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Grain growth in nanocrystalline $NbAl_3$ prepared by mechanical alloying

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Grain growth and its kinetics were studied on an intermetallic compound, $NbAl_3$ powder prepared by mechanical alloying of elemental Nb and Al powders for 1.8 Ms in an argon atmosphere at ambient temperature. The initial and grown grain sizes were measured from the X-ray line broadening of as-alloyed and annealed powders. Isochronal annealing of mechanically alloyed powders from 573 to 1373 K indicated that substantial grain growth occurs only in a temperature range of 1048 to 1173 K and ceases at 1273 K regardless of anneal time. Accordingly isothermal annealing of 1.8 to 18 ks was carried out at 1048, 1073 and 1098 K to obtain the grain growth kinetic that is described by $\ln(dD/dt) = \ln(r_0/3) - 2.0 \ln D$ where D is the measured grain size and r_0 a constant. This r_0 depends on temperature according to $r_0 = r'_0 \exp(-Q/kT)$ where Q is the activation energy for grain growth, k the Boltzmann constant and T the absolute temperature. Arrhenius plots of r_0 against the reciprocal of temperature yield a straight line, from whose slope the activation energy for grain growth is deduced to be 162 ± 2 kJ mol^{-1}. Of significance is the fact that the ultimate grain size at 1273 K is approximately 70 nm, which will not grow by further annealing even at 1373 K.

1. Introduction

Reliable structural materials have recently been sought for high-temperature aerospace applications. Such materials must have high-temperature strength combined with a low density and some ductility or toughness at both elevated and ambient temperatures. So far, various intermetallic compounds have been considered to be ideal materials, but brittleness at ambient temperature is by far the greatest impediment to finding useful compositions among many intermetallic compounds. Among them, however, niobium aluminides and titanium aluminides could be potential candidates for such applications because of their high melting points, low densities and attractive high-temperature mechanical properties. They have good oxidation resistance but they are brittle and weak when conventional cast and wrought processing methods are employed.

One of the alternative processing methods is mechanical alloying (MA) of elemental powders to produce alloyed powders that may be amorphous, metastable or intermetallic phases of ultra-fine grain sizes, but the MA powders have eventually to be consolidated into the bulk. When conventional powder metallurgy processing such as hot pressing, hot extrusion and hot isostatic pressing (HIPping) is employed for consolidation of MA powders, they experience somewhat extended heating that may result in excessive grain growth. Instead of the conventional consolidation, electro-discharge consolidation (EDC) has successfully been utilized to consolidate the powders produced by rapid solidification [1–3] and mechanical alloying [4–7]. Briefly, EDC employs a high voltage (up to 30 kV), high density (up to 150 kA cm^{-2}) current pulse (approximately 300 μs) instantly discharged from a capacitor bank to the powders under an external pressure [7]. One of the distinct characteristics of EDC is the capability of consolidating powders without altering the microstructures inherent in rapid solidification or mechanical alloying. For example, nanophases (2 to 6 nm grain sizes) of $NbAl_3$ or TiAl with a small amount of Ti_3Al powder produced by mechanical alloying could be consolidated into bulk pieces that have resultant grain sizes of the order of 15 to 100 nm depending on the input energy [5, 6].

Of great interest is that, when the resultant grain sizes in both the above-mentioned systems are greater than their critical sizes, a positive Hall–Petch relationship between the hardness and the reciprocal of $D^{1/2}$ exists [4], while there exists a negative Hall–Petch relation when they are smaller than their critical sizes [5, 6]. This fact suggests that EDC consolidates with grain sizes of a few tens of nanometres are rather ductile compared to those of larger grain sizes. At this moment, the reason for softening in ultra-fine grain size materials is somewhat speculative; deformation within grain boundaries, not by the dislocation mechanism in the matrix, is predominantly responsible for softening since grain boundaries occupy an extremely large portion of the material (20–50 vol %) [8]. A

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preliminary observation of microstructures of EDC consolidates by high-resolution transmission microscopy (HREM) indicates that crystalline grains of a few tens of nanometres are separated from neighbouring grains by a fuzzy grain boundary configuration [9].

