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Solid-state reactions in the Al–Fe system induced by ball milling of elemental powders

F. CARDELLINI, V. CONTINI*, G. MAZZONE*
*Enea, Centro Ricerche Energia Casaccia, Divisione Nuovi Materiali C.P. 2400, 00100 Rome, Italy and also *Istituto Nazionale per la Fisica della Materia, Unità di Perugia, Perugia, Italy*

Elemental aluminium and iron powders have been mechanically alloyed in the atomic Al: Fe ratios of 1:1 and 1:3. The structural evolution of the samples was followed by X-ray diffraction and differential calorimetry. Extended milling caused the formation of an almost completely disordered b c c solid solution instead of the equilibrium B2 and DO_3 compounds. Upon heating to 700 °C the formation of the B2 phase was observed in the equiatomic samples and no significant variation of the long-range state of order in the iron-rich samples. Upon heating of samples pre-milled for short or intermediate times, at about 400 °C, the nucleation and growth of Al_5Fe_2 was observed which, upon further heating to 700 °C, transformed to the B2 phase or to the b c c solid solution, depending on the sample composition. These results suggest that the solid-state reactions proceed through diffusion of iron atoms in the aluminium layers, and that for an iron concentration in these layers below about 50 at%, the Al(Fe) solid solution could be in a metastable phase.

1. Introduction

The transition metal aluminides and, among these, the iron aluminides, are of considerable interest from a technological point of view because of their excellent oxidation and corrosion resistance, particularly at high temperature. However, iron aluminides, like most intermetallic compounds, suffer from limited ductility. For this reason, several studies have been made to improve the mechanical properties of Al–Fe based alloys through control of their microstructure [1].

A possible route to achieve a non-conventional microstructure is the use of high-energy ball milling. In fact, the ability of high-energy ball milling to impart to metallic particles a very high amount of cold work has been exploited to promote near room-temperature solid-state reactions, leading to a variety of alloy phases with nanometric grain size [2, 3]. In particular, the synthesis of intermetallic compounds has been achieved in a number of cases [4] using, where necessary, a combination of ball milling and heat treatment [5].

The reactions induced by ball milling have been the subject of several studies which have proved that in some cases these reactions cannot be described as simple layer-growth processes [6]. The structural evolution during ball milling of Al–Fe mixtures at different compositions has been followed by means of X-ray diffraction [7] showing that at both 80 and 50 at % Fe, the intensity of the aluminium peaks decreases with milling time. A similar behaviour is also exhibited by the Al–Ni system. In this case, the decrease of the aluminium peaks during the first hour of milling has been attributed to a selective change of the absorption of diffracted X-rays due to refinement of the particle size [8]. In addition, transmission electron microscopy (TEM) observations have shown that, contrary to what could be naively deduced from the diffraction patterns, nickel is the dominant moving species [5, 8].

In order to study the effect of high-energy ball milling upon Al–Fe mixtures in the bcc phase field, and to compare these results with those observed in the Al–Ni system, we have performed structural and thermal studies of samples having atomic compositions $Al_{50}Fe_{50}$ and $Al_{25}Fe_{75}$.

2. Experimental procedure

Aluminium powder of 99.95% purity (particle size 50–100 μm) and iron powder of 99.999% purity (particle size 5–10 μm) both by Koch Chemicals, were mixed at the compositions 25 and 50 at % Al. Milling of these mixtures was performed for different lengths of time in steps of 30 min, alternated with rest intervals of 10 min, using an air-cooled SPEX 8000 mixer/mill equipped with a hardened steel vial of 66 cm^3 and two balls of 13.5 mm diameter and 10 g weight (ball to powder ratio 6:1). To prevent sample oxidation, the powders were sealed in the vial under an argon atmosphere and a fresh sample was used for each ball-milling run.

