Pergamon

NanoStructured Materials, Vol. 7, No. 6, pp. 691-697, 1996
Elsevier Science Ltd

0965-9773/96 $15.00 + .00

PII S0965-9773(96)00032-3

INFLUENCE OF Fe AND Cr ON THE DISORDERING BEHAVIOR OF MECHANICALLY ALLOYED NiAl

B.S. Murty, J. Joardar and S.K. Pabi

Department of Metallurgical and Materials Engineering,
Indian Institute of Technology, Kharagpur - 721302, India

(Accepted April 1996)

Abstract — *The role of Fe and Cr on the disordering behavior of mechanically alloyed nanocrystalline NiAl has been investigated. The results of milling with WC media show that NiAl is only partially ordered in the as-milled stoichiometric composition. Addition of 20 at.% of Fe or Cr results in a completely disordered NiAl structure. The change in the long range order parameter with increase in Fe or Cr is insignificant up to 8 at.%, and then it decreases rapidly to zero at concentrations higher than 16 at.%. The deformation induced defects introduced by high energy ball milling seem to contribute significantly to the disorder. Large amount of Fe contamination (~18 at.%) from stainless steel milling media has also caused complete disorder in NiAl. Contamination from steel milling media may, therefore, be useful to ductilize the otherwise brittle aluminides through the introduction of disorder.*

INTRODUCTION

Mechanical alloying (MA) by high energy ball milling (1) has been quite successful in the production of amorphous phases (2-5), nanocrystalline alloys (6,7) and intermetallics (8-10). It has also been observed to enhance solid solubility limits (7,11,12) and even to achieve alloying in liquid immiscible systems (13). Among all the intermetallics produced by MA, aluminides of Ti, Fe and Ni have received wide attention due to their potential structural engineering applications. The importance of non-equilibrium processing of these aluminides lies on the possible ductilization of these otherwise brittle intermetallics by grain refinement (14), and/or by the introduction of disorder (15). However, initial studies on rapid solidification of several ordered aluminides (16,17) failed to produce disordered structure, though grain refinement to nanoscale has been reported. In contrast, MA has been successful in disordering highly ordered Ni_3Al and Ni_3Ge (18). Investigation on vapor deposited NiAl (19) has also shown disordered NiAl formation when the crystallite size is lower than a critical value (~5 nm). Schröpt *et al.* (20) have recently reported that the long range order parameter (S) of NiAl, mechanically alloyed in stainless steel grinding media, decreases with increase in Fe content in the powder blends of nominal composition $(Ni_xFe_{1-x})Al$ where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0. However, the effect of Fe or Cr contamination from the milling media has been overlooked in this study. Nevertheless, complete disordering was achieved by them only in pure FeAl (x = 0). Preliminary experiments (21) in our laboratory have shown the formation of disordered NiAl in an elemental blend of nominal composition $Ni_{50}Al_{50}$ in stainless steel grinding media. It is known that Cr and Fe lower the ordering energy of NiAl (15). In the present paper, a detailed investigation on the role of both Fe and Cr on the disordering tendency in thermodynamically stable B2 NiAl (ΔH_f = -72 kJ/mol) is presented. The effect of contamination from milling media on the creation of disorder is also highlighted in this report.

EXPERIMENTAL

High purity (> 99.5%) Ni, Al and Fe or Cr elemental powder blends with initial particle size of < 45 μm (-325 mesh) were mechanically alloyed in a high energy planetary ball mill (Fritsch pulverisette-5) at a milling speed of 300 rpm. Various elemental blends of composition $Ni_{50-x}Al_{50-x}M_{2x}$ (where x = 0, 1, 4, 8 and 10; M = Fe or Cr) have been studied in the present investigation. MA was performed with WC milling media in toluene medium at a ball to powder weight ratio of 10:1. In order to study the influence of Fe and Cr contamination, an elemental blend of $Ni_{50}Al_{50}$ composition has also been milled in stainless steel and hardened chrome steel vials under similar milling conditions. The evolution of different phases and their ordering behavior was analyzed by x-ray diffraction (XRD) in a Philips 1710 diffractometer using CuKα radiation. Refinement of the crystallite size and strain induced during MA was determined from the variance analysis of XRD peak profile of the most intense peak (110) of NiAl, after eliminating instrumental peak broadening contribution (22). The S of NiAl was calculated (23) by comparing the ratio of observed (100) superlattice peak intensity to the (110) fundamental peak intensity with that from the standard XRD data file for NiAl. The extent of contamination in stainless steel and hardened chrome steel media was estimated by means of a Shimadzu AA670 atomic absorption spectroscope.

