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Composition and structure variations during mechanical alloying to produce the intermetallic Cr_2Nb

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The evolution of the mechanical alloying process by ball-milling elemental chromium and niobium powders has been studied as a function of milling time. Evaluation of the layered structure of the alloyed powders by energy dispersive spectroscopy and X-ray analysis has been made. Although the Cr_2Nb hexagonal phase forms after 15 h milling time, when much of the powder presents the equilibrium range of composition, further milling to 25 h produces the disappearance of this phase. This behaviour is explained in terms of chemical disorder induced by the deformation process such that structure stability is not possible when a high degree of order is required.

1. Introduction

Mechanical alloying is a process that can be used to produce alloys, without melting, with very fine microstructures. It has extensively been used to prepare dispersion strengthened materials in the case where high melting point dispersoids are desired for high-temperature applications of aluminium alloys [1, 2]. Also this technique has recently been successfully used to obtain high-strength high-conductivity copper alloys [3] because large volume fractions of very fine dispersoids can be very homogeneously distributed within the matrix.

A large effort in this field has been devoted to produce amorphous materials from elemental powders of transition metals [4–7] or even from elemental powders of intermetallic compounds [8]. Another aspect that appears of interest is that of preparing crystalline intermetallic compounds from elemental powders. Such materials are of interest because their high melting points make them attractive for high-temperature applications. However, in many cases, they are very difficult or impossible to produce by conventional casting techniques.

In our present study we have attempted to produce the intermetallic compound Cr_2Nb by mechanical alloying and to follow the evolution of the process as a function of time. The choice of material has been made because its crystalline structure is a complex Laves phase with a high degree of order. Thus the evolution of the mixing processes together with the degree of ordering necessary to form the compound have been followed as a function of milling time.

2. Experimental procedure

Elemental powders of chromium and niobium of sizes 100 to 150 μm were used with a weighed composition of 52 wt % Cr and 48 wt % Nb. Mechanical alloying of these powders was performed using a Fritsch Mini-Planetary ball mill (Pulverisette 7) with hardened steel containers and balls, the weight ratio of balls to powder was 4. Alloying of the powders was carried out for different periods of time, 5, 10, 15, 20 and 25 h. These powders were evaluated by metallographic observations, X-ray analysis and microhardness tests. The powders milled for 10 h were given an annealing treatment at 1100 °C for 3 h and re-milled for a further 10 h. Consolidation of the powders, which had been milled for 15 h, was carried out by hot isostatic pressing at a temperature of 1450 °C and 50 MPa for 20 min. X-ray analysis of the alloyed powders was performed using a Scintag Pad V powder diffractometer with copper radiation. Metallographic observations of the alloyed powders and consolidated materials were made by scanning electron microscopy. Also chemical analysis was performed using a Cambridge Stereoscan 250 scanning microscope equipped with energy-dispersive spectroscopy (EDS) facilities.

The mechanical properties of the powders were evaluated as a function of milling times by hardness testing using a Vickers microhardness tester with 100 and 300 g loads. The consolidated material was also given compression tests using a Schenck Universal testing machine. The compression specimens were cut by spark-erosion in the form of cylinders of 3 mm diameter and 7 mm height.

3. Results

The chromium and niobium powders are particularly well suited for ball-milling because the equilibrium between the fracture and welding processes that take place during mechanical alloying easily reach an equilibrium and therefore no other product need be added [2] in order to help the process. The general morphology of the milled powders is shown in Fig. 1.

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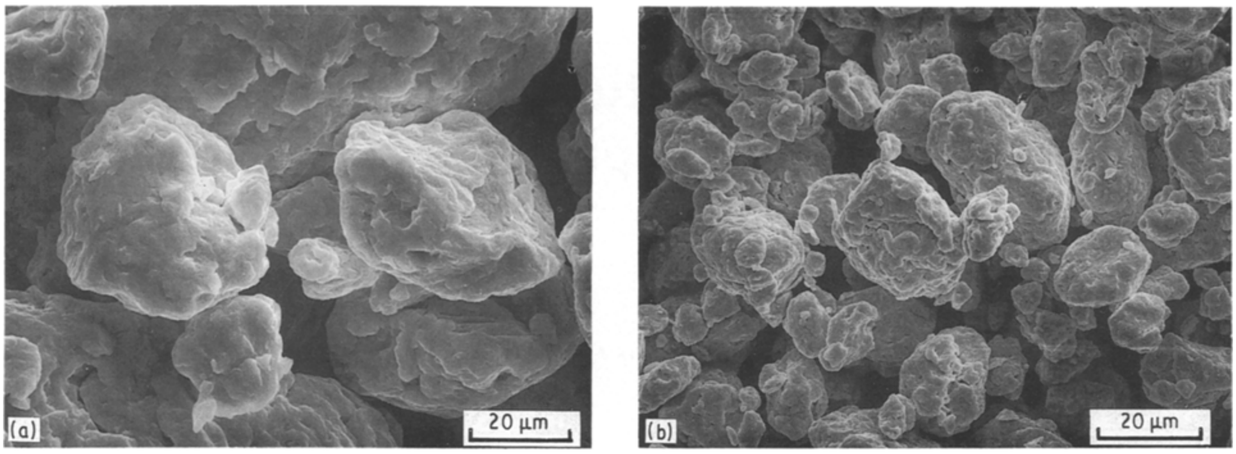


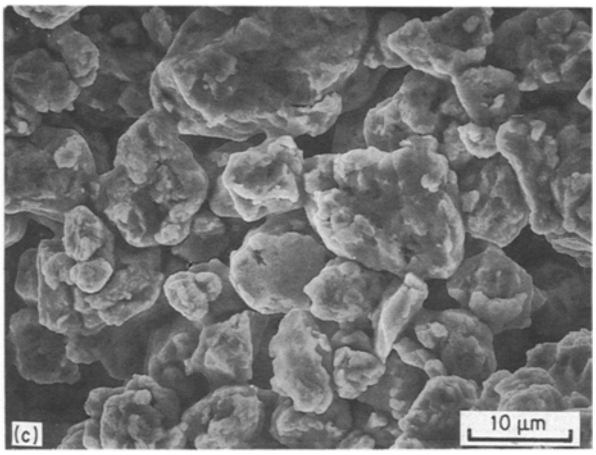


Figure 1 General morphology of alloyed powders after milling for different times: (a) 5 h, (b) 15 h, (c) 25 h.

