

# Tribochemical equilibrium in mechanical alloying of metals

K. B. GERASIMOV, A. A. GUSEV, E. Y. IVANOV, V. V. BOLDYREV  
*Institute of Solid State Chemistry, 630091, Novosibirsk 91, Derzhavina 18, USSR*

The structure of the product in mechanical alloying depends both on the elemental composition and the milling conditions. An increase of ball energy led to more pronounced crystallinity of the product. Mechanical alloying at small ball energy leads to the formation of amorphous alloys for Zr–Co and Cu–Ti systems. Demixing of  $Ti_3Cu_4$  into crystalline TiCu and  $TiCu_4$  and demixing of  $Zr_{50}Co_{50}$  into  $Zr_3Co$  and  $ZrCo_2$  was found. The results are explained on the basis of the concept of tribochemical equilibrium.

## 1. Introduction

To account for mechanical alloying the following knowledge is used [1]: plastic deformation and grinding of particles in mixtures of metals and alloys in high-energy mechanical activators result in the formation of composite species with a developed interface between the starting components. If the starting components are sufficiently plastic, the composite has a layered structure; if they are brittle, it predominantly consists of equiaxed particles. The process further proceeds through a solid-state reaction. The driving force of this reaction, the negative energy of component mixing, is considered to be a necessary condition for the occurrence of mechanical alloying.

The composition of the end products of mechanical alloying depends upon many factors: the composition of the starting mixture, the solubility of the elements in each other, the existence of intermediate compounds on the equilibrium phase diagram, the conditions of nucleation for intermediate phases, etc. If the mutual solubility of the elements is limited, and the nucleation of equilibrium crystalline intermediate phases is hindered, amorphous alloys can form as well as supersaturated solid solutions and other metastable phases.

Thus, in the literature an analogy is drawn between mechanical alloying and solid-state transformation in layered film systems [2]. The mechanisms of both these processes are considered to be essentially identical, and the role of mechanical treatment supposedly reduces to the formation of the composite from dispersed particles of the starting components, and to the facilitation of diffusion due to generation of non-equilibrium defects.

It is known, however, that under mechanical action different chemical reactions may proceed, which are rather specific and cannot be accounted for by the usual mechanisms of thermal and/or pressure initiation [3]. Such mechanochemical reactions are the probable reason that there is a considerable amount of experimental data concerning mechanical alloying which are beyond the scope of a simple diffusional model. Thus, for example, in the amorphization by

mechanical alloying of elements, equilibrium crystalline intermetallic compounds often form as the intermediate products [4, 5]. In the case of mechanical alloying, the ranges of concentration in which complete amorphization is attained are considerably wider than in the case of amorphization of layered film systems by heterodiffusion. Neverov *et al.* [6] have studied mechanical alloying in Bridgeman anvils for a number of pairs of metallic elements, and have revealed the information of solid solutions with concentration which considerably exceed the ultimate solubility in the solid phase for a number of systems with a positive heat of component mixing. Loeff and Bakker [7] found the decomposition of La–TM (TM = Ag, Ni, Co) intermetallic compounds into elemental constituents as a result of ball milling.

It may be expected that specific mechanochemical processes (if any) will significantly depend on the type of apparatus in which mechanical alloying is carried out, and also on the operating parameters of the apparatus such as the rotational speed of the vials, the material and size of the grinding balls, their total mass, and the mass of the treated powders.

Unfortunately, studies on the effect of these parameters in the course of mechanical alloying are practically absent from the literature. Weeber *et al.* [8] have compared amorphization during mechanical alloying of zirconium with nickel in vibratory and planetary ball mills. They found that in mills of different types the process proceeds in different ways: in a vibratory mill the amorphous alloy forms from the elements directly, and in a planetary mill the formation of a metastable crystalline intermetallic compound is observed as the intermediate product.

In this paper we present the results obtained for mechanical alloying in a planetary ball mill under different conditions. The average kinetic energy of the balls was altered by changing their mass (dimension) and their velocity (centrifugal acceleration). The system zirconium–cobalt was chosen as the basic subject of research; some results were also obtained for the systems titanium–copper and titanium–aluminium.

