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SINTERING OF $Fe_{0.912-X}Mn_XAl_{0.075}C_{0.01}CU_{0.003}$ ALLOYS WITH X=0.412 AND 0.162

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ABSTRACT

Powders of $Fe_{0.912-x}Mn_xAl_{0.075}C_{0.01}Cu_{0.003}$ alloys, with x=0.412 and 0.162, were obtained after a ball milling process during 10 hours period using a 4:1 ball mass to powder mass ratio. These powders were compacted and later sintered in hydrogen atmosphere at 900, 1000, 1100, 1200 and 1300 °C during periods varying from 2 to 48 hours. X-ray diffraction results of the milled powders showed the coexistence of the elements and a ternary Fe-Mn-Al fcc phase. Mössbauer spectra of these samples were fitted with two hyperfine field distributions, one with low fields (fcc phase) and other with high fields (Fe with some impurities of Mn and Al atoms). After sintering at 900 and 1000 °C during short times (2 and 4 hours), the samples with x=0.412 showed the austenitic structure but low sinterability, while the x=0.162 sample showed the bcc and fcc phases. For longer periods (48 hours) at 1200 °C, few pores were observed, proving a significant sample sintering but accompanied with a decreasing sample density due to vaporization of some elements from the alloy surface.

INTRODUCTION

During the last years many research works were performed about the use of mechanical alloying (MA) in the preparation of binary metallic systems [1,2] and metallic oxides in general. The alloys based in Fe-Mn-Al are of great importance for obtaining non-magnetic steels with good mechanical and resistance to corrosion/oxidation properties [3]. Studies on these types of alloys, prepared by mechanical alloying, show that they can present BCC and FCC phases depending on milling time and composition. For Al contents ≥ 10 at.% and milling times bigger than 8 hours the stable phase is BCC [4], which is ferromagnetic (F) for low Mn contents and paramagnetic (P) for high Mn contents. For Al ≤ 10 at.% and milling times bigger than 12 hours the FCC phase is the stable, with an antiferromagnetic (AF) character for high Mn contents and P for low Mn contents [5,6,7]. Our interest in this system is to report the structural and magnetic properties of alloyed and semi-alloyed powders of the system FeMnAlCCu prepared by mechanical alloying [7] and then sintered. C and Cu are added in order to improve their mechanical and corrosion resistance properties.

EXPERIMENTAL PROCEDURE

Elemental powders with ≥ 99.9% purity were mixed in order to obtain the stoichiometry $Fe_{0.912-x}Mn_xAl_{0.075}C_{o.01}Cu_{0.003}$ with x=0.412 and 0.162. A planetary high-energy ball mill (Pulverisetti 5) with balls and jars of hardened stainless steel at 280 rev./min. was used. The jars were sealed and evacuated until $5x10^{-2}$ mbar, with the powder and the balls inside. The ball mass to powder mass relation of 4:1 and a milling time of 10 hours were used. Compacted pills were sintered with a flux of 0.5 lit/min. ultrahigh purity H_2 atmosphere at temperatures of 900, 1000, 1100, 1200 and 1300 °C during 2 hours. Additional sintering was performed during 4 and 48 hours at 1200 °C. For each condition three pills were prepared in order to obtain a better statistics. X-ray diffraction (XRD) patterns were taken using a Rigaku diffractometer using the Cu-Kα line. Scanning electron microscopy (SEM) analysis was performed using a JEOL equipment. Mössbauer spectra were collected using a conventional spectrometer with a 57-Co(Rh) source and α-Fe as calibration sample.

EXPERIMENTAL RESULTS

Mechanical alloying

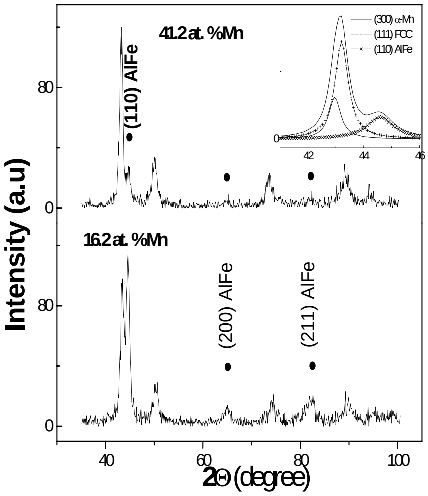

Fig. 1. XRD of the milled powder during 10 hours.

