], MARCELA LIEBLICH[1]

[1] *Physical Metallurgy Department, Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, Spain*
[2] *UNIVAP, Av. Shishima Hifumi 2911, 12244-000 Sao José dos Campos-SP, Brazil*
[3] *DEMa-UFSCar, Sao Carlos-SP, Brazil*

Received 26 July 2005, accepted 25 October 2005

After 80 h of milling the elemental powders, mechanical alloying of $Al_{90}Fe_5Nd_5$ produces a nanostructured composite, which consists of nanocrystals of fcc-Al and some $Al_{11}Nd_3$ precipitates, embedded in an amorphous matrix. This composite has a Vickers hardness of 2.8 GPa and is thermally stable up to about 340 °C. Above this temperature it decomposes into $Al_{11}Nd_3$ and $Al_{10}Fe_2Nd$ phases.

K e y w o r d s: nanostructures, mechanical alloying

1. Introduction

In the last twenty years, high strength amorphous Al alloys have been developed by non-equilibrium techniques [1, 2]. In some Al-TM-RE (TM = Transition Metal, RE = Rare Earth) alloys, the strength has been improved by the partial crystallisation of amorphous precursors which gives rise to nanostructured composites consisting of Al nanocrystals embedded in a remaining amorphous matrix, with ultimate tensile strength reaching 1550 MPa [1].

Amorphous and nanocrystalline states in the $Al_{90}Fe_5Nd_5$ alloy have been obtained by melt spinning and gas atomisation processes and widely studied by the authors [3–6]. The $Al_{90}Fe_5Nd_5$ amorphous melt spun ribbon evolved with thermal treatments, as determined by DSC, through three exothermic reactions [3]: the primary crystallisation of fcc-Al phase from the amorphous matrix at around 230 °C forming a nanostructured state; the precipitation of a metastable ternary phase and the equilibrium $Al_{11}Nd_3$ phase at 355 °C; and the transformation of the metastable

*corresponding author, e-mail: age@cenim.csic.es

ternary phase into the equilibrium $Al_{10}Fe_2Nd$ phase at 540 °C. $Al_{90}Fe_5Nd_5$ powder produced by means of gas atomisation also resulted in an amorphous state that accounted for up to 42 % volume fraction of the batch [4]. With thermal treatments, the atomised powder evolved to the equilibrium state through three exothermic reactions, in a similar way as the melt-spun ribbon. In this case, however, reactions occurred at slightly different temperatures: 240 °C, 360 °C and 530 °C. From those studies the results showed that both materials, melt-spun ribbons and gas atomised powder presented a high thermal stability up to about 240 °C for the amorphous state and up to 360 °C for the nanostructured state. Both materials also presented a high hardness: 2.1 GPa and 2.8 GPa for the as-spun ribbon and as-atomised powder, respectively.

In the present work, the effect of mechanical alloying on Al, Fe and Nd elemental powder mixtures, in the atomic fraction of 90-5-5 has been studied and the results compared with those of amorphous and nanostructured $Al_{90}Fe_5Nd_5$ alloys previously obtained by melt-spinning and gas atomisation.

2. Experimental procedure

Mechanically alloyed $Al_{90}Fe_5Nd_5$ at.% powder was produced by milling the elemental powders under argon atmosphere in a SPEX 8000 high-energy shaker mill using hardened steel vials and balls. The ball-to-powder weight ratio used was 15 : 1 and 1–2 wt.% of stearic acid was added to minimise the agglomeration of powder. The powder was studied after 3, 6, 9, 12, 20 and 80 hours milling.

The evolution of the mechanically alloyed powder was followed by X-ray diffraction (XRD), using CuK_α radiation and silicon as a reference element. The change of fcc-Al crystallite size with milling time was determined by measuring the Bragg (111) and (200) peak widths at half the maximum intensity and applying the Scherrer formula [7]. The thermal stability of the mechanically alloyed powders was examined by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min under pure argon flow. Milled powders were also submitted to heat treatments at 350 and 450 °C for 1 hour. Structural characterisation was performed by scanning electron microscopy (SEM) equipped with an energy dispersive analysis unit (EDS) and transmission electron microscopy (TEM). Vickers microhardness was measured on polished powder particle cross-sections by applying a load of 25 g for 15 seconds.

