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Synthesis of nanocrystalline NiAl over a wide composition range by mechanical alloying

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Abstract. The paper reports the synthesis of nanocrystalline NiAl by mechanical alloying of pure metal mixture and a mixture of prealloyed powder with Ni/Al. A large number of compositions have been studied to establish the phase field of NiAl in the milled state. The phase field of NiAl in the ball milled condition was found to be much wider (10–68 at.% Ni) than its equilibrium phase field (45–59 at.% Ni). The metastable equilibrium achieved by mechanical alloying was identical for a given composition irrespective of the starting ingredients. The crystallite size of NiAl reached a minimum (5 nm) at the phase boundary of NiAl/Ni_3Al.

Keywords. Nanocrystals; nickel aluminides; mechanical alloying.

1. Introduction

The high specific strength, high melting point and good oxidation resistance of NiAl have made it an advanced high temperature material (Miracle 1993; Noebe *et al* 1993). However, this aluminide lacks room temperature ductility and sufficient creep resistance. Mechanical alloying (MA) by high energy ball milling, has the potential to enhance the room temperature ductility of NiAl by bringing it to a nanocrystalline state and also improve upon its creep property by homogeneous dispersion of ceramic particles in its matrix (Benjamin 1976; Koch 1991; Gleiter 1990, 1992; Shingu 1992; Murty 1993; Das and Pabi 1996). Several reports on the synthesis of aluminides in general (Atzmon 1988; Ivanov *et al* 1990; Hwang *et al* 1992; Itsukaichi *et al* 1992, 1993; Nash *et al* 1992; Scwarz *et al* 1992; Cardellini *et al* 1994) and on NiAl in particular (Atzmon 1988; Itsukaichi *et al* 1992, 1993; Cardellini *et al* 1994) by MA evidence the dependence of the structure on the particular milling technique. The equilibrium phase field of NiAl extends over 45–59 at.% Ni. Itsukaichi *et al* (1993) studied different compositions in Al–Ni–Ti system after milling in a conventional ball mill and have reported the binary NiAl phase field to extend from 20 to 65 at.% Ni, after 500 h of milling. However, it is apparent from their report that they studied only two binary compositions, namely, $Al_{75}Ni_{25}$ and $Al_{50}Ni_{50}$ in the above composition range. Cardelline *et al* (1994), working with a Spex Mill, observed the formation of NiAl at compositions of $Al_{67}Ni_{33}$ and $Al_{50}Ni_{50}$. The present paper reports the synthesis of NiAl over a wide composition range of 10–68 at.% Ni by MA of both pure metal mixture and a mixture of an alloy powder (Al–50 wt.% Ni, i.e. $Al_{70}Ni_{30}$) and pure metals in a planetary mill.

2. Experimental

High purity Ni and Al (99·9%) are mixed in proportions of $Al_{100-x}Ni_x$ ($x = 10, 25, 40, 50, 65$ and 68) and mechanically alloyed in a planetary mill (Fritsch Purverisette-5) at 300 rpm using WC container with 10 mm diameter WC balls and a ball to powder weight ratio of 10:1. A Ni–Al alloy powder of composition Al–50 wt.% Ni ($Al_{70}Ni_{30}$) was also ball milled under identical conditions with and without the addition of Al or Ni to achieve compositions of $Al_{100-x}Ni_x$ ($x = 10, 25, 30, 40, 50, 65$ and 68). The mechanically alloyed powders were characterized by a Philips PW 1840 X-ray diffractometer with CuKα radiation at regular intervals of milling. The effective particle size was calculated from the X-ray peak broadening after separating the contribution of strain according to the standard procedure (Murty *et al* 1993).

