



# Metastable Ti–Al phases obtained by mechanical alloying

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## Abstract

The Ti–Al phase formation occurring during mechanical alloying was investigated, special attention being paid to avoid contamination. The compositions  $\text{Ti}_{10}\text{Al}_{90}$ ,  $\text{Ti}_{25}\text{Al}_{75}$ ,  $\text{Ti}_{33}\text{Al}_{67}$ ,  $\text{Ti}_{43}\text{Al}_{57}$ ,  $\text{Ti}_{44}\text{Al}_{56}$ ,  $\text{Ti}_{50}\text{Al}_{50}$  and  $\text{Ti}_{70}\text{Al}_{30}$  were investigated. In all cases the resulting phase composition of the mechanical alloys does not depend on the initial state, i.e. pure metals or compounds. The mechanical alloying of samples having compositions falling into the region of  $\gamma$ -TiAl result in a metastable h.c.p. phase. The mechanical alloy  $\text{Ti}_{70}\text{Al}_{30}$  has an h.c.p. structure if the treatment intensity is low, or a b.c.c. structure if the treatment intensity is rather high. The compositions  $\text{Ti}_{25}\text{Al}_{75}$  and  $\text{Ti}_{33}\text{Al}_{67}$  transform into the same phase, possibly having the  $\text{TiAl}_2$  structure. Annealing of  $\text{Ti}_{25}\text{Al}_{75}$  reveals an intermediate phase, possibly  $\text{Ti}_2\text{Al}_5$ . This phase results also from the mechanical alloying of  $\text{Ti}_{10}\text{Al}_{90}$ . A possible mechanism of mechanical alloying is discussed. It is shown that the results are in good accordance with the model of local melting.

**Keywords:** Mechanical alloying; Titanium; Aluminium; Metastable phases; Aerospace alloys

## 1. Introduction

In recent years the Ti–Al alloys have received particular attention as a promising structural material for aerospace application. The present approach to engineering these materials involves a compositing technique based on powder metallurgy. The difficulties encountered in preparing the powders of these alloys by conventional metallurgy or rapid solidification technique have recalled the attention to mechanical alloying (MA).

There are several tens of papers concerning phase formation by MA of the Ti–Al system (Fig. 1). Unfortunately, data of different investigators often do not agree with each other. For instance, MA of the alloys with composition  $\text{Ti}_{50}\text{Al}_{50}$  may result in the formation of: h.c.p. phase,  $\alpha_2$  [4]; mixture of  $\alpha_2$  and  $\gamma$  phases or amorphous alloy, depending on milling conditions [5]; single  $\gamma$  phase [6]. In addition, some results seem to be inexplicable. Formation of amorphous alloys by MA in the Ti–Al system observed in Ref. [7] for the composition  $\text{Ti}_{100-x}\text{Al}_x$  with  $x = 20$ –50 is in contradiction with the existing viewpoint. To prevent the amorphous state from transformation into the more stable thermodynamically crystalline phase

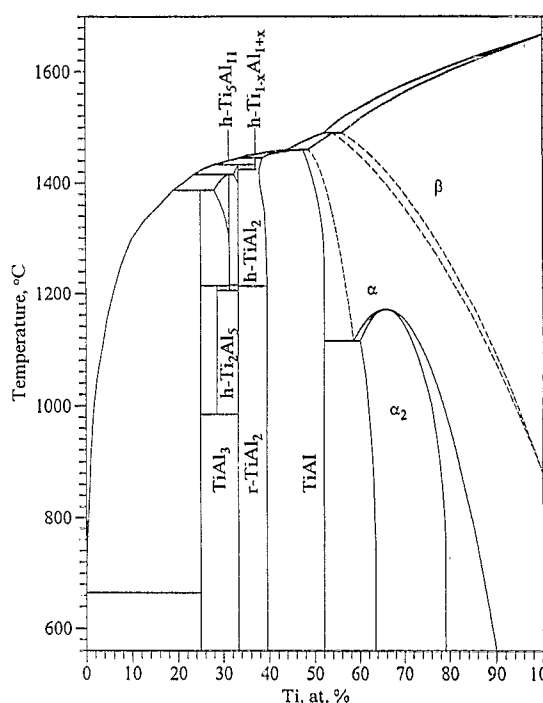


Fig. 1. Phase diagram of Ti–Al system [1–3].

