NANOCRYSTRALLINE PHASES IN Cu-Ni, Cu-Zn AND Ni-Al SYSTEMS BY MECHANICAL ALLOYING

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Abstract- Nanocrystalline solid solutions and intermetallic phases in Cu-Ni (enthalpy of formation, $\Delta H_f \approx 2kJ/mol$), Cu-Zn($\Delta H_f \approx -8kJ/mol$) and disordered Ni_3Al ($\Delta H_f = -42kJ/mol$) in Ni-Al system formed during mechanical alloying (MA) through conventional continuous diffusive mixing mechanism. In contrast, nanocrystalline ordered NiAl ($\Delta H_f = -72kJ/mol$) and $NiAl_3$ ($\Delta H_f = -39kJ/mol$) formed during MA by a discontinuous additive mixing mechanism. Ternary additions of Fe and Cr made the as-milled NiAl phase disordered, and the alloying mechanism changed over to the continuous diffusive mode. ©1997 Acta Metallurgica Inc.

INTRODUCTION

The formation of nanocrystalline phases during mechanical alloying (MA), to a large extent, is dictated by the inherent deformation characteristics of the ingredients (1). The accompanying alloying mechanism, on the other hand, evoked contradictory view points (2). In order to draw a comprehensive hypothesis, the present study of the formation of solid solutions and intermetallics in Cu-Ni, Cu-Zn and Ni-Al systems has been undertaken. Here, the enthapy of formation (ΔH_f) ranges from slightly positive in Cu-Ni to highly negative in Ni-Al (3,4). The contribution of ternary alloying addition of Fe and Cr on the mode of formation of NiAl phase during MA has also been highlighted.

EXPERIMENTAL

The MA was performed by means of a high energy planetary ball mill (Fritsch pulverisette-5) at a rotational speed of 300 rpm and ball to powder weight ratio of 10:1. The binary blends studied include $Cu_{100-x}Ni_x$(x=5,10,50,70,90), $Cu_{100-x}Zn_x$(x=30,50,65,85) and $Ni_{100-x}Al_x$ (x=21,25,50,65,75). Milling was usually carried out with elemental powders of ≤ 45 μm size for 20h. In some experiments a conventionally prealloyed Ni-30at.%Al powder containing NiAl, Ni_2Al_3 and $NiAl_3$ phases were used as a ingredient. The various stages of phase formation during MA were monitored by x-ray diffraction (XRD) analysis of the milled products using CuKα radiation. The average crystallite sizes were estimated from the XRD peak profile analysis by variance method (5).

RESULTS AND DISCUSSION

MA of elemental blends for 20h resulted in the formation of solid solutions and intermetallic phases in the binary Ni-Al and Cu-Zn systems (Table 1), which did not change with further milling. In Ni-Al system, the metastable equilibrium after MA was the same in all the composition studied irrespective of the starting ingredients being either blends of pure metals or a prealloyed powder blended with Ni or Al. The extent of crystallite refinement in the Ni-Al intermetallics has been quite significant when compared to Cu-Zn intermetallics (Table 1), possibly due to the relatively brittle nature and higher melting points of the Ni-Al intermetallics as compared to the various intermetallic phases of Cu-Zn system. The finest of the Ni-Al intermetallics was the NiAl phase (~5 nm) at the $NiAl$-Ni_3Al metastable phase boundary ($Ni_{65}Al_{35}$), while the smallest crystallite size in Cu-Zn system was observed for α phase in $Cu_{50}Zn_{50}$, which is close to the metastable α-β phase boundary composition. This suggests restricted growth of the crystallites due to the mutual hindrance in the two-phase product. Ball milling of Cu-Ni system resulted relatively coarse crystallite size (~30 nm) after 20h of milling, possibly due to the ductile nature of the fcc solid solution.

It is of interest to note, that the disordered NiAl produced by MA of ternary blends, viz., $Ni_{40}Al_{40}(Fe/Cr)_{20}$, was coarser when compared to the partially ordered binary NiAl synthesised under identical conditions (Table 1). Such difference in the extent of refinement can be attributed to the change in the deformation behaviour in NiAl due to the introduction of disorder, which is expected to trigger additional silp sytems (4).

In Cu-Ni system, the lattice parameter of Cu and Ni gradually approached each other with the progress of milling indicating a continuous diffusive mode of mixing (6,7) during MA (Fig. 1). This has occured in spite of the existence of a thermodynamic driving force for segregation. Similar mixing phenomenon has been reported earlier in immiscible Fe-Cu system (8), which is known to have an even higher ΔH_{mix} ($\approx 10 kJ/mol$) (3).

MA of all the Cu-Zn blends lead to the formation of Zn-rich phases, viz. ε and γ, in the initial stages of milling as reported earlier (9). Prolong milling resulted a gradual

TABLE 1

Phase Formation Charecteristics in the Different Systems during MA

System	Composition	Product phases	C.S. (nm)	Product nature	$\Delta H_{f/mix}$ kJ/mol	Alloying mechanism
Cu-Ni	$Cu_{50}Ni_{50}$	Cu(Ni) Ni(Cu)	~30	DO	~2	CD
Cu-Zn	Cu-15 to 50at.%Zn	α	20	DO	-8	CD
	Cu-65 to 85at.%Zn	ε	85	DO	-9	CD
Ni-Al	Ni-21 to 25 at%Al	$NiAl_3$	~20	O	-39	DA
	$Ni_{50}Al_{50}$	NiAl	10	O	-72	DA
	$Ni_{75}Al_{25}$	Ni_3Al	~8	DO	-42	CD
Ni-Al-Fe/Cr	$Ni_{40}Al_{40}Fe_{20}$	NiAl	25	DO	-	CD
	$Ni_{40}Al_{40}Cr_{20}$	NiAl	19	DO	-	CD

