Effect of non-stoichiometry on the ordering behaviour of nanocrystalline NiAl produced by mechanical alloying

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Nanocrystalline materials are usually characterized by a large proportion of atoms, even to the extent of 50%, residing at grain boundaries and at the surface, which account for various novel properties of these materials [1, 2]. In recent years, considerable attention has been paid to the development of nanocrystalline aluminides of Ti, Fe and Ni by mechanical alloying (MA) [2–4]. Earlier modelling studies have predicted that the ductility of otherwise brittle NiAl intermetallics could be enhanced by the introduction of disorder into the aluminide [5]. In these previous studies it is suggested that a low antiphase boundary energy may activate non-conventional $\langle 1\,1\,1 \rangle$ slip in NiAl resulting in improved ductility. NiAl is known to remain ordered till its melting point [5] and earlier attempts to create disorder in it by rapid solidification were unsuccessful [5]. Kizuka *et al.* [6] report that vapour deposited NiAl is disordered, when the crystallite size is $\leqslant 5$ nm. An earlier investigation of AB-type highly ordered conventionally processed aluminides, e.g. FeAl and CoAl [7], has revealed the definite role of composition in the long range order parameter, S, showing a maximum in S at the stoichiometric composition. (AB-type alluminides represent intermetallics with stoichiometric ratio 1:1. Here B and B^A correspond to aluminium and the other element, respectively). The present paper reports the effect of non-stoichiometry on the degree of ordering in mechanically alloyed NiAl. The interrelation between S, root-mean-square (r.m.s.) strain and the crystallite size of nanocrystalline NiAl synthesized by MA is also investigated.

A wide range of elemental blends with nominal compositions of Ni_xAl_{100-x} ($x = 25$, 40, 50 and 65) were ball milled in a high energy planetary mill (Fritsch pulverisette-5). Similar experiments were also performed with powder blends of a commercial Ni–Al alloy powder ($Ni_{30}Al_{70}$) blended with Al or Ni to achieve nominal compositions of Ni_xAl_{100-x} ($x = 25$, 30, 40, 50 and 65). The initial particle size of all the powder ingredients was $<45\ \mu m$ (-325 mesh) with a purity level of $>99.5\%$. Milling was carried out for 20 h in toluene using tungsten carbide (WC) vial and WC balls of 10 mm diameter. A ball to powder weight ratio of 10:1 and a rotational speed of 300 r.p.m. were used during milling. The milled powders were characterized by X-ray diffraction (XRD) with CuK_α radiation in a Philips PW 1710 diffractometer. The crystallite size was determined from the XRD peak profile analysis by the variance method [8] after eliminating the instrumental broadening component. The S of NiAl was estimated [9]

by comparing the ratio of the intensity of the $(1\,0\,0)$ superlattice peak and the $(1\,1\,0)$ fundamental peak of NiAl with standard data.

Fig. 1 shows the formation of NiAl in the elemental blend of $Ni_{40}Al_{60}$ within 8 h of MA. The NiAl thus formed was found to be ordered, as indicated by the $(1\,0\,0)$ superlattice peak (arrowhead) in the XRD pattern. Fig. 1 also reveals the presence of some residual Ni even after 20 h of milling. Ordered NiAl formation was also observed in all other elemental blends in the compositional range 25–65 at % Ni (i.e. 25, 40, 50 and 65 at % Ni) within 8–14 h of milling, as has been reported elsewhere [10]. A marked relation between S and the composition of NiAl was observed in the present study. S was found to increase up to 40% Ni, but it dropped with further increase in the Ni content. An almost identical correlation between S and Ni content was also found in the NiAl produced by MA of the commercial alloy powder blended with Al or Ni (Fig. 2). XRD of the as-received alloy powder showed the presence of ordered NiAl, Al_3Ni_2 and Al_3Ni. The results in Fig. 2 illustrate that, irrespective of the starting ingredients of the blends, the maximum in S is manifested in the MA product
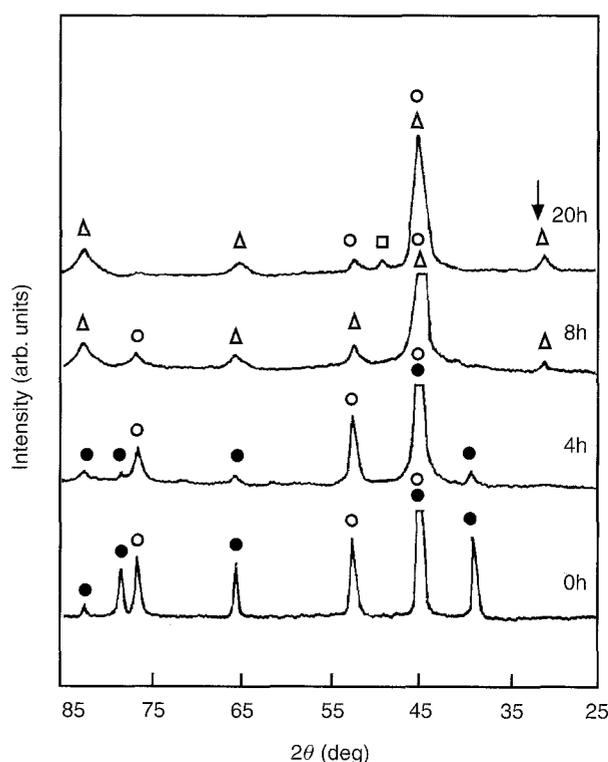