3. Results

3.1 *Pure metal mixture of* $Al_{100-x}Ni_x$ ($x = 10$–68)

Mechanical alloying of Ni and Al powder mixture having nominal composition $Al_{90}Ni_{10}$ has not shown the formation of any new phase, in the X-ray diffraction (XRD) pattern even up to 30 h of milling (table 1). The ball milling did not cause any noticeable shift in the Al peaks, while the solubility of Al in Ni (Pearson 1974) calculated from the observed peak shift of Ni (figure 1), asymptotically reached 8·5 at.% after 30 h of milling. The particle size of Ni and Al after 30 h of milling reached about 12 and 20 mm respectively (table 1).

In the case of $Al_{75}Ni_{25}$ composition, the XRD peaks for Ni and Al were observed up to 12 h of milling, as shown in figure 2. The Ni peak shift at this stage showed that Ni has taken about 17 at.% Al in solution. After 14 h of milling, NiAl and small Al_3Ni peaks appeared in addition to Ni and Al peaks. Further milling up to 18 h resulted in the disappearance of Ni and Al peaks, while the Al_3Ni peaks also disappeared after 20 h of milling leaving behind single phase NiAl with some WC contamination (figure 2). It may be noted that the NiAl, formed during MA in this alloy as well as in all other compositions studied, was ordered as indicated by the (100) superlattice reflection shown by arrowhead in figure 2.

In $Al_{60}Ni_{40}$ the formation of single phase NiAl was complete after 16 h of milling. In contrast, in $Al_{50}Ni_{50}$ residual Ni peaks persisted at this stage which disappeared only after 24 h of milling. In both the compositions the particle size of NiAl was 10–12 nm after 30 h of milling. Figure 3 is an electron micrograph of NiAl crystallites of $Al_{50}Ni_{50}$ composition which confirms their nanocrystalline nature. $Al_{35}Ni_{65}$ also manifested similar mode of alloying as $Al_{50}Ni_{50}$ excepting that here Ni peaks disappeared after

Table 1. Phases present and their crystallite sizes after 30 h of MA.

Composition (at.% Ni)	Pure Ni and Al mixture		Alloy powder + Al or Ni	
	Phases	Crystallite size (nm)	Phases	Crystallite size (nm)
10	Ni, Al	12, 20	NiAl, Al	11, 15
25	NiAl	15	NiAl	19
30	—	—	NiAl	12
40	NiAl	12	NiAl	11
50	NiAl	9	NiAl	9
65	NiAl	5	NiAl	5
68	NiAl, Ni_3Al	5, 5	NiAl, Ni_3Al	5, 5

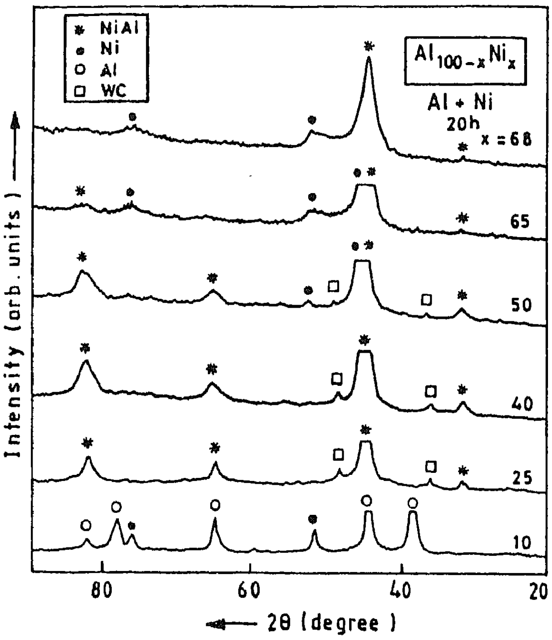

Figure 1. XRD patterns of Ni and Al mixtures of $Al_{100-x}Ni_x$ ($x = 10$–68) after 20 h of MA.

