

Stability of nanocrystalline disordered NiAl synthesized by mechanical alloying

J. JOARDAR[†], S. K. PABI[‡], H.-J. FECHT[§] and B. S. MURTY^{†*}

[†] School of Materials Science and Engineering, Seoul National University,
Seoul 151-742, Kwanak-ku, South Korea

[‡] Department of Metallurgical and Materials Engineering, Indian Institute of
Technology, Kharagpur-721 302, India

[§] Materials Division, University of Ulm, Albert Einstein Alee 47, D-89081 Ulm,
Germany

[Received in final form 27 March 2002 and accepted 3 April 2002]

ABSTRACT

The thermal stability of highly disordered mechanically alloyed nanocrystalline NiAl has been evaluated. The reordering of disordered NiAl(Cr) shows extremely fast kinetics on isothermal annealing at and above 673 K, while the process is quite sluggish below this temperature. On the other hand, significant reordering in NiAl(Fe) takes place even at 573 K. A unique dependence of reordering on the grain growth of the nanophase is evident during thermal treatment. Rapid grain coarsening begins only as the absolute temperature approaches approximately $0.4T_m$, where T_m is the melting point of the aluminide.

§ 1. INTRODUCTION

Notable studies were made in recent years on the stability of ordered lattice structure of aluminides such as Ni₃Al (Zhou and Bakker 1995), FeAl (Pochet *et al.* 1995) and NiAl (Schröpf *et al.* 1994, Murty *et al.* 1996a) under high-energy ball milling. The destabilization of the ordered structures of these intermetallics was realized by the introduction of deformation-induced defects and/or the presence of ternary elements in the form of external additions and/or contamination. However, such a structure has a large stored energy owing to the high density of deformation-induced defects (Hellstern *et al.* 1989). This is in addition to the excess free energy due to the large grain-boundary volume fraction in the nanocrystalline structure (Baró *et al.* 1993), which consequently presents a highly metastable state. It is expected that such a metastable structure may instigate reversion to the ordered state and may show grain coarsening under favourable thermal conditions. The metastability of mechanically disordered nanocrystalline Ni₃Al is well documented (Hahn and Vedula 1989, Yavari 1993). These studies indicate distinctly independent stages of reordering and grain coarsening. The present work evaluates the stability of disordered, nanocrystalline NiAl produced by mechanical alloying (MA) (Murty *et al.* 1996a) in the temperature range 573–873 K, which covers the ductile-to-brittle transition temperature range of NiAl (Noebe *et al.* 1993). This work has been

* Email: bsm@metal.iitkgp.ernet.in

prompted by the pronounced influence of grain size on the ductility of brittle NiAl as observed in the ductile-to-brittle transition temperature range (Noebe *et al.* 1993).

§ 2. EXPERIMENTAL DETAILS

Highly disordered NiAl was synthesized by MA of an elemental powder blend of Ni₄₀Al₄₀Fe₂₀ and Ni₄₀Al₄₀Cr₂₀ compositions in wear-resistant cemented carbide (CC) vials with CC grinding balls, as well as from an equiatomic Ni₅₀Al₅₀ elemental blend using stainless steel (SS) grinding materials. MA was performed using powders of about 325 mesh (less than 45 µm) in a Fritsch P5 planetary ball mill under controlled conditions as mentioned elsewhere (Murty *et al.* 1996a). For comparison, MA of an equiatomic blend was also milled using CC materials. The as-milled powders were characterized by X-ray diffractometry by means of a Philips PW1710 diffractometer using Co K_α radiation. The disordered and partially ordered NiAl specimens were subjected to isothermal annealing in the temperature range 573–873 K for various periods up to 12 h. The heat-treated samples were subsequently analysed by X-ray diffractometry for an estimation of the long-range-order parameter *S* of NiAl and its average coherent domain size. *S* was determined using the relation (Guinier 1963)

$$S = \left(\frac{(I_{100}/I_{110})_{\text{obs}}}{(I_{100}/I_{110})_{\text{std}}} \right)^{1/2}, \quad (1)$$

