

Ball-milling of elemental powders—compound formation and/or amorphization

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Mechanical alloying of elemental powders has been carried out by ball-milling in a number of systems containing boron and silicon with chromium and niobium. Detailed analysis of the milled powders has been performed by X-ray diffraction and electron microscopy as a function of milling time. Compound formation occurs in both chromium and niobium silicides but only in niobium containing borides, whilst chromium containing borides never form up to 80 h milling time. In all cases, partial amorphization was observed after 60 h milling indicating that the amorphization process is independent of the different paths followed by the different systems. Amorphization is related to the degree of atomic disorder produced during the milling process.

1. Introduction

Solid-state amorphization can be achieved by different routes involving diffusion and/or plastic deformation processes as follows. (i) Alternated layer deposition of different elements, followed by heat treatments which allow diffusion of one element into another [1]. In this case, amorphization seems to occur within a limited layer thickness and is determined by the very different diffusivities of the two elements. (ii) Cold deformation processes such as rolling or wire-drawing of layered composites of different elements [2]. In this case the amorphization process appears to be produced after very large strains and is also limited [3] to a certain layer thickness which is determined by the total strain. (iii) Mechanical alloying of either elemental powders [4] or intermetallic compounds [5]. When starting from elemental powders, the general conditions for amorphization have been related to a negative heat of mixing of the elements and to the different diffusivity of these elements, similar to case (i). However, in the mechanical alloying process, a blend of elemental or alloy powders is subjected to highly energetic compressive impact forces in a ball-mill. These impact forces result in repeated cold welding and fracture of the powder particles. The heavy plastic deformation can generate a large number of point defects, which at low temperature can modify not only the diffusion behaviour but also the chemical order of the crystalline structure [6]. Indeed, the effect that the high energy disordered states, created by milling, could have on the amorphization process of intermetallic compounds needs to be given particular attention, as this will make it differ from any equilibrium process.

This work is a comparative study of the different structures obtained by ball-milling, as a function of time, of a number of alloys based on chromium and niobium with boron and silicon. We have tried to establish whether compound formation or amorphization

occur due to the effect of the different diffusivity of the elements or rather by mechanisms that depend on atomic order.

2. Experimental procedure

The systems studied here were CrB, CrB₂, CrSi₂, NbSi₂, NbB, NbB₂ and Cr₂Nb. Some physical properties of these systems are listed on Table I, and it can be seen that in all cases the enthalpies of compound formation are negative and the crystallographic structures are rather complex. Also Cr₂Nb and NbB₂ are the only compounds which can form within a range of compositions, i.e. they are not line compounds.

Ball-milling of the elemental powders was carried out in all cases, such that the weighed amounts of the powders corresponding to each composition were mechanically alloyed in a planetary ball-mill (Pulverisette 7) with a weight ratio of balls to powder of 4. The steel containers were loaded under an argon atmosphere and only opened at the end of each run when the milling period was completed. For each set of powders, the milling process was carried out for different periods of time ranging between 5 and 80 h. Complete microstructural analysis of all the powders was performed by X-ray diffraction (XRD), using a Philips powder diffractometer with Copper radiation. Also scanning electron microscope (SEM) observations and EDX chemical analysis of the powders were carried out using a Cambridge Stereoscan 360 microscope. TEM observations of the milled powders were made with a Philips CM 12 transmission electron microscope at 120 kV. Preparation of powder samples for the SEM involved mounting in a carbon resin and polishing to a final finish of 20 nm, no attack being used. For TEM observations, no thinning technique was necessary as the powders observed were 100–200 nm in size.

3. Results

X-ray spectra obtained from the milled powders as a function of milling time are shown in Figs 1–5. From these diagrams we observe that compound formation occurs in some of the systems, namely NbB, NbB₂, CrSi₂ and NbSi₂. The kinetics of compound formation are however different: the compounds NbB and NbSi₂ are totally formed after 5 h milling, whilst the NbB₂ forms after 15 h and the CrSi₂ forms slowly over a period of 10 to 40 h. After compound formation, increasing milling times produce broadening of the peaks and a decrease in peak height indicating a continuous decrease in crystallite size. At the same time, the increase in background observed in the area under the main peaks (in particular after 60 h for the NbB system) provides evidence for partial amorphization. These trends are also observed in the case of the CrB and CrB₂ systems. In these cases (see Fig. 2) the borides do not form and only the chromium peaks are observed. Since the boron peaks of the elemental powders before milling were well identified as the rhombohedral phase, their disappearance from the spectra of the milled powders suggest that this element has amorphized and only contributes to the much higher background observed.

In the case of the NbSi₂ and Cr₂Nb systems, the quasi-disappearance of the main peaks after 60 h milling provides strong evidence for partial amorphization (see Figs 4 and 5). However the compound NbSi₂ forms after milling for only 5 h, and its presence is observed until the onset of partial amorphization whilst the case of the Cr₂Nb system, as already mentioned elsewhere [7], is more specific. After 15 h milling, the hexagonal Laves phase forms (even though this phase only appears at high temperature in the phase diagram) and after 20 and 25 h milling, only chromium and niobium peaks are present. It is the

quasi-disappearance of these peaks after milling for 60 h that reveals the presence of an amorphous phase.

Measurements of crystallite sizes have been made from the width at half maximum of the peaks using the Scherrer formula [8] in all cases. The plot of decrease in crystallite size as a function of milling time is shown in Fig. 6 for all the systems. The minimum crystallite sizes are observed in the 60 h milled powders for the NbSi₂, CrB₂ and Cr₂Nb systems, indicating that a more severe breakdown in crystal size occurs in these systems.

In order to follow the process of mixing the elemental powders during milling, microstructural observations were made by atomic number contrast in the SEM using backscattered electrons. In this case, the areas with higher concentration of the elements of low atomic number will appear dark, and those with more concentration of elements with higher atomic number will appear light. In this way, boron, silicon and chromium-rich areas will appear dark in the systems studied here.