The structural characterization of the powders was performed by X-ray diffraction (XRD) and their thermal stability was tested in a differential scanning calorimeter (DSC). XRD patterns were obtained using crystal-focused and monochromated $CoK_{\alpha 1}$ radiation in a Debye–Scherrer diffractometer equipped with a curved 120° position-sensitive detector. Thermal measurements from 100–700 °C were performed in a computer-assisted Perkin–Elmer DSC7 calorimeter operated in the specific heat mode at a constant heating rate of 0.25 K s^{-1}.

3. Results

3.1. The effect of milling

XRD patterns of samples milled for short times do not show any significant change in the ratio of the intensities of Al (1 1 1) to Fe (1 1 0) + Al (2 0 0). A progressive decrease of this ratio, accompanied by an asymmetric displacement to lower angles of the Fe + Al peaks, was observed for longer milling times until, after 10 h milling of samples at the equiatomic composition (Fig. 1) and 5 h milling of iron-rich samples (not shown), the aluminium reflections were no longer visible. The remaining peaks, with the exception for the equiatomic sample of a weak superstructural reflection at the (1 0 0) position, corresponded to a b c c solid solution having a lattice parameter expanded by about 2% at the equiatomic composition and by about 1.3% in the other case. Further milling did not cause any other significant change; in particular no superstructural reflection was observed to grow in the iron-rich samples.

As milling proceeded, a considerable broadening of the Fe + Al peaks was also observed which could be analysed on the basis of the procedure suggested by Williamson and Hall [9]. The accuracy of this analysis was affected by the fact that in the first stages of milling the aluminium peaks overlapped with the iron peaks. In any case, the size of the coherent domains decreased to about 10 nm after 10 h milling. Following this procedure, a quantity usually called the atomic level strain, can also be deduced. Actually, from a plot of the width of the Bragg peaks as a function of exchanged momentum, it is possible to deduce a quantity which can be written as $\Delta a/a$ where a is the lattice parameter of the substance and Δa is approximately proportional to the width of the distribution function of a in the sample. The values of $\Delta a/a$ as a function of milling time are shown in Fig. 2. In analogy with Oleszak and Shingu [7], $\Delta a/a$ is observed to go through a maximum, particularly pronounced in the iron-rich samples, at a value of milling time corresponding to the disappearance of the aluminium reflections.

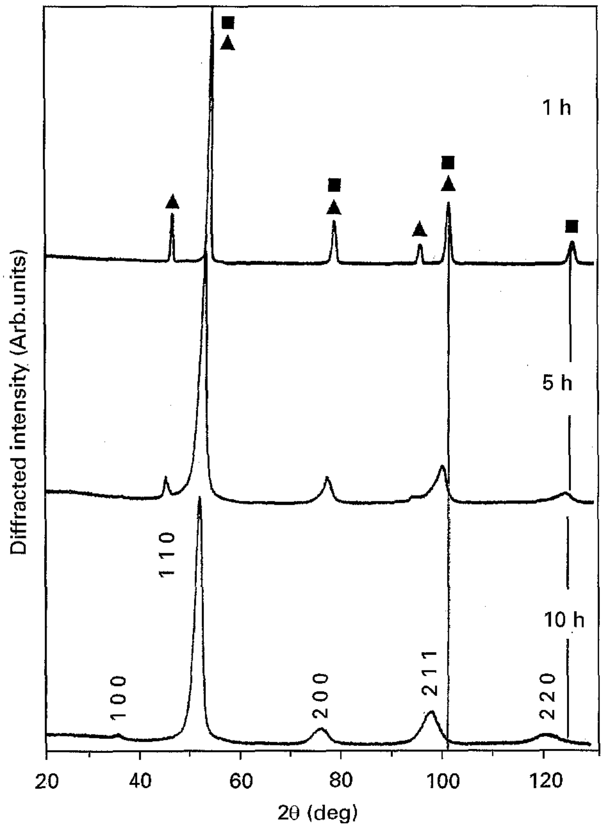

Figure 1 XRD patterns of equiatomic samples milled for different times. (▲) Al, (■) Fe.

