ON THE MECHANISM OF MILLING INDUCED DISORDERING IN AlFe

M.T. CLAVAGUERA-MORA[*], J. ZHU[*], M. MEYER[**], L. MENDOZA-ZELIS[**],
F.H. SANCHEZ[**], N. CLAVAGUERA[***]
*Grup de Física de Materials I, Dept. de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.
**Departamento de Física, Universidad Nacional de La Plata, C.C.67, 1900 La Plata, Argentina.
***Grup de Física de l'Estat Sòlid, Dept. ECM, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

ABSTRACT

The evolution of the B2-AlFe phase during mechanical grinding in Ar has been examined as a function of milling time by X-Ray diffraction, transmission Mössbauer spectroscopy and differential scanning calorimetry. Short and long range disorder was observed to increase with the mechanical treatment up to the attainment of a steady state. The evolution of the long range order parameter and of the local atomic configurations at Fe sites were analyzed in terms of possible mechanisms for milling induced disordering. The kinetics of the thermal reordering was studied under continuous heating and isothermal calorimetric regimes. Modeling of the reordering processes by diffusion controlled growth of pre-existing ordered grains is presented as well as the estimated values of both the enthalpy and the activation energy of the reordering process. The results are consistent with a non uniform distribution of disorder throughout the sample and will be compared with preceding information on related systems.

INTRODUCTION

Disorder induced by mechanical work in intermetallic compounds with the B2 or DO_3 structure is a well known phenomenon and their stability under ball-milling has been extensively examined in the last decade. Thirty years ago Huffman et al. [1] studied the modification induced by cold working in a series of Al-Fe alloys with different Al content. Among several other recent works, Pochet et al. [2] have presented a detailed study of the order-disorder transition induced by milling B2-AlFe. It is rather well established that this compound, as well as the B2-AlRu [3], undergoes a transition to a metastable partially disordered state accompanied by a reduction in particle and domain size and microstrain storage.

Hyperfine interaction techniques, such as Mössbauer effect (ME) spectroscopy, may prove useful in the study of these mechanically induced transformations due to their ability of sensing the ^{57}Fe surroundings. From the ME spectra, the magnetic hyperfine field (HF), electric quadrupole splitting (QS) and the isomer shift (IS) at a given Fe site, can be obtained. The combination of the information coming from X-Ray diffraction (XRD) should help to observe how long range (LR) disorder correlates with short range (SR) structures.

On the other hand, differential scanning calorimetry (DSC) allows us to follow the time/temperature evolution in the approach towards the equilibrium state, giving indirect information about the nature of the disorder induced during milling.

We present here some results on the mechanical grinding of the intermetallic compound AlFe, obtained by ME, XRD and DSC carried out with the aim of studying the evolution of mechanically induced short- and long-range order during the transformation.

EXPERIMENT

The starting AlFe alloy was prepared by heating in vacuum a mixture of the elemental pure powders in equiatomic proportion. The ingot was ground and annealed in vacuum for several hours at 550°C to remove the remaining stress and improve the order. Samples of 250 mg were sealed into cylindrical vials under Ar atmosphere, after several Ar washings, and mechanically ground with a Retsch MM2 horizontal vibratory mill operating at 30 Hz. We used 5cm^3 vials and one ball (9 mm diameter) of stainless steel. The estimated milling intensity under these conditions was 450 m/s^2 [2]. Milling times, t_m, ranged between 3 and 120 min.

After each milling experiment the samples were characterized by XRD and ME spectroscopy at room temperature. XRD patterns were obtained in reflection geometry using a Philips PW1710 diffractometer with Cu Kα radiation. ME experiments were carried out with a conventional spectrometer under transmission geometry, employing a ^{57}CoRh radioactive source. The quoted values of IS are relative to α-Fe.

The milled samples have been analyzed with a Perkin Elmer DSC7 calorimeter under dried Ar atmosphere and using Cu pans. Continuous heating experiments were done at heating rates ranging from 10 to 80°C/min. Sequential isothermal plus continuous heating measurements were also performed.