RESULTS AND DISCUSSION

The XRD patterns in Figure 1 show evidence for the formation of NiAl during MA of $Ni_{50}Al_{50}$ blend in WC media within 8 h of milling. Some residual Ni was found at this stage and the amount gradually diminished to an insignificant level as the milling continued up to 20 h. In all the ternary compositions studied, *i.e.* $Ni_{50-x}Al_{50-x}M_{2x}$ (x = 1, 4, 8, 10 and M = Fe or Cr), the alloying characteristics manifested by the time of evolution of NiAl structure and disappearance of residual Ni were similar to binary $Ni_{50}Al_{50}$. However, the extent of disorder in ternary systems was markedly different from that in the binary $Ni_{50}Al_{50}$ milled in WC milling media. Figure 2 shows the XRD patterns of ball milled (20 h) ternary compositions containing various levels of Fe or Cr. It is evident that the intensity of (100) superlattice reflection of NiAl structure gradually decreases with increase in Fe or Cr content, and ultimately the peak disappears in $Ni_{40}Al_{40}Fe_{20}$ and $Ni_{40}Al_{40}Cr_{20}$ compositions milled for 20 h. The variation of S of NiAl with increase in Fe or Cr content in milled (20 h) ternary blends (Figure 3) shows that the effect of either ternary addition on S is similar. The decrease in the S with the increase in Fe or Cr in NiAl lattice is in agreement with the large reduction in antiphase boundary energy predicted by various earlier models (24, 25).

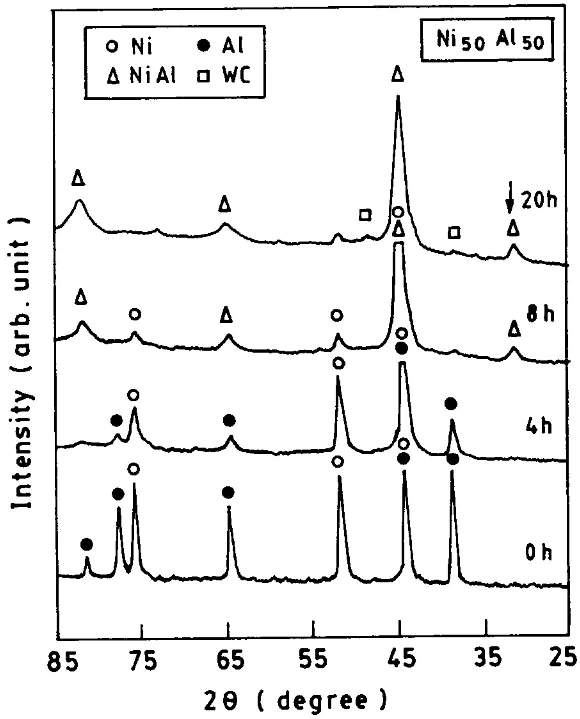

Figure 1. XRD patterns of $Ni_{50}Al_{50}$ at different milling times, showing the evolution of NiAl phase (arrow-head indicates (100) superlattice reflection).

It is of interest to note that the S of NiAl produced in the present study by MA for 20 h is considerably lower (~ 0.5), even in the absence of ternary additions, as compared to that reported earlier (~ 0.8) (20) for 100 h of milling in stainless steel media at a speed of 170 rpm. It is apparent that the higher milling speed (300 rpm) and higher density of WC media used in the present study impart a higher impact energy, which can induce a larger concentration of crystal defects resulting in more disorder in NiAl. Possibly for the same reason, a completely disordered NiAl could be produced in the present study with just 20 at.% of Fe, whereas the earlier investigation (20) reports complete disorder only in binary FeAl. It may be pointed out that NiAl produced by the conventional ingot metallurgy route is almost perfectly ordered (S~1) (26) and the critical temperature of ordering lies in proximity of liquidus temperature (15).