at least one of the following conditions must be fulfilled [8]. The constituents should have substantially different atomic radii or the difference in the diffusion rates of atoms of components may be large. In both cases difficulties for crystallisation arise, so the amorphous state becomes more favourable. Neither condition is fulfilled in the Ti–Al system. The atomic radii of Ti and Al are close, and the values of the interdiffusion coefficients of Ti and Al are also close [9].

One can imagine various reasons for the disagreement of the data obtained by different investigators. However, an unusual phase composition may often be explained as a result of contamination of the alloy, mainly by oxygen and nitrogen. The formation of a metastable f.c.c. phase in the mechanical alloys  $Ti_{75}Al_{25}$  [10] is due to impurities of oxygen and nitrogen [11]. Contamination can take place even if MA is carried out under high purity argon [11,12]. In this case the impurities are likely to appear from the surface of powders (oxide and adsorbed layers) or from contamination of the gas atmosphere caused by periodic sampling, as in the Zr–Ni system [13]. Another source of impurities may occur when the product forms a compact coating on the balls and vial walls. In this case, agents such as hydrocarbons or alcohols, for instance methanol [12], are used to facilitate sampling. These agents may react chemically with the products of the MA [14], changing the phase constitution of the product.

The sensitivity of the phase composition of a mechanical alloy to contamination complicates the interpretation of MA results. To obtain reliable data about MA in systems containing highly active metal, one should take care in reducing the impurity content, especially with regard to non-metals (O, N, C).

The aim of this work is to investigate MA in the Ti–Al system, with the contamination reduced to a minimum. In addition, it is intended to reveal whether the principle proposed in Ref. [4] is applicable to the Ti–Al system. This principle states, that the result of MA does not depend on the initial state (elements or intermetallic compounds) and is determined by the elemental composition only.

## 2. Experiment

To reduce contamination by oxygen and nitrogen associated with the surface, we have discarded the use of fine dispersed powder. Titanium was taken in the form of coarse filings (about 0.5 mm) obtained from a crystal bar made via the iodide-process. Aluminium was prepared from wire (diameter 0.4 mm) cut into pieces about 2 mm long. Both the metals are greater than 99.99% pure. No sampling during alloying was

made. The compact products were stripped from the balls by a file.

The intermetallic compounds  $TiAl_3$ ,  $TiAl$  and the  $\alpha_2$  phase of the composition  $Ti_{70}Al_{30}$  were prepared by a pyrometallurgical process under argon atmosphere. Powders from the ingots were prepared in a vibration mill under argon. The size fraction 0.2–0.5 mm was used in the experiments.

The mechanical treatment was carried out in a centrifugal ball mill of the model AGO-2M. This mill is characterised by a high power (up to 1.5 kW per two vials, depending on the operational mode) and water cooling of the vials during milling. The vials were designed to allow pumping and subsequent filling by an inert gas (Ar or He) up to pressure of 1 MPa. High pressure in the vials facilitates heat transport between the balls and the vial walls, hence reducing the average temperature [15]. The excess gas pressure that persisted in the vials after the mechanical treatment evidences that air did not permeate into the vial. The powder load was about 10 g per vial; the load of the steel balls was 200 g. High power applied to the milled substance allows fast alloying. Structure changes were completed in all cases in 2–3 h (for comparison, such a state was reached in Ref. [5] after 100–200 h).

The samples were examined after mechanical treatment by X-ray diffraction (XRD) using  $Cu K\alpha$  radiation and by differential scanning calorimetry (DSC) (Setaram DSC-111).