Although the surface roughness did not change much with increasing number of milling hours, the powder size decreased considerably from about 50 µm after 5 h to about 5 to 10 µm after 25 h milling time.

The different stages of powder mixing are shown in Figs 2 and 3. The atomic number contrast obtained by using backscattered electrons shows different layers where the zones corresponding to higher niobium contents appear lighter. The different grey levels indicate different degrees of mixing achieved after the different number of milling hours. In this way it

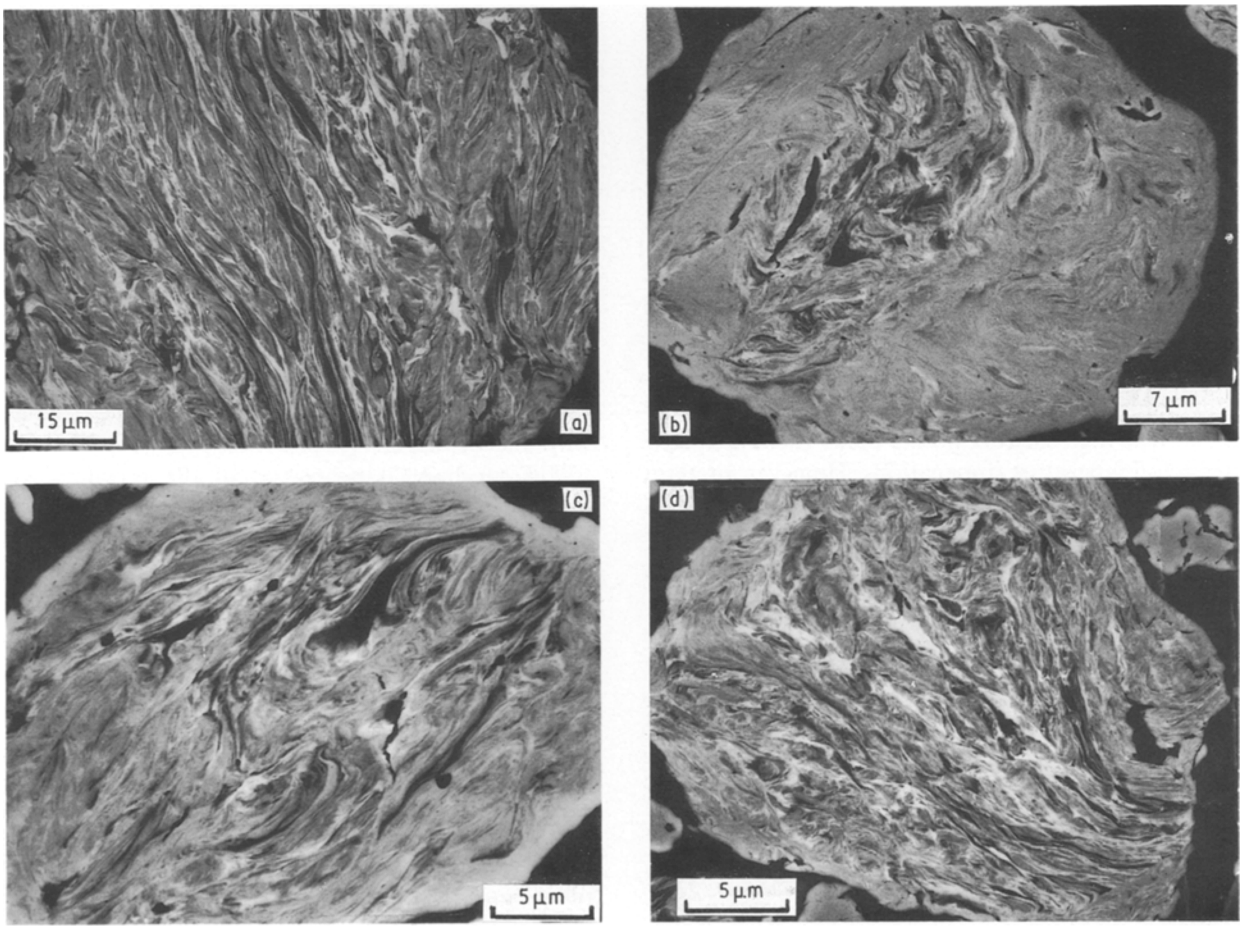


Figure 2 Typical layered structures of milled powders indicating the degree of alloying as a function of milling time: (a) 5 h, (b) 15 h, (c) 20 h, (d) 25 h.

