PHASE RELATIONS IN THE $LaNi_{5-x}Cu_x$, $LaNi_{5-x}Al_x$ AND RELATED SYSTEMS

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PHASE RELATIONS IN THE $LaNi_{5-x}Cu_x$, $LaNi_{5-x}Al_x$ AND RELATED SYSTEMS*

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ABSTRACT

The Ni in $LaNi_5$ can be partially replaced by other elements. Limits of solid solubility were determined in the $La(Mn,Ni)_5$, $La(Fe,Ni)_5$, $La(Ni,Al)_5$ and $La(Ni,Cu)_5$ systems. Sections of the quaternary $La(Mn,Ni,Al)_5$, $La(Ni,Cu,Al)_5$, $La(Fe,Ni,Cu)_5$ and $Y(Mn,Ni,Al)_5$ systems were also investigated. All solutes increase unit cell constants. $YMnNi_4$ has the $MgCu_4Sn$ -type structure (a_o = 6.97Å).

INTRODUCTION

The binary compound $LaNi_5$ is of interest because of its capacity to absorb large amounts of hydrogen, and to discharge hydrogen at relatively low pressure. Research has shown that substitution of alloying elements into $LaNi_5$ causes modification of the hydrogen desorption pressure. This paper is concerned with the effect on the crystal structure and unit cell constants of Mn, Fe, Cu and Al substitutions.

EXPERIMENTAL METHODS

Alloys were prepared by arc melting on a water-cooled Cu hearth under Argon with metals of 99.9% purity or better. Specimens were homogenized in evacuated vycor capsules. Xray diffraction patterns were taken with Fe or Cu K_α radiation by the Debye-Scherrer method. Patterns were indexed with the aid of a Bunn

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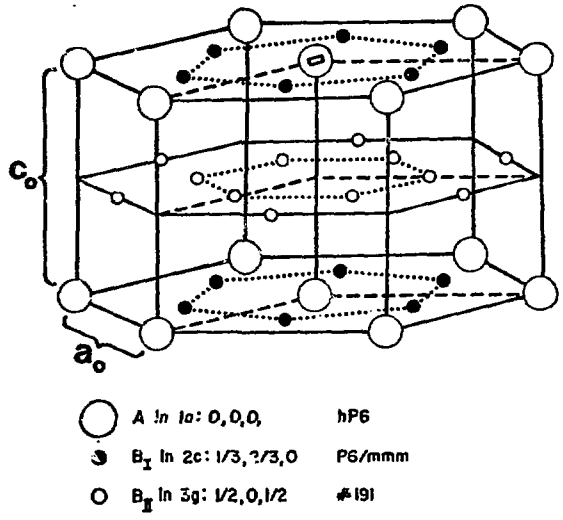

Fig. 1. $CaCu_5$ -type structure

chart, and unit cell constants were calculated from the two highest angle reflections. The assignment of elements to lattice sites was verified by comparison of calculated and observed intensities. The extent of the single phase field was estimated from the change of slope of unit cell constant curves and from the appearance of extra lines on the diffraction patterns.

THE COMPOUND $LaNi_5$

$LaNi_5$ has the hexagonal $CaCu_5$-type structure shown in Figure 1. The a_o is 5.016 Å, c_o is 3.982 and V/M = 86.7 Å^3. The 1a site at 0,0,0, is always occupied by a large atom, in this paper by a rare earth or yttrium atom. The 2c and 3g sites are occupied by Ni atoms. The 2c and 3g sites are not equivalent, and the substitution of other elements into one or both of these sites is of major importance in modification of unit cell size and hydriding characteristics.

TERNARY SYSTEMS

Mn was substituted for part of the Ni in $LaNi_5$ by Lundin and Lynch[1] who reported beneficial changes in the hydriding characteristics. Fig. 2 shows our data for unit cell constants. Much less Fe than Mn could be substituted for Ni, but Fe also raises the unit cell constants (Fig. 3).