## 3. Results

### 3.1. Region of the $\gamma$ -TiAl phase

The compositions  $Ti_{50}Al_{50}$ ,  $Ti_{43}Al_{57}$  and  $Ti_{44}Al_{56}$  were investigated. The MA of all these materials as well as the mechanical treatment of  $\gamma$ -TiAl leads to formation of an h.c.p. product (Fig. 2). DSC traces (Fig. 3(a)) exhibit a single exothermic effect of  $2.7 \pm 0.4$  kJ mol<sup>-1</sup>. The X-ray analysis of the annealed products reveals single  $\gamma$ -TiAl.

The activation energy of transformation of the h.c.p. phase into the equilibrium tetragonal phase was determined from the Kissinger plot. It equals to  $260 \pm 43$  kJ mol<sup>-1</sup>. This value is in good agreement with the activation energy for diffusional growth of TiAl layers,  $234 \pm 19$  kJ mol<sup>-1</sup> [9].

### 3.2. $Ti_{70}Al_{30}$ composition

Results of both MA and mechanical treatment of  $\alpha_2$  were identical. In contrast to the previous composition, the phase constitution of the products depends on treatment conditions (Fig. 4): a treatment with low power (approximately 2 W g<sup>-1</sup>) leads to the h.c.p.

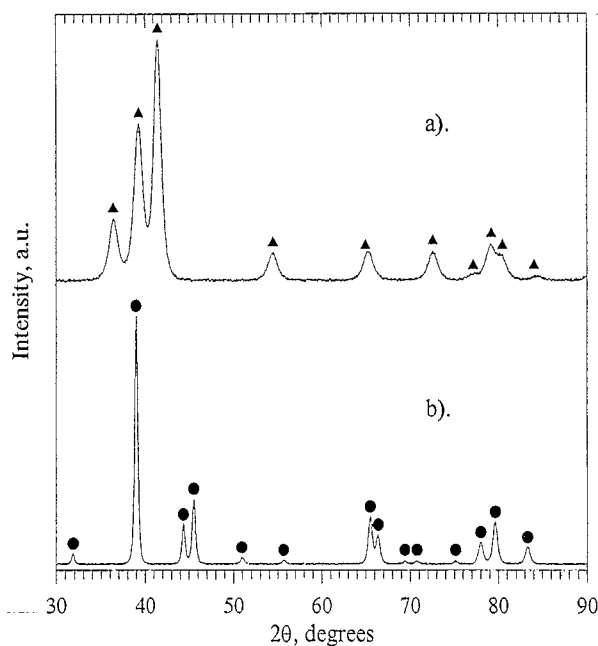


Fig. 2. XRD patterns of mechanical alloy  $Ti_{50}Al_{50}$ , after MA (a) and after annealing (b): ▲ h.c.p.; ●  $\gamma$ -TiAl.

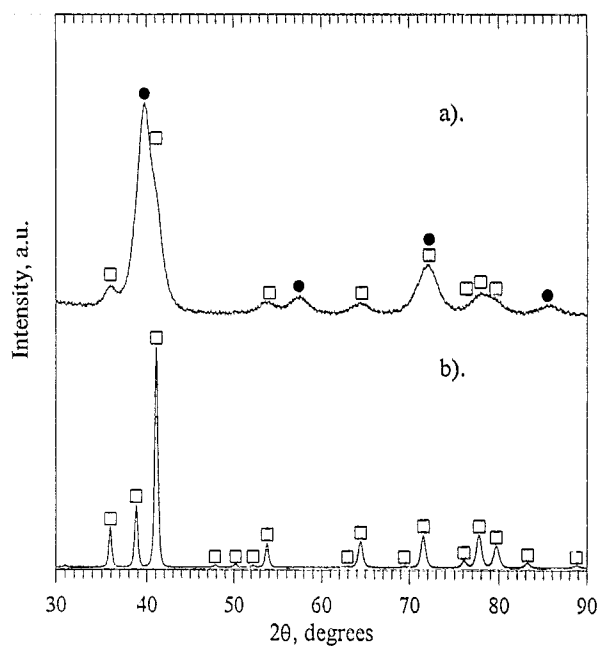


Fig. 4. XRD patterns of mechanical alloy  $Ti_{70}Al_{30}$ , after MA (a) and after annealing (b): ● b.c.c.; □  $\alpha_2$  phase.