Figure 1 XRD patterns of $Ni_{40}Al_{60}$ at different milling times showing the evolution of the NiAl phase. The arrowhead indicates the $(1\,0\,0)$ superlattice reflection. ($\bigcirc$) Ni, ($\bullet$) Al, ($\triangle$) NiAl, ($\square$) WC.
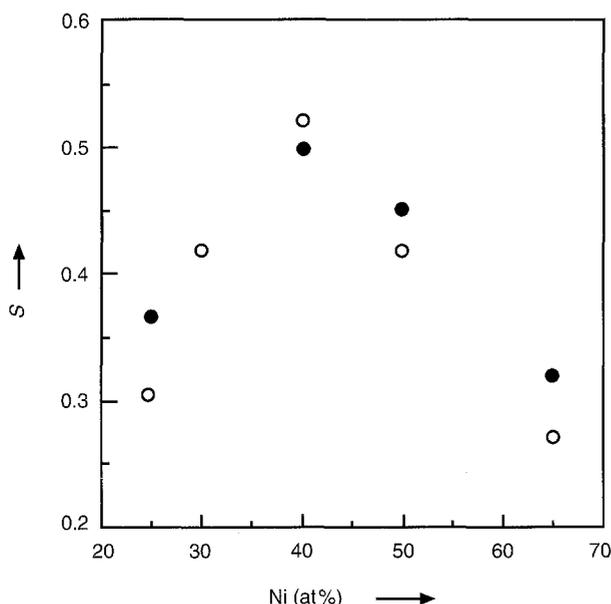
Figure 2 Variation of long range order parameter, *S*, of NiAl with composition: (○) alloy + Ni/Al, (●) Al + Ni.

Figure 3 Variation of crystallite size (□) and r.m.s. strain (■) of NiAl with composition.

between 40 and 50 at% Ni. This is contrary to the expected maximum at the stoichiometric composition of 50 at% Ni, which corresponds to the minimum of the enthalpy of formation ($\Delta H_f \sim -72\,\mathrm{kJ\,mol^{-1}}$) [5] of NiAl. The observed discrepancy may be attributed to Al depletion due to oxide formation, which causes Ni-enrichment of the alloy. This was confirmed by chemical analysis that revealed that the compositions of the alloy powders obtained by MA of elemental blends of 40 and 50 at% Ni are in fact 46.4 and 55.4 at% Ni, respectively. Thus, the maximum in *S* may be obtained for an elemental blend of nominal composition of about 45 at% Ni. Such changes in composition during milling have also been reported in earlier works [11, 12]. A similar maximum in *S* was observed earlier by Xiao and Baker [7] in conventionally prepared ordered body centred cubic (B2) FeAl at 49.8 at% Fe. The role of vacancies in Fe-rich alloys and anti-site defects in Al-rich compositions on the lowering of *S* has been suggested in the above investigation [7]. Therefore, the contribution of point defects to such behaviour in mechanically alloyed NiAl cannot be ruled out. A considerably low value of *S* for NiAl (~0.5) has been recorded in the present study, compared with the high level of *S* (~1.0) in NiAl produced by conventional methods [5]. This difference may be due to the introduction of defects by high energy ball milling as reported in earlier studies on RuAl [13]. Disordering of mechanically alloyed NiAl by the addition of alloying elements (Fe and Cr) has been reported by the present authors elsewhere [14].

A progressive decrease in NiAl crystallite size with increasing Ni content has been observed, as shown in Fig. 3. The decrease in crystallite size may be attributed to the increase in inherent brittle character of Ni-rich NiAl due to solid solution strengthening, which consequently favours fragmentation during MA. The coexistence of NiAl and Ni₃Al at higher Ni concentrations (68 at% Ni)
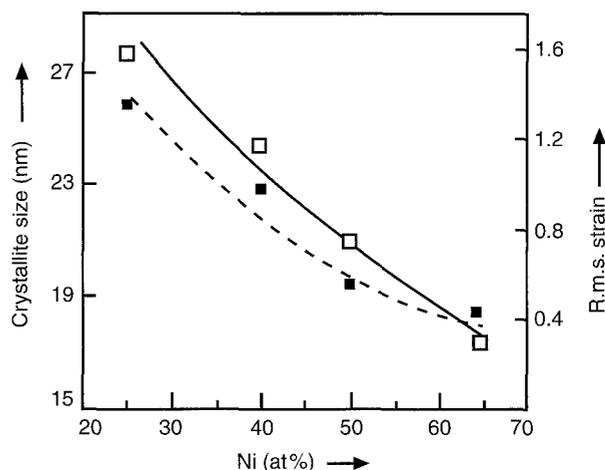
seems to promote grain refinement further (Fig. 3). It is plausible that two brittle intermetallics mutually hinder crystal growth during the welding stage of the MA process. With the appearance of disordered Ni₃Al in the milled product, a marked reduction in r.m.s. strain occurs, probably due to the ease of migration of dislocations to crystallite surfaces in the disordered structure.

Acknowledgements

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