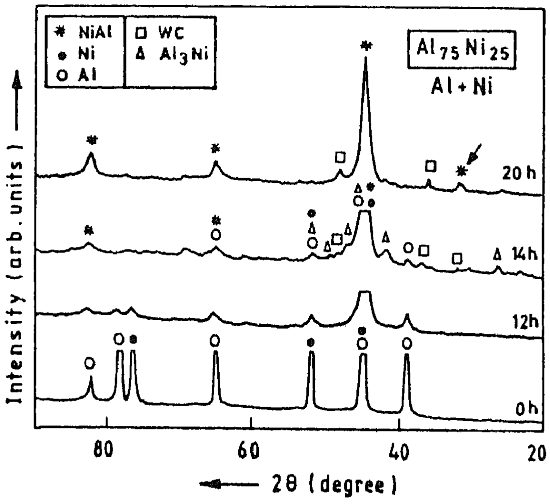

Figure 2. XRD patterns of Ni and Al mixture of $Al_{75}Ni_{25}$ at different durations of MA. The arrowhead indicates superlattice reflection (100) of NiAl.

30 h of milling. The effective particle size NiAl in this alloy, however, was very small (5 nm) after 30 h of milling (table 1).

In $Al_{32}Ni_{68}$ composition NiAl and Ni peaks were observed in the XRD pattern after 20 h of milling (figure 1). Further milling up to 30 h has resulted in the replacement of Ni with Ni_3Al (figure 4). In contrast to NiAl, no superlattice reflections of Ni_3Al could be observed indicating that the Ni_3Al phase formed was disordered (figure 4). The particle size of NiAl and Ni_3Al were about 5 nm after 30 h of milling.

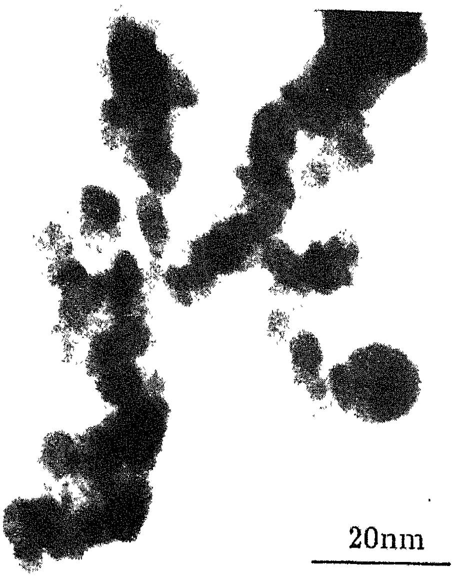

Figure 3. Electron micrograph of NiAl of $Al_{50}Ni_{50}$ composition showing its nanocrystalline nature.

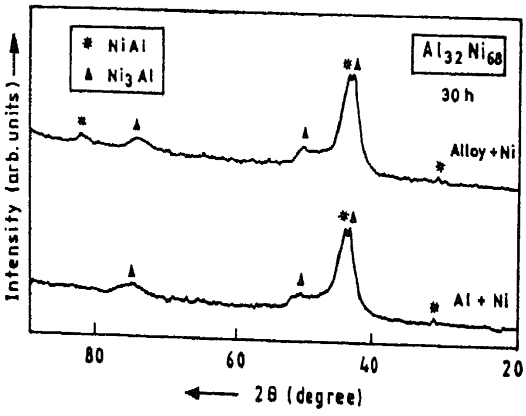

Figure 4. XRD patterns of pure metal mixture and mixture of alloy powder and Ni of $Al_{32}Ni_{68}$ after 30 h of MA.

3.2 *Ball milling of alloy powder* ($Al_{70}Ni_{30}$)

The modulation of the XRD patterns of alloy powder in course of ball milling is displayed in figure 5. The Al_3Ni, Al_3Ni_2 and NiAl phases were present in the as received alloy powder. Within 4 h of milling Al_3Ni peaks disappeared, Al_3Ni_2 followed suit after 8 h with concommittant large peak shift of the NiAl. Further milling up to 30 h retained the single phase NiAl structure with gradual reduction in particle size to 12 nm (table 1). WC contamination became significant after 30 h of milling (figure 5).