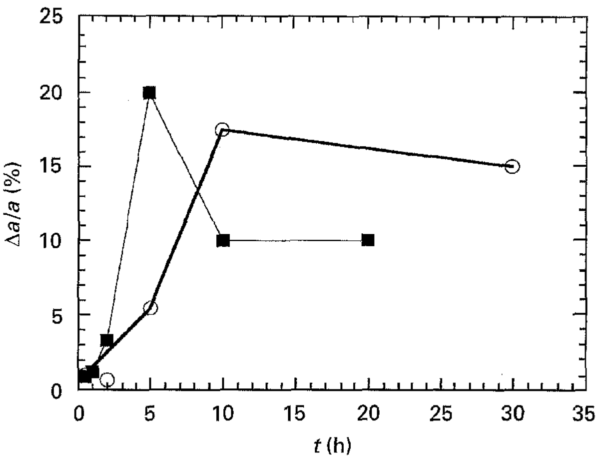

Figure 2 The variation of $\Delta a/a$ as a function of milling time. (○) $Al_{50}Fe_{50}$ (■) $Al_{25}Fe_{25}$. (—) A guide to the eye.

3.2. The effect of temperature

The effect of temperature has been studied by means of DSC scans from 100–700 °C performed at a constant heating rate of 0.25 K s^{-1}. For a very short premilling time (0.167 h) the DSC thermograms at the two compositions were very similar, displaying in both cases a small low-temperature endotherm probably due to a modest gas release and three well-developed exothermal peaks (Fig. 3). XRD patterns recorded after heating the equiatomic samples to suitable intermediate temperatures (Fig. 4) showed that the first two peaks correspond to different stages of growth of Al_5Fe_2, with unreacted iron and aluminium still being the majority components. The third peak occurs at a temperature very near to the melting point of aluminium and the corresponding XRD pattern shows the disappearance of aluminium together with a marked decrease of iron, further growth of Al_5Fe_2 and the formation of a B2 phase with a lattice parameter about 1.5% larger than that of pure iron. The sequence of solid state reactions described above was observed also in iron-rich samples premilled for 0.167 h.

The DSC scans of equiatomic samples milled up to 2–3 h showed a very deep exothermal peak centred at

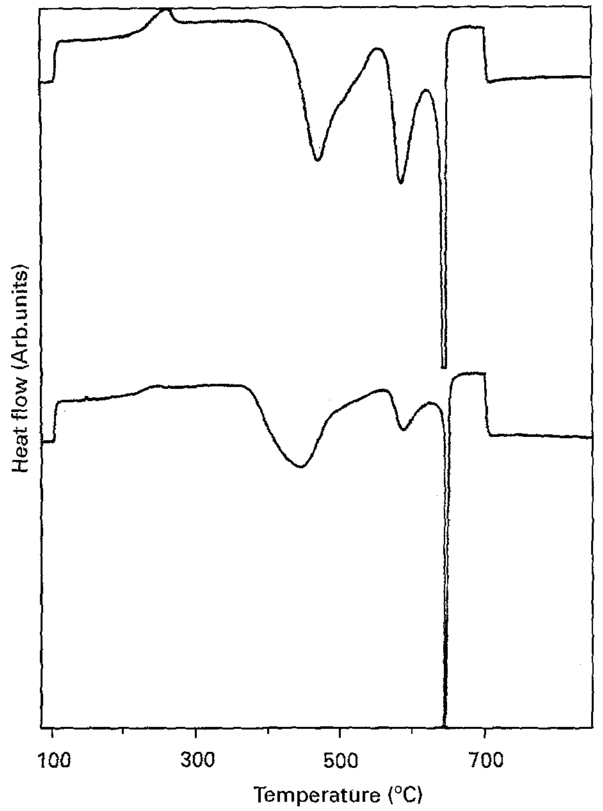

Figure 3 DSC scans of samples milled for 10 min. Upper curve: $Al_{50}Fe_{50}$, lower curve: $Al_{25}Fe_{75}$. Endothermal effects appear along the positive direction of the ordinate.