where *I* denotes the integrated intensity with suitable background correction. Since the most intense (110) peak of NiAl overlaps with the most intense (111) peak of Ni, which persists in a minor amount even after MA for 20 h, the peaks were separated by deconvolution using Gaussian functions. However, it may be noted that this causes some degree of error in the calculated order parameter, depending on the accuracy of such fitting, especially when the intensity of superlattice reflection is very low. Therefore, the lowest *S* data within the maximum range of error are reported. The crystallite size was estimated by peak-profile analysis based on the variance method (Wilson 1962) after eliminating the instrumental broadening constituent and separating the contribution to peak broadening from lattice strain. The *S* and the crystallite sizes of the mechanically alloyed NiAl product prior to thermal treatments are given in table 1.

In addition, differential scanning calorimetry (DSC) analysis using a Perkin-Elmer DSC7 was also performed on the samples in order to provide insight into the thermal stability. DSC investigations were carried out under an argon atmosphere at various heating rates, namely 10, 20, 40 and 60 K min⁻¹.

Table 1. Characteristics of mechanically alloyed NiAl prior to isothermal treatments.

Starting blend composition	Grinding material	Contamination from milling media	Long-range-order parameter <i>S</i>	Average crystallite size (nm)
Ni ₅₀ Al ₅₀	SS	≈ 18 at.% Fe	≈ 0.15	12
Ni ₅₀ Al ₅₀	CC	—	≈ 0.50	15
Ni ₄₀ Al ₄₀ Fe ₂₀	CC	—	≈ 0.10	23
Ni ₄₀ Al ₄₀ Cr ₂₀	CC	—	≈ 0.15	19

§ 3. RESULTS AND DISCUSSION

3.1. Reordering

Figure 1(a) shows the variation in S of disordered NiAl(Cr), mechanically alloyed using CC grinding balls, with annealing duration at different annealing temperatures. A sharp rise in S occurs after isothermal holding for less than 0.5 h at and above 673 K. Longer annealing periods, however, result only in a marginal rise in S . Interestingly, at the lower temperature of 573 K, S for NiAl(Cr) shows a gradual rise with increase in the annealing time and reaches only about 0.25 after 12 h. This is in sharp contrast with mechanically alloyed NiAl(Fe), which shows a considerable rise in S within 0.5 h even at 573 K (figure 1(b)). Furthermore, the final value of S for NiAl(Fe) after annealing for 12 h at 573 K is substantially higher ($S \approx 0.4$) than in NiAl(Cr) ($S \approx 0.25$) attained under identical conditions. However, S at a higher temperature (873 K) reaches nearly the same value in both alloys ($S \approx 0.65$) after long annealing times (12 h). It may be noted that complete reordering ($S = 1.0$) could not be achieved even after long annealing at 873 K in both the alloys.

S for isothermally annealed NiAl, synthesized by MA using SS grinding materials, has lower values at any given annealing temperature in the range 573–873 K (figure 2(a)) than S for as-milled NiAl(Fe) from a $\text{Ni}_{40}\text{Al}_{40}\text{Fe}_{20}$ blend milled using CC grinding balls (figure 1(b)). Such a difference in the reordering behaviour cannot be attributed solely to the presence of ternary iron addition in the latter since a similar level of iron (about 18 at.%) has been detected in the form of contamination in the former also (table 1). It is worthwhile noting that a low value of S for NiAl is possible with a deviation from the equiatomic composition (Murty *et al.* 1996b). This may be evaluated, quite conveniently, by quantitative X-ray analysis, using a direct comparison method, of the disordered samples prior to the thermal treatment. The