Figs 7 to 10 show the evolution of the elemental mixing of the powders for the boron-containing systems. We see that in these cases, there is no layered

TABLE I Physical properties of the different systems

Compound	ΔH (kJ mol ⁻¹)	T_M (°C)	Line compound	Crystal structure
Cr ₂ Nb	-21	1770	No	Cubic (C15)
CrB	-75	2100	Yes	Orthogonal (<i>B</i> _f)
CrB ₂	-94	2200	Yes	Hexagonal (C 32)
CrSi ₂	-80	1490	Yes	Hexagonal (C 40)
NbSi ₂	-138	1900	Yes	Hexagonal (C 40)
NbB	-220	2260	Yes	Orthogonal (<i>B</i> _f)
NbB ₂	-250	2900	No	Hexagonal (C32)

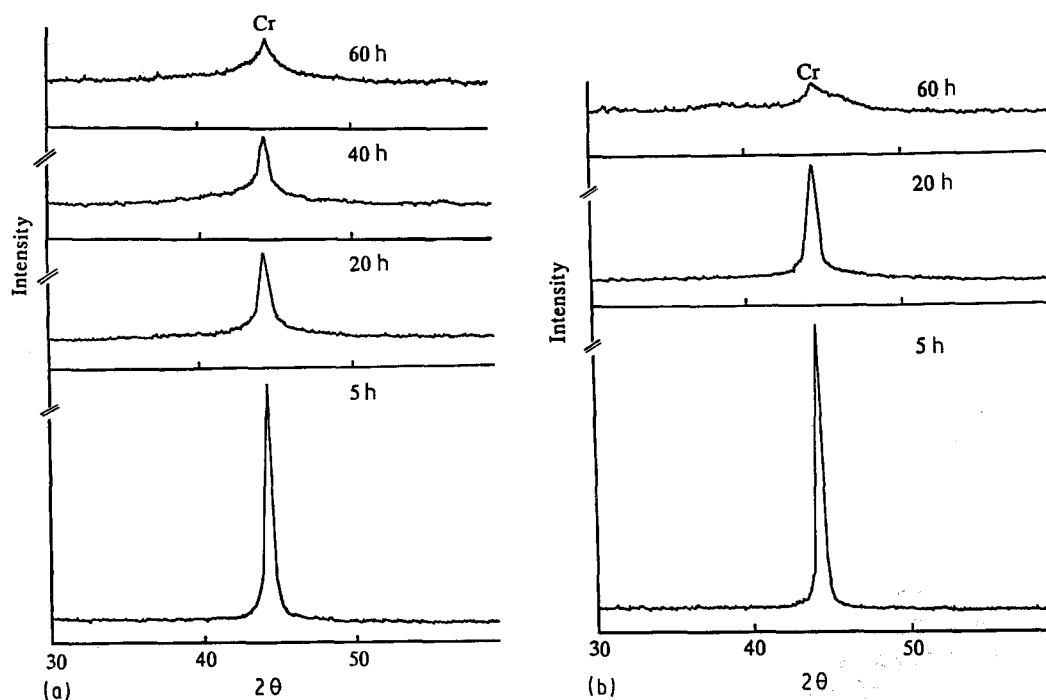


Figure 1 X-ray spectra from milled powders in (a) CrB and (b) CrB₂ MA systems. Only chromium peaks are observed.

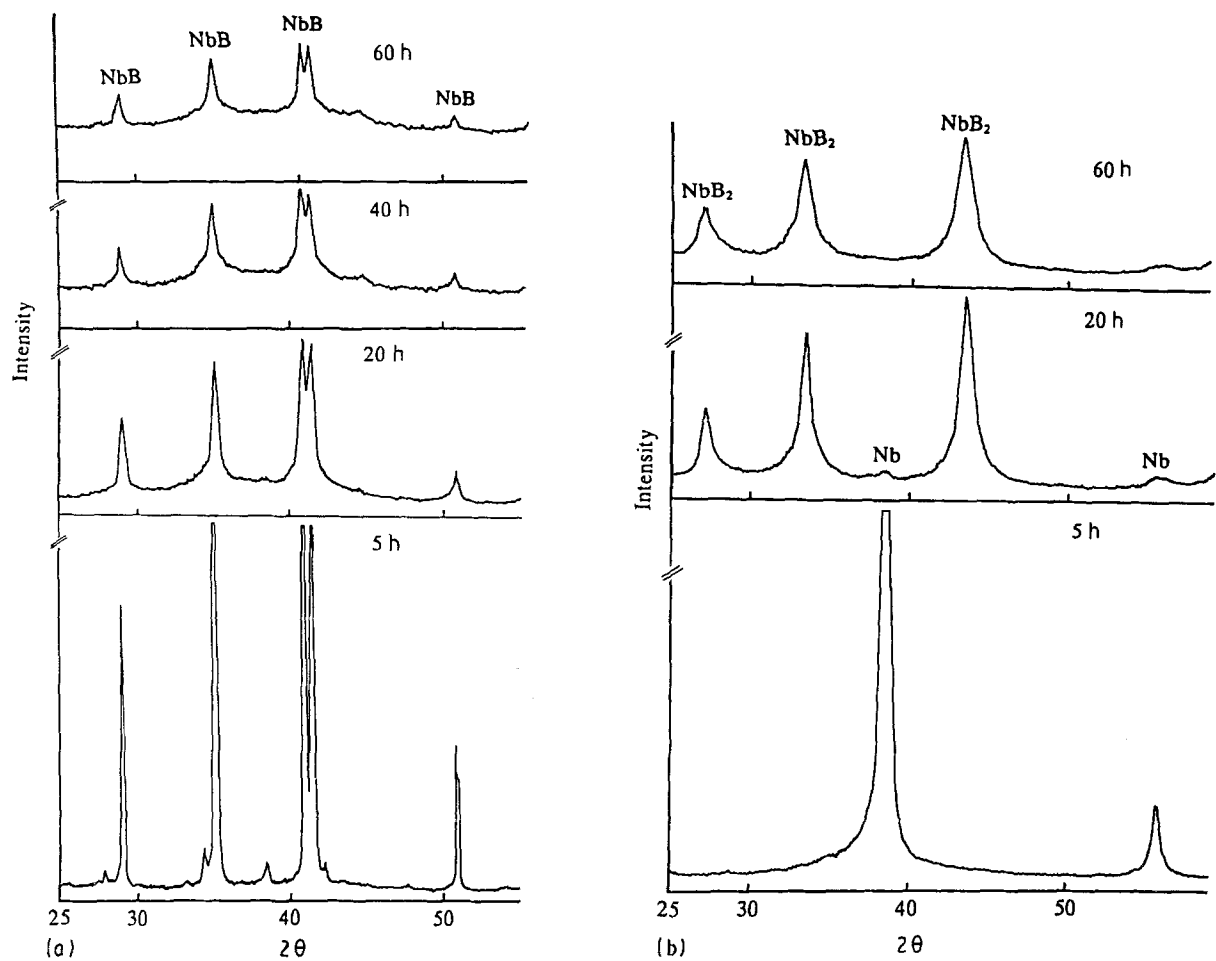


Figure 2 X-ray spectra from (a) NbB and (b) NbB₂ MA systems after milling for different times. Note formation of compounds.

