AI-Mn-Ni (Aluminum-Manganese-Nickel)

V. Raghavan

The previous review/compilation of the data on this ternary system by [1993Suz] and [1995Vil] presented a liquidus projection, partial isothermal sections, and vertical sections from the work of [1938Kos] and [1944Ray]. Among the more recent work included in the above are an isothermal section at 1000 °C from [1977Cha] and a vertical section along the Ni₃Al-Ni₃Mn join from [1988Wac]. Recently, [1993Pov] found an Al-rich ternary phase at the composition Mn_3NiAl_{10} and [1998Kai] determined three isothermal sections at 1100, 1000, and 850 °C.

Binary Systems

The Al-Mn phase diagram [1996Liu, 1996Mul] depicts a number of complex intermediate phases in the Al-rich region, see [Massalski2] for a list. In the midatomic region, two intermediate phases with simple structures are present: the body-centered-cubic (bcc) phase (called γ) and the close-packed-hexagonal (cph) phase (ε). The homogeneity ranges of these phases determined by [1996Liu] and [1996Mul] are significantly different from each other. The phase boundaries of [1996Liu] are used tentatively in this review. The Al-Ni phase diagram [1993Oka] shows five intermediate phases: NiAl₃ (D0₁₁, Fe₃C-type orthorhombic), Ni₂Al₃ (D5₁₃-type hexagonal), NiAl (B2, CsCl-type cubic, also denoted β), Ni₅Al₃ (Ga₃Pt₅-type orthorhombic), and Ni₃Al ($L1_2$, AuCu₃-type cubic; also denoted γ'). The Mn-Ni phase diagram given in [Massalski2] appears to be obsolete. Figure 1 shows the Mn-Ni diagram computed by [2005Guo], incorporating the recent experimental results of [2002Din]. [2002Din] investigated 47 binary alloys in the composition range of 25 to 70 at.% Ni, using annealing times of 3 to 7 months between 850 and 500 °C. They found only the B2 and $L1_0$ structures around the midcomposition. Likewise, [1995Col] found only the $L1_0$ structure between 565 and 500 °C. In Fig. 1, MnNi (HT) (HT stands for hightemperature form; denoted aMnNi by [2005Guo]) has the B2, CsCl-type cubic structure. MnNi (LT) (denoted βMnNi by [2005Guo]) has the $L1_0$, AuCu-type tetragonal structure. Two other Mn-rich compounds are known: MnNi₂ and $MnNi_3$ ($L1_2$, AuCu₃-type cubic).

Ternary Phases

[1995Vil] listed six ternary phases. Two of these are based on the binary B2 phase and two others are based on the binary L_1 phase. AlMnNi₂ is a Heusler-type phase that forms through a second-order transition from B2 below 500 °C [1998Sut]. Mn₆Ni₂Al₃₁ is orthorhombic, space group *Cmcm* [Pearson3]. The structure of Mn₃NiAl₁₀ found by [1993Pov] is not known. It appears to be related to Fe₃NiAl₁₀ and could be a quasi-crystalline phase, see [2005Rag] for a brief discussion. It crystallizes at 980 °C and forms tie-lines at 900 °C with *B*2 and Mn_2Al_3 phases [1993Pov].

Isothermal Sections

With starting metals of Al (99.7 wt.%), Mn (99.9 wt.%), and Ni (99.9 wt.%), [1998Kai] induction melted alloys under Ar atm. Diffusion couples were annealed at 1100 to 850 °C for 2 to 336 h. The microstructures were examined by optical microscopy. The compositions of coexisting phases after the diffusion anneal were measured by the energy dispersive x-ray spectroscopy. Combining their experimental results with those of [1994Jia], [1998Kai] constructed three isothermal sections at 1100, 1000, and 850 °C, which are redrawn in Fig. 2 to 4 to agree with the accepted binary data.