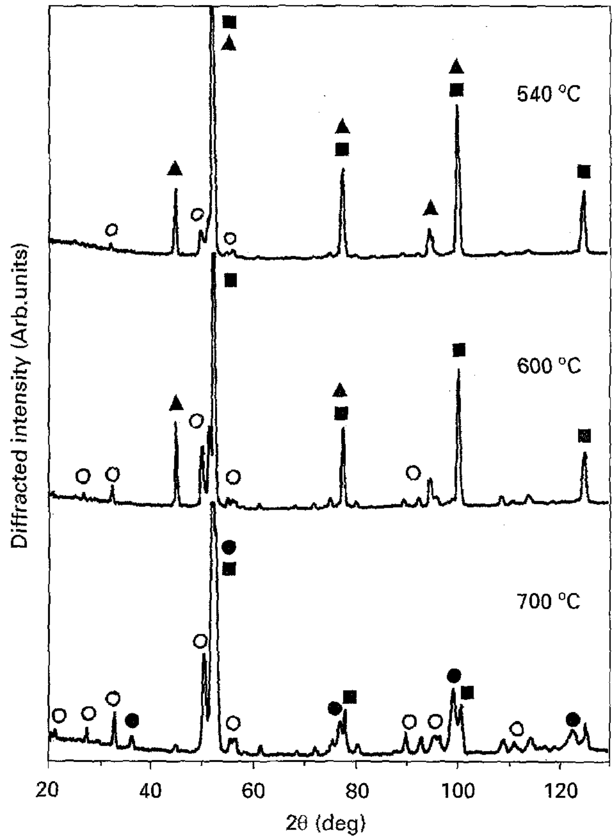

Figure 4 XRD patterns of equiatomic samples milled for 10 min and heated to different temperature. (▲) Al, (■) Fe, (●) AlFe, (○) Al_5Fe_2.

about 380 °C followed by a broad heat release extending to about 600 °C. For even longer times of milling the main exothermal peak became less and less pronounced with decreasing total area, until it became a weak heat release distributed over the whole range of temperature explored by the DSC (Fig. 5). The XRD patterns of equiatomic samples heated to 430 °C are shown in Fig. 6. It is observed that the main

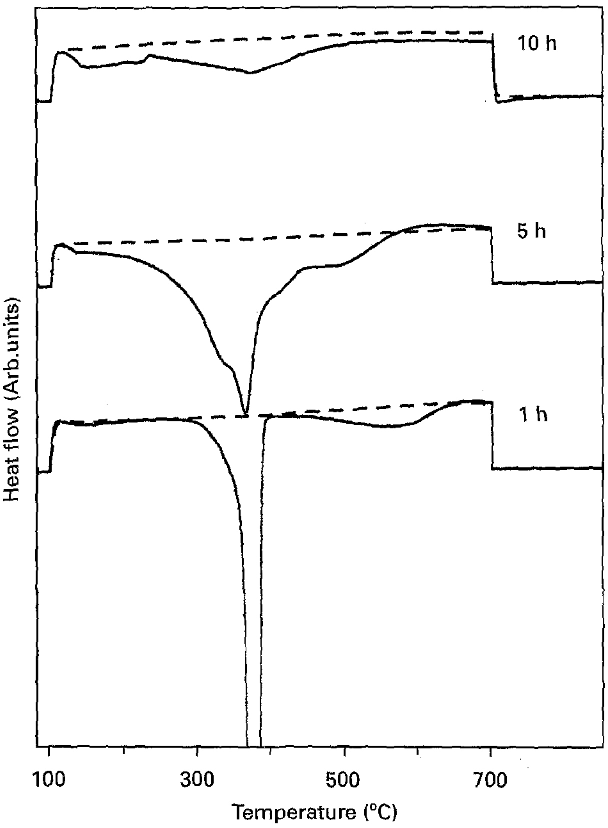

Figure 5 DSC scans of equiatomic samples milled for different times.