3. Results and discussion

The XRD patterns of the mechanically alloyed powders are illustrated in Fig. 1. It can be observed that the patterns from powders milled for short periods of time, up to 12 h, only present peaks from the fcc-Al phase, which become broader with increasing milling time, indicating crystal deformation and grain size refinement. In the sample milled for 20 h, the fcc-Al peaks become narrower and increase

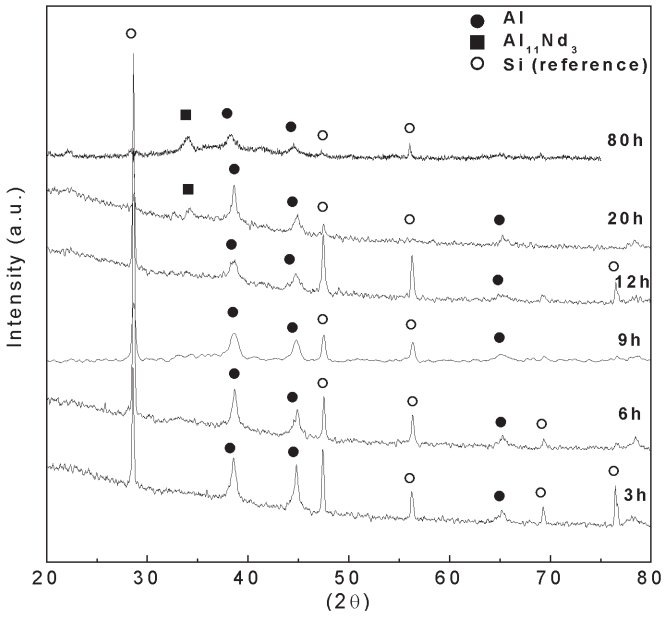

Fig. 1. XRD patterns of $Al_{90}Fe_5Nd_5$ powder, milled for 3, 6, 9, 12, 20 and 80 h.

in intensity. In addition, new peaks, belonging to the equilibrium $Al_{11}Nd_3$ phase, appear. The narrowing of the fcc-Al peaks, that is indicative of an increase in fcc-Al phase grain size estimated as about 20 nm [7], could be related with some dynamic recovery often found in alloys presenting a low melting point [8–13]. After 80 h milling an amorphous halo appears and the fcc-Al peaks become broader, the fcc-Al grain size being estimated in about 10 nm [7]. These X-ray diffraction results suggest that partial amorphisation of the $Al_{90}Fe_5Nd_5$ alloy was obtained by milling.

SEM observations of samples milled for 3 h showed some unalloyed Fe particles, whereas for longer milling times powders presented full homogenisation. Analysis performed by EDS showed that the nominal alloy composition was obtained in all samples.

TEM investigation of sample milled for 80 h showed the presence of a nanocomposite structure. Figure 2 presents an example where nanocrystals of about 10 to 20 nm can be observed. The corresponding electron diffraction patterns allow the identification of fcc-Al and $Al_{11}Nd_3$ intermetallic compound, as was expected from the X-ray diffraction patterns.

In order to examine the thermal stability of the mechanically alloyed $Al_{90}Fe_5$-

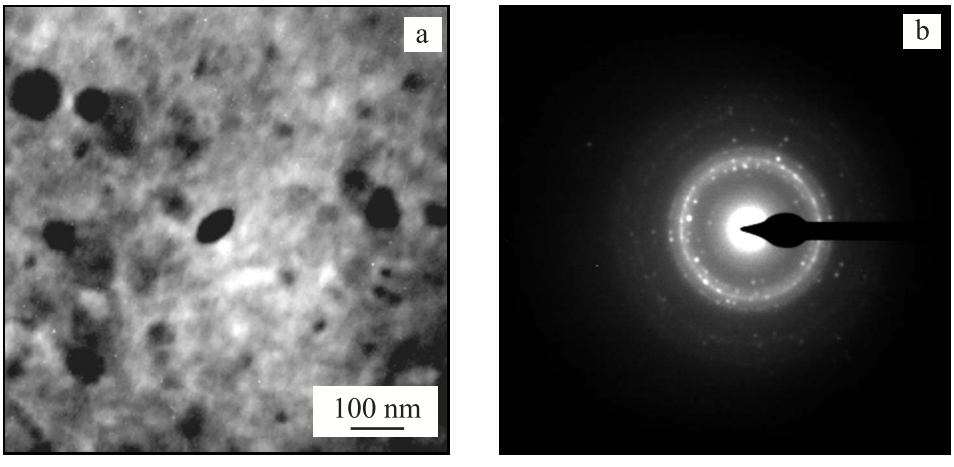

Fig. 2. (a) TEM micrograph and (b) corresponding diffraction patterns of $Al_{90}Fe_5Nd_5$ powder milled for 80 h.