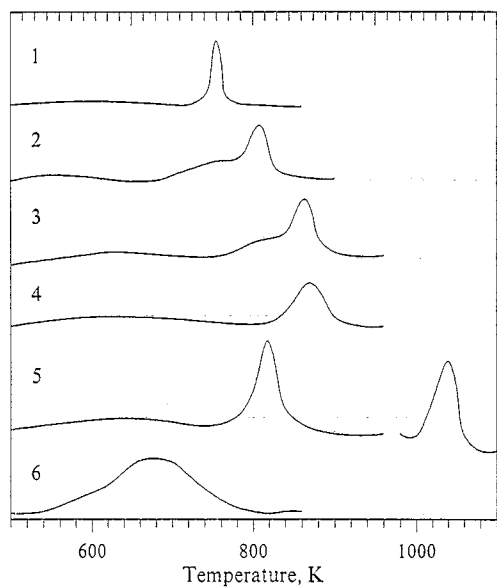


Fig. 3. DSC records of annealing mechanical alloys. (1)  $Ti_{50}Al_{50}$ ; (2)  $Ti_{70}Al_{30}$ , h.c.p phase; (3)  $Ti_{70}Al_{30}$ , b.c.c. phase; (4)  $Ti_{33}Al_{67}$ ; (5)  $Ti_{25}Al_{75}$ , curve above 950 K was recorded on a different device; (6)  $Ti_{10}Al_{90}$ .

structure only. In the case of elevated power (7–8  $W g^{-1}$ ) a b.c.c. structure was found.

DSC traces in the case of a b.c.c. phase show an exothermic effect of approximately  $2 kJ mol^{-1}$  (Fig. 3(b)) which is associated with the transition of metastable b.c.c. into the equilibrium phase  $\alpha_2$ . The XRD patterns of the samples after annealing contains only reflections of  $\alpha_2$ .

### 3.3. $Ti_{33}Al_{67}$ and $Ti_{25}Al_{75}$ compositions

Both MA and the mechanical treatment of the corresponding intermetallic compounds lead to a tetragonal phase (Fig. 5) whatever the milling conditions. The phase has the lattice parameters  $a = 0.397 nm$  and

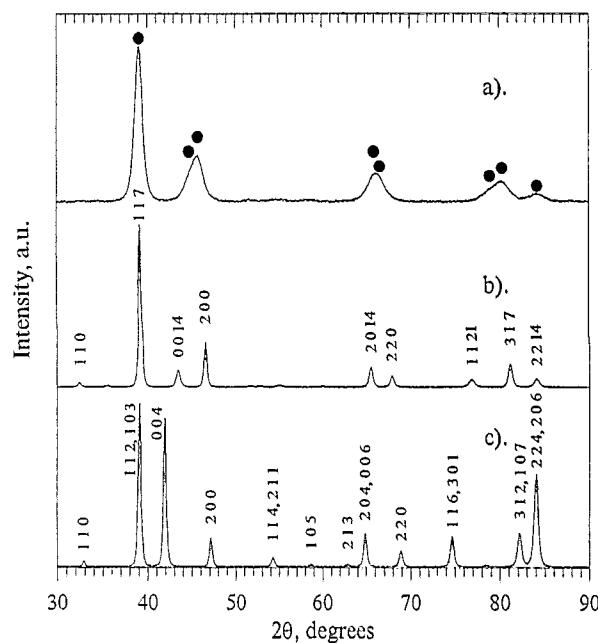


Fig. 5. XRD patterns of mechanical alloy  $Ti_{25}Al_{75}$ . (a) After MA: ● peak positions expected for the tetragonal phase with  $a = 0.397 nm$ ,  $c = 0.405 nm$ . (b) After low-temperature annealing (up to 870 K); indices correspond to the  $Ti_2Al_5$  phase. (c) After high-temperature annealing (up to 1100 K); indices correspond to the  $TiAl_3$  phase.