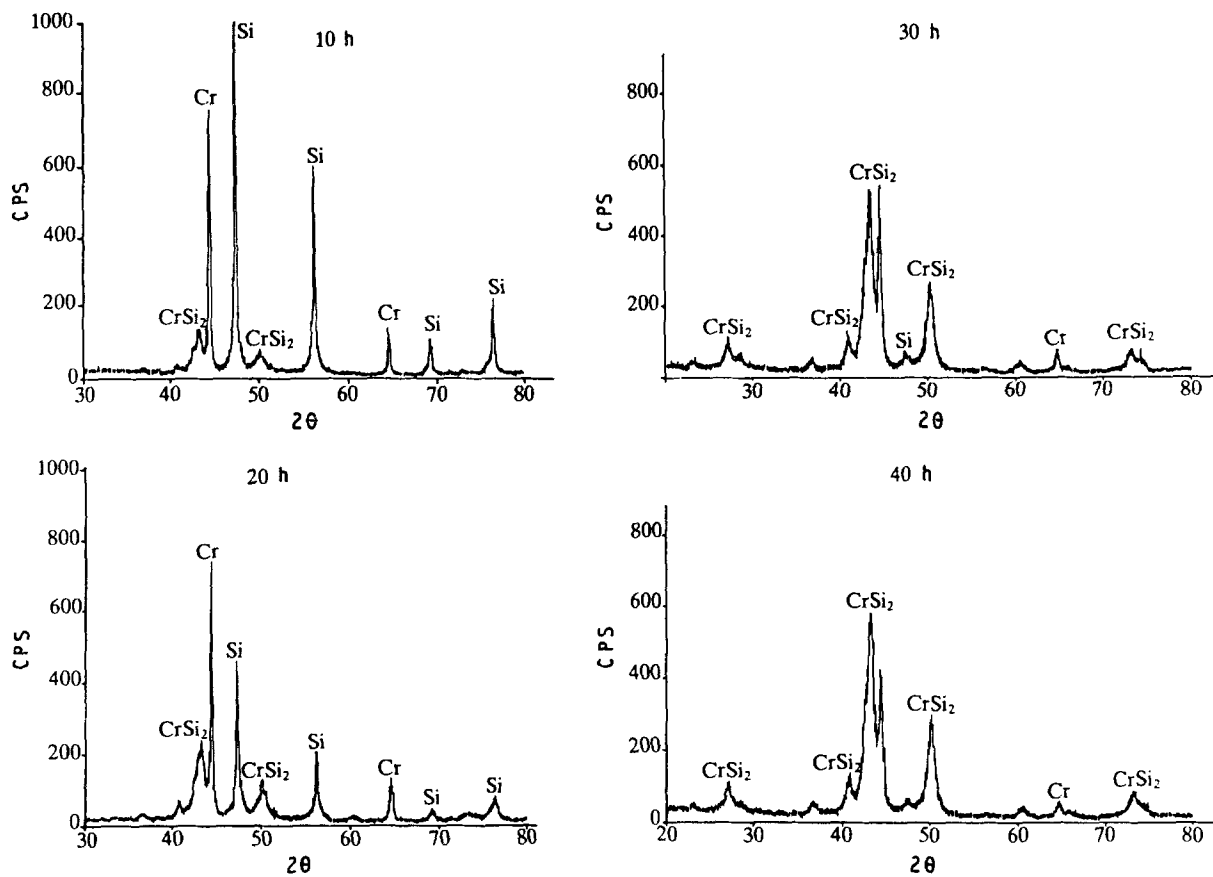


Figure 3 X-ray spectra from milled powders of the CrSi₂ system. Note the presence of Cr, Si and CrSi₂ peaks up to 40 h milling.

structure present: instead mixing of the elements appears to occur locally from outside the particles, with the boron particles becoming smaller and better distributed as a function of time (see Figs 7 and 8). This

process is continuous in the case of CrB and CrB₂ systems where the compounds did not form, behaving as though solid solutions of the two elements were finally obtained as confirmed by the X-ray spectra. At the same time the powders appear more fragile and become smaller as they fracture thoroughly after 60 and 80 h milling time.

In Figs 9 and 10, we see that the NbB and NbB₂ systems show a similar boron distribution in milled powders before compound formation. However, as soon as the boride peaks are detected, the powder particles show a homogeneous contrast with no darker or lighter areas, confirming complete mixing of the elements. At the same time the homogeneous powder particles appear very small (about 100 nm after 60 and 80 h milling) indicating the extent of fracture occurring in these fragile borides.

Fig. 11 shows the aspect of the NbSi₂ and CrSi₂ powders which appear very small and homogeneous in composition between 5 and 60 h, similarly to the niobium borides. In the case of the Cr₂Nb system, the layered structure observed within the milled powders up to 25 h milling [7] continues to be present after 60 h milling as observed in Fig. 12. The chemical compositions analysed from these layers correspond to chromium-rich (darker) or niobium-rich (lighter) areas, but always within the average global composition necessary to form the stable inter metallic compound corresponding to the equilibrium phase diagram (47 to 52 wt % Nb).

Finally, Figs 13 and 14 show a selection of the observed milled powders under TEM. It can be seen that in all cases diffuse rings are present in the diffraction patterns, together with some intense spots. These

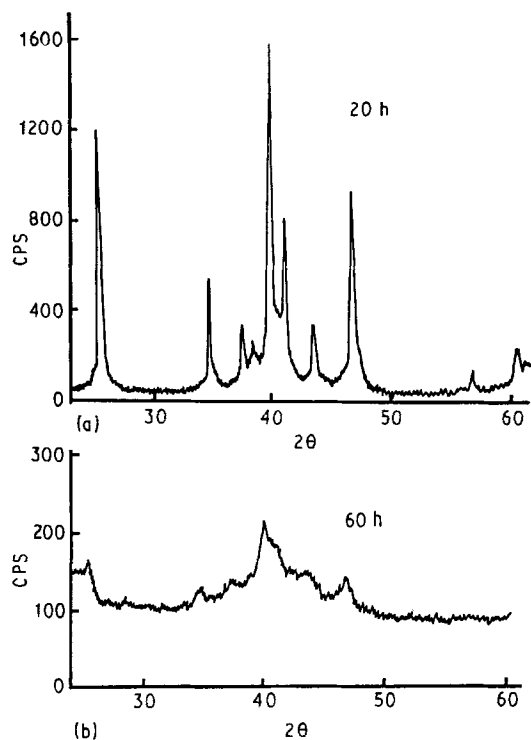


Figure 4 X-ray spectra from milled powders of the NbSi₂ system. The presence of NbSi₂ peaks after 20 h milling (a) confirms the formation of the compound, whilst the quasi-disappearance of those peaks after 60 h milling, (b) provides evidence for amorphization.