Nd_5 powders and their phase transformations during heat treatments, samples were submitted to DSC studies. Figure 3 illustrates the DSC traces of the as-milled 80 h powder, which shows three exothermic peaks. The first one is broad and overlapped with the second one and takes place at 340 ℃, with a heat released of 18 J/g. The second peak is larger, with a heat released of 50 J/g, and occurs at around 380 ℃. A small peak at higher temperature, 540 ℃, can also be distinguished. Comparison with the three transformation peak temperatures also shown in Fig. 3 of the corresponding ribbon, that occurred at 230, 355 and 540 ℃ [3], and atomised powder that occurred at 240, 360 and 530 ℃ [4], shows the absence of the exothermic peak between 220 and 240 ℃ in the mechanically alloyed material. In melt-spun ribbons and gas-atomised powder, the first exothermic peak corresponded to primary crystallisation of the amorphous precursor, forming a nanocomposite of fcc-Al nanocrystals in a remaining amorphous matrix. This nanocomposite structure is already formed in the material after 80 h milling and this is the reason why the exothermic peak associated with its formation is not observed in the as-milled material. To estimate the volume fraction of the remaining amorphous phase present in the material milled for 80 h, the heat released in the exothermic transformation that occurred at 340 ℃, 18 J/g, was compared with the heat released by the ribbon, about 100 J/g, that was wholly amorphous [3]. From this comparison, it follows that volume fraction of amorphous phase in the MA material was about 20 %. This amount of heat released is close to that released by the size fraction of 25 to 50 μm in the helium-atomised powder [4].

To identify the phase transformations that take place during heating, milled

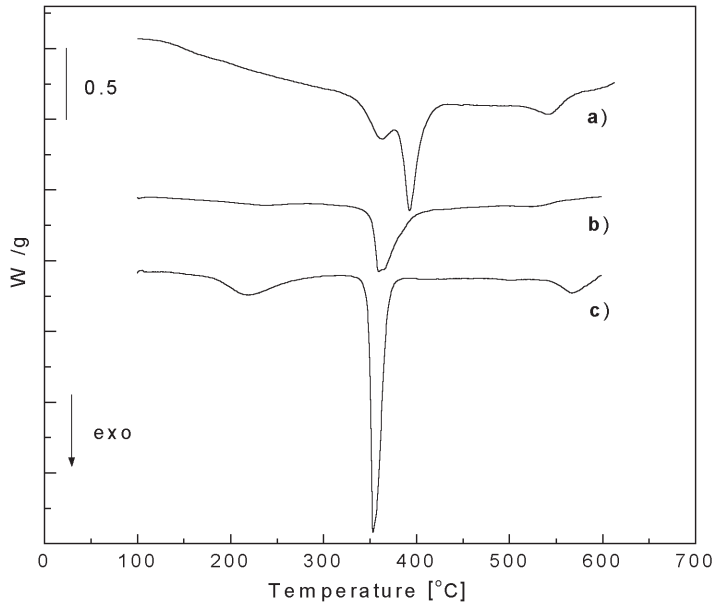

Fig. 3. DSC traces of $Al_{90}Fe_5Nd_5$ alloy. (a) 80 hours mechanically alloyed powder, (b) gas-atomised powder [4], and (c) melt-spun ribbon [3].

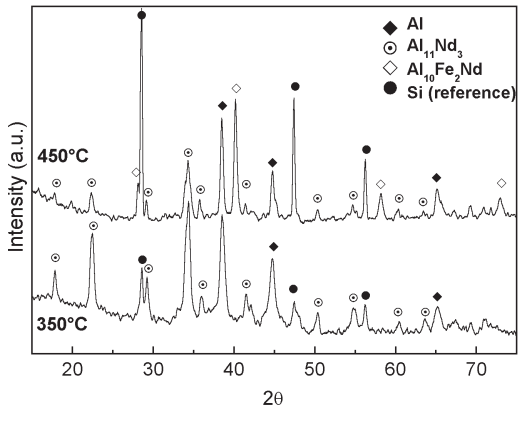

Fig. 4. XRD patterns of $Al_{90}Fe_5Nd_5$ powder milled for 80 h and thermally treated for 1 h at 350 and 450 °C.

samples were submitted to thermal treatments for 1 hour at 350 and 450 °C, i.e. above first and second exothermic peaks. The corresponding diffraction patterns

are shown in Fig. 4. XRD of the sample milled for 80 h and heat treated at 350 ℃ shows an increase in the intensity of the fcc-Al and $Al_{11}Nd_3$ peaks with respect to the as-milled condition shown in Fig. 1. After the 450 ℃ heat treatment, the ternary equilibrium $Al_{10}Fe_2Nd$ phase [4] was also present. This indicates that the first exothermic peak is due to the appearance and growth of $Al_{11}Nd_3$ together with the growth of fcc-Al, while the second exothermic peak corresponds to the formation of the ternary $Al_{10}Fe_2Nd$ phase. No sign of the metastable ternary phase, which appears during the evolution of the ribbon [3] and atomised powder [4] towards the equilibrium $Al_{10}Fe_2Nd$ phase, was detected in the mechanically alloyed powders.