$c = 0.405$  nm, as determined from XRD patterns (here and below  $a$  and  $c$  are parameters of subcell in the case of superlattice). The low value of  $c/a = 1.02$  coupled with the peak broadening lead to overlapping of the reflections: (200) and (002), (220) and (202), (311) and (113). Nevertheless, the tetragonal structure is reliably recognised from the asymmetric character of the broadening.

The products of MA undergo different changes depending on the composition. Heating the powder of  $Ti_{33}Al_{67}$  is characterised by a single exothermic effect (Fig. 3(c)). The annealing product contains only the equilibrium phase r-TiAl<sub>2</sub>. The value of the heat effect estimated from the DSC data is about 1 kJ mol<sup>-1</sup>. Thermograms of  $Ti_{25}Al_{75}$  (both mechanical alloy and intermetallic compounds after mechanical treatment) are identical and characterised by two heat effects (Fig. 3(d)). The magnitude of the low temperature one is  $3.0 \pm 0.4$  kJ mol<sup>-1</sup>. XRD patterns of the samples annealed up to 870 K (slightly higher than the end of the low-temperature peak) exhibit reflections of the tetragonal phase with a  $c/a$  ratio substantially higher than that of the phase obtained by MA. The observed  $c/a$  value is 1.067. The high-temperature heat effect is due to the transition of the metastable phase into the equilibrium compound TiAl<sub>3</sub>. The XRD patterns of samples annealed up to 1150 K contain only the reflections of this phase.

### 3.4. $Ti_{10}Al_{90}$ composition

This composition was represented in the MA experiments as a mixture of the elements, Al + TiAl<sub>3</sub>, Al +

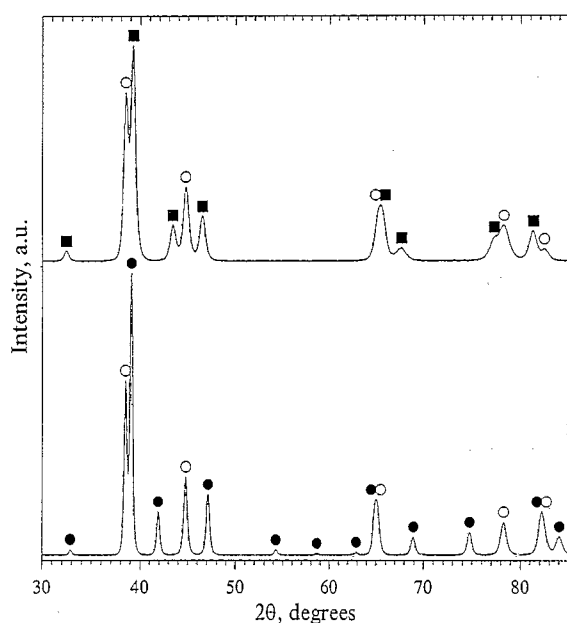


Fig. 6. XRD patterns of mechanical alloy  $Ti_{10}Al_{90}$ . After MA (a) and after annealing (b): ○ Al; ● TiAl<sub>3</sub>; ■ tetragonal phase, possibly  $Ti_2Al_5$ .

TiAl and Al +  $\alpha_2$ -phase. In all cases the products of the MA are identical and represent a mixture of Al and the tetragonal phase with  $c/a = 1.067$  (Fig. 6). The products of the MA have a remarkably low peak broadening. Annealing of the product take place at substantially lower temperatures than for the other mechanical alloys (Fig. 3(e)). The heat effect is very diffuse and has a value  $2.0 \pm 0.7$  kJ mol<sup>-1</sup>.