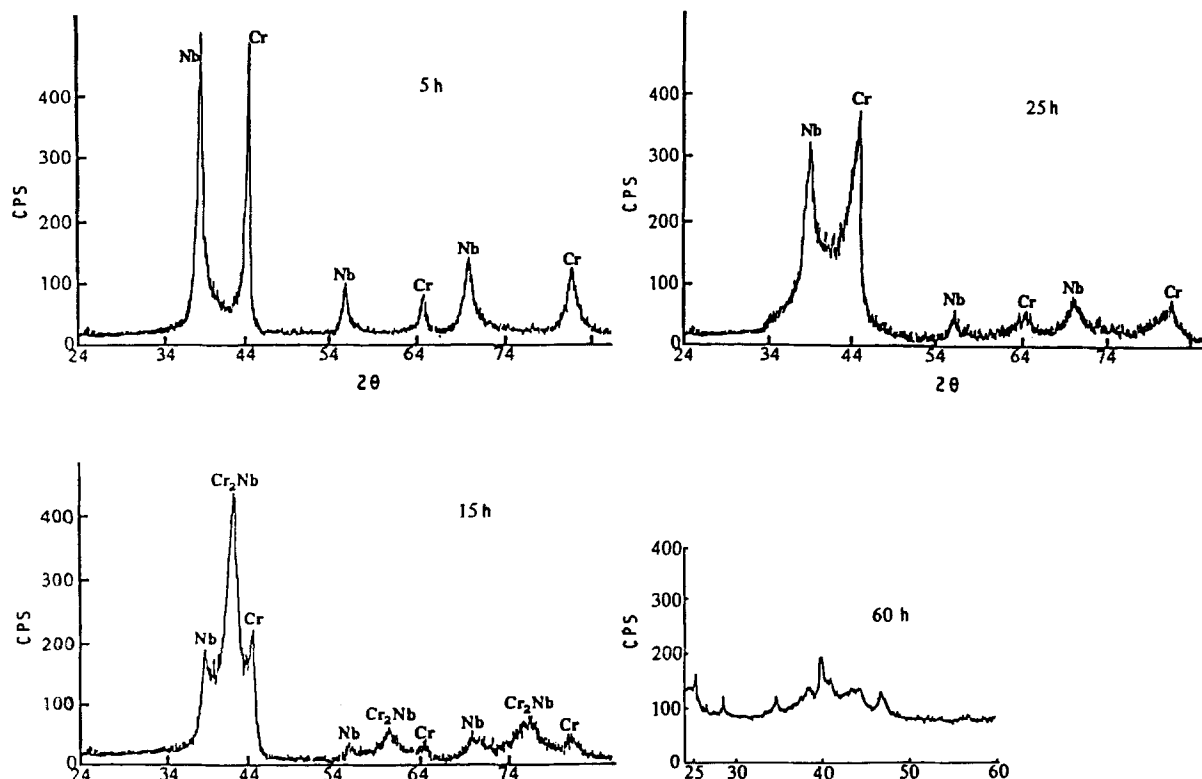


Figure 5 X-ray spectra from milled powders of the Cr₂Nb system. Note the appearance of the intermetallic hexagonal phase after 15 h, its disappearance after 25 h, and the evidence for partial amorphization after 60 h milling.

confirm the presence of an amorphous phase in the powders. Dark-field images obtained using the intense spots show that small crystallites are embedded in the amorphous matrix. The size of these crystallites corresponds well with the measured values from the X-ray spectra. Also, it is interesting to note that in most of the systems the small or large powders studied by TEM have similar appearance for a given milling time, in particular in terms of the crystallite size and distribution.

4. Discussion

We here take into account the capacity of these systems to form stable compounds, and the path followed by the systems to partial amorphization. In the early stages of milling, fracture and cold welding of the powders occur and if both elemental powders show similar plasticity, a layered structure will form. This is the case for the Cr_2Nb system. However, in the case of brittle powders, plastic deformation will not occur and the layered structure will not be observed. Indeed,

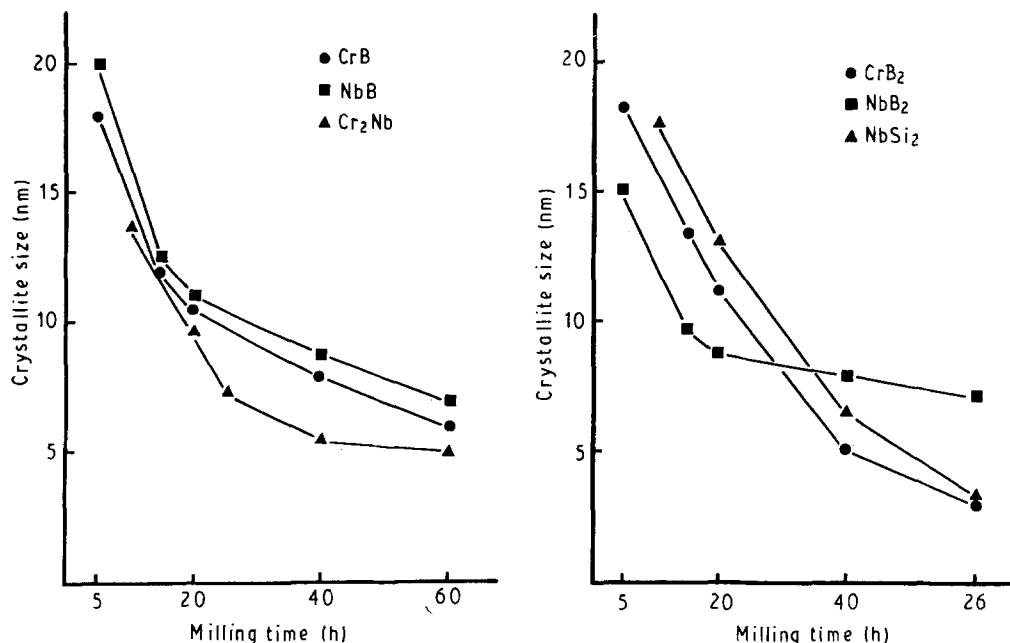


Figure 6 Plots of crystallite sizes as a function of milling time for all the powders. Note that a fastest decrease in crystal size occurs in the systems NbSi_2 , CrB_2 and Cr_2Nb , respectively.