Al can be substituted up to approximately $LaNi_{3.5}Al_{1.5}$ (Fig. 4). The Al atoms show a preference for occupancy of the 3g sites over the 2c sites, as determined by comparison of calculated and

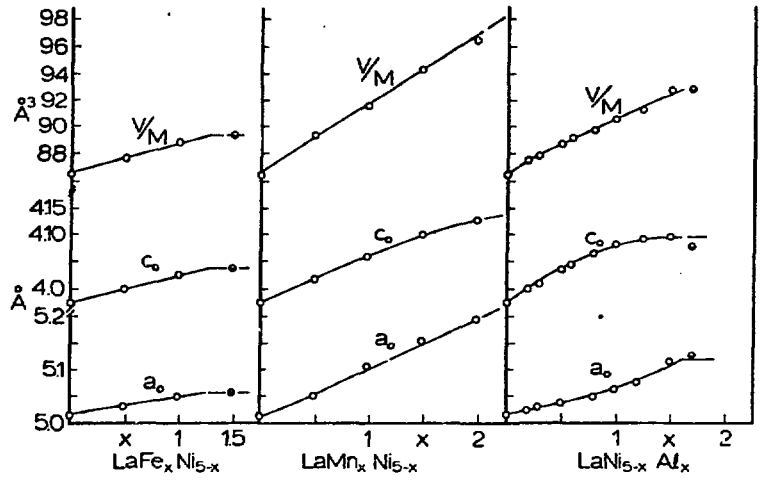

Fig. 2. Unit cell constants in $LaMn_xNi_{5-x}$ alloys
Fig. 3. Unit cell constants in $LaFe_xNi_{5-x}$ alloys
Fig. 4. Unit cell constants in $LaNi_{5-x}Al_x$ alloys