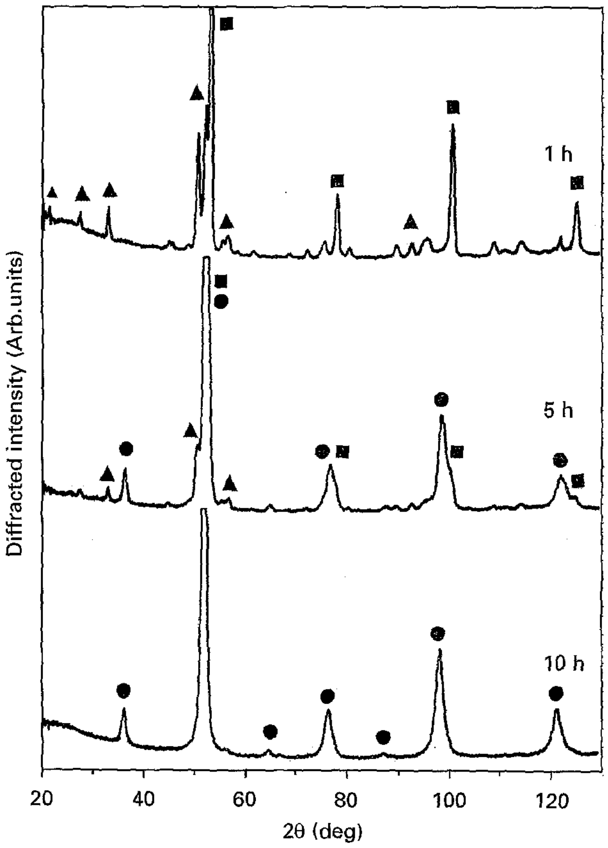

Figure 6 XRD patterns of equiatomic samples milled for different times and DSC heated to 430 °C. (■) Fe, (●) AlFe, (▲) Al_5Fe_2.

exothermal peak is associated with the nucleation and growth of Al_5Fe_2 which is the first phase to nucleate upon heating of samples milled for up to 5 h. In the samples milled for longer times the nucleation of Al_5Fe_2 was by-passed and heating to 430 °C caused only an increase in the (1 0 0) reflection and a decrease in the width of all reflections.

The sample milled for 5 h is the crossing-point between the two regimes and its DSC pattern shows a pronounced low-temperature shoulder of the main peak. The XRD pattern recorded after DSC heating to 340 °C showed the appearance of a weak (1 0 0) superstructural reflection but no trace of Al_5Fe_2 which, together with an increase of the intensity of the (1 0 0) reflection, was detected after heating to 430 °C (Fig. 6). This finding shows that there is partial ordering of the b c c solid solution at a temperature lower than that required for the nucleation of Al_5Fe_2. Finally, upon heating to 700 °C, it was observed that the XRD patterns of all equiatomic samples milled for more than 1 h were very similar showing the presence of the ordered B2 phase. From the peak width of the samples heated to 700 °C it can be deduced that the value of $\Delta a/a$ is about 1 order of magnitude smaller than before heat treatment, and that no significant growth of the size of the ordered domains has occurred.

A similar sequence of phase transformations was observed upon heating to 430 °C the iron-rich samples for which all solid-state reactions occurred for shorter milling times (Figs 7 and 8). In addition, in these samples, a lower amount of Al_5Fe_2 and a much weaker intensity of the (1 0 0) reflection were observed. Upon heating to 700 °C, the transition to a b c c phase was complete for all samples milled for 1 h or more; at the same time the intensity of the (1 0 0) reflection decreased to the point of becoming hardly visible. Also in this case there was a marked reduction of $\Delta a/a$ to an almost negligible value and no significant growth of the coherent domains. Finally, no trace of the (1/2, 1/2, 1/2) superstructural reflection typical of the DO_3 structure was observed in any of these samples.