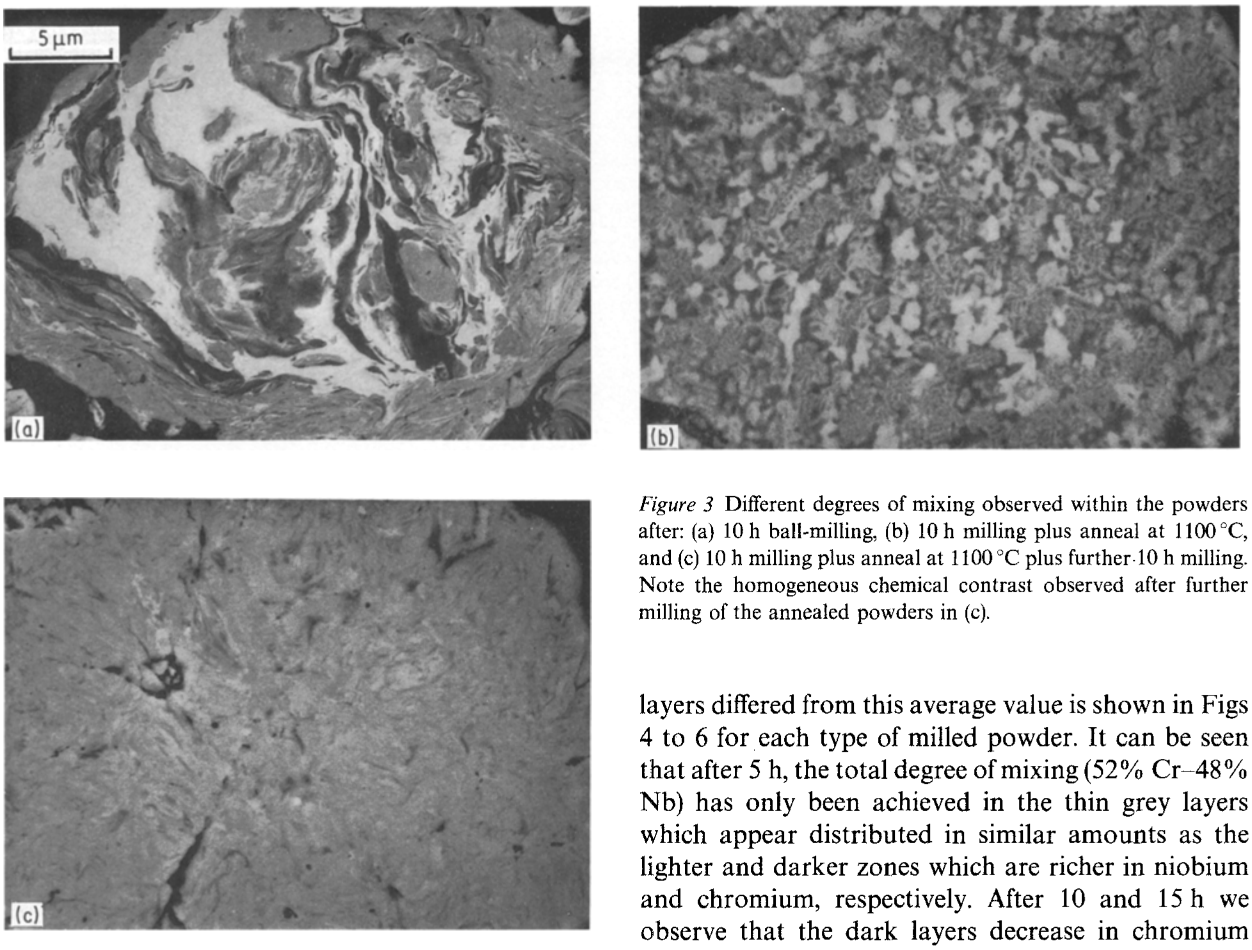


Figure 3 Different degrees of mixing observed within the powders after: (a) 10 h ball-milling, (b) 10 h milling plus anneal at 1100 °C, and (c) 10 h milling plus anneal at 1100 °C plus further 10 h milling. Note the homogeneous chemical contrast observed after further milling of the annealed powders in (c).

appears that after 15 h (Fig. 2) the mixing is more complete as observed by the general grey contrast within most of the powder particles. Only the centre of the powders appears to consist of layers. However, after longer milling times such as 20 or 25 h, the layered structure is again observed. In order to obtain a more quantitative understanding of the extent of alloying during milling, quantitative chemical analysis was performed by EDS. The general results showed that the global composition of the powders was always 52%Cr–48%Nb irrespective of the milling time. The extent by which the composition of the different layers differed from this average value is shown in Figs 4 to 6 for each type of milled powder. It can be seen that after 5 h, the total degree of mixing (52% Cr–48% Nb) has only been achieved in the thin grey layers which appear distributed in similar amounts as the lighter and darker zones which are richer in niobium and chromium, respectively. After 10 and 15 h we observe that the dark layers decrease in chromium content from 80% to 74% and 66% respectively. At the same time the grey zones with average composition occupy most of the particle volume, with layers being most visible at the centres. The white layers also showed a decrease in niobium content at this stage. After 20 and 25 h milling, the compositions of the black layers correspond to the average values 52% Cr–48 Nb whilst those of the grey ones are only slightly poorer in chromium at about 45% and 47%, respectively. Only the white layers remain rich in niobium, even though these zones occupy much less of the particle volume. Fig. 3 shows the aspect of the powder particles after milling for 10 h, annealing at 1100 °C and re-milling after annealing. It appears that