RESULTS AND DISCUSSION

Disordering process

The XRD patterns of milled samples show the reflections characteristic of the bcc phase with B2 ordering. But, as milling proceeds, the intensity of the superstructure peaks decreases as a consequence of induced disorder. Additionally, all the peaks broaden because of both particle and domain size reduction and also the increase in stored microstrain. For the analysis of the diffractograms we use a full pattern fitting procedure DBWS-9411 [4], which allows the simultaneous refinement of the LR order parameter, S, the lattice parameter, a, the average size of the coherent regions for diffraction, L, and the mean square deviation of the unit volume deformation (microstrain), ε.

All these parameter evolve rapidly with the milling time, as presented in Fig. 1. Their behaviour may be described as follows: 1) there is an increment in a with t_m; 2) S decreases monotonically up to t_m=10 min when it reaches a steady state value of about 0.32; 3) L decreases rapidly in the first minutes of milling and more slowly afterwards, reaching a final value of about 59 nm); 4) ε increases with a decreasing rate up to a stationary value of 2.6% for t_m=120 min. It is worth noticing that the observed reduction in particle size is not as large as the one reported in previous work on similar system [2,3,5], probably due to the characteristics of our milling device.

The ME spectra obtained after various grinding times (t_m) show all a broad absorption peak at low velocities, characteristic of paramagnetic Al-Fe phases, without any trace of ferromagnetic components. To analyze these unresolved doublets, several kinds of fits were attempted, including broadened Lorentzians, Voigt profile lines and model-independent hyperfine field distributions (histograms). Good fits were obtained with Voigt-shaped doublets, which give account of Gaussian distribution of the quadrupole splitting defined by its mean value <QS> and standard width σ. The proposed fitting allows also for a linear correlation
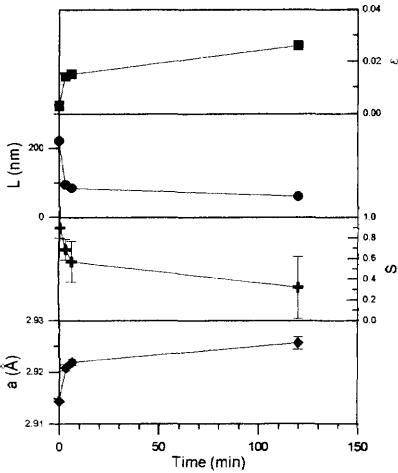
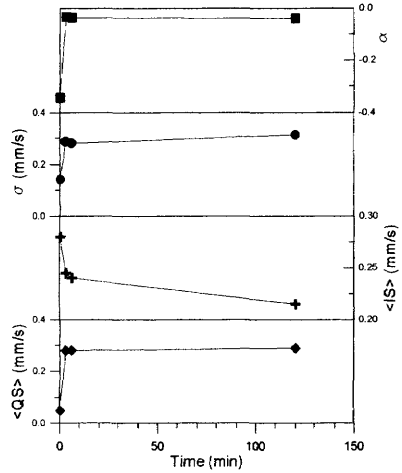Fig. 1.- Evolution of **a**, **S**, **L** and ε with milling time.

Fig. 2.- Evolution of <QS>, <IS>, σ and α with milling time.

between IS and QS: $IS = IS_0 + \alpha QS$. The <QS> and σ values resulting from these fits show a rapid increase with t_m, as shown in Fig. 2, reflecting the departure from cubic symmetry of the local charge distribution around Fe sites and the wide variety of local configuration produced by milling.

Since the LR parameter S experiences a sudden drop in the first few minutes of milling, with a simultaneous important increase in the accumulated microstrain ε, the combination with ME results is consistent with the interpretation that lattice disorder is the main mechanism for the observed evolution with milling time. First, there is some similarity between the evolution of <QS> and ε with t_m, both being related with SR disorder. The large number of possible local configurations for the Fe neighbourhood render difficult, at this stage, to model the local environments in order to predict values of <QS>.