## 2. Experimental details

Chips of zirconium and titanium powder with a particle size of about 1 mm were used. The other metals were used as powders with a particle size of about 100  $\mu\text{m}$ . We abandoned the use of dispersed metal powders since they are usually contaminated by oxides (especially zirconium and titanium), and oxygen has a pronounced effect on the results; amorphization is accelerated, the temperature and the heat of crystallization of amorphous alloys fall off considerably, and so on.

Mechanical treatment was conducted in planetary ball mills with hardened steel vials at accelerations of 300, 600 and 900  $\text{m sec}^{-2}$ . Steel balls 5, 7 and 10 mm in diameter were used for grinding. The ball charge was 100 g and the mass of the powders being treated was 10 g. To prevent oxidation, the treatment was carried out in hermetically sealed vials filled with argon. Sampling in the course of treatment was performed in an argon glove box.

Samples were examined by X-ray techniques (using  $\text{CoK}\alpha$ -radiation for the samples containing copper, and  $\text{CuK}\alpha$  radiation for the rest), and also by differential thermal analyses and differential scanning calorimetry (Setaram DSC-111). Elemental compositions were determined by chemical analyses. Intermediate phases and intermetallic compounds were specially prepared by alloying elements in a vacuum furnace. Ingots were turned over and remelted several times and then were subjected to homogenizing annealing. Powders from the ingots were prepared in a vibrating mill in an inert atmosphere.

The sampling of powders for the analyses was conducted at the following intervals after the beginning of the mechanical alloying: 0.25, 0.5, 1, 2, 4 h etc. If two sequential analyses yielded practically indistinguishable results, the process was terminated. To be certain that further treatment would bring about no changes in the product, in several experiments mechanical alloying was carried out for more than 10 h. In most cases the process was terminated after 2 or 4 h.

## 3. Results and discussion

The experiments showed that increased kinetic energy of the balls due to an increase of their diameter and/or of the rotating speed of the vials leads to a rise in the degree of crystallinity. The operating conditions of the mill which provide complete amorphization depend on the composition of the starting charge or, in other words, the concentration ranges for amorphization in mechanical alloying depend on the operating conditions of the mill. Thus, the composition  $\text{Zr}_{67}\text{Co}_{33}$  became amorphous only under the "softest" of the conditions employed: a centrifugal acceleration of 300  $\text{m sec}^{-2}$ , and a ball diameter of 5 mm (Fig. 1).

Under all other operating conditions the amorphization was either incomplete or only crystalline products formed. For the composition  $\text{Zr}_{50}\text{Co}_{50}$  (Fig. 2) analogous transitions from amorphous alloys to crystalline ones were observed under more severe conditions; the limiting conditions which provided

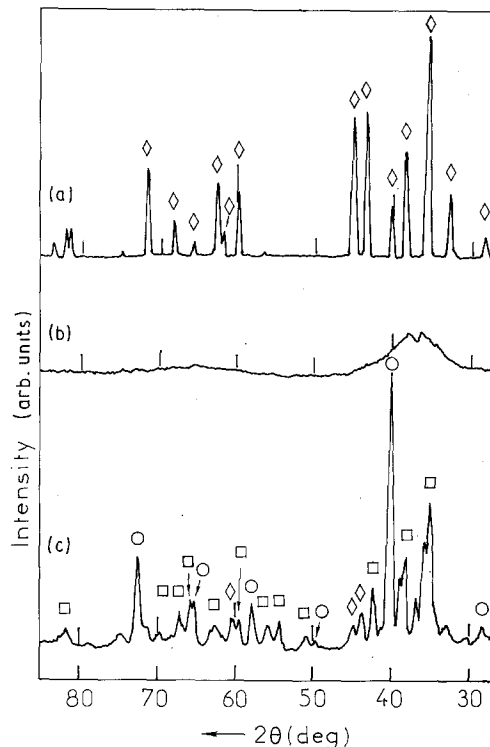


Figure 1 X-ray diffraction patterns of  $\text{Zr}_2\text{Co}$ : (a) the starting intermetallic; (b) after treating in a mill at an acceleration of 300  $\text{m sec}^{-2}$  with balls 5 mm in diameter; (c) after treating at an acceleration of 600  $\text{m sec}^{-2}$  with balls 7 mm in diameter ( $\text{CuK}\alpha$  radiation). ( $\diamond$ )  $\text{Zr}_2\text{Co}$ , ( $\circ$ )  $\text{ZrCo}$ , ( $\square$ )  $\text{Zr}_3\text{Co}$ .