Fig. 1 shows the XRD patterns of samples milled during 10 hours. It can be noted in the x=0.412 sample the peaks (300) of □-Mn, the (110), (200) and (211) of the Al-Fe alloy and all those of a ternary FCC phase [8]. For the x=0.162 sample only very intensive peaks of the Al-Fe alloy and those of the FCC phase are observed. Fe-Mn-Al alloys produced by melting and with the same compositions of the present MA samples show the FCC structure [8, 9]. The □-Mn peak of the x=0.412 sample is due high Mn content and the low milling time. Mössbauer spectra of these samples (not showed) were fitted with two hyperfine field distributions, one with low fields which corresponds to the detected FCC phase which is AF and disordered [9], and other with high fields corresponding to the Fe-Al alloy which is F and disordered [10].

Sintering

After the sintering processes during 2 hours at all temperatures, the XRD results show that the x=0.412 samples presented only the FCC phase which corresponds to the alloy, while the x=0.162 sample presents the coexistence of BCC and FCC phases. These results are similar to those obtained for melted samples with these compositions [11]. Between 900 and 1100 ºC the mass loss is less than 1%, and this can due to three facts: first, the compaction processes were realized without lubricant which in general evaporates at low temperatures in the sintering process; second, the powders were previously alloyed by MA and the Al is not in the elemental state but alloyed in the Fe-Al bcc phase avowing its evaporation; and finally the Al content of the samples is very low. Then the mass loss is attributed to the evaporation of the surface contaminants and of Mn, which presents the highest vapor pressure. Between 1100 and 1300 ºC it can be observed a notable decrease in mass, near 6.5%, attributed to the Mn loss. At these temperatures the sintering process is dominated by both vapor transport [12] and diffusion processes. The variation of the length and diameter behave in a similar way, showing the isotropy of the samples. This isotropy comes from the low ratio between these two parameters (0.2), which permits to obtain a homogeneous value of the green density of the pill after pressed.

The density vs. temperature curve (not showed here), after the sintering process for the x=0.412 samples, shows that the density at 1200 ºC is nearly 8% bigger than that at 900 ºC. Fig. 2(a) shows the micrograph obtained by SEM of the sample treated at 900 ºC. It can be observed that local contact points between particles begin to form. The number of these points increases at 1200 ºC, explaining the increasing density at this temperature.

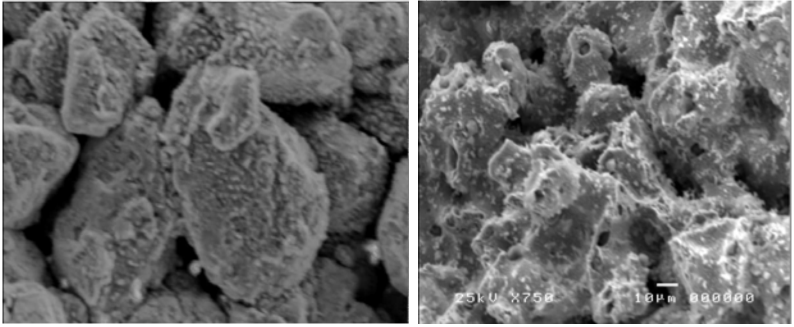
(a)25kVx750 (b)25kVx750

Fig. 2. SEM micrograph of sintered x = 0.412 sample for (a) 900 ºC, (b) 1200 ºC.

The density for 1300 ºC is nearly 28% bigger than that for 900 ºC. The SEM micrograph (Fig. 2(b)) of this sample shows more spherical and closed pores, and a broadening of the necks between particles.

The effect of sintering time in the dimensions, mass and density, at 1200 ºC, was studied in the samples with x=0.162 and 0.412 and different behaviors were detected. For the x=0.162 sample the dimensions (height and diameter) remain practically constant with a contraction near 1.5% for 2 and 4 hours and 2% for 48 hours, and the mass remains practically constant for 2 and 4 hours and decreases nearly 3% for 48 hours. The density presents a value of ~5.31 g/cm3 for 2 and 4 hours and of ~5.12 g/cm3 for 48 hours. However, for x=0.412 big changes were obtained. The dimensions changed from ~3% for 2 and 4 hours to ~4.6% for 48 hours while the mass changed from ~3% at 2 and 4 hours to ~29% for 48 hours. The density changed from 5.42 g/cm3 to 4.17 g/cm3. The big density change can be attributed not only to mass loss (of Mn atoms) but also to the advanced sintering process as was proved by SEM (not showed here) which shows that for 48 hours all the particles are practically joined with isolated and spherical pores. The same SEM results was obtained for the x=0.162 sample. Microprobe maps of the distribution of the different elements showed that they are homogeneously distributed in the surface samples as a consequence of the previous mechanical alloying of the powders. XRD patterns and energy spectra after the sintering process during 4, 12 and 48 hours at 1200 °C, were obtained. The XRD of x=0.412 samples for 4 hours presents only the peaks of the FCC structure while that for 48 hours presents additional peaks corresponding to α-Al2O3 phase. These results show that the sample present an oxidation process with sintering time. The oxide phase formation was proved by microprobe analysis (not showed) which shows small peaks of