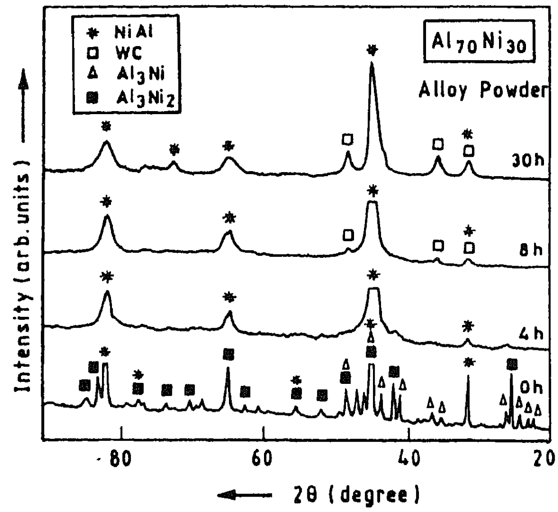

Figure 5. XRD patterns of alloy powder ($Al_{70}Ni_{30}$) at different durations of milling.

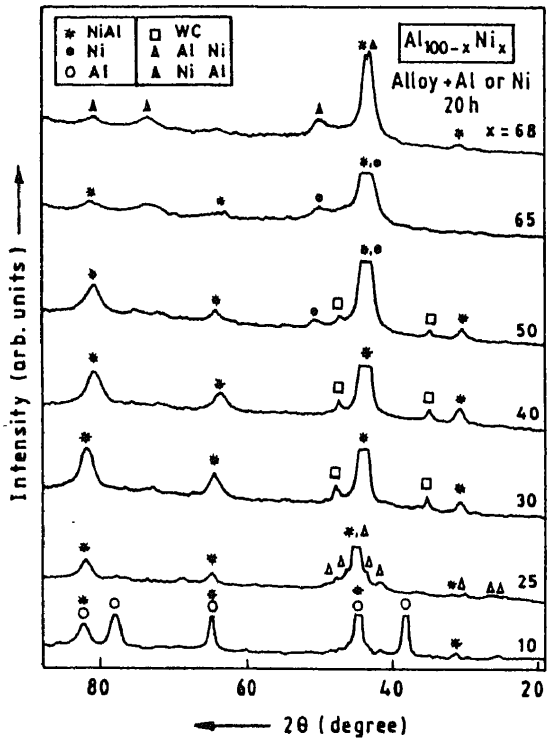

Figure 6. XRD patterns of mixture of alloy powder and Al or Ni of $Al_{100-x}Ni_x$ ($x = 10$–68) after 20 h of MA.

3.3 *Mixture of alloy powder and Al/Ni of* $Al_{100-x}Ni_x$ ($x = 10$–68)

The XRD patterns of the above mixtures of different compositions corresponding to $Al_{10-x}Ni_x$ ($x = 10, 25, 30, 40, 50, 65$ and 68) after 20h of mechanical alloying are displayed in figure 6. The results after 30 h of milling are summarized in table 1. Mechanical alloying of mixture of alloy powder and Al of $Al_{90}Ni_{10}$ composition resulted in the disappearance of Al_3Ni and Al_3Ni_2 after 16 h of milling. However, the Al and NiAl peaks persisted even after milling up to 30 h. No peak shift in Al was observed. The $Al_{75}Ni_{25}$ obtained from the mixture of alloy powder and Al showed the presence of NiAl, Al_3Ni and Al_3Ni_2 up to 16 h of milling. Milling for 20 h resulted in the disappearance of Al_3Ni_2 (figure 6). Further milling up to 30 h yielded single phase NiAl.