On the other hand, the decrease of <IS> with t_m is a clear indication of the reduction in in the number of Al neighbours of Fe atoms as a consequence of local departures from the B2 ordering. In a very simple model, IS for a given Fe site may be expressed in terms of the number of Al near and next near neighbours. Then, if an statistical distribution of disorder is assumed, a predicted value of <IS> may be obtained from the measured value of S. The experimental values of <IS> follow the predicted trend, but are always higher. For instance, in the steady state (S=0.32) a value of 0.19 mm/s is expected against the measured one of 0.21 mm/s. An opposite situation is to consider that the sample is composed of alternating completely ordered (S=1) and disordered (S=0) regions. The experimental values of <IS> lie within the predictions for these two situations. That is, the actual distribution of disorder in the samples consists probably of quite ordered regions embedded in less ordered ones.

357

Reordering process

Milled samples have been analyzed by DSC under continuous heating regime. All of them show a broad asymmetric exothermic peak in the temperature range between 110 and 250°C, which may be considered as consisting of two overlapped peaks, (see Fig. 3). An average activation energy for this process has been estimated as $E_a=1.1\pm0.1$ eV, by the Kissinger plot, shown in Fig. 4.

To analyze the kinetics of this transformation, we measured the calorimetric signal under isothermal regime at selected temperatures, T_a, ranging between 90 and 160°C. Fig. 5 shows the obtained DSC curves for samples with S=0.4 at four different values of T_a. The calorimetric signal shows practically no transformation for T_a=90°C and otherwise an exothermic exponentially decreasing signal, which becomes more important when increasing T_a. These results are characteristic of a thermally activated growth process. Continuous heating analysis of samples previously annealed for 1 hour, at several values of T_a, are shown in Fig. 6. It is readily seen how the onset temperature of the exothermic peak shifts to higher temperatures as T_a increases.

Reordering kinetics

The reduction of both S and L are indirectly affecting the calorimetric measurements on the milled samples. The exothermic effect observed at temperatures in the range 110-250°C, when continuously heating the milled samples corresponds to a transformation whose enthalpy increases with t_m.

An empirical kinetic analysis of the evolution of the calorimetric signal has been accomplished by assuming that the isothermal calorimetric signal obtained corresponds to the reordering process from an initial state where ordered and disordered zones coexist. The statistical distribution of ordered zones was replaced by a density of ordered grains of given initial radius r_o, whose growth is driven by:

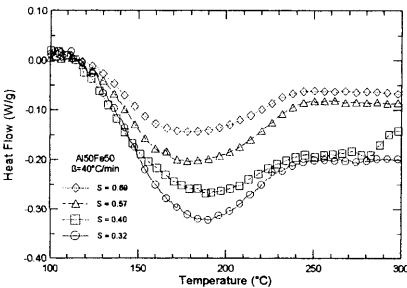$$\frac{dr}{dt} = \frac{D}{r^m} \quad \text{with} \quad D = D_o \exp(-E_o / kT) \tag{1}$$

Fig. 3.- Continuous heating DSC curves of samples milled at different times.
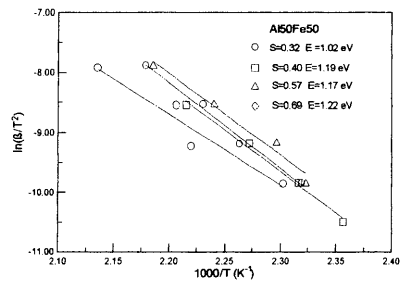
Fig. 4.- Kissinger plot of the evolution of peak temperature with heating rate, β.
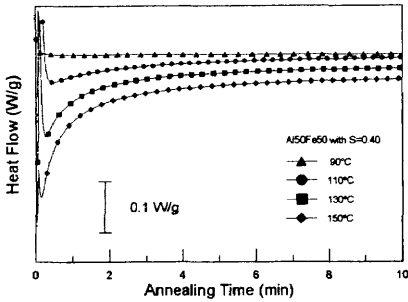
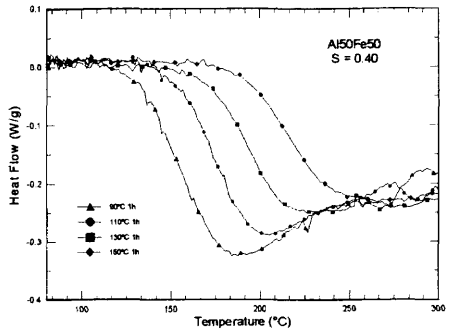Fig. 5.- Isothermal DSC curves obtained by annealing at several temperatures.