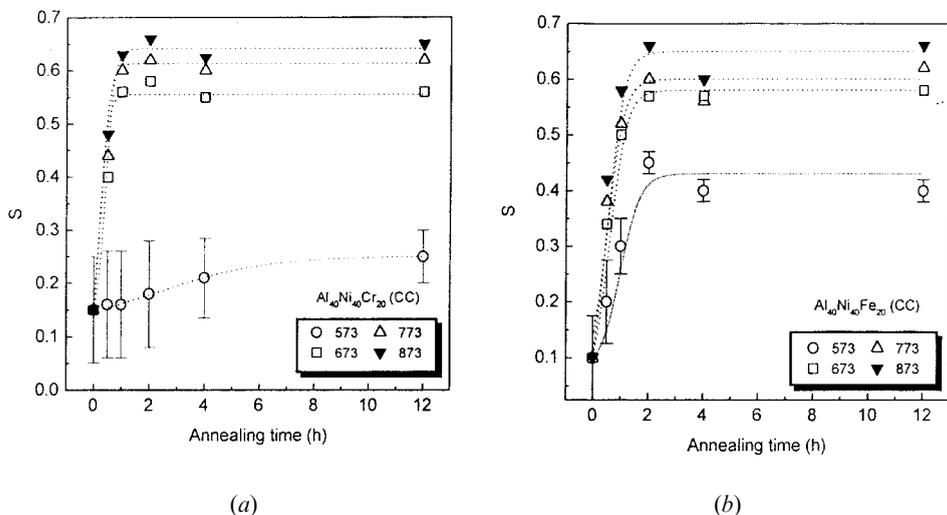


Figure 1. Variation in S for NiAl on annealing of (a) $\text{Al}_{40}\text{Ni}_{40}\text{Cr}_{20}$ and (b) $\text{Al}_{40}\text{Ni}_{40}\text{Fe}_{20}$ blends, mechanically alloyed using CC grinding balls.

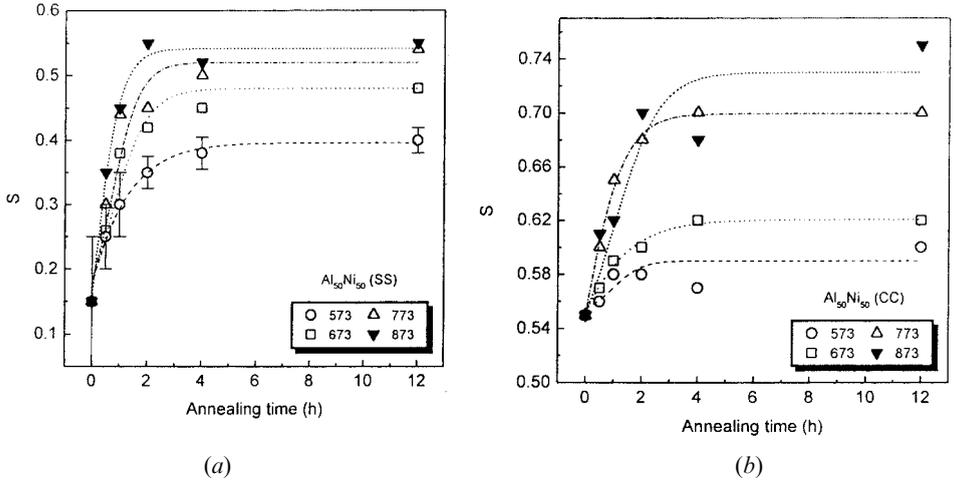


Figure 2. Variation in S during the annealing of NiAl from $\text{Al}_{50}\text{Ni}_{50}$ blends mechanically alloyed using (a) SS and (b) CC grinding materials.

volume fraction C_{Ni} of Ni and the volume fraction C_{NiAl} of NiAl are given (Cullity 1978) by

$$\frac{I_{\text{Ni}}}{I_{\text{NiAl}}} = \frac{R_{\text{Ni}}C_{\text{Ni}}}{R_{\text{NiAl}}C_{\text{NiAl}}}, \quad (2)$$

where $C_{\text{Ni}} + C_{\text{NiAl}} = 1$ and the constant R is given by the expression

$$R = \frac{1}{v^2} \left[|F^2| p \left(\frac{1 + \cos^2(2\theta)}{\sin^2 \theta \cos \theta} \right) \right] \exp(-2M). \quad (3)$$