When an EDC consolidate in the negative Hall–Petch region is annealed at high temperatures (1073 to 1273 K) for a few hours, the grain size is increased, resulting in an increase in hardness [5, 6]. This suggests the possibility that nanophase intermetallic compounds produced by EDC can be mechanically fabricated into a desired shape at rather low temperatures and then annealed to higher strengths. In order to fully take advantage of this practice, a knowledge of grain growth and its kinetics must be obtained on powders of an intermetallic compound such as $NbAl_3$ prepared by mechanical alloying. Isochronal and isothermal annealings were therefore conducted at elevated temperatures.

2. Experimental procedure

31.85 g of aluminium powder (99.5 %, – 325 mesh) and 38.15 g of niobium powder (99.8 %, – 325 mesh) were jar-milled for 90 ks (25 h), 180 ks (50 h), 360 ks (100 h), 720 ks (200 h), 1080 ks (300 h), 1440 ks (400 h) and 1800 ks (500 h) in a stainless steel container having the dimensions of 130 mm diameter and 80 mm length, with a ball to powder ratio of 30:1 under an argon atmosphere. After mechanical alloying for the predetermined periods of time, MA powders were examined by X-ray diffraction (XRD) using a copper target (K_α) from 15 to 80° for 2θ at 40 kV with a scanning speed of $0.02^\circ\ s^{-1}$, to determine phase formation and line-broadening.

Powders (20 mg) produced by 360, 720, 1080 and 1800 ks MA were analysed by using differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7) at a heating rate of $40\ K\ min^{-1}$ to observe the effect of MA time on the phase formation. To further identify the phase changes with temperature by XRD, heating was interrupted at various temperatures during a DSC run [5].

MA 1800 ks powders that are a mixture of mostly $NbAl_3$ (grain size 8 nm) and a very small amount of Nb_2Al (grain size 6 nm) were isochronally annealed for 1.8, 3.6 and 10.8 ks at 573, 723, 873, 973, 1048, 1073, 1098, 1173, 1273 and 1373 K in a vacuum of 10^{-3} Pa. After anneals, powders were analysed for their grain sizes by X-ray line broadening.

The line-broadening width B was obtained from one-half the difference between the two extreme angles $2\theta_1$, and $2\theta_2$ at which the intensity is zero by assuming the diffraction line is triangular in shape, so that $B = (\theta_1 - \theta_2)$. Since both θ_1 and θ_2 are very nearly equal to θ_B, $\theta_1 + \theta_2 = 2\theta_B$. If λ is the wavelength of X-rays, the grain size D is given by

$$D = 0.94\lambda/B\cos\theta_B \qquad (1)$$

To remove the strain effect, the measured D values for (1 0 1), (1 1 0), (1 1 2), (0 0 4) and (2 0 0) reflections of $NbAl_3$ were processed further in a relation described by

$$B\cos\theta_B = 0.94(\lambda/\bar{D}) + 2\varepsilon\sin\theta_B \qquad (2)$$

where ε is the effective strain associated with MA and ultra-fine grain size and $\bar{D}$ is the true grain size obtained by extrapolating $\sin\theta$ to zero to eliminate the strain term in Equation 2.

Isothermal annealings of MA 1800 ks powders were carried out at 1048, 1073, 1098 and 1173 K in a vacuum for up to 18 ks, and the grown grain sizes were measured in a similar manner to that described above. These data are used for calculating the grain growth rate ($d\bar{D}/dt$) to deduce the grain growth kinetics.