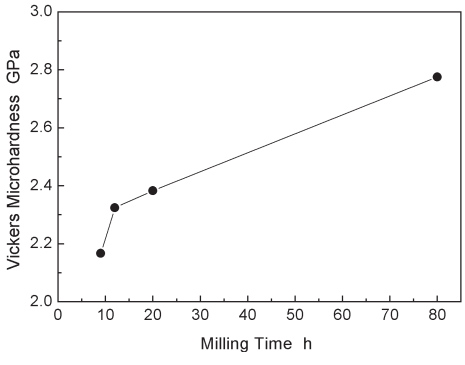

Fig. 5. Vickers hardness versus milling time of as-milled $Al_{90}Fe_5Nd_5$.

Vickers microhardness values of milled powders are shown in Fig. 5. As can be seen, hardness increases with milling time. Hardness value of the powder milled for 80 h (2.8 GPa) is similar to that of as-atomised powder particles in the size range of < 25 μm in diameter [4]. This hardness is higher than those reported in the literature for other nanostructured materials, i.e. 2.4 GPa for Al-Y-Ni [14] and 2.7 GPa for Al-Ni-Mm (Mm = Mischmetal) [15].

4. Conclusions

Mechanical alloying for 80 h of Al, Fe and Nd elemental powders to form $Al_{90}Fe_5Nd_5$ alloy produced, without thermal treatments, a nanocomposite structure that consisted of fcc-Al nanocrystals and some $Al_{11}Nd_3$ intermetallic phases in an amorphous phase. The crystallisation path of this amorphous phase is slightly different from that followed by melt spinning ribbon and gas atomised powder of the $Al_{90}Fe_5Nd_5$ alloy. The differences result from the fact that with mechanical alloying only partial amorphisation is obtained and this amorphous phase has a different composition from the fully amorphous phase obtained by melt spinning. The hardness of the nanocomposite alloy obtained by mechanical alloying is similar to that of the helium atomised powder particles in the size range of < 25 μm.

Acknowledgements

Financial support of Fapesp and Capes, "Phase transformations in nanostructures and development of ceramics and metallic nanocomposites", the Scientific Cooperation

Programme of the Spanish Ministry for Education and Culture and MAT2003-00722 are acknowledged.

REFERENCES

[1] MASUMOTO, T.: Mater. Sci. Eng. A, *179–180*, 1994, p. 8.
[2] PAIK, J. H.—BOTTA FILHO, W. J.—YAVARI, A. R.: Mater. Sci. Forum, *225–227*, 1996, p. 305.
[3] CARDOSO, K. R.—GARCÍA-ESCORIAL, A.—BOTTA, W. J.: J. Non-Crystalline Solids, *273*, 2000, p. 266.
[4] CARDOSO, K. R.—GARCÍA-ESCORIAL, A.—LIEBLICH, M.—BOTTA, W. J.: Mater. Sci. Eng. A, *315*, 2001, p. 89.
[5] YAVARI, A. R.—BOTTA FILHO, W. J.—RODRIGUES, C. A. D.—CARDOSO, K. R.—VALIEV, R. Z.: Scripta Mater., *46*, 2002, p. 71.
[6] CARDOSO, K. R.—GARCÍA-ESCORIAL, A.—LIEBLICH, M.—BOTTA, W. J.: Mater. Sci. Eng. A, *344*, 2003, p. 57.
[7] CULLITY B. D.: Elements of X-ray Diffraction. London, Addison-Wesley 1978.
[8] BENAMEUR, T.—INOUE, A.: Mater. Sci. Forum, *269–272*, 1998, p. 163.
[9] BENAMEUR, T.—INOUE, A.: Mater. Trans. JIM, *36*, 1995, p. 240.
[10] SURYANARAYANA, C.: Progress Mater. Sci., *46*, 2001, p. 1.
[11] ECKERT, J.—SCHULTZ, L.—HELLSTERN, E.—URBAN, K. J.: Appl. Phys., *64*, 1988, p. 3224.
[12] SAJI, S.—ABE, S.—MATSUMOTO, K.: Mater. Sci. Forum, *88–90*, 1992, p. 367.
[13] SHERIF EL-ESKANDARANY, M.—AOKI, K.—SUMIYAMA, K.—SUZUKI, K.: Acta Mater., *50*, 2002, p. 1113.
[14] INOUE, A.—TOMIOKA, H.—MASUMOTO, T. J.: Mater. Sci., *18*, 1983, p. 153.
[15] HONG, S. J.—KIM, T.-S.—KIM, H. S.—KIM, W. T.—CHUN, B. S.: Mater. Sci. Eng. A, *271*, 1999, p. 469.