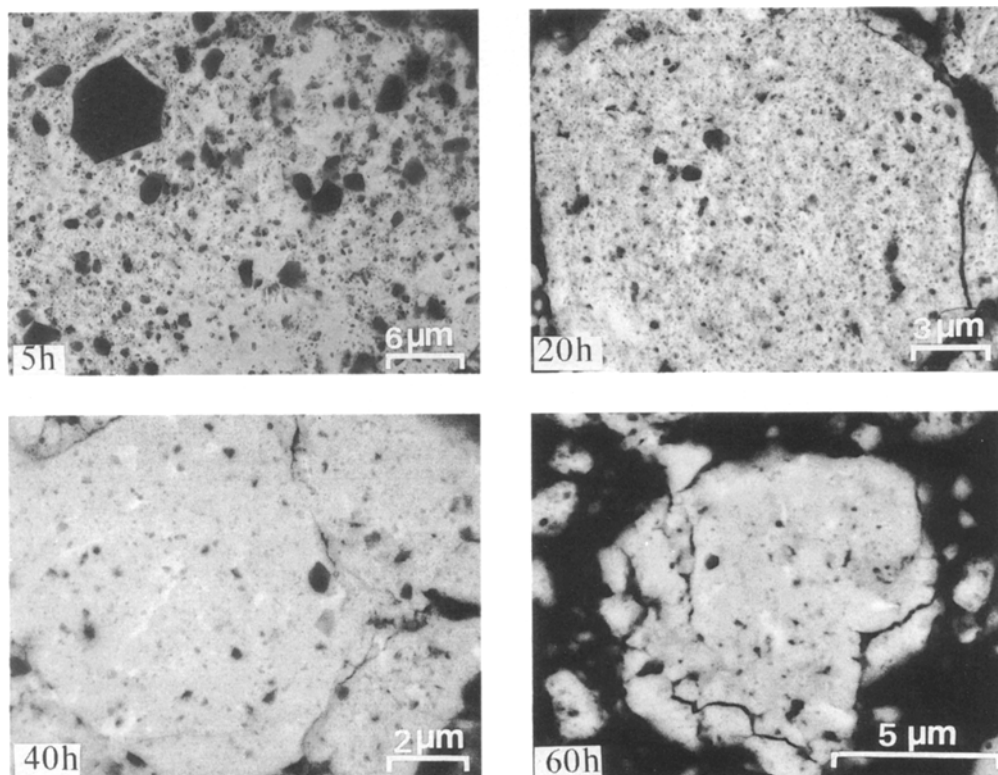


Figure 7 Observed boron distribution (dark) in milled powders of the CrB system after different milling times.

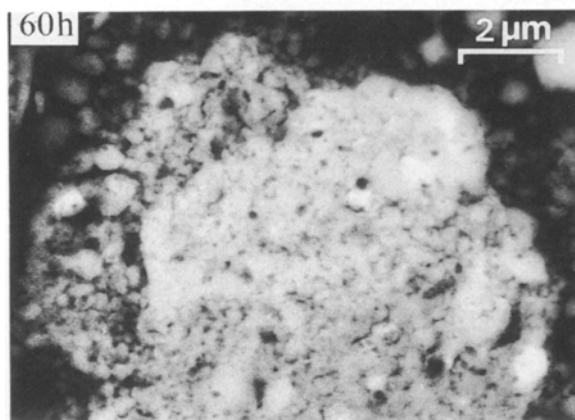
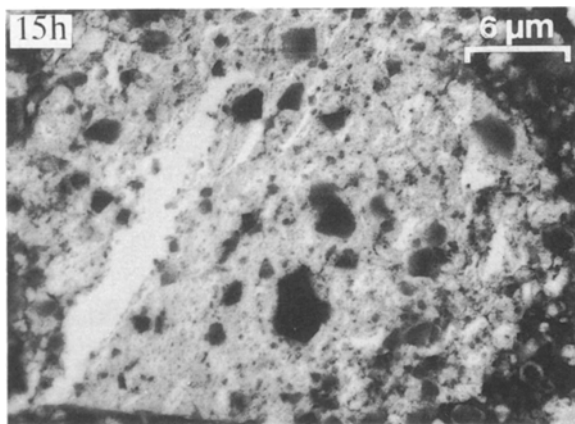


Figure 8 Observed boron distribution (dark) in milled powders of the CrB_2 system after different milling times.

boron and silicon are brittle elements and these powders will fracture rather than plastically deforming. In this way, mixing of the elements occurs after fracturing, with local diffusion from the outside towards the inside of the powders. In this way, the systems where no compound formation is observed (i.e. CrB and CrB_2) show a more homogeneous distribution of finer boron particles with increasing milling time (see Figs 7 and 8). Finally a homogeneous solid solution is observed after 60 h milling when partial amorphization occurs. The systems where compound formation occurs (see Figs 9 and 10) reach a homogeneous chemical composition at the milling time for which compound formation is observed (since they are line compounds). These compounds are very brittle and continue to fracture, becoming very small powders after 60 h milling, but with no change in chemical composition taking place.

Since partial amorphization seems to occur similarly in all cases, independently of the diffusion process involved with or without layered structures, and with or without compound formation) it must be assumed that the amorphization process must be due to structural rather than compositional destabilization. In this context we can relate the amount of local disorder causing amorphization in the cases where compound formation or solid solutions exist. Indeed the crystallite sizes observed in NbSi_2 (with compound formation) or in CrB_2 (solid solution) are the same after 60 h milling, indicating that local amorphization occurs after break down of the crystals to the same