3. Results and discussion

Low-angle XRD spectra of MA powders are presented in Fig. 1 for 720 to 1800 ks to illustrate the phase formation. At shorter MA times, all the expected peaks of Al and Nb elemental powders are observed, although the minor peaks of higher indices lose their intensities as MA proceeds and the major but weak-intensity peaks of Al (1 1 1) and Nb (1 1 0) persist up to 720 ks. As seen from this figure, Nb_2Al is first formed along with elemental Al at 720 ks. This Nb_2Al, however, appears to transform into $NbAl_3$ as MA further proceeds.

The line-broadening width B was obtained as described above. Using Equation 1, the elemental particulate or compound grain size D was calculated. The D values calculated for Nb(1 1 0) and Al(1 1 1) up to

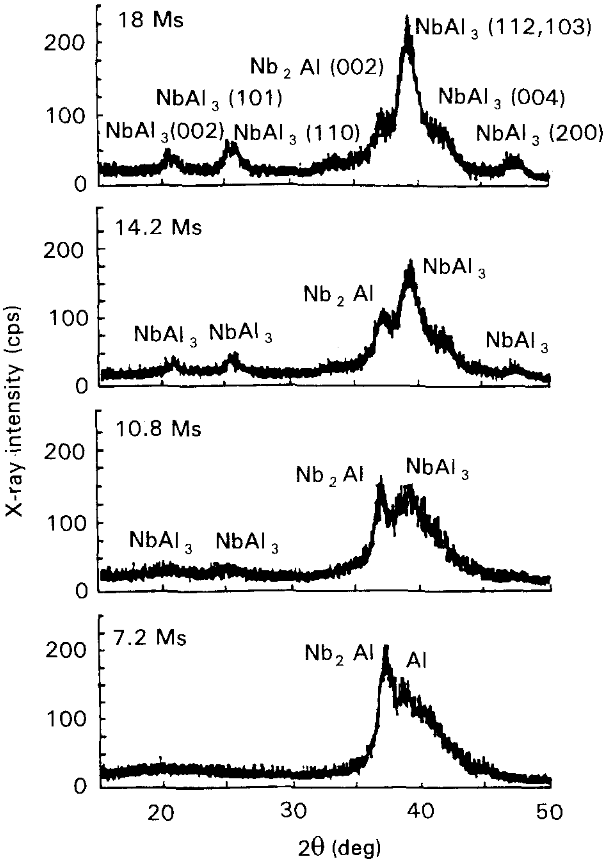

Figure 1 X-ray diffraction spectra of MA powders as a function of the MA time for Nb–54.5 wt % Al powder mixture.

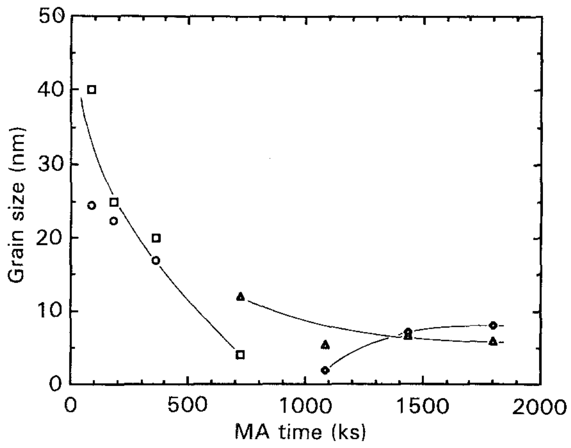

Figure 2 Elemental particulate and grain sizes measured from the line-broadening versus MA time for Nb–54.5 wt % Al mixture: (○) Al, (□) Nb, (△) Nb_2Al, (◇) $NbAl_3$.

720 ks, and those for Nb_2Al (0 0 2) and $NbAl_3$ (1 1 0) are plotted against MA time in Fig. 2 for an Al–54.5 wt % Nb alloy mixture. Here, due to the assumption of a triangular shape, the error associated with calculating the D values will be of the order of ± 0.5 nm. The elemental particulate size decreases sharply with increasing MA time up to 720 ks, when the grain sizes of newly formed phases of Nb_2Al and $NbAl_3$ are of the order of a few nanometres.