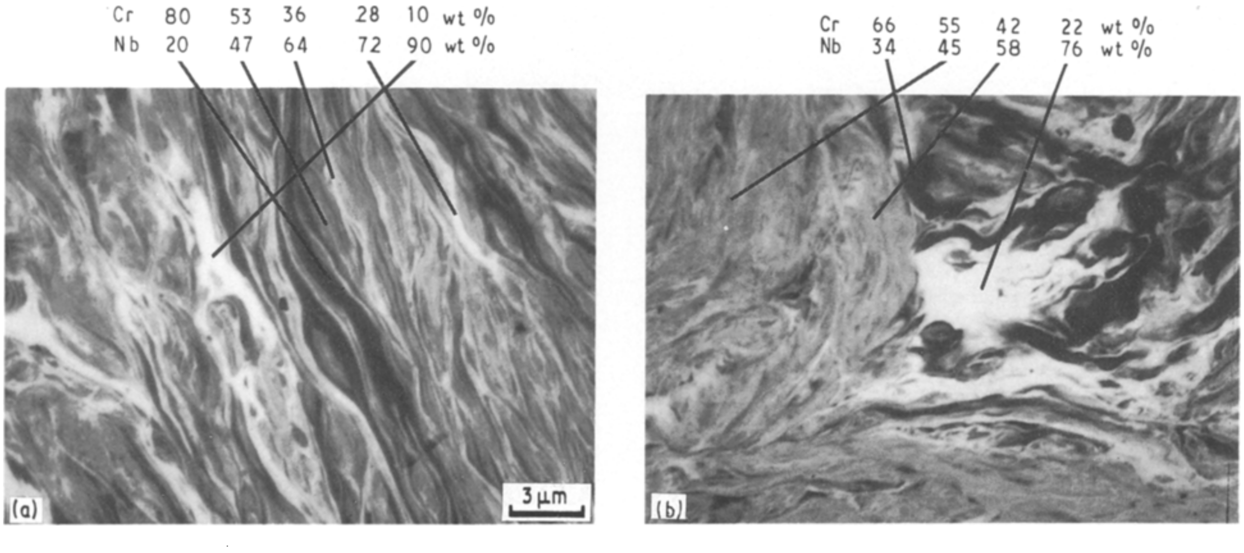


Figure 4 Chemical compositions measured from the typical characteristic layers observed in the milled powders: (a) 5 h, (b) 15 h.

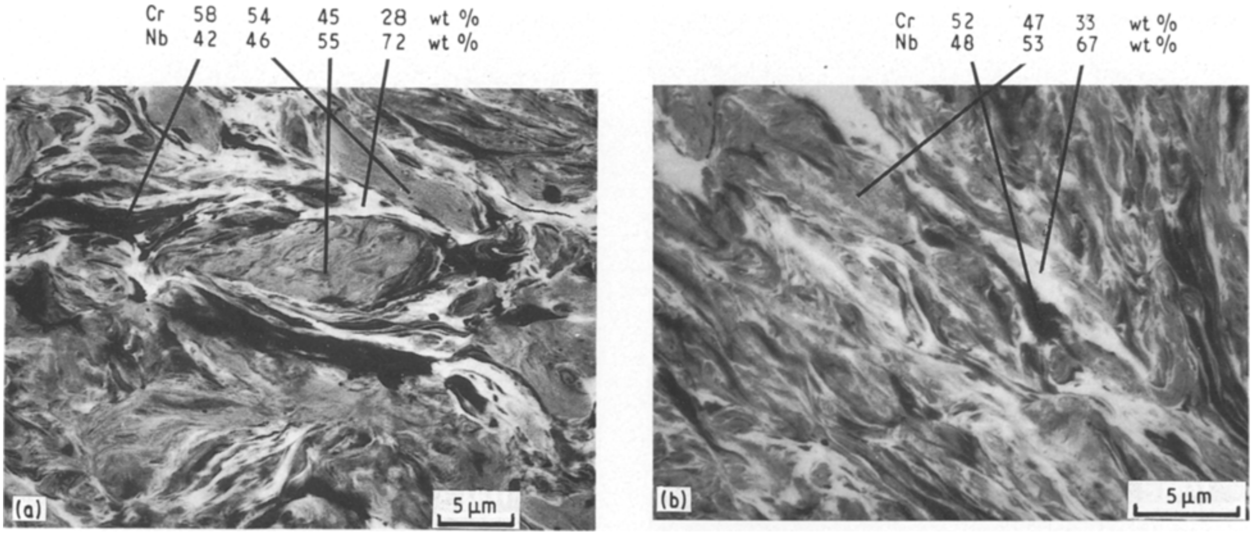


Figure 5 Chemical compositions measured from the typical characteristic layers observed in the milled powders: (a) 20 h, (b) 25 h.

the annealing produces demixing to a certain extent, whilst further mechanical alloying for 10 h produces a very homogeneous amount of mixing. In Fig. 6 the composition of the chemical analysis for the different zones produced after annealing shows that the chemical compositions range from 46 to 56 wt % Nb in most of the regions with only some areas being poorer in niobium.

The results obtained from X-ray diffraction analysis of the powders are shown in Figs 7 and 8. After 5 h milling only the diffraction peaks corresponding to chromium and niobium are present. After 10 h a new phase appears and it is only after milling for 15 h that the strong peaks corresponding to the Cr_2Nb (hexagonal) phase are quite evident. On further milling, i.e. after 20 h, the peaks of Cr_2Nb are much less intense and after 25 h milling these peaks totally disappear and only the chromium and niobium peaks are once more observed.

In order to understand the effect of mechanical alloying on the appearance and disappearance of the intermetallic phase Cr_2Nb, a simple experiment was