In order to study the effect of Fe and Cr contamination from milling media, MA of $Ni_{50}Al_{50}$ has been carried out in hardened chrome steel as well as stainless steel media under identical conditions. The NiAl produced in chrome steel media after 20 h of milling was found to be ordered with S = 0.48, which is quite close to that obtained by milling with WC media (0.5) as shown in Table 1. In contrast, the NiAl synthesized in stainless steel milling media was found to be completely disordered after 20 h of milling.

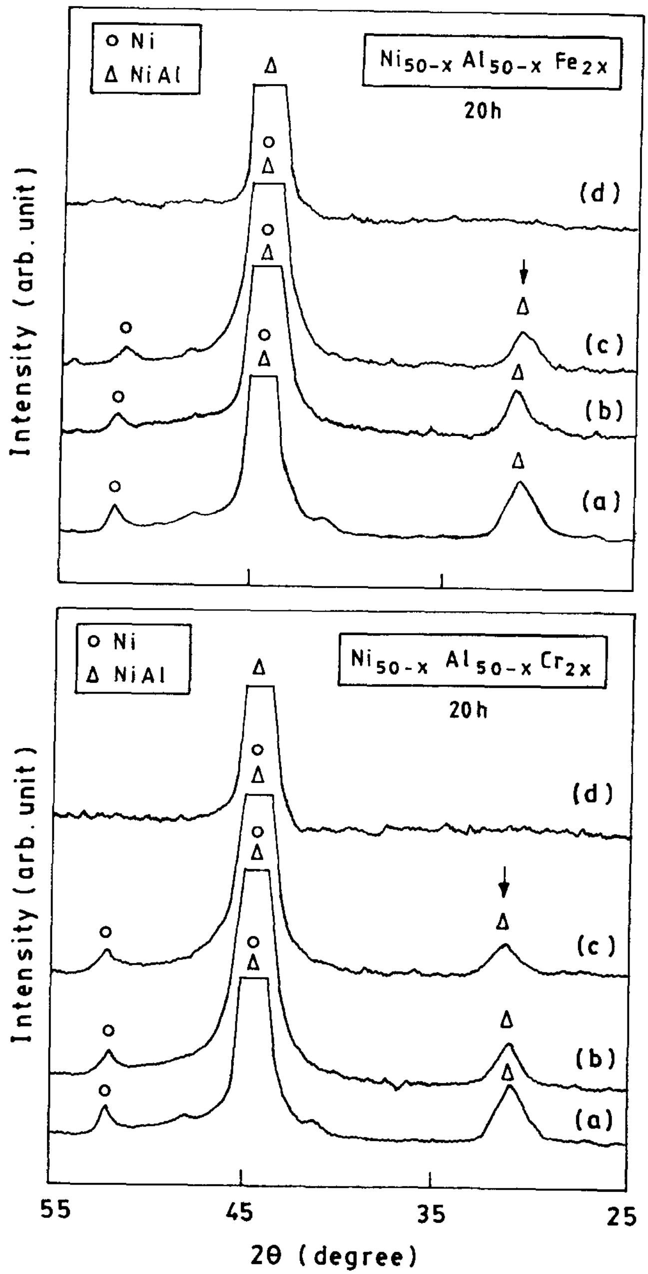

Figure 2. XRD patterns of mechanically alloyed $Ni_{50-x}Al_{50-x}M_{2x}$ (M= Fe or Cr) after 20 h of milling with (a) x = 0, (b) x = 1, (c) x = 4 and (d) x = 10 (arrow-head indicates (100) superlattice reflection).

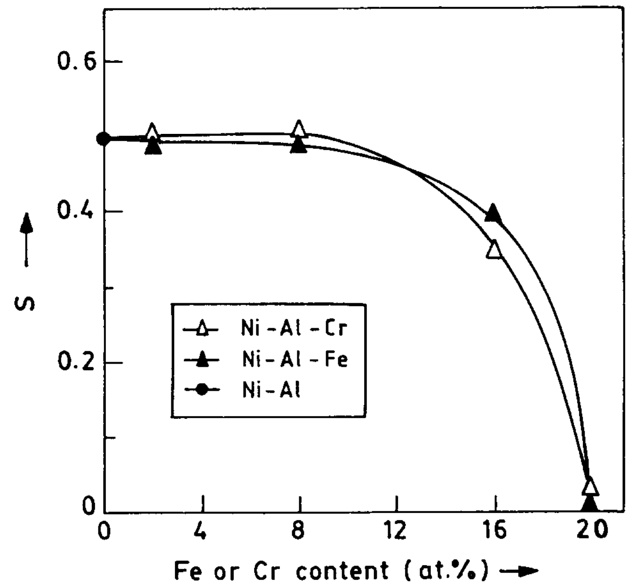

Figure 3. Variation of S of NiAl with Fe or Cr addition.