Since the line broadening is caused by reduction of grain size as well as plastic strain produced during mechanical alloying, the real grain size $\bar{D}$ must be obtained by eliminating the second strain term in Equation 2 by extrapolating the curve of $B\sin\theta_B$ versus $\sin\theta_B$ to $\theta_B = 0$. This strain term for as-alloyed powders contains plastic strain of the order of a few per cent due to plastic deformation of the powder during MA [9] and the macroscopic strain associated with a large volume fraction of grain boundaries due to the reduction of grain sizes to nanometres. An example of this exercise is shown in Fig. 3, where the line-broadening data for MA 1800 ks powders annealed at 873–1273 K for 3.6 to 18 ks in a vacuum are plotted according to Equation 2. The grain sizes thus obtained are summarized in Table I.

For studying the grain growth kinetics in a nanophase $NbAl_3$, MA 1800 ks powders were used since the previous X-ray and DSC studies on MA powders [5] indicate that MA of 1800 ks produces almost 100 % $NbAl_3$, and a very small fraction of the remaining Nb_2Al will be transformed into $NbAl_3$ when it is heated to a temperature higher than 673 K. Depicted in Fig. 4 is the isochronal annealing of MA 1800 ks powders that have formed $NbAl_3$ with a very small fraction of Nb_2Al and without any elemental phase after MA, to show how the grain size of $NbAl_3$ is increased. It is seen from this figure that grain growth does not occur up to 673 K. At this temperature the DSC data for MA 1800 ks powders [5] indicate that the transformation to $NbAl_3$ is complete. Significant grain growth can be observed in the temperature range of 973 to 1173 K, while the grain growth appears to cease at 1273 K regardless of anneal time and the grain size remains unchanged even at 1373 K.

TABLE I Grain sizes of $NbAl_3$ (MA 1800 ks) after annealing at various temperatures for various periods of time

Temperature (K)	Grain size (nm)			
	1.8 ks	3.6 ks	10.8 ks	18 ks
573	–	–	10.5	–
723	–	–	13.0	–
873	13.6	15.0	17.5	20.5
973	17.5	21.8	22.6	24.5
1048	21.9	27.0	38.0	45.0
1073	22.7	31.3	40.8	52.2
1098	28.1	35.0	49.8	56.5
1173	36.0	42.7	61.0	70.0
1273	58.0	67.0	68.0	68.8
1373	–	–	70.0	–

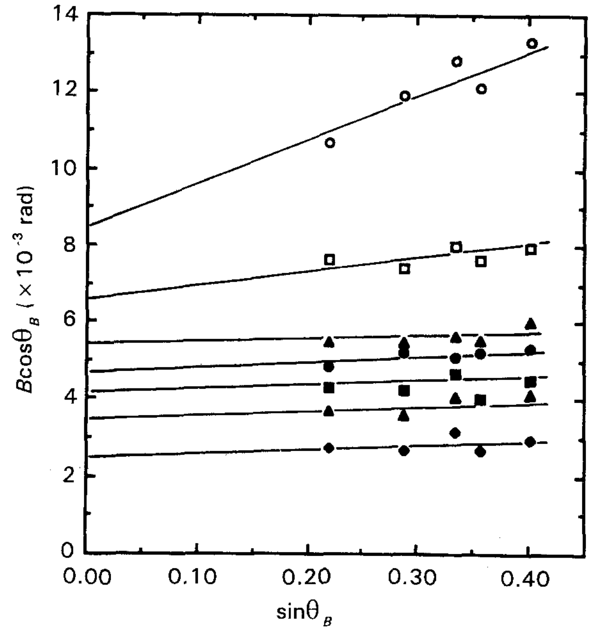

Figure 3 $B\cos\theta_B$ versus $\sin\theta_B$ as a function of anneal temperature for MA 18 ks $NbAl_3$ powders annealed for 3.6 ks at the respective temperature: (○) 873 K, (□) 973 K, (△) 1048 K, (●) 1073 K, (■) 1098 K, (▲) 1173 K, (◇) 1273 K.