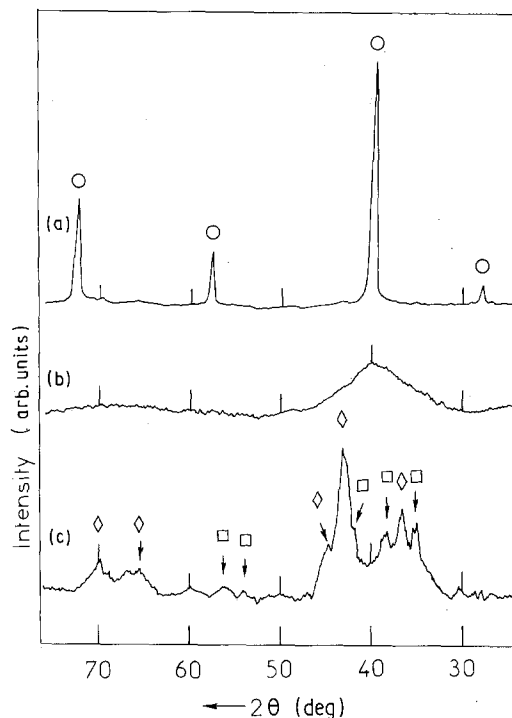


Figure 2 X-ray diffraction patterns of  $\text{ZrCo}$ : (a) the starting intermetallic; (b) after treating in a mill at an acceleration of 600  $\text{m sec}^{-2}$  with balls 5 mm in diameter; (c) after treating in a mill at an acceleration of 900  $\text{m sec}^{-2}$  with balls 10 mm in diameter ( $\text{CuK}\alpha$  radiation). ( $\circ$ )  $\text{ZrCo}$ , ( $\diamond$ )  $\text{Zr}_2\text{Co}$ , ( $\square$ )  $\text{Zr}_3\text{Co}$ .

complete amorphization were an acceleration of 600  $\text{m sec}^{-2}$ , and a ball diameter of 7 mm. An increase in diameter of the balls up to 10 mm at an acceleration of 600  $\text{m sec}^{-2}$  resulted in peaks of the intermetallic

compound ZrCo occurring in the X-ray diffraction patterns of the product in addition to an amorphous halo. An exoeffect corresponding to the crystallization of the amorphous phase remained on the DSC curves, but its magnitude decreased. At an acceleration of  $900 \text{ m sec}^{-2}$ , a completely amorphous product was obtained for none of the ball diameters used. For balls 10 mm in diameter the product was completely crystalline, as evidenced by the absence of an exoeffect on the DSC curves. The X-ray diffraction patterns of the product contained reflections from the intermediate compounds  $\text{ZrCo}_2$  and  $\text{Zr}_3\text{Co}$  (Fig. 2).

One could suppose that such a composition of the product is due to incompleteness of mechanical alloying, for example because of hindered diffusion. Special experiments, however, showed that if a powder of the intermetallic compound ZrCo was taken as the starting material, mechanical treatment under the same conditions resulted in the formation of exactly the same mixture of intermediate crystalline phases (Fig. 2). Moreover, at a given elemental composition of the starting mixture and under given operating conditions of the mill the phase composition of the products is always the same, whatever the starting phase composition: a mixture of two ( $\text{Zr}_2\text{Co} + \text{ZrCo}_2$ ) or three ( $\text{Zr}_2\text{Co} + \text{ZrCo} + \text{ZrCo}_2$ ) intermediate phases.

From these results it follows that mechanical alloying in high-energy apparatus basically differs from solid-state diffusive reactions, in that besides the processes which lead to averaging of the composition over volume, the reverse processes of disproportionation involving the establishment of tribochemical equilibrium [9] take place. Tribochemical equilibrium differs basically from true chemical equilibrium; specifically, the Gibbs phase rule is not satisfied for it. The position of tribochemical equilibrium depends on the conditions of mechanical treatment.