Fe, Mn, and O, and a big peak of Al. The presence of O in the surface, in spite of the pure H2 flux, can be attributed to the air trapped in the pores of the original green compacted. This O, as well as the Al atoms, diffuses to the surface by thermal effects in order to produce the passive layer of alumina. Similar results were obtained for the x=0.162 samples, but in this case the XRD pattern presents additional peaks of the bcc phase.

Table 1 reported the microprobe chemical analysis, of the MA powders and of the sintered samples during 48 hours. From this table it can be derived the behavior of the elementary mass content for the sintered samples during 48 hours pustule in the previous paragraph.

	Mn[wt %]	**Fe[wt %]**	**Al[wt %]**	**Cu[wt %]**	**Si[wt.%]**	**T[^{o}C]**	**Time [h]**
Nominal	42.80	52.79	3.82	0.36			
MA	39.18	51.90	3.65	0.34	4.93		10
Sintered	20.55	71.63	3.30	0.48	4.04	1200	48
Nominal	16.75	78.85	3.82	0.36			
MA	15.54	77.69	3.64	0.33	2.80		10
Sintered	17.75	80.87	1.92	0.45		1200	48

Table 1. Chemical analysis obtained by microprobe of the mechanically alloyed powders and of the surface of the sintered samples for the different times.

The first that it can be noted is the appearing of Si in the analysis which can be attributed to the material of the used detector which decreases the real content of the other elements. The analysis of the sample with bigger Mn content was obtained from the surface after sintering while that of the sample with low Mn content was obtained from its bulk. About the surface of the first sample, the following facts can be noted: the Mn loss is bigger than 50%; the Fe and Cu contents increase as a consequence of the balance, and the Al content remains nearly constant. For the second sample it can be noted the following: compared with the theoretical values, Mn and Fe contents are almost constant and the Al content decreases. Then in the sintering process the Mn of the surface volatilizes, Mn and Fe in the bulk remain constant and part of the bulk Al migrate towards the surface in order to produce alumina.

XRD and Mössbauer results of the cleaned surface of all the samples demonstrated that for low sintering times the phase is fcc and AF for x=0.412 and fcc (P) + bcc (F) for the 0.162 sample, but for 48 hours they present the two phases showing, in according with the structural phase diagram [8], that the composition move to the low Mn composition proving again the Mn loss. Fig. 6 shows the Mössbauer spectra (left) and their corresponding hyperfine field distributions (right) for the sample with x= 0.412: a) sintering during 2 h; b) milling during 48 h.

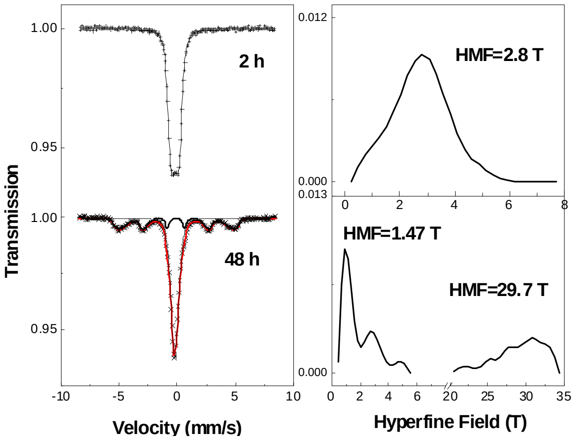

Fig. 3. Mössbauer spectra (left) and their corresponding hyperfine field distributions (right) for the sample with x= 0.412: a) sintering during 2 h; b) milling during 48 h.

CONCLUSIONS

The use of alloyed or semi-alloyed powders give the better sintering conditions; after any one of the sintering process used in this work the sample with bigger Mn content stabilizes in the fcc phase while that with lower Mn content stabilize in the bcc and fcc phases; the best sintering temperature was that of 1200 ºC during 2 hours due that it produces the biggest densification without an exaggerate loss of mass; and that for 48 hours of heat treatment an alumina layer is formed for the two types of samples.

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