Fig. 6.- Continuous heating after previous isothermal annealing at several temperatures.

where the values of r_0, E_0 and m are adjusted from the experimental data.

The calculated isothermal curves for samples with S=0.4 are presented in Fig. 7. In view of the approximate nature of the calculations, the agreement between calculated and observed heat evolution is quite good. When annealing at 90°C the reaction rate calculated is very low and the predicted signal will be almost indistinct from the noise in the DSC curve. However, at higher values of T_a, the height and decay rate of the continuously decreasing experimental curves are well reproduced. The calculated curves have been constructed with the following optimized parameters: r_0=7 nm, E_0=0.91 eV and m=5. Good agreement is also obtained in reproducing the calorimetric data for samples milled during different times by use of the same values of E_0 and m. However, the value r_0 of is quite sensitive to the milling duration [8].

The ideal grain growth model for a single phase material will follow equation (1) with a value of m=1. However, most experimental studies have demonstrated that grain growth results in a value of m well above the ideal one [8].
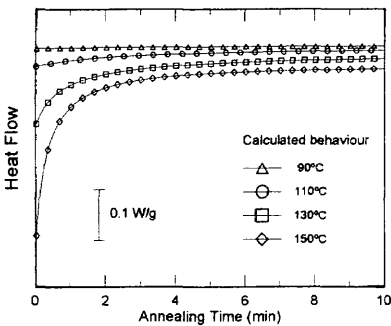

Fig. 7.- Calculated isothermal DSC curves when annealing at several temperatures.

In AlFe, the main factor impeding diffusion suggested is the low vacancy concentration on the Al sites [9]. The value of r_0 obtained suggests that antiphase boundaries of small dimensions are created by milling [1].

A complementary test of the goodness of the kinetic analysis is obtained by simulation of the continuous heating DSC curves. The results of that analysis indicate that both the peak onset temperature and the reaction rate of the experimental curves are well reproduced [10]. Also the calculated DSC heating curves of previously annealed samples show good agreement with the experimental data.

CONCLUSIONS

Room temperature milling of AlFe at an intensity of 450 m/s^2 leads to a final value of **S** of about 0.32 after a long milling time. Although the particle size decreases during milling, the disorder is mainly due to lattice disorder, probably originated by a high density of antiphase domain boundaries. The SR order evolution also indicates highly disordered local environments, but is consistent with a non statistical order distribution throughout the sample.

In the calorimetric studies a rapid evolution towards equilibrium is observed at temperatures around 150°C under isothermal annealing, and in the range 100-150°C under continuous heating regime. The kinetics of the reordering process is described in terms of already existing ordered regions which grow with an activation energy of about 1.1 eV. Growth is probably limited by the displacement of the antiphase boundaries and enhanced by the large number of vacancies created during milling.

REFERENCES

1. G.P.Huffman and R.M.Fisher, J.Appl.Phys. **38**, p. 735 (1967).
2. P.Pochet, E.Tominez, L.Chaffron and G.Martin, Phys. Rev **52**, p. 4,006 (1995).
3. E. Hellstern, H.J. Fecht, Z. Fu and W.L. Johnson, J.Appl.Phys **65**, p. 305 (1988).
4. R.A. Young, A. Sakthivel, T.S. Moss and C.O. Piva-Santos, J.Appl.Phys.**28**, p. 366 (1995).
5. I. Boerner and J.Eckert, Proceedings of Ismanam 95, Mat.Sci Forum (Trans. Tech Publ, 1996).
6. S. Nasu, U. Gonser and R.S. Preston, J.Physique **41**, p. C1-385 (1980).
7. J.H. Hsu and C.L. Chien, Hyp.Int. **69**, p. 451 (1991).
8. U. Köster, Mater. Sci. Forum, **235-238**, p. 377 (1997).
9. R. Feldwisch, B. Sepiol and G. Vogl, Il Nuovo Cimento **18D**, p. 247 (1996).
10. M. T. Clavaguera-Mora, J. Zhu, M. Meyer, L. Mendoza-Zelis, F.H. Sanchez and N. Clavaguera, Mater. Sci. Forum, **235-238**, p. 541 (1997).