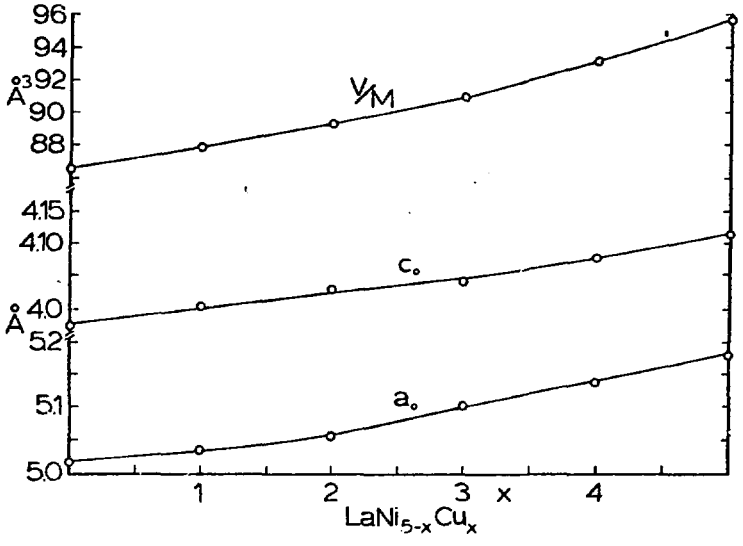

Fig. 5. Unit cell constants in $LaNi_{5-x}Cu_x$ alloys

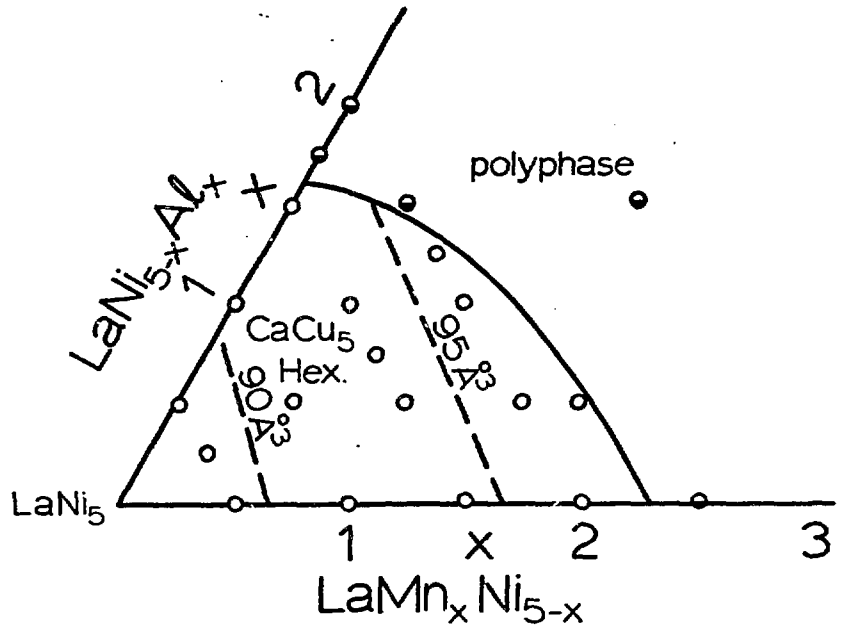

Fig. 6. Extent of $CaCu_5$ -type phase and V/M in $La(Mn,Ni,Al)_5$ system.

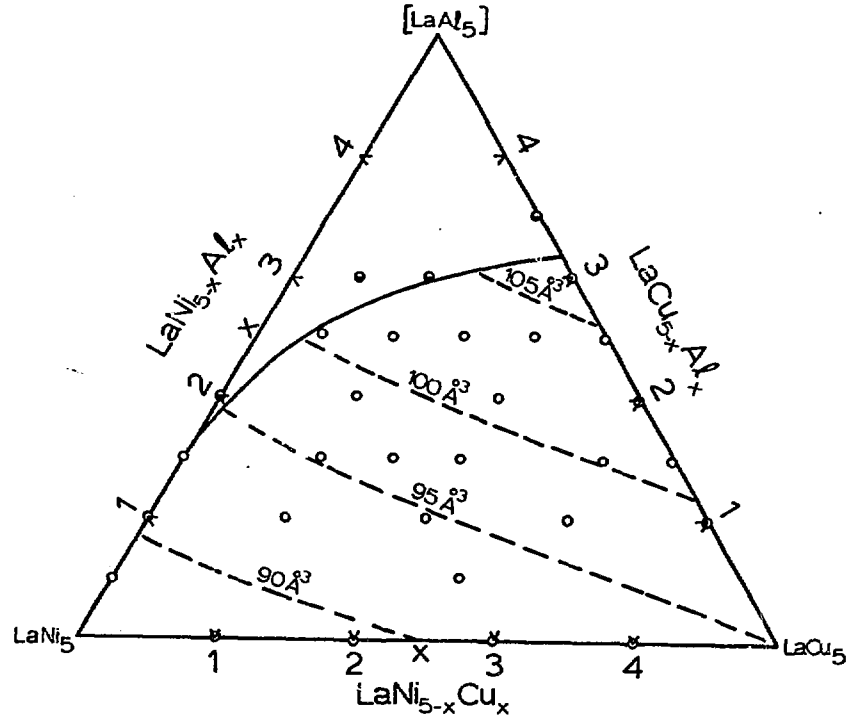

Fig. 7. Extent of $CaCu_5$ -type phase and V/M in $La(Ni,Cu,Al)_5$ system.

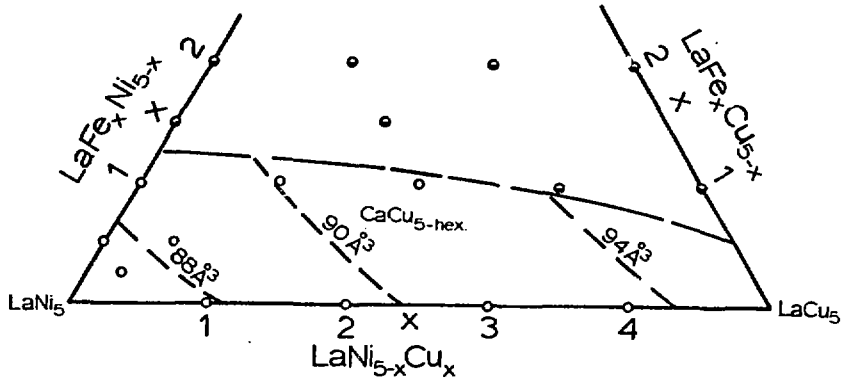

Fig. 8. Extent of $CaCu_5$ -type phase and V/M in $La(Fe,Ni,Cu)_5$ system.