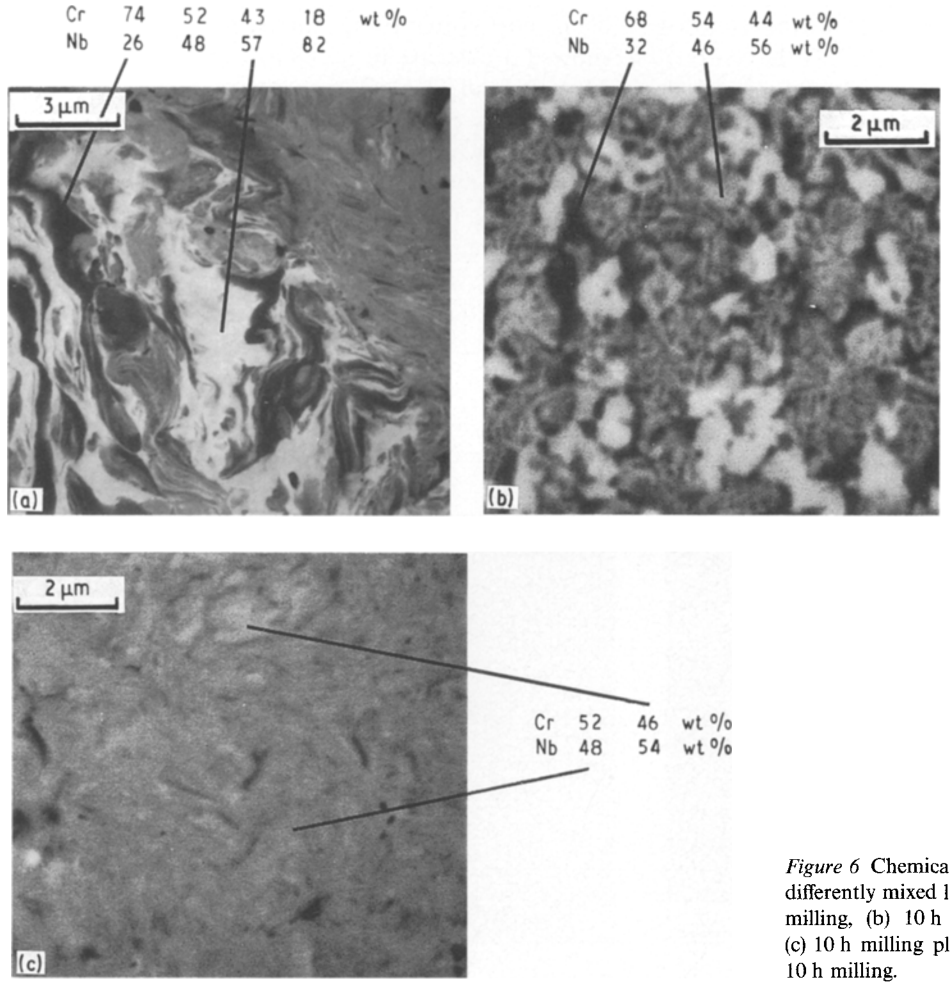
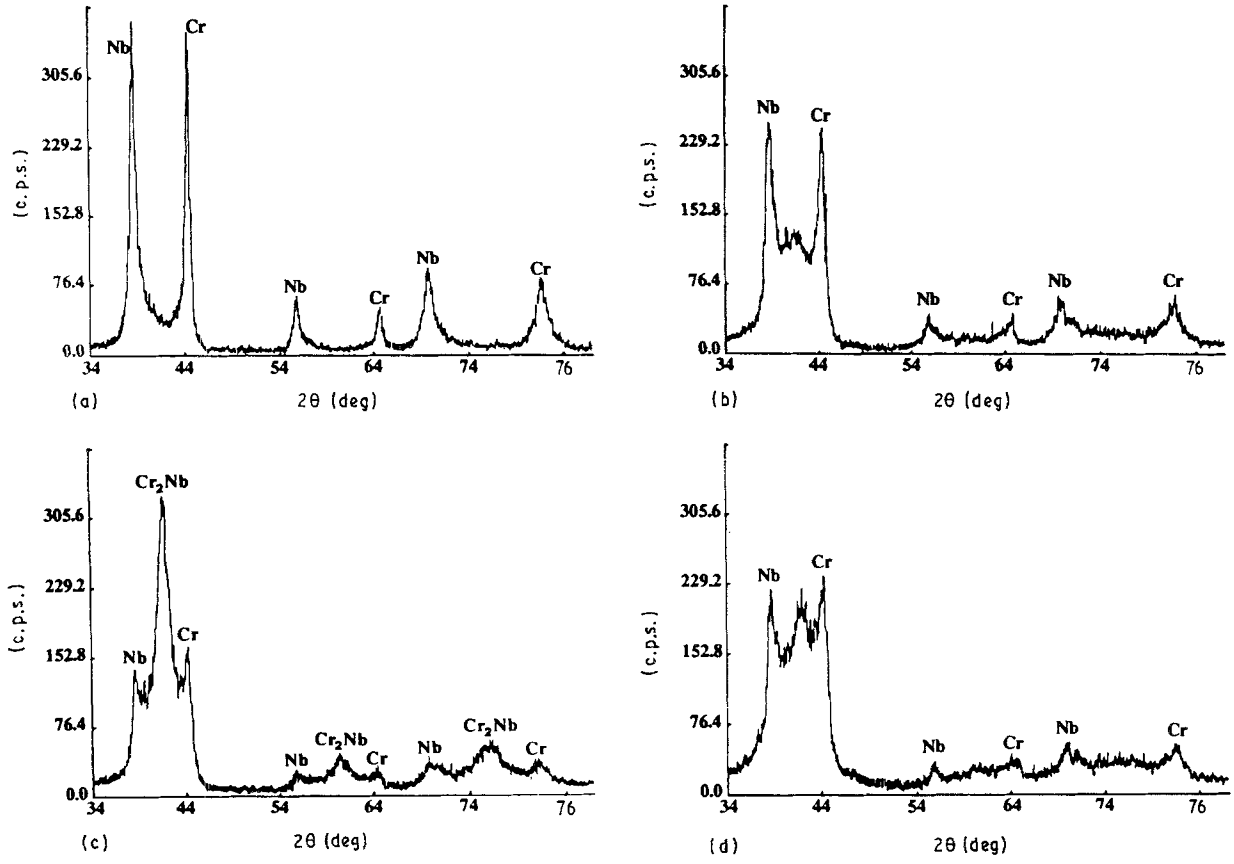


Figure 6 Chemical compositions measured from the differently mixed layers of the powders after: (a) 10 h milling, (b) 10 h milling plus anneal at 1100 °C, (c) 10 h milling plus anneal at 1100 °C plus further 10 h milling.

X-RAY ANALYSIS FROM MECHANICALLY ALLOYED Cr-Nb POWDERS.