The level of Fe contamination as determined by the atomic absorption spectroscopy for the above two cases (Table 1) shows a much higher value (~18 at.%) for stainless steel milling media, as compared to that from hardened chrome steel media (~5 at.%). The difference in the contamination levels in these two cases can be attributed to the higher wear resistance of hardened chrome steel, as compared to that of stainless steel. Thus, it is quite evident that a minimum Fe content of about 18 at.% is essential to induce a complete disorder in NiAl, and the higher impact energy in WC media, as compared to that in steel media, does not significantly affect this amount under the present milling conditions.

TABLE 1
Level of Fe Contamination in NiAl Synthesized in $Ni_{50}Al_{50}$ and its S after Milling for 20 h at 300 rpm in Different Milling Media

Milling Media	S	Fe Concentration (at.%)
WC	0.5	---
Chrome Steel	0.48	5
Stainless Steel	0	18

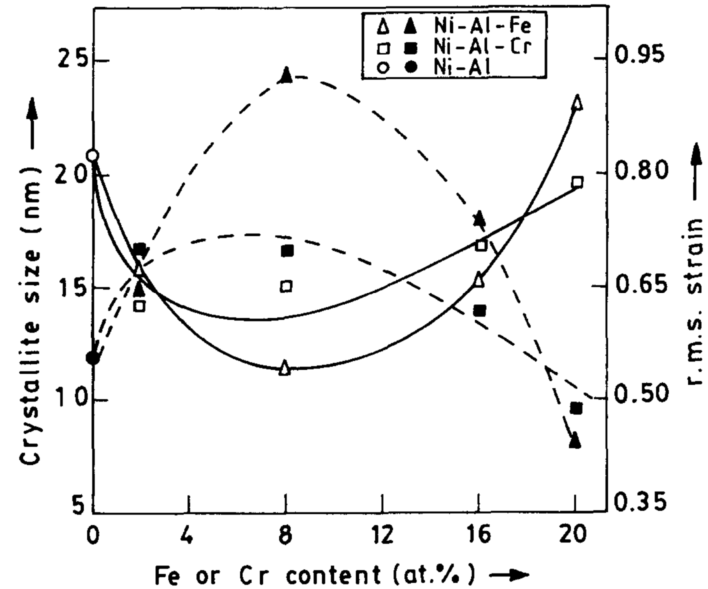

Figure 4. Change in crystallite size (open symbols) and r.m.s. strain (closed symbols) of NiAl with the variation in Fe or Cr concentration.

The crystallite size after prolonged milling (20 h) in WC medium shows a minimum at ~8 at.% Fe in Ni-Al-Fe system, whereas in Ni-Al-Cr system a minimum is observed at ~6 at.% Cr (Figure 4). The r.m.s. strain in these samples was found to reach a peak value at the corresponding minimum in crystallite sizes. This behavior probably indicates an initial solid solution strengthening due to ternary addition that enhances the brittle character of the intermetallic. In consequence, the fragmentation stage would dominate over the cold welding process in the course of MA, leading to a decrease in crystallite size. The increase in r.m.s. strain could be caused by the dislocation pileups during deformation as observed in other systems (6). The subsequent coarsening after a critical level of alloying addition indicates predominance of cold welding over fragmentation. This apparently suggests an increase in ductility of the intermetallic at these higher levels of ternary addition. It is interesting to note a simultaneous sharp drop in S in these compositions (Figure 3). The drop in the r.m.s. stain at higher alloying addition could be due to the stress relaxation associated with disordering. This is in agreement with investigation (15) on conventionally processed NiAl in Ni-Al-Fe and Ni-Al-Cr systems, where triggering of additional slip systems has been observed through introduction of disorder. Finally, it is apparent from the present study that Fe contamination from steel milling media may be useful to enhance the ductility of Ni-aluminides by promoting disorder.