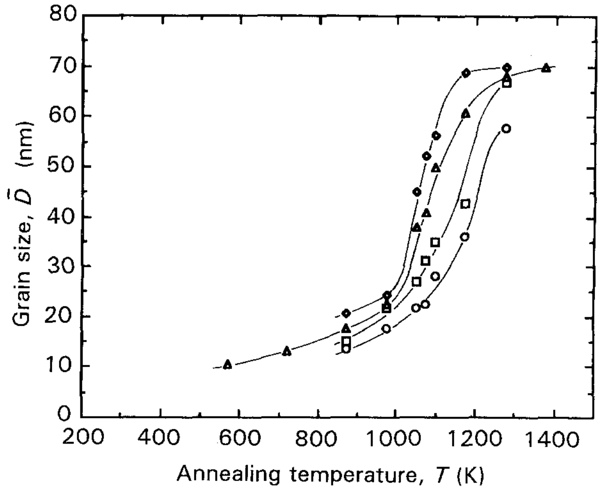

Figure 4 Measured grain sizes plotted against anneal temperature as a function of anneal time for $NbAl_3$ produced by MA 1800 ks: (●) as alloyed; (○) 1.8 ks, (□) 3.6 ks, (△) 10.8 ks, (◇) 18.0 ks.

The data shown in Fig. 4 are converted into the isothermal annealing curves in Fig. 5 for the temperatures of 1048 to 1098 K which exhibit faster grain growth rates. Smooth curves can be drawn through the data points in this temperature range. In order to test whether these isothermal curves are controlled by a single kinetics, the grain growth rate $d\bar{D}/dt$ was calculated from the curves shown in Fig. 5 at these three temperatures. The results are plotted as $\ln (d\bar{D}/dt)$ versus $\ln \bar{D}$ in Fig. 6, where straight lines having the same slope of -2.0 can be drawn through the data points at all temperatures. This indicates that the grain growth in this temperature range is really controlled by a single kinetics. From Fig. 6, the kinetic equation can be obtained as follows:

$$\ln(d\bar{D}/dt) = \ln(r_0/3) - 2.0\ln\bar{D} \qquad (3)$$

which leads, by integrating Equation 3 with respect to time t, to

$$\bar{D}^3 - \bar{D}_0^3 = r_0 t \qquad (4)$$

This r_0 has a temperature dependence described by the equation

$$r_0 = r_0' \exp(-Q/kT) \qquad (5)$$

where r_0' is a frequency term, k the Boltzmann constant, Q the activation energy for grain growth and T the absolute temperature.

Fig. 7 shows Arrhenius plots of r_0 versus $1/T$, where a straight line can be drawn through the data points and a slope of 162 ± 2 kJ mol^{-1} can be calculated for the activation energy for grain growth. The values of r_0 and r_0' are summarized in Table II, from which the average $\bar{r}_0'$ can be deduced to be