Thus for samples of different phase compositions corresponding to the elemental composition  $\text{Zr}_{6.7}\text{Co}_{3.3}$  (as well as in the case of  $\text{Zr}_{50}\text{Co}_{50}$ ), the starting materials were mixtures of the elements, one intermetallic compound and various mixtures of intermediate phases, and the following states corresponding to the establishment of tribochemical equilibrium were obtained. At the minimum kinetic energy of the balls an amorphous alloy forms. The halo in the X-ray diffraction pattern of this alloy has a valley (Fig. 1b) which points to separation in the amorphous alloy and the presence in it of rather extended regions which differ in composition. As this alloy crystallizes, a mixture of the three phases  $\text{Zr}_3\text{Co}$ , ZrCo and  $\text{Zr}_2\text{Co}$  forms, the last one being in the smallest quantity (Fig. 1c). Increased kinetic energy of the balls leads to an increased degree of crystallinity of the product. At the mean energy of the balls the crystalline phases  $\text{Zr}_3\text{Co}$  and ZrCo form, while at the maximum energy ( $900 \text{ m sec}^{-2}$ , balls 10 mm in diameter), the disproportionation of ZrCo occurs into  $\text{ZrCo}_2$  and  $\text{Zr}_3\text{Co}$ , and the product contains only these two last intermediate compounds.

The alternating processes of amorphization and crystallization could be proposed as a possible mechanism of disproportionation of equilibrium intermetallic compounds under conditions of mechanical

treatment. Local overheating upon collision of the balls are the cause of the crystallization. Provided that the nucleation of equilibrium crystalline phases during crystallization of an amorphous alloys is constricted for some reason, this mechanism could account for the results obtained.

Note, however, that an amorphous alloy having the composition  $\text{Zr}_{6.7}\text{Co}_{3.3}$  and obtained by melt-quenching crystallizes with the formation of one intermetallic compound  $\text{Zr}_2\text{Co}$  [10, 11]. Moreover, the samples of the amorphous alloy  $\text{Zr}_{50}\text{Co}_{50}$  that we obtained by the mechanochemical method also crystallized, usually with the formation of one phase, ZrCo. A mixture of phases in the crystallization of an amorphous alloy, having this composition and obtained by mechanical alloying of the elements, was formed only when the mechanical alloying was carried out for a relatively short period of time. In this case the DSC curves contained three well-separated exoeffects (Fig. 3c) which corresponded to the sequential crystallization of the phases  $\text{Zr}_3\text{Co}$ , ZrCo and  $\text{ZrCo}_2$  as shown by X-ray phase analysis. In full agreement with other work [10, 11] the temperature of the crystallization increases with increasing cobalt content. Thus, amorphization in mechanical alloying of this composition was reached earlier than was averaging of the composition over volume. However, as the duration of mechanical alloying increased only one exoeffect remained on the DSC curves (Fig. 3a), and only one phase (ZrCo) formed as the product of the crystallization.

The following experiment is the most convincing evidence that the disproportionation of intermetallics under conditions of mechanical treatment is not

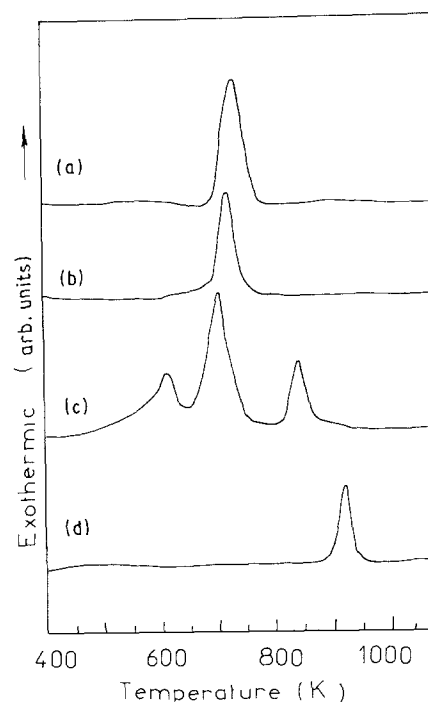


Figure 3 DSC curves for: (a) amorphous alloy  $\text{Zr}_{50}\text{Co}_{50}$ ; (b) amorphous alloy  $\text{Zr}_{6.7}\text{Co}_{3.3}$ ; (c) amorphous alloy  $\text{Zr}_{50}\text{Co}_{50}$ , obtained by mechanical alloying of the elements at an acceleration of  $600 \text{ m sec}^{-2}$  with balls 5 mm in diameter for 1 h (amorphization is carried to completion but the averaging of the alloy composition over volume is not yet attained); (d) a supersaturated solution of aluminium in titanium,  $\text{Ti}_{50}\text{Al}_{50}$ .