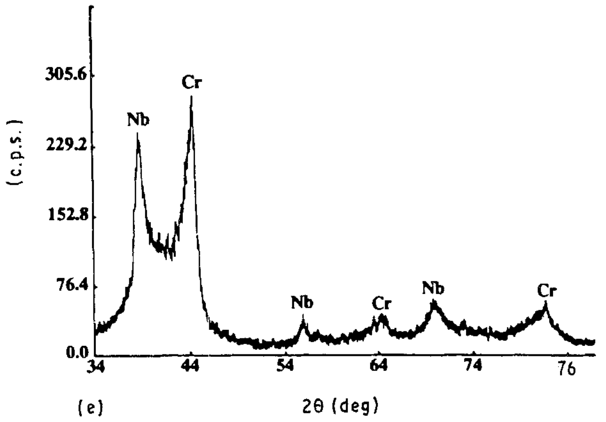


Figure 7 General X-ray diffraction data obtained from the powders milled for different times. Note the presence of peaks corresponding to the Cr_2Nb hexagonal phase after 15 h milling and their disappearance after milling for 25 h. (a) 5 h, (b) 10 h, (c) 15 h, (d) 20 h, (e) 25 h.

performed: the 10 h milled powders (where the presence of the intermetallic phase was beginning to be detected) were annealed at 1100 °C for 3 h and then used for X-ray analysis. At this stage the presence of intense peaks corresponding to both Cr_2Nb cubic and hexagonal phases was observed as shown in Fig. 8. This figure also shows the X-ray results of the powders after re-milling the annealed powders for 10 h. It is seen that re-milling the annealed powders leads to the disppearance of the Cr_2Nb peaks, only the chromium and niobium peaks are once more observed. Consolidation of the 15 h milled powders produced a material with practically full density (measured as 7.4 $g\,cm^{-3}$), almost no porosity was observed. Fig. 9a shows the general aspect of the structure obtained after consolidation. The material consists of some large grey areas with an average composition 52% Cr–48% Nb and within which small grains (about 1 µm size) can be seen in Fig. 9b. These figures also show the presence of darker and lighter zones which, similar to the milled plus annealed powders, had the composition 68% Cr–32% Nb and 44% Cr–56% Nb, respectively. Also, both Cr_2Nb intermetallic phases were present.

Hardness results from the powders and consolidated materials are given in Table I. Maximum hardness of the powders was achieved after about 15 to 20 h milling times. Any further milling produced little effect on hardness.

The inherent brittleness of the consolidated material did not allow the possiblity of evaluating the yield strength from the compression tests. All specimens tested failed by cleavage at a stress of 1800 MPa before yielding. Fig. 10 illustrates the main features of these fractured specimens.

TABLE I Hardness values of powders and consolidated material

Milling time (h)	H_v (kg mm^{-2})
5	510 ± 55
10	620 ± 50
15	750 ± 55
20	780 ± 50
25	730 ± 50
Consolidated material	1100 ± 60

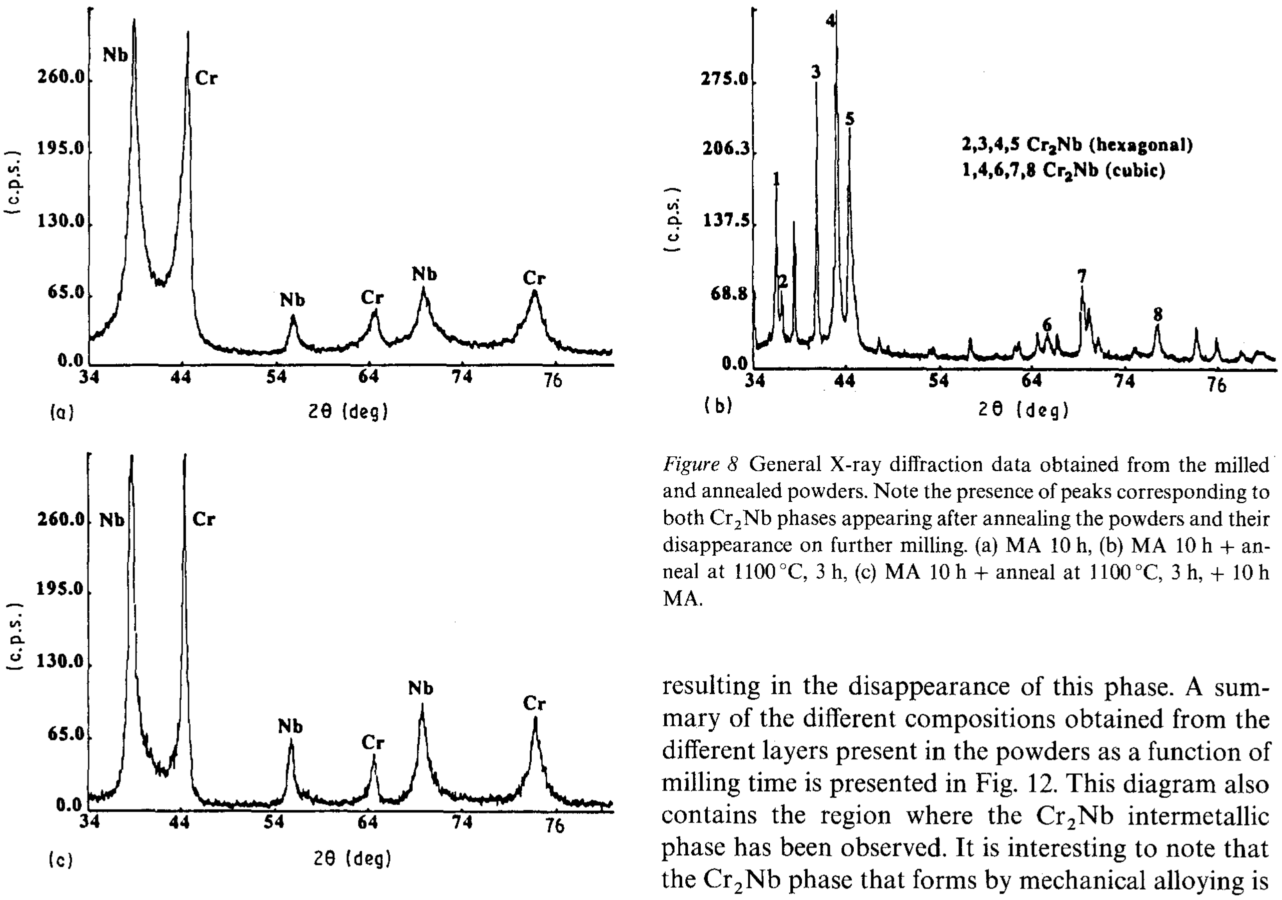


Figure 8 General X-ray diffraction data obtained from the milled and annealed powders. Note the presence of peaks corresponding to both Cr_2Nb phases appearing after annealing the powders and their disappearance on further milling. (a) MA 10 h, (b) MA 10 h + anneal at 1100 °C, 3 h, (c) MA 10 h + anneal at 1100 °C, 3 h, + 10 h MA.