## 4. Discussion

It is obvious that some extent of contamination is unavoidable in practice. For instance, the surface of the fine product of MA undergoes oxidation when the product is being analysed. However, this contamination affects only the surface layers and does not change the structure in the bulk as determined by diffraction methods. In contrast, oxygen and nitrogen from the surface of the original metals can be built into the structure of the product. In the latter case the results may be biased. Conventional chemical analysis is unable to distinguish between these cases.

To establish whether the phase belongs to the Ti–Al system, or has to be attributed to impurities, we wish to propose a method that seems to be more reliable. The atomic radii of both Ti and Al are close, all equilibrium compounds and solid solutions, excluding  $\beta$ -Ti and its solid solutions, are based on close packing, h.c.p or deformed f.c.c. Hence the dependence of the volume per atom  $V_{at}$  on Ti content is a steady function (Fig. 7). The structure of the products of MA is unlikely to deviate from close packing and hence should behave according to this dependence. However, if the compound contains oxygen or nitrogen in interstitial positions,  $V_{at}$  should deviate from the curve on Fig. 7 toward higher values. The metastable f.c.c. mentioned above [10] has a lattice parameter  $a = 0.422$  nm, so the value of  $V_{at}$  equals  $18.78 \times 10^{-3}$  nm<sup>3</sup>. This is far outside the margins of the plot on Fig. 7. Iron is another impurity that can originate from the material of the ball and the vial. The Fe atoms substitute for Ti and Al. The atomic radius of Fe is smaller than those of Ti and Al. Hence ternary compounds Al–Fe–Ti containing small amounts of Fe [16] should exhibit a deviation of  $V_{at}$  toward lower values than the  $V_{at}$  of equilibrium phases with the same Al:Ti ratio (Fig. 7).

Therefore, in order to acquire proof as to whether the phase found in the products of MA is characteristic of the Ti–Al system or whether its existence is due to foreign constituents, we will compare the  $V_{at}$  of the products of MA with the values predicted by Fig. 7. The values of  $V_{at}$  were calculated from the cell parameters determined by XRD for all phases observed, including the metastable ones. It was found that these

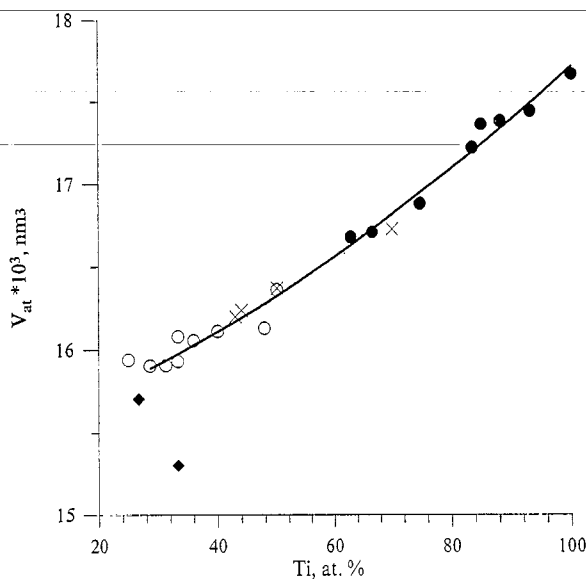


Fig. 7. Dependence of volume per atom in alloy for various compositions: ● solid solutions based on  $\alpha$ -Ti, calculated from the data in Ref. [24]; ○ intermetallic compounds, calculated from the data in Ref. [1]; × mechanical alloys obtained in the present work; ◆ intermetallic compounds  $\text{TiAl}_2\text{Fe}$  and  $\text{Ti}_8\text{Al}_{22}\text{Fe}_3$ , calculated from the data in Ref. [16], Ti content is calculated for corresponding compositions without Fe.

values are in a good agreement with the dependence of Fig. 7.

In addition, the products of MA in each experiment were subjected to annealing. The phase composition of the annealing products were examined to check whether there is accordance with those predicted by the equilibrium phase diagram (Fig. 1). If a mechanical alloy contains noticeable amounts of foreign constituents, one would observe the presence of stable phases composed of the impurities after annealing. In this regard we assume that the expected impurities (O, N, Fe) form strong compounds with Ti and Al that cannot be decomposed at relatively low (up to 1270 K) temperatures and can be detected in the products of annealing.