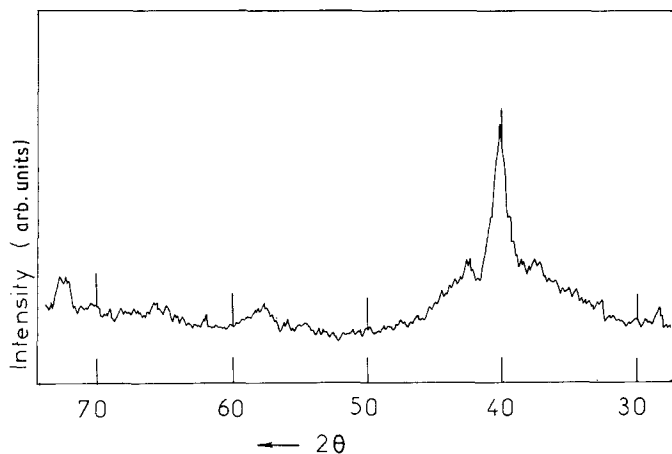


Figure 4 X-ray diffraction pattern of the amorphous alloy  $Zr_{50}Co_{50}$  treated in a mill at an acceleration of  $900 \text{ msec}^{-2}$  with balls 10 mm in diameter for 6 min. The diffraction peak at  $\theta \approx 20^\circ$  corresponds to the intermetallic  $ZrCo$  ( $CuK\alpha$  radiation).

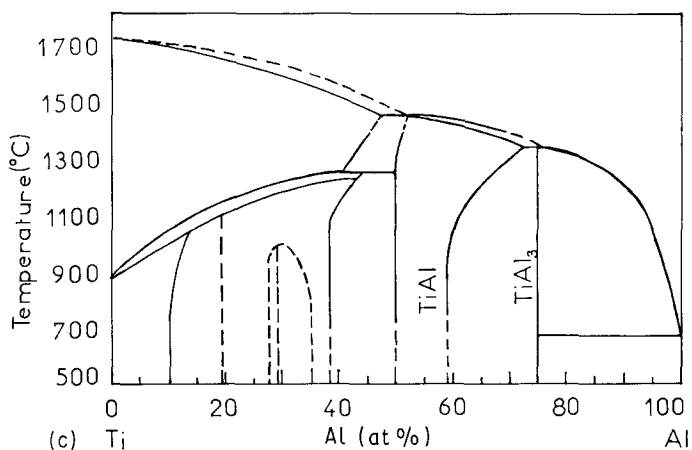
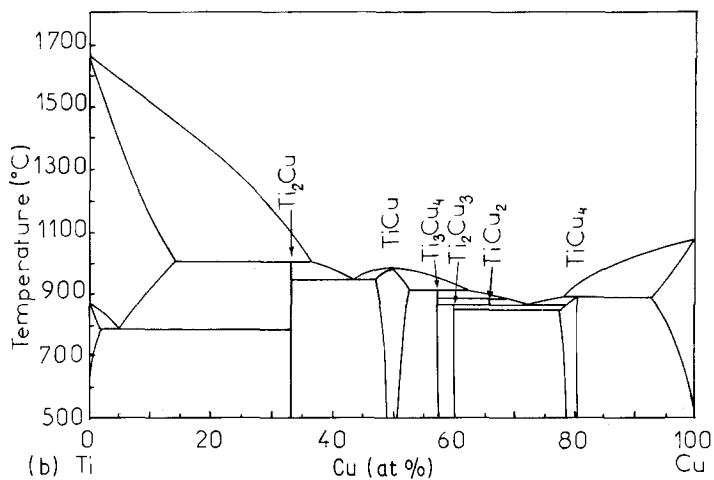
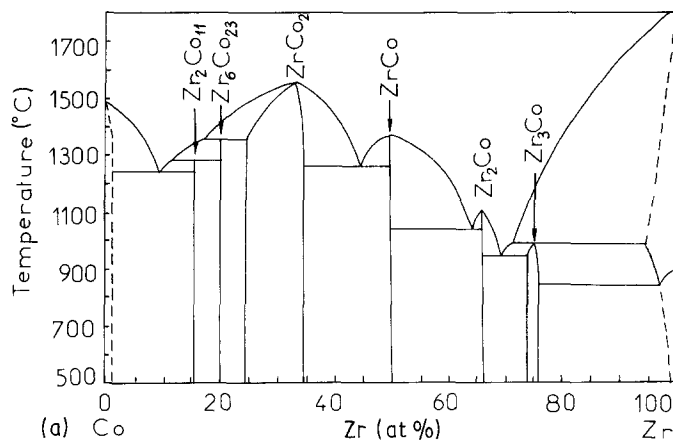