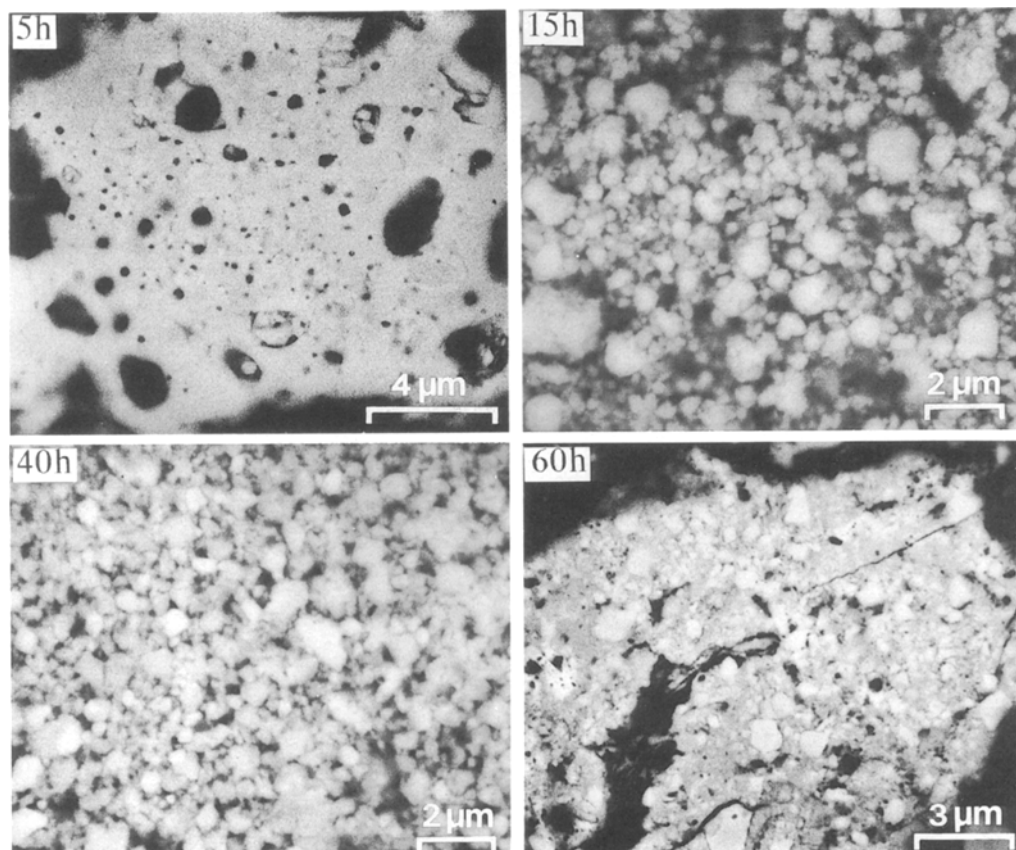


Figure 9 Milled powders observed in the NbB system. Note that boron (dark) particles are seen only before compound formation occurs (5 h).

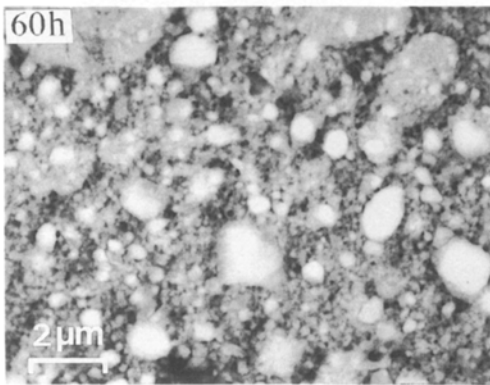
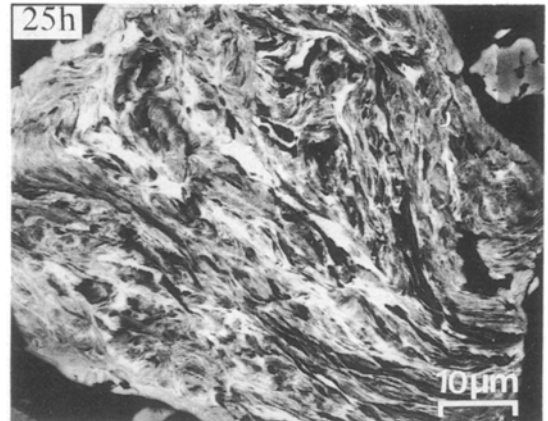
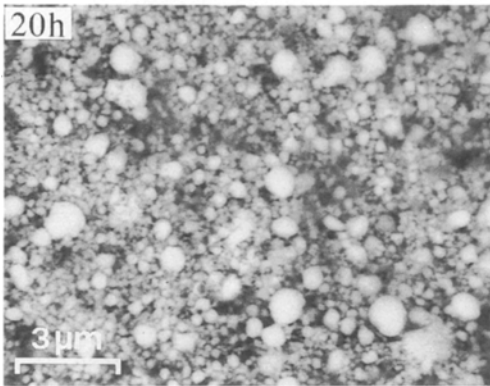
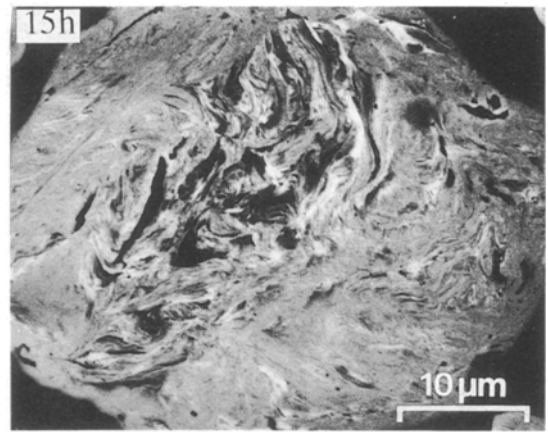
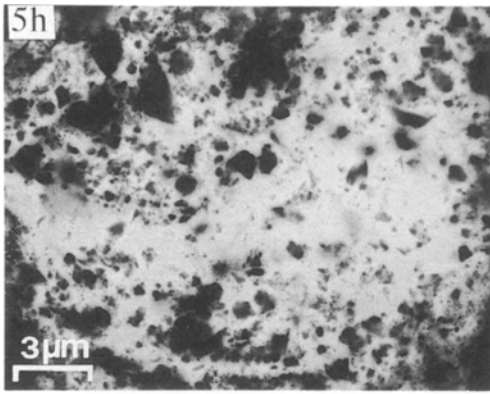


Figure 10 Milled powders observed in the NbB_2 system. Note that boron particles are seen up to 15 h milling when compound formation occurs.

Figure 12 Layered structures observed in the milled powders of the Cr_2Nb system after different milling times.