$$\bar{r}_0' = 5.86 \times 10^8 \text{ nm}^3 \text{ s}^{-1} \qquad (6)$$

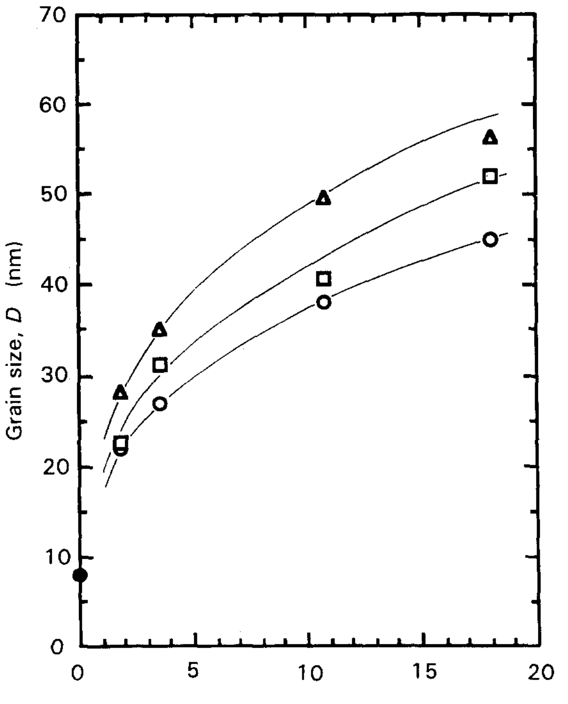

Figure 5 Isothermal annealing of MA $NbAl_3$ powders at (○) 1048, (□) 1073 and (△) 1098 K; (●) as alloyed (1800 ks).

which is within an experimental error of the order of 0.03×10^8 nm^3 s^{-1}.

Depicted in Fig. 8 are plots of $\ln(\bar{D}^3 - \bar{D}_0^3)$ versus $\ln[t \exp(-Q/kT)]$, and it is clearly seen that a single straight line with a slope of 1 can be drawn through the data points. This fact verifies that a single kinetic law prevails over data points obtained in the temperature range of 1048 to 1098 K, i.e. Equation 4 is valid. The reason that the exponent of $\bar{D}$ in Equation 4 is 3 is considered to be that the grain growth occurs in three dimensions [10, 11].

At this moment the reason that the grain growth ceases at and above 1273 K regardless of anneal time (see Fig. 4) to result in the ultimate grain size of ~70 nm is not obvious. However, judging from preliminary observations of the nanophase structures of as-alloyed powders and annealed powders by high-resolution transmission microscopy (as shown in Fig. 9a and b, respectively) the width of grain boundary is quite thick, of the order of approximately 1.5 nm, and the crystal orientations of neighbouring grains are quite random so as not to constitute low-angled grain boundaries. Accordingly it is speculated that grain growth can occur by growing larger grains whose crystal orientations are not too much different from each other, at the expense of neighbouring small grains. But once the growing grains face against grains

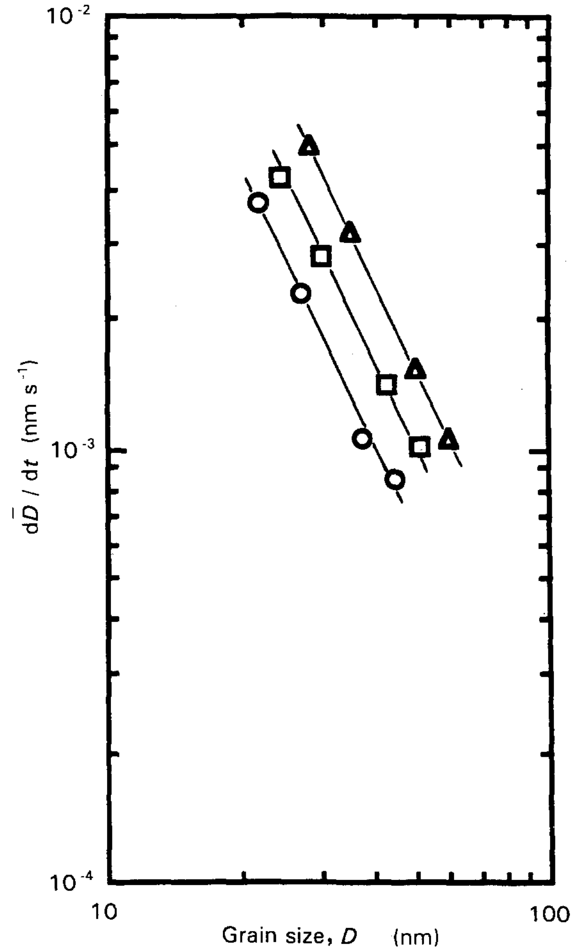

Figure 6 Ln ($d\bar{D}/dt$) versus ln ($\bar{D}$) for $NbAl_3$ MA powders: (○) 1048 K, (□) 1073 K, (△) 1098 K. $d\bar{D}/dt$ was calculated using the isothermal data shown in Fig. 5. Slope = -2.0 ± 0.7.

