Aluminium – Magnesium – Nickel

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Literature Data

The Al-Mg-Ni system has been examined first in 1924. From the results of thermal analysis and metallography [1924Fus] concluded that the Mg_2Al_3-$NiAl_3$ section is a quasibinary one. In [1934Fus] Fuss presented a projection of the liquidus surface in the Al-Mg_2Al_3-NiAl area showing the lines of double saturation on it. An essential conclusion was that a ternary eutectic equilibrium does not exist in the shown part of the phase diagram. However, [1943Mon, 1944Cha, 1952Han] reported that the invariant eutectic equilibrium exists and is reached independently of the heat treatment and the compositions of the phases, except of solid solution of magnesium in aluminium. These conclusions were based on experimental data obtained on as-cast, annealed and rapidly quenched alloys; their liquidus projection is essentially different from the one without the eutectic invariant reaction proposed by [1934Fus].
[1968Var] studied the structure of the Al-Mg-Ni alloys containing 1 at.% Ni in as-cast conditions. The intermetallic phases were separated by high temperature centrifuging and identified by X-ray analysis. As a result, the $AlNi_3$ and Al_3Ni_2 phases were found to coexist in the alloy 1Ni-15Mg-Al (at.%).
The assessment by [1993Pri] took into account the works published up to 1991 and deals with the Al-rich part of the Al-Mg-Ni ternary system Al-Mg_2Al_3-Ni_2Al_3.
Later experimental investigations of the ternary system were mainly motivated by the search for new hydrogen storage materials [1998Ori, 2000Yua, 2000Aiz, 2001Gua]. From these studies information on new ternary phases was obtained. [1998Ori] examined the crystallization processes of Al_x-Mg_{1-x}-Ni alloys which were mechanically alloyed under an argon atmosphere by planetary ball milling for 4800 min at ambient temperature and 400 rpm. A phase with CsCl type crystal structure was found in alloys with x = 0.3-0.5 and an amorphous phase formed in alloys with $x < 0.2$.
[2000Yua] synthesized Al_x-Mg_{2-x}-Ni (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) samples by a diffusion method. Mixtures of pure Al, Mg and Ni powders were grounded and pressed into pellets under a pressure of 30 MPa. The pellets were annealed at 540-550°C for 4 h and then cooled to room temperature. X-ray diffraction and SEM were applied to investigate their structure. A new phase of cubic crystal structure of Ti_2Ni type was observed in the alloys, so that with x = 0.5 only this phase and a trace of magnesium were detected.
[2001Gua] studied by X-ray diffraction the Ni_2Mg_3Al ternary alloy prepared from components of purities better than 99.95 % by compacting their mixtures at 30 MPa and annealing them at 540-550°C for 4 h under 0.5 MPa argon atmosphere. The composition of the alloy prepared coincided actually with the composition of a new ternary phase found in the investigation by [2000Yua]. [2001Gua] confirmed the existence of the new ternary phase with the composition Ni_2Mg_3Al and studied its crystal structure using more advanced X-ray techniques. As a result, the crystal structure of Ni_2Mg_3Al is established and described in more detail than by [2000Yua].
[1991Han] addressed some thermodynamic aspects on the effect that aluminium has on magnesium-nickel melts in presence of $3.8\text{-}8.6\cdot10^{-4}$ mass% O. [2000Aiz] studied the effect that the substitution of aluminium by magnesium has on hydrogen absorption by a material based on Mg_2Ni.

Binary Systems

The Al-Mg and Al-Ni binary phase diagrams are accepted from [2003Luk], [2003Sal], respectively. The Mg-Ni phase diagram is accepted from [1998Jac]. [1998Jac] made a thermodynamic assessment of the Mg-Ni binary system using the experimental characteristics of the Mg-Ni phase diagram from [1934Hau, 1978Bag, 1996Mic]. The calculated phase diagram is in a good agreement with the data from the experimental works.

Solid Phases

The data on the relevant binary phases and ternary phases are listed in Table 1. [2001Gua, 2000Yua] found a new ternary phase of the same stoichiometry Ni_2Mg_3Al; its structural characteristics were determined and described in detail by [2001Gua]. Although the ternary alloys in both works were prepared in similar ways the Ni_2Mg_3Al alloy contained different phases in addition to the main phase. Therefore, the real composition of the compound discovered may differ slightly from the stoichiometry given.