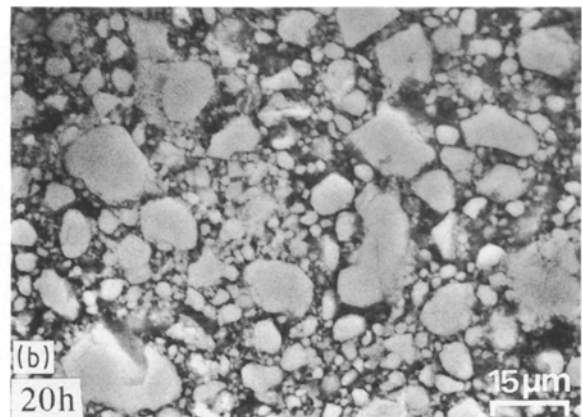
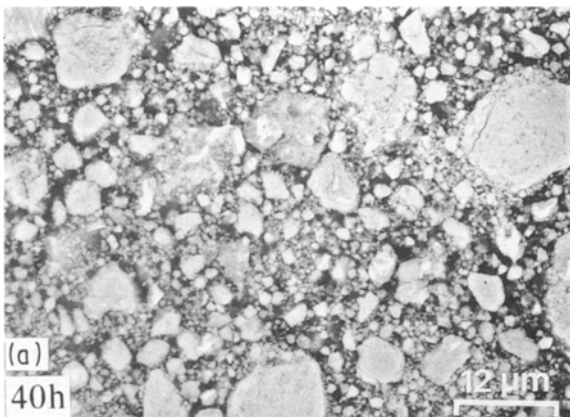


Figure 11 Homogeneous compositions observed in milled powders of the (a) CrSi_2 and (b) NbSi_2 systems where compound formation occurs.

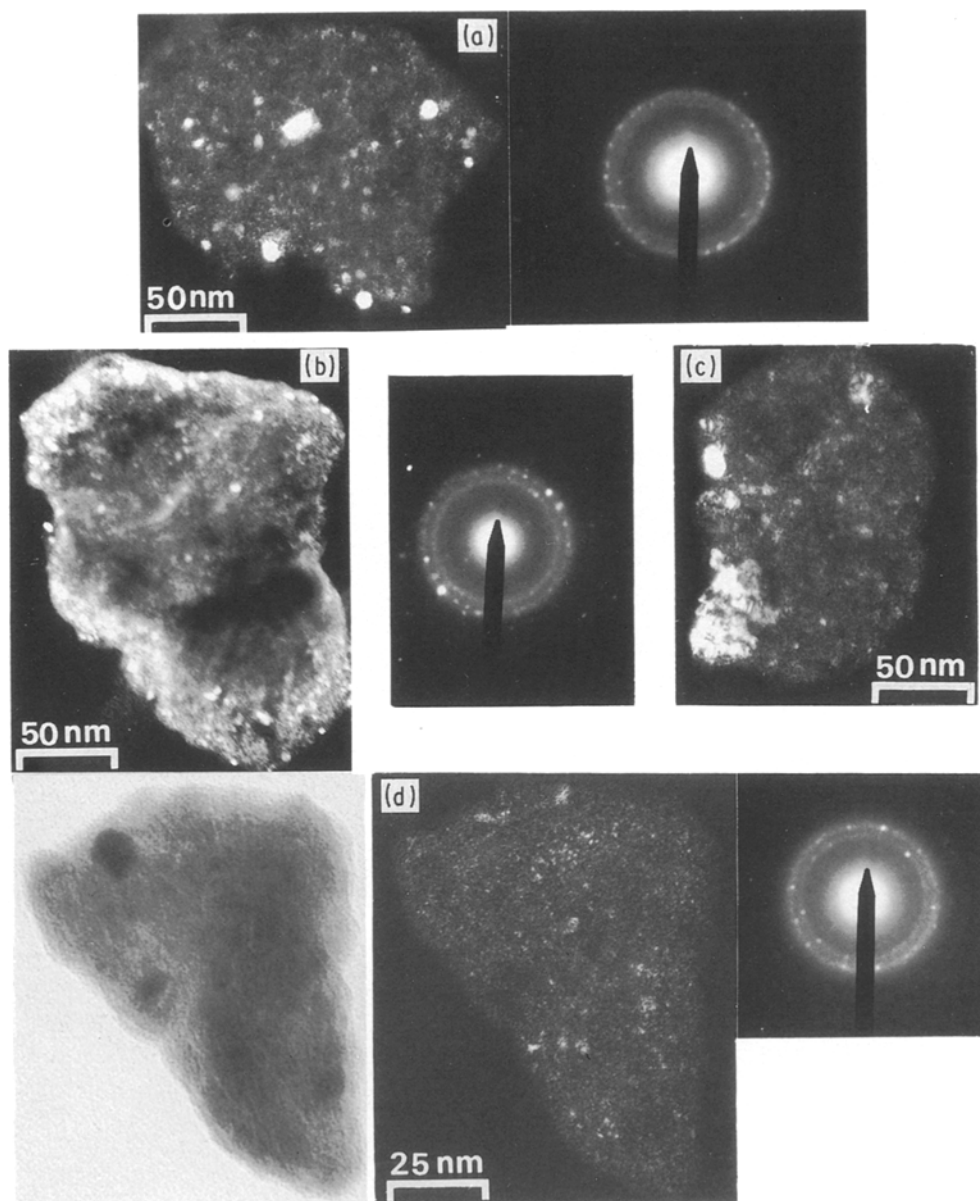


Figure 13 Typical TEM observations from milled powders in (a) CrB system after 60 h milling, and in the NbB system for (b) 40 h, (c) 60 h and (d) 80 h milling. Note the presence of diffuse rings in all the diffraction patterns, providing evidence for partial amorphization. The white particles observed in the dark field images made using the bright diffraction spots confirm the existence of crystallites embedded in an amorphous matrix.

extent. Therefore, the free energy increase corresponding to the disordered metastable solid solution or to the disordered destabilized compound appears to be equivalent.

A detailed comparison of the amorphization paths followed by these systems shows that in cases where the formation of a more stable compound occurs first (as for NbB, NbB₂ and NbSi₂ with the highest negative enthalpy of compound formation between -250 and -140 kJ mol⁻¹, respectively) further milling results in the formation of an amorphous phase containing crystallites of the remaining compound. In this way the amorphization process by ball-milling can be seen as a continuous increase in the volume fraction of zones with local disorder of their crystallographic structures. Such atomic disorder, as a function of milling time, has already been observed in other intermetallics during ball-milling [6] confirming that

chemical disorder is the precursor of amorphization [9]. These recent investigations have shown that ball-milling generates thermodynamic non-equilibrium states of disorder equivalent to the high temperature ones.