Figure 5 Equilibrium phase diagrams for the systems (a) Zr-Co [14], (b) Ti-Cu [15], (c) Ti-Al [16]. (○)  $Ti_3Cu_4$ , (◇)  $TiCu$ , (□)  $TiCu_4$ .

associated with the intermediate formation of an amorphous alloy. As noted above, if mechanical treatment is conducted long enough to attain tribochemical equilibrium, the phase composition of the products is determined only by the elemental composition of the starting charge and the conditions of the mechanical treatment. The transition from amorphous material to crystalline solid and the reverse process can be brought about by changing the operating conditions of the mill. Mechanochemically, under "soft" conditions (at small energy of the balls) we obtained the amorphous alloy  $Zr_{50}Co_{50}$ , and then treated it in the mill under such conditions that disproportionation of the intermetallic compound  $ZrCo$  into  $ZrCo_2$  and  $Zr_3Co$  occurred. X-ray phase analysis of samples taken in the course of this treatment showed that at first the formation of the intermetallic  $ZrCo$  from the amorphous alloy occurred (Fig. 4), and only then did it decompose into  $Zr_3Co$  and  $ZrCo_2$ .

It would be most natural to attempt to attribute the crystallization of amorphous alloys during mechanical treatment to local overheating in the collision zone. Direct experimental temperature measurements in the collision zone are lacking in the literature. Theoretical estimations are based on many assumptions and give rather ambiguous values [12]. Experimental determinations of the averaged temperature of the internal walls of the vial can hardly be used in this case. Note, however, that the temperatures of crystallization for amorphous alloys obtained mechanochemically and having the compositions  $Zr_{67}Co_{33}$  and  $Zr_{50}Co_{50}$  differ from one another insignificantly (see Fig. 3), whereas the most severe conditions of treatment under which it is still possible to attain complete amorphization differ considerably. A strong dependence of temperature in the collision zone on the relative amount of cobalt and zirconium seems to be improbable.

It is impossible, in our opinion, to account for the amorphous-to-crystalline transition only by the temperature effect upon collisions. It would probably be very useful to present the results obtained during mechanical alloying and mechanical treatment of metallic systems under different operating conditions of the apparatus as diagrams of "mechanochemical equilibrium". It is clear that chemical composition should be plotted on the abscissa, but it is not clear what quantity would be plotted on the ordinate. The average kinetic energy of the balls which we used apparently cannot be such a quantity for the following reasons. Mechanical action produced by colliding balls on the material being treated is more intense the greater the energy of the balls, and the smaller the region in which it is localized. The dimensions of this region must depend on the diameter of the balls and on the ratio between the mass of powder being treated and that of the balls.

Further, it is not yet clear how to determine the average kinetic energy of the balls. If it is assumed that during the rotation of the vials the balls do not slip on the walls, the velocity of the balls at the moment of separation from the wall can be easily calculated. This assumption, however, is hardly true for real systems,

and, at least, it needs an experimental verification. Redistribution of the velocities of the balls on their collisions with each other and with the wall of the vial still further complicates the problem. It is for these reasons that we do not present herein the average kinetic energies (calculated) of the balls at the moment of separation, but confine the discussion to only qualitative considerations.