C.S.= Crystallite size after 20h MA; O = Ordered; DO = Disordered
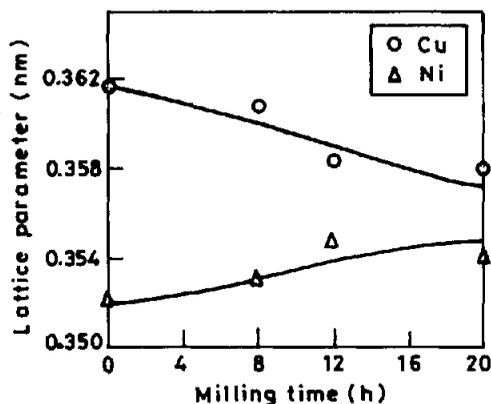CD= continuous diffusive; DA= Discontinuous additive

Fig.1. Variation of lattice parameter of Cu and Ni with the progress of MA.
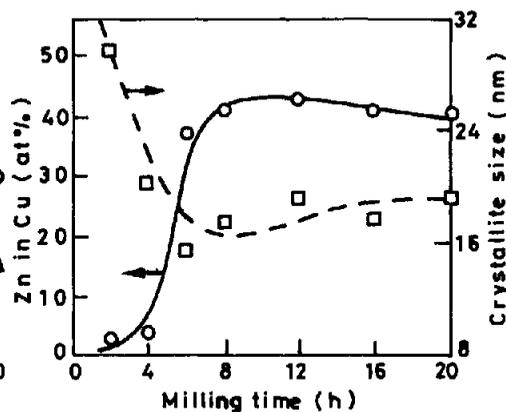
Fig.2. Amount of Zn in Cu (o) and crystallite size of Cu (□) vs. milling time.

transformation to near-to-equilibrium phases. The formation of Zn-rich phases in the early stages of MA in preference to Cu-rich phases even in the Cu-rich blends, can be attributed to the higher diffusivity of Cu in Zn at the milling temperature (~ 473K) than vice-versa (9,10). The diffusion of Zn into Cu becomes appreciable (Fig. 2) only after Cu reaches nanocrystalline state (~20 nm).

Studies on Ni-Al system revealed contrasting alloying behaviour in Ni_3Al as against NiAl and $NiAl_3$. In the as-milled state the Ni_3Al was disordered. The lattice parameter of Ni gradually changed to Ni_3Al, which evidenced continuous diffusive mixing mechanism. On the other hand, insignificant shift in Ni or Al peaks occured prior to the formation of ordered binary NiAl and $NiAl_3$, and the crystallite size of the intermetallic at the onset of its formation was equal to the sum of the individual crystallite sizes of the two elements at that stage (Fig.3(a)).This suggests a discontinuous additive mode of mixing (7) in ordered NiAl and
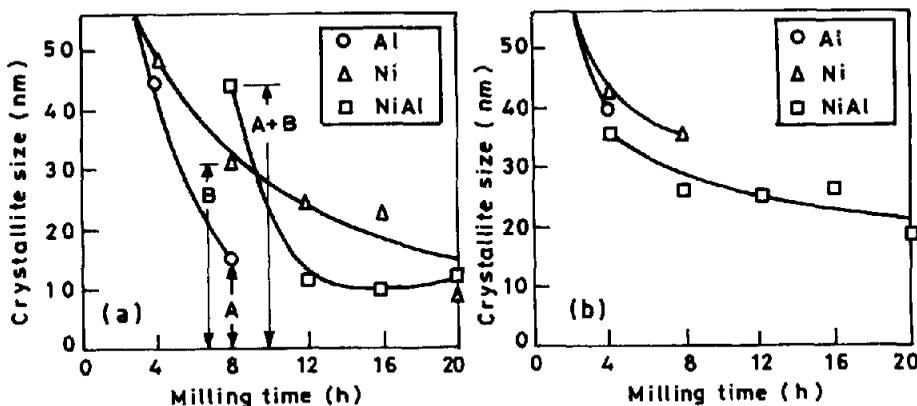

Fig.3. Crystallite size of the constituents in course of MA, indicating (a) discontinuous additive mixing in $Ni_{50}Al_{50}$ and (b) gradual diffusive mixing in $Ni_{40}Al_{40}Cr_{20}$ composition.

NiAl$_3$, which are known to have highly negative values of ΔH_f (Table 1). While Ni$_3$Al can be easily disordered due to its low ordering energy ($\Delta H_{ord}\approx-8$kJ/mol), disordered NiAl cannot be produced even by splat cooling (4). The present results of MA suggest that discontinuous additive mode of mixing is favoured only when the ΔH_f is highly negative (≤-40kJ/mol), as well as, the product phase is ordered. When the as-milled NiAl was made disordered by the ternary additions of Fe or Cr, the alloying mechanism changed from discontinuous additive mixing mode to continuous diffusive mode (cf. Fig. 3(b)).

CONCLUSIONS

1. During MA nanocrystalline solid solutions/intermetallic phases in Cu-Ni and Cu-Zn system form by the continuous diffusive mixing mechanism.

2. In Ni-Al system, the nanocrystalline disordered Ni$_3$Al also forms by continuous diffusive mixing. In contrast, NiAl and NiAl$_3$ remained ordered in the as-milled state, and the alloying took place by the discontinuous additive mode of mixing. Ternary addition of Fe and Cr resulted in the formation of disordered NiAl by continuous diffusive mixing mechanism.

ACKLOWLEDGEMENT

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