where v is the volume of the unit cell, F is a structure factor, p is a multiplicity factor, θ is the Bragg angle and $\exp(-2M)$ is a temperature factor. Since the Bragg angles of the Ni 111 and NiAl 110 peaks differ only marginally, the temperature effect may be safely ignored (Cullity 1978). A detailed analysis based on the above expression reveals the existence of about 20% free nickel in the as-milled $\text{Ni}_{50}\text{Al}_{50}$ blend milled with SS grinding materials as against only 5% with CC grinding balls for the same composition and about 5% and 9% in $\text{Ni}_{40}\text{Al}_{40}\text{Fe}_{20}$ and $\text{Ni}_{40}\text{Al}_{40}\text{Cr}_{20}$ blends, respectively. The lower amount of unreacted nickel milled using CC grinding balls may be attributed to the involvement of higher impact energy compared with that milled with SS grinding materials. The higher level of unreacted nickel in the case of milling with SS indicates aluminium-rich NiAl and therefore shows a lower S on isothermal annealing because of a non-stoichiometric effect (Murty *et al.* 1996b). The marginally higher level of unreacted nickel (9%) in $\text{Ni}_{40}\text{Al}_{40}\text{Cr}_{20}$ possibly leads to a more aluminium-rich NiAl as against that in $\text{Ni}_{40}\text{Al}_{40}\text{Fe}_{20}$ (5%). With excess aluminium in NiAl, more vacancies are created in the nickel sublattice (Bradley and Taylor 1937), which is expected to slow down the reordering process in view of slow vacancy migration kinetics at lower temperature. This possibly explains the sluggish reordering process in NiAl(Cr) at 573 K compared with NiAl(Fe) (figure 1 (a) and (b)).

For a comparative study, the reordering process of partially disordered NiAl ($S = 0.55$) obtained by MA of an equiatomic $\text{Ni}_{50}\text{Al}_{50}$ blend with CC was analysed.

As shown in figure 2(b), S for NiAl reaches about 0.7 after isothermal holding for less than 873 K, which is the maximum temperature investigated in the present work. It is clearly evident that a higher level of S (about 0.7) is attained on reordering in the case of binary NiAl when compared with ternary NiAl(Fe/Cr). This may possibly be due to the absence of ternary elements. The inability to reach complete ordering ($S = 1.0$) even in binary NiAl on long annealing (12 h) at 873 K could be attributed to the possible inherent disorder in the nanocrystalline state as described in the next section.

3.2. Grain growth

Figure 3(a) illustrates the stability of nanostructured NiAl(Fe) at elevated temperatures. As is evident from the figure, considerable hindrance against grain coarsening is apparent at or below 673 K. Similar behaviour has also been identified in all other samples investigated in the present work. The grain-coarsening temperature T_{gc} at which significant grain growth is observed in the short time of 1 h is found to be 773 K for NiAl(Fe), which is close to $0.4T_m$ (T_m is the melting point of NiAl). It is worthwhile mentioning that an empirical relation similar to $T_{gc} \geq 0.32T_m$ has been postulated earlier for nanocrystalline pure metals (Lian *et al.* 1995). The variation in the crystallite size of the as-milled NiAl with various nominal compositions during isothermal annealing at 873 K (figure 3(b)) reveals a lower degree of coarsening in the presence of chromium. This suggests that chromium is more effective than iron in restricting the grain growth of nanocrystalline NiAl.

Figure 4(a) shows the DSC plots at different heating rates for the as-milled NiAl (using CC grinding balls) obtained from the binary equiatomic composition. An exothermic peak appears between 573 and 773 K, with the peak being at 650 K for 10 K min^{-1} (figure 4(a)). The observation that significant reordering and grain coarsening take place in this temperature range suggests that the two phenomena occur simultaneously (figures 1–3). The presence of a small amount of unreacted nickel in the as-milled sample suggests that the exothermic heat effect is also partially due to