Invariant Equilibria

At least one invariant four-phase equilibrium and one three-phase equilibrium exist in the ternary Al-Mg-Ni system, besides those in the adjacent binary systems. They are in the region of aluminium-rich alloys. The four-phase equilibrium is of eutectic type at a temperature of 449°C [1944Cha, 1952Han, 1993Pri]. The temperature of this equilibrium is assumed to be only by a few tenths of a degree lower than that of the binary eutectic reaction $L \rightleftharpoons (Al)+Mg_2Al_3$, which is reliably confirmed to be at 450.5°C [2003Luk]. Type and temperature of the three-phase equilibrium however are not firmly established. It is of eutectic nature and takes place at a temperature between 449°C, where the four-phase eutectic equilibrium is, and 552°C the melting temperature of Mg_2Al_3, [1993Pri].
The characteristics of the three-phase and four-phase invariant equilibria are listed in Table 2 according to [1993Pri] with some correction for (Al) and Mg_2Al_3 by [2003Luk]. Concentration of the liquid phase in the three-phase invariant equilibrium is not determined exactly, but taking into account its temperature it is reasonable to assume that it is close to the $L \rightleftharpoons (Al)+Mg_2Al_3$ eutectic point in the binary Al-Mg system. The reaction scheme for Al-$NiAl_3$-Mg_2Al_3 region is shown in Fig. 1.

Liquidus, Solidus Surfaces

The liquidus surface of the Al-Mg-Ni system in Al-NiAl-Mg_2Al_3 region is shown in Fig. 2. It is a compilation of the [1952Han, 1934Fus] data with some corrections drawn out that the next phase after $NiAl_3$ should be Ni_2Al_3 [1968Var, 2003Sal], rather than $NiAl_2$, as it was proposed by [1934Fus]. The temperatures of the invariant reactions in the binary systems are also corrected to comply with the today accepted binary descriptions of Al-Mg and Al-Ni [2003Luk, 2003Sal].
The projection of the solidus surface in the Al-Mg_2Al_3-$NiAl_3$ region is plotted in Fig. 3 based on [1952Han] with correction of the (Al) and Mg_2Al_3(**β**) homogeneity ranges by [2003Luk]. The Ni_2Al_3 homogeneity range is shown according to [2003Sal].

Temperature – Composition Sections

The statement of [1924Fus] that the Mg_2Al_3-$NiAl_3$ section is a quasibinary one can not be correct taking into account the Al-Ni phase diagram [2003Sal], where the $NiAl_3$ phase is shown to form by a peritectic reaction from liquid and Ni_2Al_3.
Figure 4 gives the $NiAl_3$-Mg_2Al_3 temperature-concentration cut constructed using the data of [1952Han, 2003Luk, 2003Sal]. It can be considered as a quasibinary one only below the solidus temperature of the alloys and within the part between Mg_2Al_3 and the edge of the Ni_2Al_3 primary crystallization surface including the e_3 eutectic point.

Thermodynamics

[1991Han] showed that activity of magnesium, containing $3.8\text{-}8.6 \cdot 10^{-4}$ % O, in nickel melts increases with addition of aluminium.

Notes on Materials Properties and Applications

$NiMg_2$ base alloys with addition of Al are candidate materials for hydrogen storage [1998Ori]. Electrochemical capacity and live-cycles of $NiMg_{2-x}Al_x$ ($0 \leq x \leq 0.5$) alloys during absorption and desorption of hydrogen increase with increasing Al contents, due to increasing amount of the Ni_2Mg_3Al

phase in the alloy [2000Yua]. Addition of Al also improves the corrosion resistance of the $NiMg_{2-x}Al_x$ alloys to a certain degree because an Al_2O_3 oxide layer forms on the surface. The corrosion rate of the ternary alloys is lower than that of $NiMg_2$ [2000Yua]. Chemical modification of $NiMg_2$ alloy by aluminium addition to ($NiMg_{1.8}Al_{0.2}$) is expected not to lead to significant reduction of onset temperature for hydrogen absorbing [2000Aiz].
$NiMg_{1-x}Al_x$ phase with CsCl type crystal structure dissolves hydrogen interstitially without any structural transformation [1998Ori].