CONCLUSIONS

1. NiAl synthesized by MA of $Ni_{50}Al_{50}$ blend was partially ordered (S = 0.5), possibly due to large amount of deformation induced defects generated under the present milling conditions.

2. Ternary alloying additions of Fe and Cr to the extent of ~20 at.% to NiAl can induce complete disorder in the latter.

3. A minimum in crystallite size and a maximum in lattice strain observed with the increase in Fe and Cr additions to NiAl can be attributed to the interplay between solid solution strengthening and disordering.

4. Large amount of Fe contamination from the milling media can significantly contribute to the extent of disorder obtained by high energy ball milling of nickel aluminides.

ACKNOWLEDGMENTS

The authors are grateful to the Department of Science and Technology, Government of India for financial support in carrying our this work via Grant No. III.4(23)/92-ET. BSM is thankful to ISIRD and AR and DB for financial assistance.

REFERENCES

1. J.S. Benjamin, Metall. Trans. 1, 2943 (1970).
2. A.E. Ermakov, E.E. Yurichikov and V.A. Barinov, Phys. Met. Metall. 52, 50 (1981).
3. C.C. Koch, O.B. Cavin, C.G. McKamey and J.O. Scarbrough, Appl. Phys. Lett. 43, 1017 (1983).
4. B.S. Murty, S. Ranganathan and M. Mohan Rao, Mater. Sci. Eng. A149, 231 (1992).
5. B.S. Murty, M.D. Naik, S. Ranganathan and M. Mohan Rao, Mater. Forum 16, 19 (1992).
6. E. Hellstern, H.J. Fecht, Z. Fu and W.L. Johnson, J. Appl. Phys. 65, 305 (1989).
7. B.S. Murty, M. Mohan Rao and S. Ranganathan, Nanostruct. Mater. 3, 459 (1993).
8. M. Atzmon, Phys. Rev. Lett. 64, 487 (1990).
9. T. Itsukaichi, M. Umemoto, and J.G.C. Moreno, Scripta Metall. Mater. 29, 583 (1993).
10. A. Calka and A.P. Radlinski, J. Less Common Metals 161, L23 (1990).
11. C.C. Koch, in *Processing of Metals and Alloys*, ed., R.W. Cahn, p. 193, VCH Publications, New York (1991).
12. B.S. Murty, K.H.S. Singh and S.K. Pabi, Bull. Mater. Sci. 19, 1 (1996).
13. A.R. Yavari, Mater. Sci. Eng. A179/180, 20 (1994).
14. R. Birringer, Mater. Sci. Eng. A117, 33 (1989).
15. R.D. Noebe, R.R. Bowman and M.V. Nathal, Int. Mater. Rev. 38, 193 (1993)
16. J.A. Hornton and C.T. Liu, Acta Metall. 33, 2191 (1985).
17. K. Sumiyama, Y. Hirose and Y. Nakamura, Phys. Stat. Solidi. (a) 114, 693 (1989).
18. K. Aoki, X.M. Wang, A. Memezawa and T. Masumoto, Mater. Sci. Eng. A179/180, 390 (1994).
19. T. Kizuka, N. Mitarai and N. Tanaka, J. Mater. Sci. 29, 5599 (1994).
20. H. Schröpt, C. Kuhrt, E. Artz and L. Schultz, Scripta Metall. Mater. 30, 1569 (1994).
21. K.H.S. Singh, M. Tech. Thesis, Indian Institute of Technology, Kharagpur, India (1995).
22. G.K. Williamson and W.H. Hall, Acta Metall. 1, 22 (1953).
23. A. Guinier, *X-ray Diffraction*, p. 259, Freeman, San Francisco (1963).
24. T. Hong and A.J. Freeman, Phys. Rev. B. 43, 6446 (1991).
25. S. Guha, P.R. Munro and I. Baker, Mater. Sci. Eng. A131, 27 (1991).
26. T. Hughes, E.P. Lautenschlager, J.B. Cohen and J.O. Brittain, J. Appl. Phys. 42, 3705 (1971).