In the case of composition $Al_{60}Ni_{40}$, $Al_{50}Ni_{50}$ and $Al_{35}Ni_{65}$, the mode of alloying was quite similar to that of pure metal mixture (cf. figures 1, 6 and table 1). However, in $Al_{32}Ni_{68}$ composition, Ni_3Al formation was observed within 20 h of milling in the case of mixture of alloy powder and Ni, while in the case of pure metal mixture it took 30 h (cf. figures 1, 4 and 6).

4. Discussion

The as received $Al_{70}Ni_{30}$ alloy powder showed the presence of NiAl in addition to the equilibrium Al_3Ni and Al_3Ni_2 phases (figure 5), possibly due to the incomplete peritectic reaction between liquid and NiAl during the formation of Al_3Ni_2. The present results have demonstrated that Al_3Ni and Al_3Ni_2 become unstable during ball milling (figure 5). The narrow composition range of stability of these phases in comparison to NiAl under equilibrium conditions (Massalski 1990) points out that the stability of Al_3Ni and Al_3Ni_2 is more sensitive to structural defects as compared to NiAl. In consequence, the defects induced during milling seem to have made them unstable. However, the relative stabilities of Al_3Ni and Al_3Ni_2 are found to be different at different compositions (figure 6). Al_3Ni seems to be more stable at its stoichiometric composition, i.e. $Al_{75}Ni_{25}$ (figure 6), because only at this composition of pure metal mixture Al_3Ni forms on milling (figure 2). At any composition away from $Al_{75}Ni_{25}$, the stability of Al_3Ni appears to decrease sharply (figure 6). On the other hand, it may be postulated that the stability of Al_3Ni_2 may be more sensitive to the deformation induced defects than composition. This can explain why Al_3Ni_2 persists longer than Al_3Ni in course of ball milling at compositions other than $Al_{75}Ni_{25}$.

In the present study NiAl formation was observed by milling pure metal mixture in the range of 25 at.% Ni to 68 at.% Ni composition (table 1), while in the case of alloy powder mixed with Al or Ni, the NiAl phase was found to exist in the composition range of 10 at.% Ni to 68 at.% Ni. It may also be noted that the phases obtained after prolonged (30 h) milling of powder blend containing $\geqslant 25$ at.% Ni were identical, whether the starting materials were pure metal mixture or a mixture of the alloy powder and pure metal, which possibly points out that stability of ball milled NiAl originates from the thermodynamic rather than kinetic reasons.

It is evident from figures 3 and 4 that NiAl has exceptional ability to maintain its ordered structure while Ni_3Al is disordered (i.e. reaches higher energy state) under ball milled condition. This fact coupled with the exceptional ability of NiAl to accommodate defects away from equiatomic composition and nearly perfect lattice structure up to its surface (Noebe *et al* 1993) may enhance the stability of NiAl in the ball milled condition. The narrow equilibrium phase field of Ni_3Al in comparison to NiAl also suggests that the stability of ordered Ni_3Al is very sensitive to constitutional vacancies

(Gialancella *et al* 1992). The data on crystallite size in table 1 indicates that the effective particle size decreases with increase in Ni content in NiAl and reaches about 5 nm at the phase boundary between NiAl and Ni_3Al. In contrast, structural refinement is not so remarkable in $Al_{90}Ni_{10}$ alloy containing Al/NiAl boundaries. Probably, nanocrystalline mixture of the two brittle phases, NiAl and Ni_3Al, mutually hinder their agglomeration during ball milling.

5. Conclusion

In conclusion, Al_3Ni, NiAl and Ni_3Al phases have been synthesized by mechanical alloying in the present study. Al_3Ni and Al_3Ni_2 are found to be unstable while Al_3Ni_5 has not formed under the present milling conditions. The NiAl phase field has been extended by mechanical alloying from 10 to 68 at.% Ni. Both pure metal mixture and $Al_{70}Ni_{30}$ powder blended with pure Ni or Al give nearly identical product structure after prolonged ball milling (30 h). Finally, exceptional refinement of the crystallite size (5 nm) is achieved at the NiAl–Ni_3Al phase boundary.

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