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas2] dissolves 0.01 at.% Ni at 639.9°C [2003Sal] and 18.6 at.% Mg at 450.5°C [2003Luk]
		a = 410.5 ± 0.8	at 445°C in the alloy with 18.6 at.% Mg [1952Han]
(Mg) < 650	*hP*2 $P6_3/mmc$ Mg	a = 320.94 c = 521.07	at 25°C [Mas2] dissolves 11.5 at.% Al at 436°C [2003Luk] and < 0.04 mol% Ni at 500°C [1934Hau]
(Ni) < 1455	*cF*4 $Fm\bar{3}m$ Cu	a = 352.40	at 25°C [Mas2] dissolves 20.2 at.% Al at 1385°C [2003Sal] < 0.2 mol% Mg at 1100°C [1998Jac]
γ, $Mg_{17}Al_{12}$ < 458	*cI*58 $I\bar{4}3m$ αMn	a = 1054.38	at 41.4 at.% Al [V-C2] 39.5 to 51.7 at.% Al [2003Luk]
β, Mg_2Al_3 < 452	*cF*1168 $Fd\bar{3}m$ Mg_2Al_3	a = 2816 - 2824	60 to 62 at.% Al [2003Luk]
ε, $Mg_{23}Al_{30}$ 410 - 250	*hR*159 $R\bar{3}$ $Mn_{44}Si_9$	a = 1282.54 c = 2174.78	56.3 at.% Al [2003Luk]
$NiAl_3$ < 856	*oP*16 *Pnma* $NiAl_3$	a = 661.3 ± 0.1 b = 736.7 ± 0.1 c = 481.1 ± 0.1	[2003Sal]
Ni_2Al_3 < 1138	*hP*5 $P\bar{3}m1$ Ni_2Al_3	a = 402.8 c = 489.1	36.1 to 39.8 at.% Ni [2003Sal]
Ni_3Al_4 < 702	*cI*112 $Ia\bar{3}d$ Ni_3Ga_4	a = 1140.8 ± 0.1	[2003Sal]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
NiAl < 1651	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 286.0	42.1 to 71.3 at.% Ni [2003Sal]
Ni_5Al_3 < 723	*oC*16 *Cmmm* Pt_5Ga_3	*a* = 753 *b* = 661 *c* = 376	63 to 68 at.% Ni at 63 at.% Ni [2003Sal]
Ni_3Al < 1372	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 356.77	75.4 to 76.3 at.% Ni [2003Sal]
$NiMg_2$ < 759.31	*hP*18 $P6_222$ $NiMg_2$	*a* = 520.5 ± 0.1 *c* = 1320 ± 6	[V-C2] [1998Jac]
Ni_2Mg < 1147.60	*hP*24 $P6_3/mmc$ Ni_2Mg	*a* = 482.4 ± 0.2 *c* = 1582.6	66.2 at.% at 759.31°C to 67.34 at.% Ni at 1095.28°C [1998Jac], [V-C2]
* $NiMg_{1-x}Al_x$	*cP*2 $Pm\bar{3}m$ CsCl		In alloys with $x = 0.3 - 0.5$ prepared by mechanical alloying [1998Ori]
* $NiMg_{1-x}Al_x$	amorphous phase		In the alloys with $x < 0.2$ prepared by mechanical alloying [1998Ori]
* Ni_2Mg_3Al	*cF*96 $Fd\bar{3}m$ derived from Ti_2Ni	*a* = 1154.74 ± 0.02	[2001Gua]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Al	Mg	Ni
$L \rightleftharpoons Mg_2Al_3 + NiAl_3$	449 - 552	e_3	L	~60	~40	?
			Mg_2Al_3	61	39	0
			$NiAl_3$	75	0	25
$L \rightleftharpoons Mg_2Al_3 + NiAl_3 + (Al)$	449	E	L	64.6	34.6	0.8
			Mg_2Al_3	61	39	0
			$NiAl_3$	75	0	25
			(Al)	81.39	18.6	0.01