At 1100 °C (Fig. 2), (Ni), liquid and (γ Mn) are present along the Mn-Ni axis. The B2 phase exists over a large composition range. A two-phase equilibrium exists between B2 and the disordered bcc phase based on δ Mn. With increasing Al, the two-phase region disappears and the B2-A2 boundary becomes second order. At higher Al contents, the cph ε phase of the Al-Mn system becomes stable and forms tie-lines with B2. At still higher Al concentration, the intermediate phase γ (bcc) of the Al-Mn system is stable. Its relation to the B2 phase was not clarified by [1998Kai]. At



Fig. 1 Mn-Ni computed phase diagram [2005Guo]



Fig. 2 Al-Mn-Ni isothermal section at 1100 °C [1998Kai]



Fig. 3 Al-Mn-Ni isothermal section at 1000 °C [1998Kai]



Fig. 4 Al-Mn-Ni isothermal section at 850 °C [1998Kai]



Fig. 5 Al-Mn-Ni partial isothermal section at 700 °C [1997Mul]

1000 °C (Fig. 3), a continuous solid solution exists between (Ni) and γ Mn. The δ Mn-based bcc phase recedes into the ternary region. It forms tie-lines with B2 at lower Al contents. A second-order boundary is seen at higher Al values. Comparing Fig. 3 with the isothermal section at 1000 °C determined by [1977Cha] (not shown here), it is seen that the B2 phase extends to much lower Al contents in Fig. 3. [1977Cha] found evidence for the disordered bcc phase near the Al-Mn γ phase and suggested a two-phase field between γ (bcc) and B2. At 850 °C (Fig. 4), a continuous B2 solid solution exists between NiAl and MnNi (HT) [2001Tan]. Both (γMn) (fcc) and (βMn) (A13) form tie-lines with B2. The homogeneity region of B2 has shrunk at 850 °C, especially along the line joining the Mn corner to NiAl. In Fig. 2 to 4, the (Ni)-Ni₃Al (γ') and γ' -B2 tie-lines are from [1994Jia].

[1997Mul] found that the addition of Ni to nearequiatomic Al-Mn alloys does not result in the stabilization of the metastable τ (AuCu-type tetragonal) phase found in the Al-Mn binary system. A partial isothermal section determined by [1997Mul] at 700 °C (Fig. 5) depicts tie-lines between (β Mn) and a magnetic phase κ (in the absence of τ). The κ phase, so called by [1961Tsu], has the *B*2 structure with a = 0.2970 to 0.2920 nm [1961Tsu]. Its relation to NiAl (*B*2) (or to the martensitic tetragonal form of NiAl) is not known.

The Ni₃Al-Ni₃Mn Vertical Section

Using starting metals of Al (99.99 wt.%), Mn (99.995 wt.%), and Ni (99.999 wt.%), [1988Wac] induction melted under Ar atm 15 alloys in the composition range of Ni₇₅Mn_xAl_{25-x} ($0 \le x \le 25$). The phase equilibria were investigated by the magnetothermal analysis. The vertical section constructed by [1988Wac] along the Ni₃Al-Ni₃Mn



Fig. 6 Al-Mn-Ni vertical section along the Ni₃Al-Ni₃Mn join

join is redrawn in Fig. 6. This is in good agreement with the section determined by [1986Mas], employing metallography, x-ray diffraction, and electron probe microanalysis. However, the same section redetermined by [1998Gom] using neutron diffraction and calorimetry contradicts the above results. [1998Gom] depicted it as a pseudobinary section between two continuous solid solutions γ and γ' , ignoring the known peritectic solidification of Ni₃Al (γ'). Figure 6 includes the lattice parameter measurements of γ' ($L1_2$) at room temperature by [1986Mas].

References

- **1938Kos:** W. Koster and E. Gebhardt, The System Nickel-Manganese-Aluminum, *Z. Metallkd.*, 1938, **30**, p 291-293, in German
- **1944Ray:** G.V. Raynor, The Constitution of the Aluminum-Rich Aluminum-Manganese-Nickel Alloys, *J. Inst. Metals, London*, 1944, **70**, p 507-529
- 1961Tsu: I. Tsuboya and M. Sugihara, The New Magnetic Phase in Manganese-Aluminum-Nickel System, J. Phys. Soc. Japan, 1961, 16, p 1257
- 1977Cha: D.J. Chakrabarti, Phase Stability in Ternary Systems of Transition Elements with Aluminum, *Metall. Trans. B*, 1977, 8B, p 121-123
- **1986Mas:** N. Masahashi, T. Takasugi, O. Izumi, and H. Kawazoe, The Phase Diagram of the Pseudobinary Ni₃Al-Ni₃Mn System, *Z. Metallkd.*, 1986, **77**(4), p 212-217
- **1988Wac:** E. Wachtel, M. Vincent, and B. Predel, Constitution and Magnetic Properties of $Ni_{75}Mn_xAl_{25-x}$ ($0 \le x \le 25$). Part 1.