The oxygen content of the starting powders and of two samples of different composition milled for 5 h was determined by analysing the gas evolved after melting. The results, in oxygen wt % are: 3.1 (3) in the starting aluminium powder, 0.28 (2) in the starting iron powder, 1.2 (1) at the equiatomic composition and 0.7 (1) in the iron-rich sample. From these figures it is deduced that the milling process did not alter significantly the oxygen contamination arising from the starting powders which was about 5 at% for the aluminium powder and 1 at % for the iron powder.

A summary of the transformations observed after milling and DSC heating is given in Table I.

4. Discussion

The results of this experiment allow the sequence of solid-state reactions which take place during high-energy ball-milling of Al–Fe powder mixtures to be described.

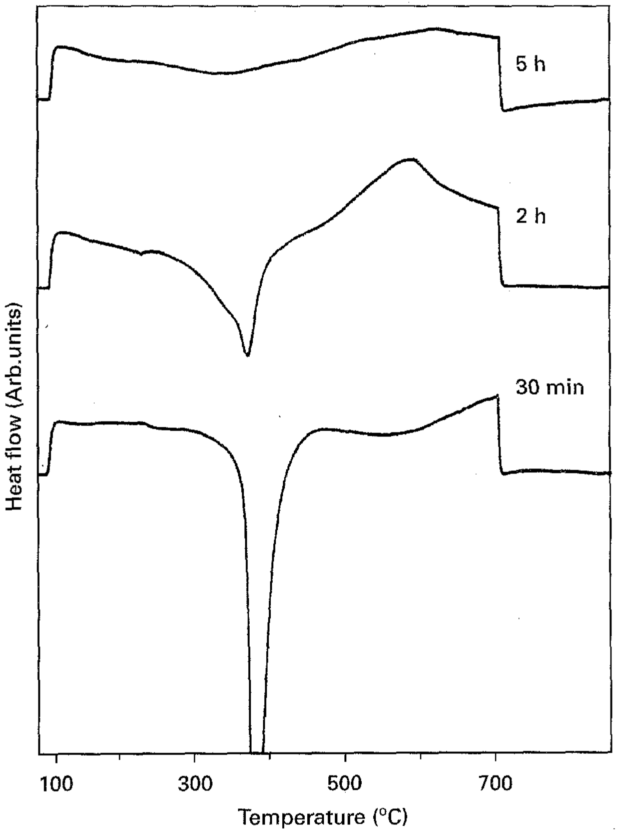

Figure 7 DSC scans of $Al_{25}Fe_{75}$ samples milled for different times.