The results obtained for the system  $Zr-Co$  show that on mechanical treatment under "severe" conditions, intermetallic compounds having a narrow homogeneity region turn out to be unstable and undergo decomposition, with the formation of intermediate compounds having wide homogeneity regions.

To establish whether this pattern extended to other systems, experiments were carried out for the system  $Ti-Cu$ . The stability of the intermetallic compounds  $Ti_3Cu_4$ ,  $Ti_2Cu$  and  $TiCu$  during mechanical treatment was investigated. In the equilibrium phase diagram (Fig. 5b), on both sides from  $Ti_3Cu_4$  on the composition axis there are intermediate compounds with a wide region of homogeneity ( $TiCu$  and  $TiCu_4$ ). It can therefore be suggested that disproportionation of this compound would be possible under conditions of mechanical treatment, and the phases  $Ti_2Cu$  and  $TiCu$  (proceeding from analogous considerations) should not decompose. The experimental results are in good agreement with our reasoning. Fig. 6b gives the X-ray diffraction pattern of  $Ti_3Cu_4$  powder after treating in a mill for 2 h with balls 7 mm in diameter and a centrifugal acceleration of  $900 \text{ m sec}^{-2}$ . For  $Ti_2Cu$  and  $TiCu$  powders after the same treatment, qualitatively similar X-ray diffraction patterns were obtained.

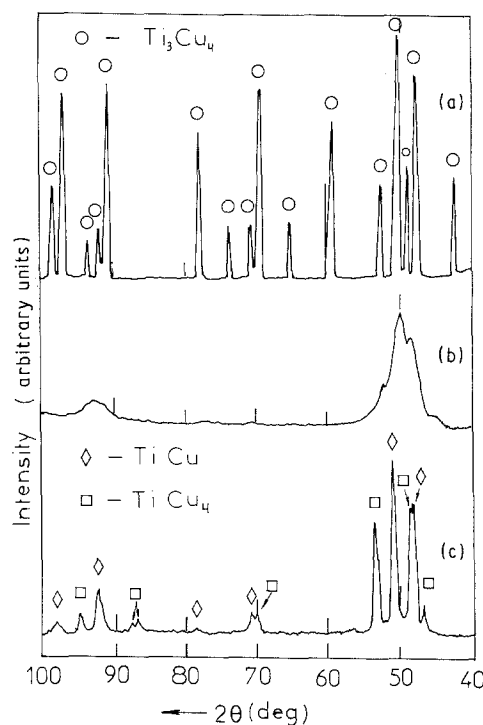


Figure 6 X-ray diffraction patterns of  $Ti_3Cu_4$ : (a) starting intermetallic; (b) after treating in a mill at an acceleration of  $900 \text{ m sec}^{-2}$  with balls 7 mm in diameter; (c) after heating of treated powder in argon up to 900 K at a rate of  $10 \text{ K min}^{-1}$  ( $CoK\alpha$  radiation). (○)  $Ti_3Cu_4$ , (◇)  $TiCu$ , (□)  $TiCu_4$ .

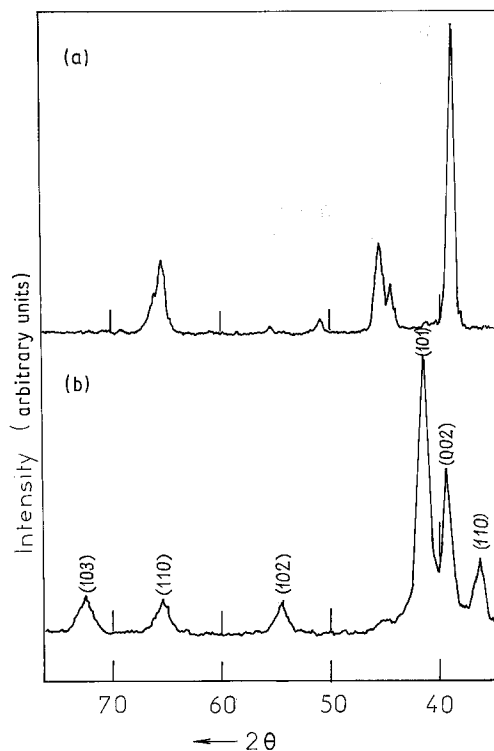


Figure 7 X-ray diffraction patterns of TiAl: (a) the starting intermetallic; (b) after treating at an acceleration of  $600 \text{ msec}^{-2}$  with balls 5 mm in diameter (CuK $\alpha$  radiation).