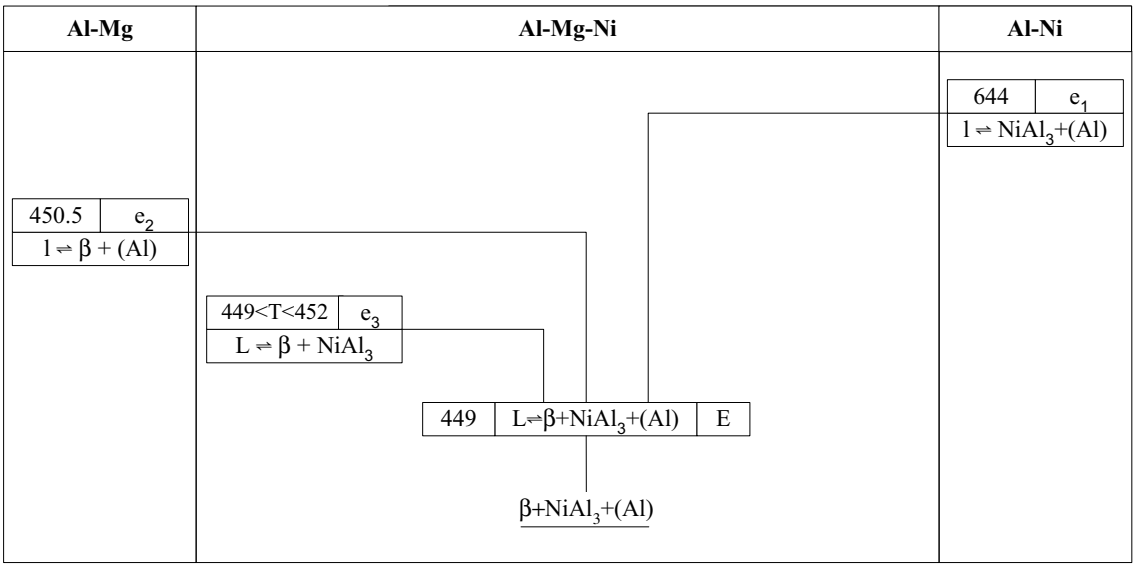

Fig. 1: Al-Mg-Ni. Reaction scheme in the partial Al-Mg_2Al_3-$NiAl_3$ system

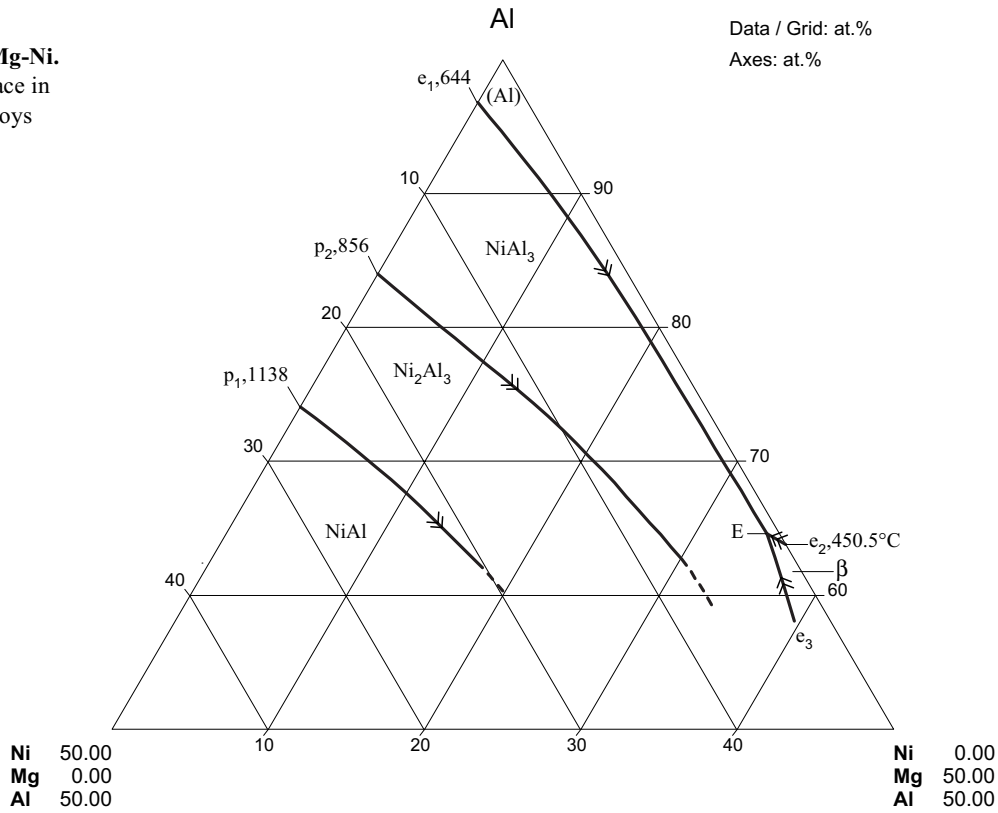

Fig. 2: Al-Mg-Ni. Liquidus surface in the Al-rich alloys