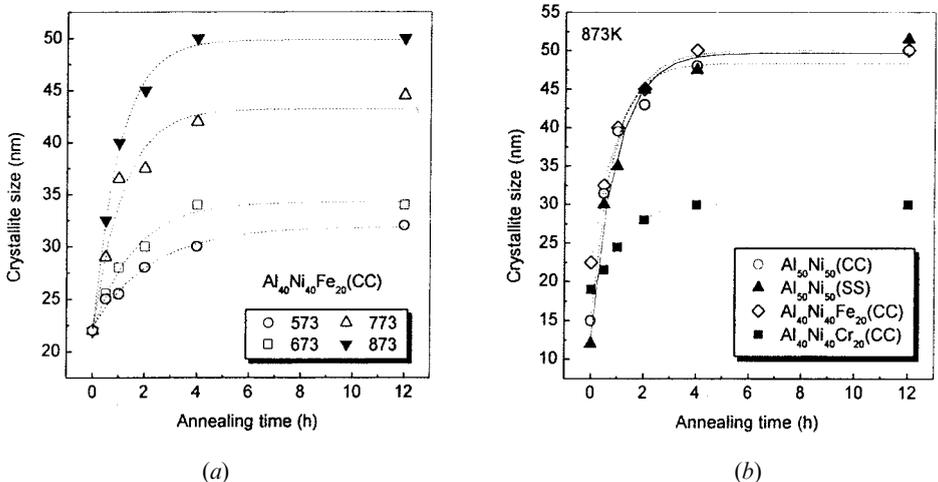


Figure 3. Variation in crystallite size during the annealing of (a) an $\text{Al}_{40}\text{Ni}_{40}\text{Fe}_{20}$ blend, mechanically alloyed using CC grinding balls and annealed in the temperature range 573–873 K and, (b) various blends annealed at 873 K after MA.

Table 2. Crystallite sizes of NiAl(Cr/Fe) ball milled with CC or SS grinding materials after isothermal holding for 12 h at different temperatures. The values within parentheses indicate the corresponding homologous temperatures T/T_m where T_m is the melting point (Hao *et al.* 1984).

Phase	Amount of Fe or Cr (at.%)	T_m (K)	Crystallite size (nm) (T/T_m)				
			RT ^a	573 K	673 K	773 K	873 K
AlNi	–	1911	15 (0.16)	32 (0.30)	35 (0.35)	48 (0.40)	50 (0.46)
AlNi ^b	18 Fe	1775	12 (0.17)	25 (0.32)	30 (0.38)	48 (0.44)	52 (0.49)
AlNi(Cr)	20 Cr	1873	19 (0.16)	21 (0.31)	20 (0.36)	26 (0.41)	30 (0.47)
AlNi(Fe)	20 Fe	1773	23 (0.17)	32 (0.32)	34 (0.38)	45 (0.44)	50 (0.49)

^aRT, room temperature (without annealing) equal to 298 K.

^bUsing SS grinding materials.

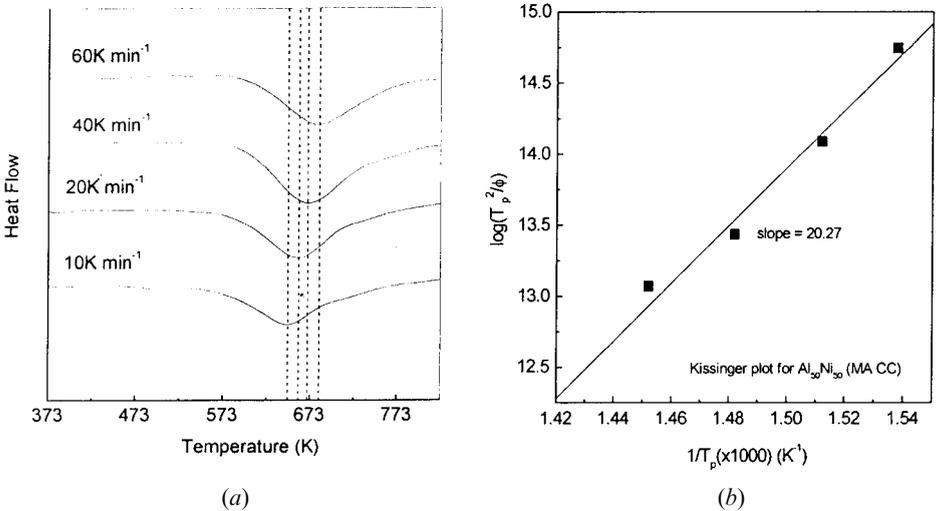


Figure 4. (a) DSC plots at different heating rates for AlNi obtained from MA of Al₅₀Ni₅₀ using CC grinding balls for 20 h; (b) Kissinger plot from the DSC data presented in (a).