None of the tests detected the presence of significant amounts of impurities in the mechanical alloys. Coupled with the attention paid to the purity of the experiments this shows that the observed phenomena are inherent to the Ti–Al system and can form the basis for discussion of the physical background of MA.

That MA can be regarded as a process leading to a simple enhancement of diffusion in the solid state, as proposed first in Ref. [17], is likely to be a common viewpoint. Nevertheless, there are some facts that cannot be explained within the framework of this approach (see e.g. Ref. [18]). The analysis of the results obtained in the present work also shows a discrepancy with this model.

The investigations have revealed that the products of the MA and the mechanical treatment of the

intermetallic compounds in the Ti–Al system are identical for all compositions considered. This phenomenon, noticed in Ref. [4] for other systems, in our opinion indicates that the nature of the phase formation during mechanical treatment is insensitive to the source of the constituents. Therefore, solid state diffusion cannot play the main role in MA, because it cannot produce a driving force for cases where the original state is represented by equilibrium compounds, as this state is already thermodynamically stable. There is another model of phase formation during MA, namely the model of local melting. It assumes melting in small regions caused by local plastic deformation under ball collision. This model has already been proposed long ago [19]. However, later it was rejected mainly because of theoretical estimations of the local temperatures. The estimations give values for local overheating of about a few tens of degrees [20]. Nevertheless there are other estimations that give values higher than 1000 K [21].

According to the existing estimations and measurements, the duration of the temperature pulse is about  $10^{-5}$  s, the dimension of the overheated regions is about 10 nm, and the cooling rate is up to  $10^6$  K  $\text{s}^{-1}$  [22]. Hence, if the model of local melting is accepted, the phase formation during MA is analogous to rapid solidification to some extent. Indeed, the rapid solidification of Ti–Al alloys having a composition falling within the homogeneity range of  $\gamma$ -TiAl leads to formation of the ordered  $\alpha_2$ -phase [23]. In our experiments, MA and mechanical treatment of intermetallic compounds of alloys of such compositions also produce the hexagonal phase. It cannot be the true  $\alpha_2$ -phase, of course, because the Ti:Al ratio is far from the homogeneity range of the  $\alpha_2$ -phase. However, it is an ordered phase, as is indicated by the low heat of annealing.

Of course, the analogy between MA and rapid solidification is not exact. In mechanical treatment the cooling takes place in the presence of original metals or equilibrium compounds; these can serve as centres of crystallisation. Nevertheless, the phase formation in MA seems to have much in common with the phase transformations taking place at the liquidus line. Thus, the formation of b.c.c. in MA of  $\text{Ti}_{70}\text{Al}_{30}$  is inexplicable from viewpoint of solid diffusion but is natural for the model of local melting, since solid solution based on  $\beta$ -Ti is a solid phase being in equilibrium with the liquid of composition  $\text{Ti}_{70}\text{Al}_{30}$  (Fig. 1).

According to the model of local melting, the MA of compositions falling into the region of a compound melted incongruently should produce the first solid phase precipitated from the melt of corresponding composition. It cannot be a strict rule, in the real case the precipitated solid can react with melt producing compounds that are closer in composition to the

equilibrium phase, non-melted regions may induce crystallisation, etc. If anything, crystallisation in the melted regions starts from the phase first precipitated from the melt. Taking into account the high rate of cooling and other phases being closer in composition to the equilibrium one, then equilibrium phase itself may have no time to form. In this case the melt will crystallise in a structure shifted by composition. Hence the model of local melting gives the following rules for the phase formation that are distinctive from the predictions of the solid diffusion model:

(1) the phase formed in MA is a high-temperature modification;

(2) the phase produced by MA of materials with compositions corresponding to incongruently melting compounds is a compound shifted in composition towards the primary phase that would have precipitated from melt.