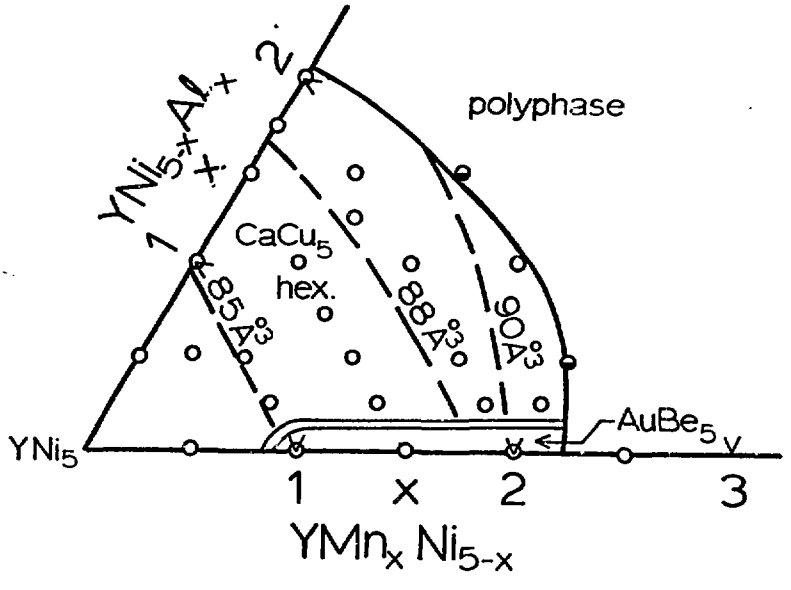

Fig. 9. Hexagonal and cubic phase composition ranges and V/M in $Y(Mn,Ni,Al)_5$ system.

observed intensities. The other solutes, Mn, Fe and Cu are too close to Ni in atomic scattering factor to justify use of intensities in site assignments. Cu can be substituted for Ni completely, with continuous solid solubility between $LaNi_5$ and $LaCu_5$ (Fig. 5).

QUATERNARY SYSTEMS

The La (Mn, Ni, Al)$_5$ system was investigated in the hope that the beneficial effects of Mn and Al might be retained in a complex alloy. The range of solid solution and the V/M (volume per formula weight) are given in Fig. 6. A similar plot for the La (Ni, Cu, Al)$_5$ system is given in Fig. 7. In this system is found the largest increase in unit cell volume, from 86.7 to 105.9 $Å^3$. Fig. 8 shows limited solubility in the La (Fe, Ni, Cu)$_5$ system.

The modifications of $LaNi_5$ described above exhibit only the hexagonal $CaCu_5$-type structure, but this is not true for other rare earth systems. The ternary system Y-Mn-Ni contains a compound based upon $YMnNi_4$ but showing a range of solid solution, with the cubic $AuBe_5$-type or $MgCu_4Sn$-type structure. The Y(Mn, Ni, Al)$_5$ quaternary is shown in Fig. 9. The significant feature is that small amounts of Al suppress the cubic compound, or conversely stabilize the hexagonal $CaCu_5$ structure at high Mn content.

The cubic $YMnNi_4$ has $a_o = 6.972$ Å. $ErMnNi_4$ also has the $AuBe_5$ structure ($a_o = 6.96$) which indicates that the smaller rare earths can be expected to form this compound. The existance of $CeMnNi_4$ ($a_o = 6.957$-7.07)[2] indicates that Ce is quadrivalent in this compound.

REFERENCES

1. Lundin, C.E. and Lynch, F.E. to Gruen, D., La-Ni-Mn Systems, private Denver Research Institute Report, February 15, 1977.

2. Kalychak, Ya. M., Bodak, O.I., and Gladyshevskii, E.I., Neorg. Mat. 12, No. 7, pp. 1149-54, July 1976.