No compound formation occurs in the case of the CrB and CrB₂ systems with heats of formation of -75 and -94 kJ mol⁻¹ respectively, whilst direct formation of the amorphous phase from the solid solution of elements takes place. This suggests that chemical disorder occurring from the early stages of milling prevents compound formation in the case of certain complex ordered structures. This means that nucleation of the compound is not possible because either the critical activation energy necessary for nucleation is too high, or the critical nucleus size is never reached. This is illustrated by the fact that the compound CrSi₂ forms after milling times between 10 and

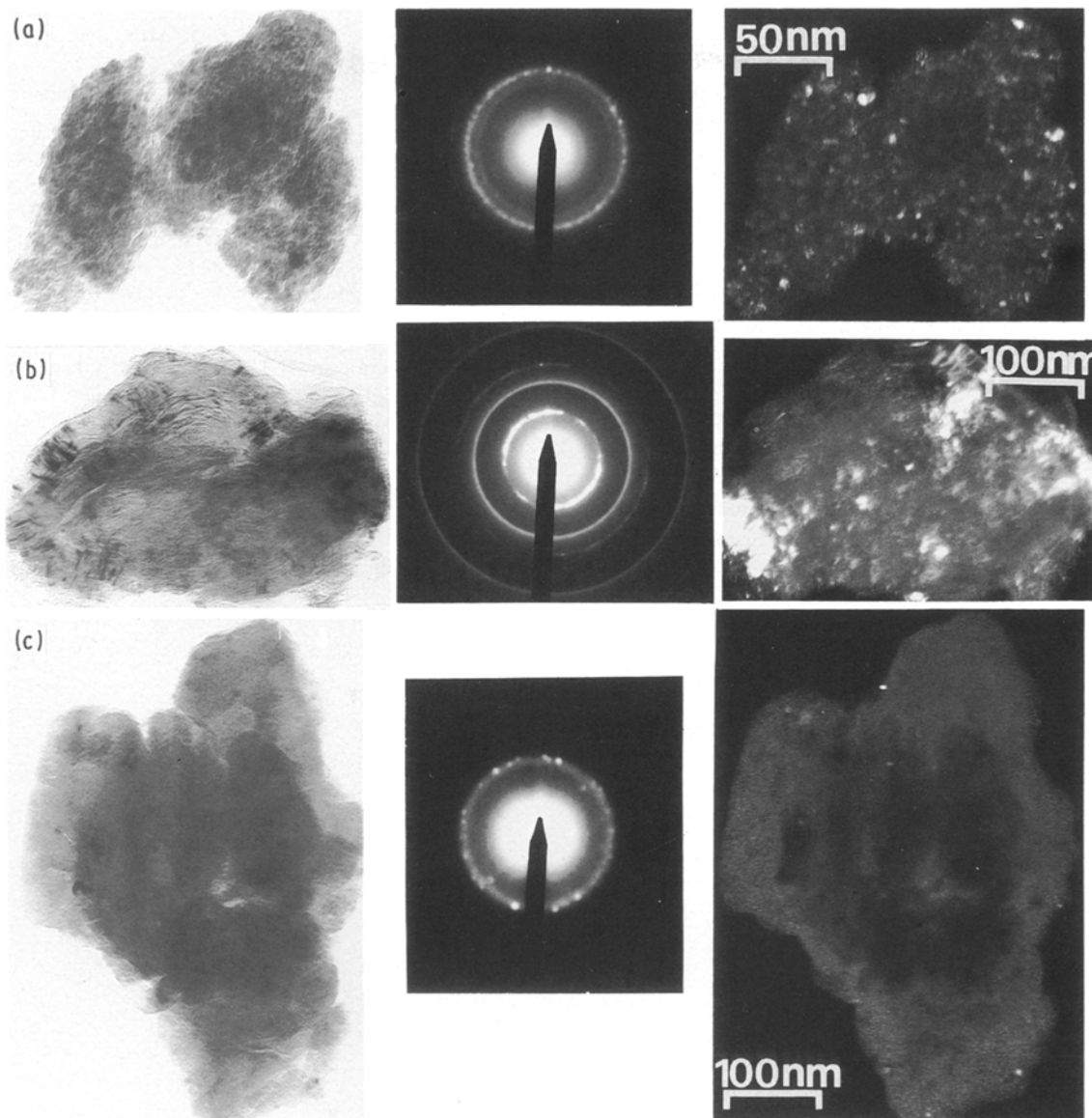


Figure 14 Typical TEM observations from milled powders after 60 h milling in (a) CrB_2 , (b) NbSi_2 and (c) Cr_2Nb systems. Note the diffuse rings present in the diffraction patterns and the extent of amorphization observed in the dark-field images.

40 h even though its enthalpy of formation, $\Delta H_f = -80 \text{ kJ mol}^{-1}$, is intermediate to those of CrB and CrB_2 .

Let us now consider the amorphization path followed by the Cr_2Nb system. The early stages of milling lead to sufficient diffusion of the elements to reach the average chemical composition necessary for compound formation [7]. However at this point (15 h), only the high-temperature hexagonal phase forms due to the high-energy state of the system. On further milling, the layered structures consisting of solid solutions of the two elements with average compositions are once more observed. Presumably these solid solutions rich in either niobium or chromium correspond to a higher energy state than the original solutions where the two elements were less mixed. If milling is continued for up to 60 h, amorphization occurs because atomic mixing gives rise to some short-range order where the free energy of the amorphous phase is equal to that of the crystalline solid solution. If, however, the stable cubic Laves phase is formed by

annealing the 10 h milled powders [7], further milling for 10 h destroys the stable crystal compound to form the solid solutions once more. These solutions lead again to amorphization after 60 h milling. Therefore it is concluded that the crystalline disordered solid solution is the precursor of the amorphous phase in this system, whether starting from the elemental powders or from the intermetallic powders.

Since sufficiently long milling times finally lead to the formation of amorphous phases, this indicates that the free energy of the system can be lowered in this way during milling whichever path is followed. Thus, the milling process induces such concentration of defects that in the early stages of mixing, rapid diffusion of the elements occurs, leading to homogeneous chemical compositions. But increasing defect concentration on further milling allow atomic mobility leading to structural disorder. In certain systems this hinders compound formation prior to amorphization, presumably because in the milling time required to reach homogeneous chemical composition, the defect

concentration has increased too much for an ordered compound to form. In other systems, however, compound nucleation is possible at earlier stages of milling. In these cases, the amorphization process occurs by the destruction of order in local regions of the small powders, as ball impact locally increases atomic mobility.

5. Conclusions

Amorphous phase formation has been observed to compete with nanocrystal phase formation of either ordered compounds or solid solutions in the different systems studied. It appears that the process of ball-milling induces high defect concentrations which lead to thermodynamic non-equilibrium states (disordered) that can hinder compound formation in some cases. Amorphization occurs locally as a means of reducing the free energy of the non-equilibrium short-range ordered state of the milled crystalline systems.

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