In the Ti–Al system the first rule is illustrated by formation of the b.c.c. phase during MA of  $Ti_{70}Al_{30}$ . The second rule is useful to rationalise the results of MA in the Al-rich region. In this region, there are many compounds formed peritectically; they all are ordered solid solutions based on the f.c.c. lattice of Al with tetragonal distortion. The energies associated with different ordering patterns probably differ very little. Therefore, many phases not present in the equilibrium phase diagram [1] may be present as products of MA. Coupled with the weakness of superlattice reflections, this circumstance presents significant problem for the phase identification of mechanical alloys.

The MA of  $Ti_{25}Al_{75}$  does not produce the corresponding equilibrium phase  $TiAl_3$ . Instead, another tetragonal phase is formed. The difficulties mentioned above and the X-ray line broadening do not allow unambiguous identification. The observed  $c/a$  ratio is 1.02. Of the phases in the equilibrium diagram, r- $TiAl_2$  or h- $TiAl_2$  have close  $c/a$  ratios. In any case, there is no compound richer in Al than  $TiAl_3$ , so the mechanical alloy  $Ti_{25}Al_{75}$  has a structure of a phase richer in Ti than  $TiAl_3$ . This is in full accordance with the predictions of the local melting model, because the cooling Ti–Al melt first produces a compound rich in a more refractory Ti. Metastability of the mechanical alloy  $Ti_{25}Al_{75}$  is also evidenced by the results of annealing. The phase formed after the first exothermic peak cannot be exactly identified. However, if only the phases present in the equilibrium diagram are to be considered, the resulting product may be recognised as the  $Ti_2Al_5$  phase, as it has a  $c/a$  ratio closest to the observed one. It is shifted in composition toward Ti-rich compounds.

When liquid is present and is in contact with the solid, phase formation is likely to be more intense than

in the case of the entirely solidified melt because of the more intense mass transport in the liquid. Hence large distances between liquidus and solidus are favourable for reaching the equilibrium state. For the compositions with less than 25 at.% Ti there is a wide temperature interval where the liquid coexists with the solid. Indeed, peak broadening in the case of  $Ti_{10}Al_{90}$  is remarkably lower than for all other compositions. The mechanical alloy  $Ti_{10}Al_{90}$  represents a mixture of Al and a tetragonal phase, but not  $TiAl_3$ , as one may expect. According to the  $c/a$  ratio it is  $Ti_2Al_5$ , just the phase obtained by low-temperature annealing of mechanical alloy  $TiAl_3$ . A possible explanation is that the cooling of the  $Ti_{10}Al_{90}$  melt leads to formation of the same solid as produced by MA of  $Ti_{25}Al_{75}$ . During the subsequent cooling this product undergoes a relaxation similar to that taking place during annealing of mechanical alloy  $Ti_{25}Al_{75}$ .

## 5. Conclusion

(1) Results of mechanical treatment in the Ti–Al system for all compositions do not depend on the initial state (mixture of elements or intermetallic compounds) and are determined by elemental composition and milling conditions only.

(2) MA of Ti–Al with a composition falling into the region of  $\gamma$ -TiAl results in formation of the h.c.p. phase, as in the case of rapid solidification. This phase is likely to be ordered.

(3) Mechanical alloys  $Ti_{70}Al_{30}$  have a b.c.c. structure if the mechanical treatment is rather intense. The h.c.p. structure is formed if the treatment is less intensive.

(4) MA of compositions with less than 33 at.% Ti leads to the formation of a metastable tetragonal phase with  $c/a = 1.02$ , that is likely to have structure of  $TiAl_2$  phase (h- or r-modification).

(5) A large difference between the liquidus and solidus lines in the case of compositions with less than 25 at.% Ti facilitates the attainment of the equilibrium state.

(6) The phase formation upon MA of the Ti–Al system cannot be explained from the viewpoint of solid state diffusion but it is in good accordance with the model of local melting.

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