The heating of the resulting powders up to 900 K was not accompanied by appreciable thermal effects and led, in the case of TiCu and Ti<sub>2</sub>Cu, to recovery of the diffraction patterns of the starting phases; in the case of Ti<sub>3</sub>Cu<sub>4</sub>, a mixture of the phases TiCu and TiCu<sub>4</sub> forms (Fig. 6c).

Supersaturated solid solutions are frequently obtained in the mechanical alloying of elements. In the system Ni–Al it is possible to obtain aluminium solutions in nickel with concentrations corresponding even to the stability region of the intermediate phase Ni<sub>3</sub>Al [13]. It was of interest to elucidate whether the formation of such solutions is accounted for only by difficulties for nucleation of an equilibrium phase (so that it is characteristic only of the processes of mechanical alloying), or whether their formation corresponds to the attainment of tribochemical equilibrium,

so that it would be possible to prepare such solutions by the mechanical treatment of equilibrium intermediate phases. To answer this question we carried out mechanical treatment of the compound TiAl. The results of the experiment are given in Fig. 7. The reflections of the phases resulting from the mechanical treatment are well indexed on the basis of a hexagonal close-packed structure with unit cell parameters  $a = 0.2848 \text{ nm}$ ,  $c = 0.4586 \text{ nm}$ , and the phase itself is apparently a titanium-based solid solution. On the DSC curves for powders of this phase an exoeffect is observed which corresponds to the transformation of it into the equilibrium starting phase TiAl.

## References

1. L. SCHULTZ and E. HELLSTERN, in "Science and Technology of Rapidly Quenched Alloys", edited by M. Tenhover, L. E. Tanner and W. L. Jonson (Materials Research Society, 1987) paper G 1.1.
2. B. M. CLEMENS, *Phys. Rev. B* **33** (1986) 7615.
3. V. V. BOLDYREV, *J. Chim. Phys.* **83** (1986) 821.
4. M. S. KIM and C. C. KOCH, *J. Appl. Phys.* **62** (1987) 3450.
5. E. A. KENIK, R. J. BAYUZICK, M. S. KIM and C. C. KOCH, *Scripta Metall.* **21** (1987) 1137.
6. V. V. NEVEROV, V. N. BUROV and P. P. ZSHITNIKOV, *Bull. Sib. Div. USSR Acad. Sci. Chem. Ser.* **5** (1983) 54.
7. P. I. LOEFF and H. BAKKER, *Europhys. Lett.* **8** (1989) 35.
8. A. W. WEEBER, W. J. HAAG, A. J. H. WESTER and H. BAKKER, *J. Less-Common Metals* **140** (1988) 119.
9. G. HEINICKE, "Tribochemistry" (Akademie-Verlag, Berlin, 1984) p. 196.
10. K. H. J. BUSCHOW, *J. Less-Common Metals* **85** (1982) 221.
11. H. U. KREBS, C. MICHAELSEN, J. REICHEL, H. A. WAGNER, J. WECKER, Q. R. ZHANG and H. C. FREYHARDT, *J. Non-Cryst. Solids* **61/62** (1984) 463.
12. R. B. SCHWARZ and C. C. KOCH, *Appl. Phys. Lett.* **49** (1986) 146.
13. E. IVANOV, T. GRIGORIEVA and G. GOLUBKOVA, in Proceedings of 2nd Japan–Soviet Symposium on Mechanochemistry, Tokyo, edited by G. Jimbo, March 1988, p. 219.
14. S. K. BATALEVA, V. V. KUPRINA, V. V. MARKOV, *Phase Diag. Metall. Syst.* **18** (1972) 33 (in Russian).
15. J. L. MURRAY, *Bull. Alloy Phase Diag.* **4** (1983) 81.
16. K. SAGEL, E. SCHULZ and U. ZWICKER, *Z. Metallkde* **47** (1956) 609.

Received 5 February  
and accepted 28 March 1990