Section II: Phase Diagram Evaluations

Paramagnetic Properties, Z. Metallkd., 1988, **79**(4), p 252-258, in German

- **1993Oka:** H. Okamoto, Al-Ni (Aluminum-Nickel), J. Phase Equilib., 1993, **14**(2), p 257-259
- **1993Pov:** K.B. Povarova, S.A. Flinn, and S.B. Maslenkov, Phase Equilibria Involving β -Phase in Ni-Al-Me (Me = Co, Fe, Mn, Cu) Systems at 900 and 1100 °C, *Metally*, 1993, (1), p 191-205, in Russian; TR: *Russ. Metall.*, 1993, (1), p 156-169
- **1993Suz:** T. Suzuki, Aluminum-Manganese-Nickel, *Ternary Alloys*, G. Petzow and G. Effenberg, Ed., Vol. 7, VCH Verlagsgesellschaft, Weinheim, Germany, 1993, p 84-99
- **1994Jia:** C.C. Jia, K. Ishida, and T. Nishizawa, Partition of Alloying Elements between γ (*A*1), γ' (*L*1₂) and β (*B*2) Phases in the Ni-Al Base Systems, *Metall. Mater. Trans. A*, 1994, **25A**, p 473-485
- 1995Col: B.R. Coles, The Equiatomic Region of the Mn-Ni System, J. Phase Equilib., 1995, 16(2), p 108-109
- 1995Vil: P. Villars, A. Prince, and H. Okamoto, Al-Mn-Ni, *Handbook of Ternary Alloy Phase Diagrams*, Vol. 4, ASM International, 1995, p 3989-3999
- **1996Liu:** X.J. Liu, R. Kainuma, H. Ohtani, and K. Ishida, Phase Equilibria in the Mn-Rich Portion of the Binary System Mn-Al, *J. Alloys Compd.*, 1996, **235**, p 256-261
- **1996Mul:** C. Muller, H.H. Stadelmaier, B. Reinsch, and G. Petzow, Metallurgy of the Magnetic τ-Phase in Mn-Al and Mn-Al-C, *Z. Metallkd.*, 1996, **87**(7), p 594-597

- **1997Mul:** C. Muller, H.H. Stadelmaier, B. Reinsch, and G. Petzow, Constitution of Mn-Al-(Cu, Fe, Ni or C) Alloys Near the Magnetic τ Phase, *Z. Metallkd.*, 1997, **88**(8), p 620-624
- **1998Gom:** V.I. Gomankov, S.M. Tretyakova, E.V. Monastyrskaya, and L.E. Fykin, Structural Diagrams of Quasi-Binary Alloys Ni₃Fe-Ni₃Al, Ni₃Mn-Ni₃Al and Ni₃Mn-Ni₃Ga, *Metally*, 1998, (6), p 104-108, in Russian; TR: *Russ. Metall.*, 1998, (6), p 125-131
- **1998Kai:** R. Kainuma, M. Ise, K. Ishikawa, I. Ohnuma, and K. Ishida, Phase Equilibria and Stability of the *B2* Phase in the Ni-Mn-Al and Co-Mn-Al Systems, *J. Alloys Compd.*, 1998, **269**, p 173-180
- **1998Sut:** Y. Sutou, I. Ohnuma, R. Kainuma, and K. Ishida, Ordering and Martensitic Transformations of Ni₂AlMn Heusler Alloys, *Metall. Mater. Trans. A*, 1998, **29A**, p 2225-2227
- **2001Tan:** Y. Tan, T. Shinoda, Y. Mishima, and T. Suzuki, Stoichiometry Splitting of β Phase in Ni-Al-Mn, Ni-Al-Co and Ni-Al-Fe Ternary Systems, *Mater. Trans*, 2001, **42**(3), p 464-470
- 2002Din: L. Ding, P.F. Ladwig, X. Yan, and Y.A. Chang, Thermodynamic Stability and Diffusivity of Near-Equiatomic Ni-Mn Alloys, *Appl. Phys. Lett.*, 2002, 80(7), p 1186-1188
- 2005Guo: C. Guo and Z. Du, Thermodynamic Optimization of the Mn-Ni System, *Intermetallics*, 2005, 13, p 525-534
- 2005Rag: V. Raghavan, Al-Fe-Ni (Aluminum-Iron-Nickel), J. Phase Equilib. Diffus., 2005, 26(1), p 70-71