TABLE II Values of the rate constant r_0 and frequency terms, r'_0 and $\bar{r}'_0$ in Equation 5

Temperature (K)	r_0 (nm^3 s^{-1})	r'_0 (nm^3 s^{-1})	$\bar{r}'_0$ (nm^3 s^{-1})
1048	4.98	$(5.90 \pm 0.03) \times 10^8$	$(5.86 \pm 0.03) \times 10^8$
1073	7.47	$(5.76 \pm 0.01) \times 10^8$	
1098	11.6	$(5.91 \pm 0.03) \times 10^8$	

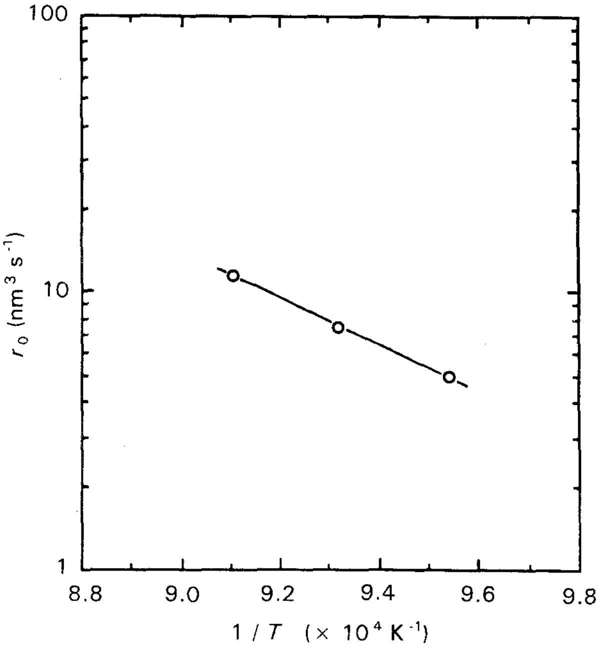

Figure 7 Arrhenius plots of the frequency term r_0 (Equation 5) against the reciprocal of anneal temperature. The slope give the activation energy of grain growth as $Q = 162 \pm 2$ kJ mol^{-1} for $NbAl_3$ annealed in the temperature range 1048–1098 K; $r'_0 = 5.858 \times 10^8$ nm^{3}s^{-1}.

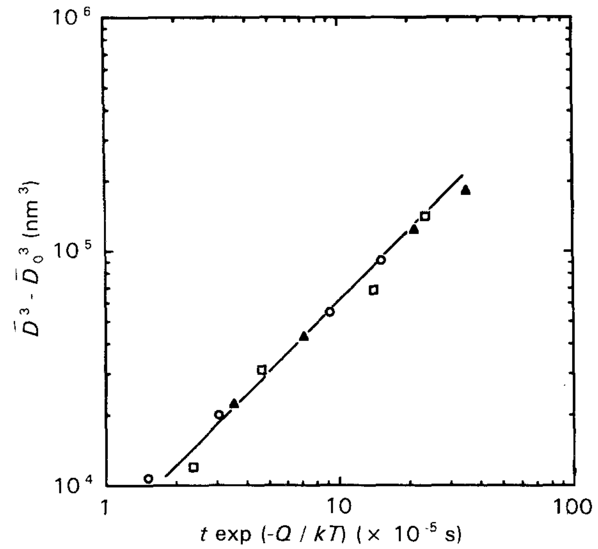

Figure 8 Normalized representation of grain growth for $NbAl_3$ powders produced by MA for 1800 ks: (○) 1048 K, (□) 1073 K, (△) 1098 K.