the dissolution of residual nickel on heating. The extent of reordering achieved at any given temperature for a given alloy composition is proportional to the grain size in the nanocrystalline state. It may be further noted that, in spite of a significant rate of grain growth, the NiAl phase retains its nanostructure within the investigated temperature range and that S for the nanocrystalline NiAl does not reach unity within this temperature range. This clearly suggests that the large fraction of grain boundaries in the nanocrystalline NiAl significantly contributes to the disorder. The present study, therefore, finds evidence for a direct correlation between the reordering and grain coarsening. Careful observation of the present results shows that saturation of the order parameter and saturation of the grain size occur at the same time for any given annealing temperature in all samples studied. This suggests that the grain growth stops once the order parameter reaches saturation, which could possibly be due to a decrease in the diffusivity in a more ordered phase.

An effort was further made to determine the activation energy of the above process based on a thermal analysis of the DSC data using Kissinger's (1957) method. Figure 4(b) shows a Kissinger plot obtained from the shift in the peak temperature of the exothermic peak profiles, where T_p is the exothermic peak temperature at different heating rates ϕ . An activation energy of 80 kJ mol^{-1} is estimated from the slope of the plot. This energy is to be associated with two processes, namely the reordering reaction as well as the grain coarsening process.

§ 4. CONCLUSIONS

- (1) The highest S (about 0.75) during reordering treatment has been obtained in binary contamination-free NiAl at 873 K, suggesting that iron and chromium reduce the reordering kinetics.
- (2) Complete reordering could not be achieved even after a long annealing time at 873 K for any of the compositions studied. This could be attributed to an inherent disorder in the nanocrystalline state.
- (3) Considerable stability against grain growth has been observed at and below 673 K. The grain-coarsening temperature appears to be close to about $0.4 T_m$.
- (4) Grain growth appears to slow down once the order parameter reaches a saturation value at any annealing temperature in all the compositions studied.

REFERENCES

- BARÓ, M. D., SURNACH, S., MALAGELADA, J., C.-MORA, M. T., GIALANELLA, S., and CAHN, R. W., 1993, *Acta metall. mater.*, **41**, 1065.
- BRADLEY, A. J., and TAYLOR, A., 1937, *Proc. R. Soc. A*, **159**, 56.
- CULLITY, B. D., 1978, *Elements of X-ray Diffraction* (Reading, Massachusetts: Addison-Wesley), p. 411.
- GUINIER, A., 1963, *X-ray Diffraction* (San Francisco, California: Freeman), p. 259.
- HAHN, H., and VEDULA, K., 1989, *Scripta metall.*, **23**, 7.
- HAO, S. M., TAKAYAMA, T., ISHIDA, K., and NISHIZAWA, T., 1984, *Metall. Trans. A*, **15**, 1819.
- HELLSTERN, E., FECHT, H.-J., FU, Z., and JOHNSON, W. L., 1989, *J. appl. Phys.*, **65**, 305.
- KISSINGER, H. E., 1957, *Anal. Chem.*, **29**, 1702.
- LIAN, J., VALIEV, R. J., and BAUDALET, B., 1995, *Acta metall. mater.*, **43**, 4165.
- MURTY, B. S., JOARDAR, J., and PABI, S. K., 1996a, *NanoStruct. Mater.*, **7**, 691; 1996b, *J. Mater. Sci. Lett.*, **15**, 2171.
- NOEBE, R. D., BOWMAN, R. R., and NATHAL, M. V., 1993, *Int. Mater. Rev.*, **38**, 193.
- POCHET, P., TOMINEZ, E., CHAFFRON, L., and MARTIN, G., 1995, *Phys. Rev. B*, **52**, 4006.
- SCHRÖPF, H., KUHRT, C., ARZT, E., and SCHULTZ, L., 1994, *Scripta metall. mater.*, **30**, 1569.
- WILSON, A. J. C., 1962, *Proc. phys. Soc.*, **80**, 268.
- YAVARI, A. R., 1993, *Acta metall. mater.*, **41**, 1391.
- ZHOU, G., and BAKKER, H., 1995, *Prog. Mater. Sci.*, **15**, 159.