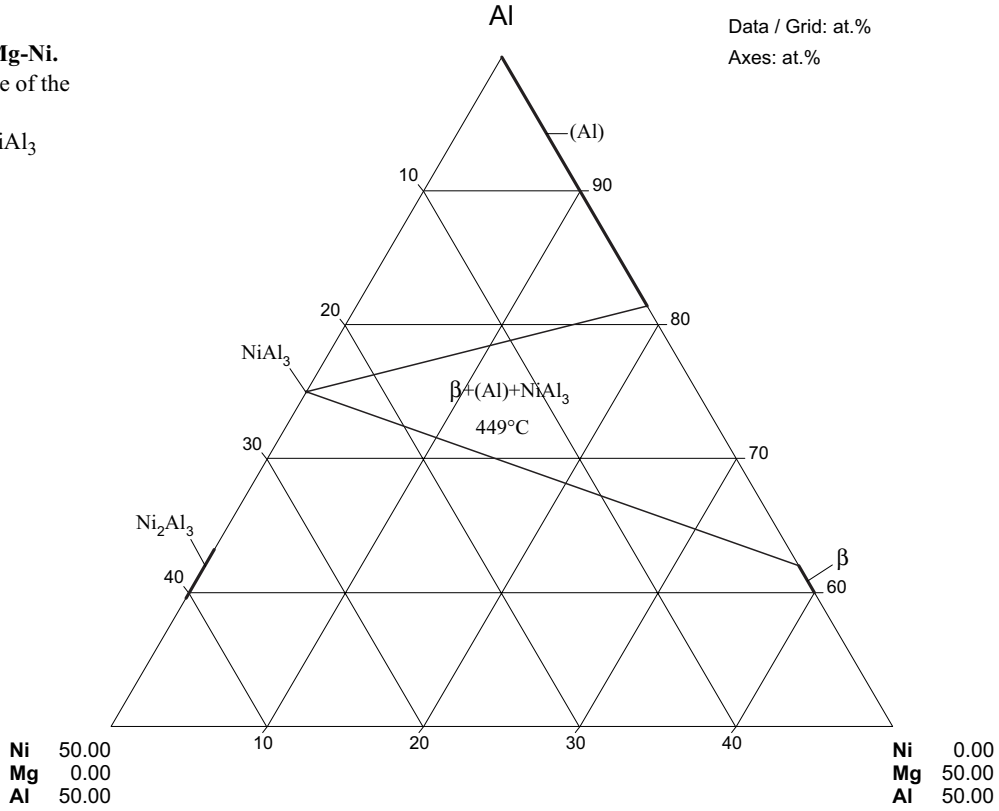

Fig. 3: Al-Mg-Ni. Solidus surface of the partial $Al\text{-}Mg_2Al_3\text{-}NiAl_3$ system

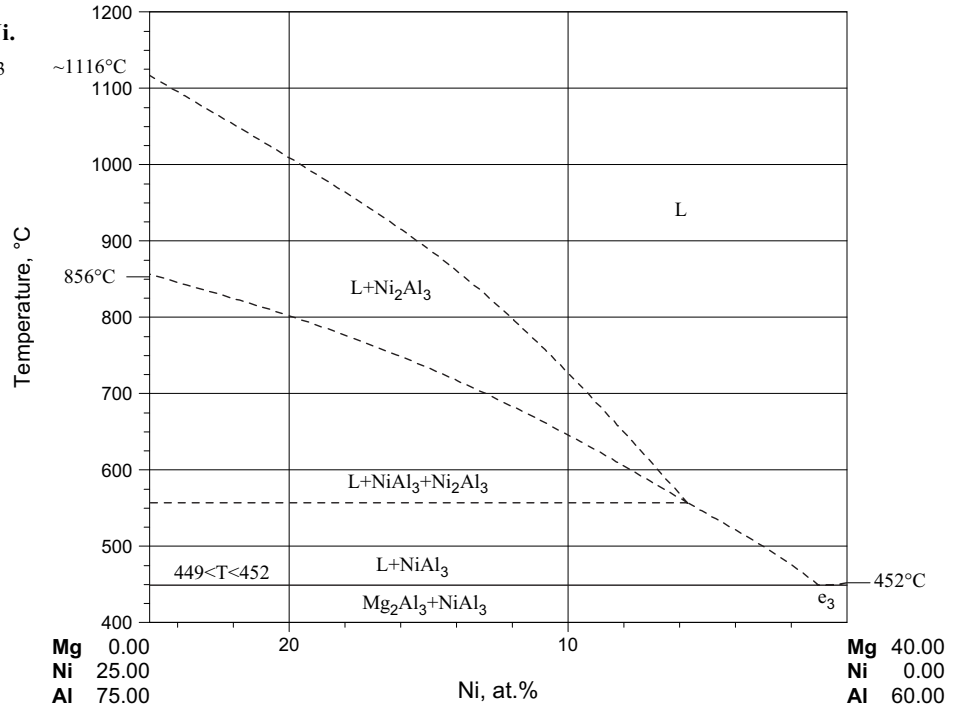

Fig. 4: Al-Mg-Ni. The $NiAl_3\text{-}Mg_2Ni_3$ vertical section