whose orientations are quite different from them, re-orientation of the neighbouring small grains is needed before further grain growth can occur. Thus, incubation of grain growth may continue until some mechanism operates to rotate the neighbouring small grains to favourable orientations so that the growing grain can consume them. The actual mechanism for grain growth in a material of nano-sized grains remains to be verified by future extensive high-resolution transmission electron microscopy work. The apparent grain growth between 550 and 670 K may be due to the crystallization of "glassy structure" [8] in the grain boundary which is quite wide (of the order of approximately 1.5 nm), as seen in Fig. 9.

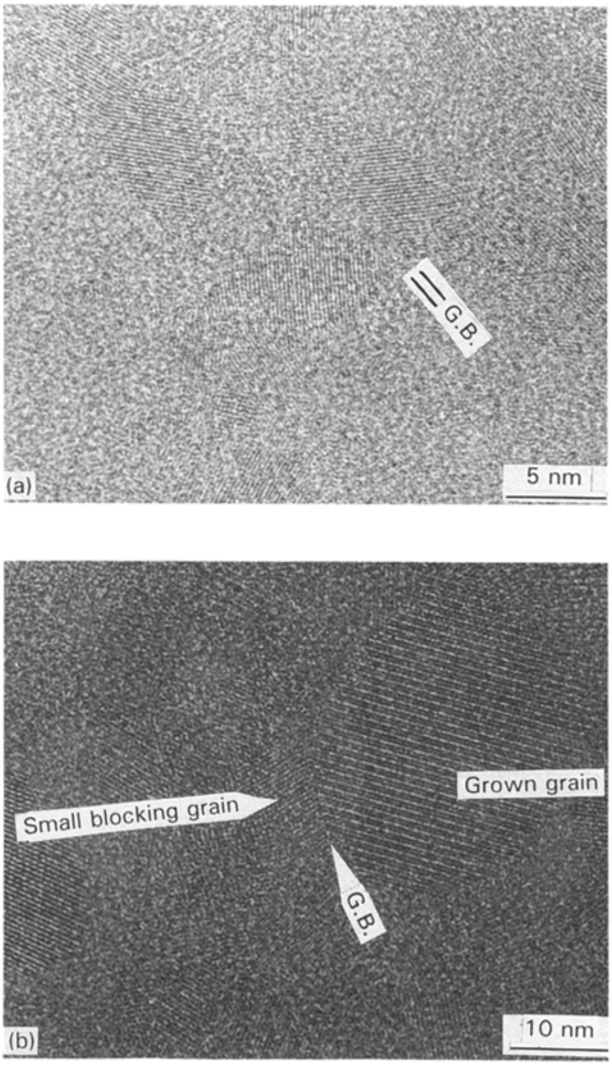

Figure 9 High-resolution transmission micrographs of $NbAl_3$ powders (a) as mechanically alloyed (1800 ks) and (b) annealed at 1373 K for 10.8 ks.

4. Conclusions

The grain growth kinetics in mechanically alloyed $NbAl_3$ powder has been studied from isochronal and isothermal annealing, with grain sizes originally of the order of a few nanometres. Grain growth occurs significantly above 973 K but ceases at 1273 K with an ultimate grain size of 69 nm. The grain growth in this temperature range is controlled by a single kinetics described by

$$\bar{D}^3 - \bar{D}_0^3 = \bar{r}'_0 t \exp(-Q/kT)$$

where $\bar{r}'_0 = 5.86 \pm 0.03 \times 10^8\ \mathrm{nm^3\ s^{-1}}$ and $Q = 162 \pm 2\ \mathrm{kJ\ mol^{-1}}$.

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