4. Discussion

In order to discuss the main aspects of this work, the equilibrium phase diagram of the chromium–niobium system is shown in Fig. 11. It can be seen that the equilibrium phase Cr_2Nb forms at a range of compositions between 47 and 52 wt % Nb. The stable structure is hexagonal at high temperature (HT) and cubic at low temperature (LT) [9].

Mechanical mixing of the elemental powders has been shown to take place as a function of time such that the local compositions in different layers continue to approach the average value (52 wt % Cr–48 wt % Nb). On the other hand, the X-ray results show that the presence of the intermetallic compound only occurs after milling for 15 h with any further milling resulting in the disappearance of this phase. A summary of the different compositions obtained from the different layers present in the powders as a function of milling time is presented in Fig. 12. This diagram also contains the region where the Cr_2Nb intermetallic phase has been observed. It is interesting to note that the Cr_2Nb phase that forms by mechanical alloying is the hexagonal structure which is stable at high temperature. There are then two aspects to be discussed from this work: the first is the effect of mechanical alloying on chemical composition, the second is that on structural stability.

Homogenization of the chemical composition as a function of milling time is such that after 25 h the powders show the equilibrium range composition practically everywhere. However, the intermetallic compound Cr_2Nb is only present when milling for a limiting period of time between 10 and 20 h. This suggests that mechanical alloying destabilizes the crystal structure. This is confirmed by the results obtained from the annealed powders, where the two crystalline Cr_2Nb phases are observed (therefore the equilibrium chemical composition has been reached)

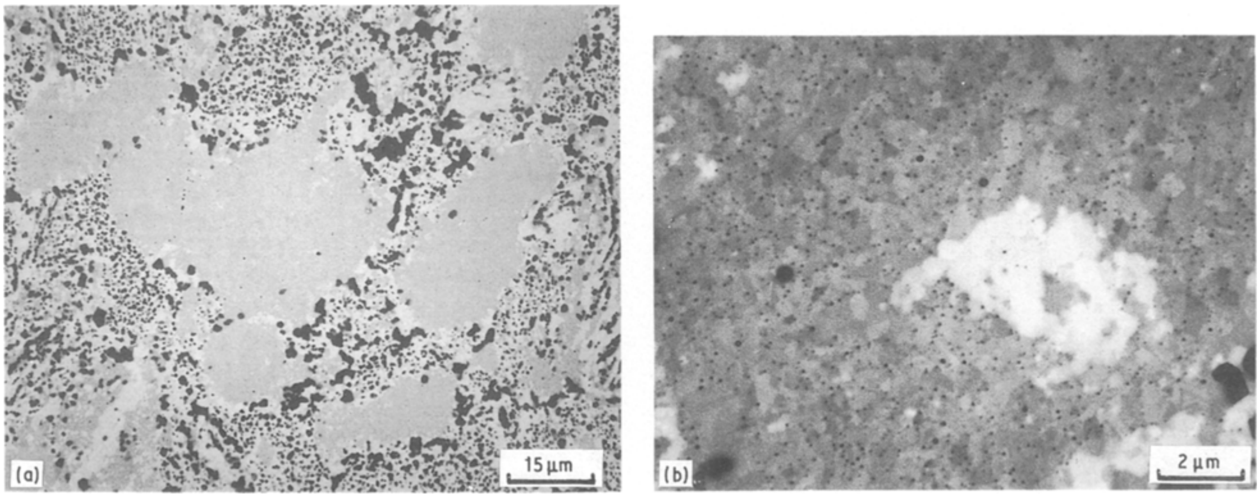
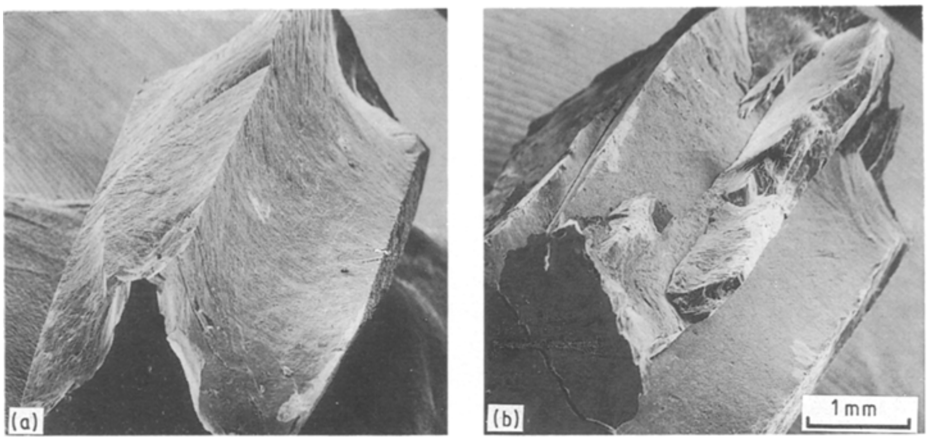


Figure 9 (a) General structure observed after consolidation of the 15 h milled powders, (b) Small grains observed within the large grey zones in (a).