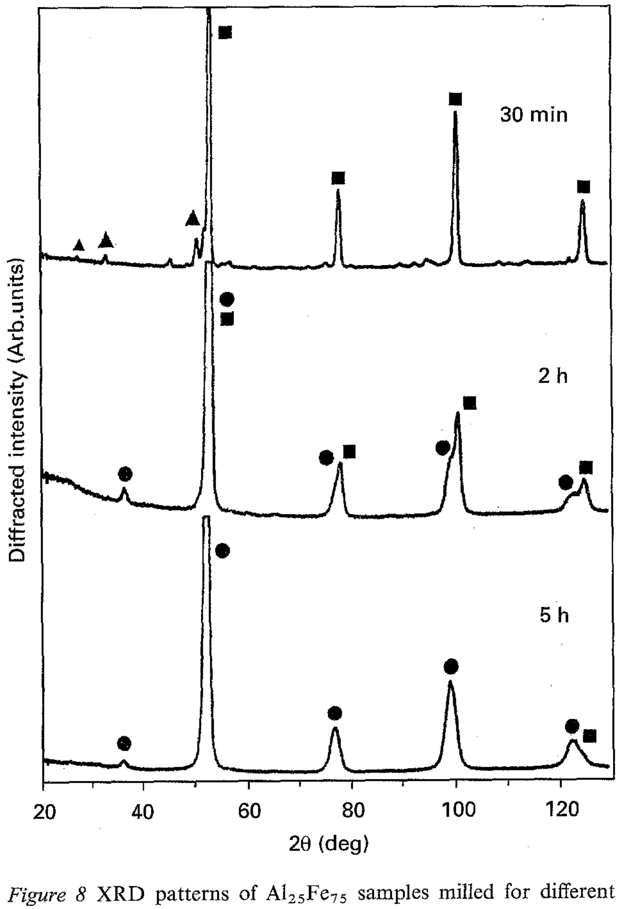

Figure 8 XRD patterns of $Al_{25}Fe_{75}$ samples milled for different times and DSC heated to 430 °C. (▲) Al_5Fe_2, (●) AlFe, (■) Fe.

The most interesting finding concerns the different reaction paths followed by the samples upon heat treatment, depending on premilling time. Upon thermal treatment, the nucleation of the Al_5Fe_2 phase in

TABLE I The sequence of reactions observed after milling (M) and after milling followed by DSC heating at 430 °C and 700 °C (M + DSC430; M + DSC700)

Milling Stage[a]	$Al_{50}Fe_{50}$			$Al_{25}Fe_{75}$		
	M	M + DSC 430	M + DSC700	M	M + DSC 430	M + DSC700
I	Al + Fe	Al_5Fe_2 + Fe + Al	Al_5Fe_2 + Fe + Al + FeAl	Al + Fe	Fe + Al + Al_5Fe_2	$AlFe_3$ dis.[b] + Fe + Al_5Fe_2
II	Al + Fe	Al_5Fe_2 + AlFe + Fe	AlFe	Fe(Al)	AlFe + Fe	$AlFe_3$ dis.
III	FeAl(B2)	AlFe	AlFe	Fe(Al)	$AlFe_3$ dis.	$AlFe_3$ dis.

[a] I, II, III refer to early, intermediate and late stages of milling.

[b] dis. refers to disordered.

slightly premilled samples has been observed at both compositions, thus suggesting that during ball milling of Al–Fe powder mixtures, iron is the dominant moving species. This behaviour is similar to that observed in the case of the Al–Ni system [5, 8] where thermal treatment leads to the formation of the Al_3Ni phase. Literature values for impurity diffusion [10, 11], extrapolated from measurements performed at higher temperatures, support this hypothesis, showing that at 500 K, the diffusion coefficient of iron in aluminium is larger than the diffusion coefficient of aluminium in iron by about five orders of magnitude.

Further support to this hypothesis arises from the experimental finding, also observed during mechanical alloying of Al–Fe powder mixtures in the 12.5–25 at % range of iron concentration [12], that the higher the iron concentration, the faster is the alloying process. In fact, the amount of diffusion occurring in unit time per unit volume of the sample is proportional to the density of the interfacial area, σ_{ij}, which, in turn, is proportional to the total surface per unit volume of one component, times the probability that an adjoining particle belongs to the other species. Neglecting in this simple calculation the difference of atomic volume between species i and j, σ_{ij} is then proportional to $c_i c_j$ if c_i and c_j are the overall atomic concentrations. If the interdiffusion is due essentially to one of the two atomic species (e.g. species i) the number n_i of atoms of i per unit volume which at time t have diffused into j will be approximately

$$n_i = c_i c_j f(t) \tag{1}$$

where $f(t)$ is a monotonically increasing function of time, independent of concentration at least during the first stages of milling when each particle acts independently from the others.

The average concentration of the ith component, x_i, in the mixed layers will then be

$$\begin{aligned} x_i = n_i/(n_i + n_j) &= c_i c_j f(t)/(c_i c_j f(t) + N c_j) \\ &= c_i f(t)/(c_i f(t) + N) \end{aligned} \tag{2}$$

where n_j is the number of atoms of species j and N is the total number of atoms per unit volume.