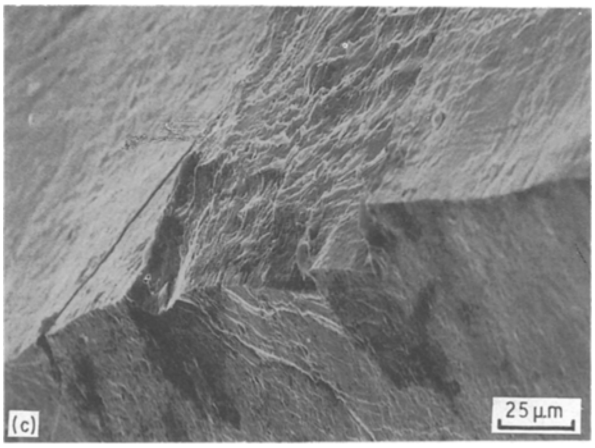


Figure 10 (a) and (b) Global cleavage fracture surfaces produced during compression tests of consolidated material, (c) Higher magnification taken from (b).

but where after further milling the disappearance of these phases occurs. At this stage the uniform equilibrium chemical composition and complete mixing are observed but only the elemental chromium and niobium phases are present. Thus the defects created by the deformation process during mechanical alloying induce sufficient chemical disorder to destabilize the intermetallic phase.

Another aspect which indicates the high-energy state of the system during mechanical alloying is the fact that the intermetallic phase that is formed after 15 h milling (when the equilibrium chemical composition is first reached) is the hexagonal phase. The equilibrium Cr_2Nb phase below 1600 °C is the complex cubic Laves phase and this phase only forms after annealing the powders. The hexagonal phase with lower symmetry than the cubic represents a state of higher energy, and because it forms by mechanical alloying it should be concluded that the high degree of order required to form the cubic structure cannot be achieved by this process alone. Several reports have been made concerning mechanical alloying of different transition metals to produce amorphous phases [4–7]. In those cases it has been argued [8] that the driving force for amorphization was a composition-induced destabilization produced by the enhanced atomic mobility in the interfacial regions of the two metals. In this way an amorphous rather than the intermetallic phase can form. Johnson [10] suggests that the energy stored in the form of defects created through the deformation process could give rise to crystalline solution destabilization rather than composition-induced destabilization if the deformation process produces chemical disorder by the formation of antiphase boundaries or atomic size defects. In this way a mechanism for energy storage equivalent to the heat of formation is provided, offering a possible mechanism for amorphization.

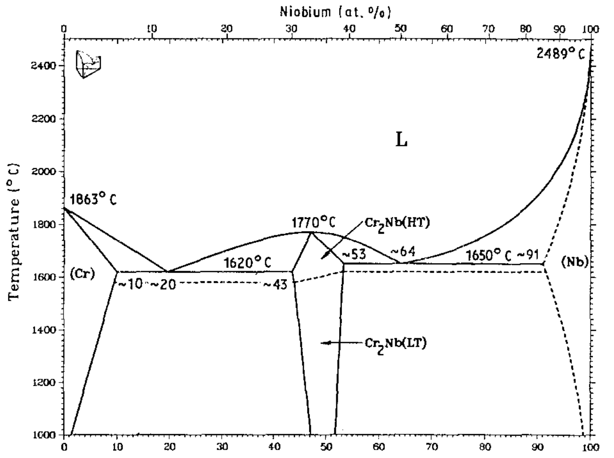


Figure 11 Equilibrium phase diagram for the chromium–niobium system.

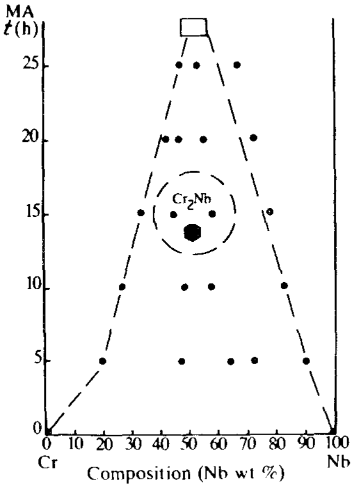


Figure 12 Diagram of the variation of chemical composition with milling time as measured from the different milled powders. Note that the total number of compositions for each given time represents the number of characteristic layers observed in the corresponding powders.

In our particular case it is evident that destabilization of the Cr_2Nb phase occurs by mechanical alloying such that only the chromium and niobium phases are observed and this can only be explained in terms of chemical disorder induced by the creation of defects produced through the deformation process.

From the measured hardness of the powders (see Table I) one observes that a saturation value was reached after about 15 h milling, indicating that the optimal degree of mixing has been reached. For this reason and because the intermetallic phase was present at this stage, powders milled for this period of time were used for consolidation. Because both hexagonal and cubic Laves phases were present in the bulk material this was similar to the milled and annealed powders where some small peaks corresponding to the chromium and niobium phases were also present. This indicates that some zones had not yet reached the equilibrium compositions as had been observed in the powders milled for 15 h. Therefore, the exposure to 1450 °C for the short period during which the consolidation was carried out was not sufficient to produce long-range diffusion. Only the formation of the cubic Cr_2Nb phase occurred by ordering in the zones where the equilibrium composition had been reached during milling.

The hardness value of the bulk material is much higher than that of the milled powders. However, the brittleness of the material indicates that this type of intermetallic would hardly be suitable for room-temperature applications. Although the lack of uniformity of bulk material (due to the existence of some zones slightly richer in chromium or niobium) may influence some of this brittle behaviour, the fracture surfaces (see Fig. 10) do not indicate any particular feature which would suggest segregation-induced fracture.

5. Conclusions

From the present study it has been possible to follow the evolution of the mechanical alloying process of chromium and niobium powders in order to form the intermetallic compound Cr_2Nb.

It appears that by this process alone it is not possible to form the equilibrium cubic Laves phase. This is due to the fact that the increase in milling time needed to achieve homogeneity in chemical composition of the powders produces an increase in chemical disorder that leads to the presence of the elemental phases of average composition. However, the short-term exposure to high temperature necessary to consolidate the powders seems to re-order the material such that the intermetallic phase is obtained. In spite of the brittleness of the bulk material, the high hardness values obtained together with its high melting point indicate that this intermetallic should be further explored for high-temperature application.

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