This equation shows that in the first stages of milling, the concentration of i in the mixed layers increases monotonically with the overall concentration of i in the sample. One can therefore conclude that if aluminium had been the dominant moving species, an increase in the overall iron concentration would have slowed down the alloying process.

Particularly interesting is the XRD pattern of the iron-rich sample premilled for 2 h and heated to 430 °C. As shown in Fig. 8, it is observed that all of the fundamental reflections are split into two components with lattice spacings differing by about 1%. Also, the intensity of the reflections of the phase with the larger lattice parameter is about 60% of the intensity of the other phase. A simple structure factor calculation shows that if one-third of the iron atoms and all of the aluminium atoms in an $Al_{25}Fe_{75}$ sample were mixed to form a B2 phase, the ratio of the intensity of a fundamental reflection of the B2 phase to that of the corresponding reflection of the remaining pure iron would be about 2:3. This analysis suggests that heating of this sample to an intermediate temperature causes the formation of the B2 phase at near equiatomic composition which, upon further heating to 700 °C, mixes with the remaining pure iron to form an almost completely disordered bcc phase having the composition Fe_3Al. Of course, the coexistence of pure iron and of a phase having nearly equiatomic composition, lends strong support to the hypothesis that iron is the dominant moving species.

The formation of an aluminium-rich metastable phase which might explain the different reaction paths followed upon thermal annealing of samples premilled for different times, has not been observed in the XRD patterns of the present samples. However, an "amorphous" phase has been repeatedly found upon extended milling of Al–Fe mixtures in the range 50–80 at % Al [13, 14]. The discovery of the formation of an "amorphous" phase in the aluminium-rich range of composition together with the experimental indication that the alloying process proceeds through iron diffusion in the aluminium-rich layers allows formulation of the hypothesis that the alloying process in ball-milled Al–Ni and Al–Fe powders proceeds in a similar way, that is through diffusion of the transition metal atom in the aluminium-rich layers and the formation of a metastable phase for aluminium concentrations in excess of 50 at %.

The occurrence of a maximum value of atomic level strain for intermediate times of milling has been observed not only upon milling of elemental powders [7, 15] but also upon grinding of intermetallic compounds [16, 17], in which case the decrease in the strain has been attributed to a lowering of the dislocation density associated with the formation of low-angle grain boundaries. In the present case, however, this mechanism seems rather unlikely if the Al–Fe B2 phase nucleates from an intermediate metastable phase according to the hypothesis advanced above. The maximum in the strain could be reasonably interpreted considering that $\Delta a/a$ also contains the effect on the lattice parameter due to local variations of the sample composition and that this effect must eventually decrease as the sample becomes progressively more homogeneous and (partially) ordered. Therefore, according to this hypothesis, the data of Fig. 2 show an increase of $\Delta a/a$ which, for intermediate milling times, is due primarily to the effect of local compositional fluctuations, while for long milling times is due essentially to the presence of residual atomic level strain of mechanical origin.

5. Conclusion

In conclusion, the present study has presented evidence that the sequence of solid-state reactions induced by thermal treatment of slightly premilled Al–Fe powder mixtures is different from that followed by the same mixtures upon extended milling. This finding shows that the result of ball milling cannot be simply explained as caused by progressive refinement of the multilayered particles until the diffusion distance during the impact becomes comparable with the average spacing of the unreacted layers. In addition to the temperature increase during the ball–powder collision, other mechanisms are operative because of the high density of lattice imperfections induced by extensive plastic deformation, in the presence of which it is reasonable to suppose that the energy barriers leading to different reaction paths may undergo selective modifications.

Finally, careful analysis of the reactions and of the reaction rates observed at different compositions suggests that atomic mixing proceeds through diffusion of iron in the aluminium layers and that at high aluminium concentrations the Al(Fe) solid solution could be in a metastable phase.

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