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Al-Mn-Pd (Aluminum-Manganese-Palladium)

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A number of reports in recent years on the phase equilibria in the Al-rich region of this system [1991Yok, 1992Yok, 1993Aud, 1995God, 1999Gru, 2000Kle] have confirmed the simultaneous presence of a decagonal and an icosahedral quasicrystalline phase, in addition to several quasicrystalline approximants.

Binary Systems

The Al-Mn phase diagram [1997Oka] shows a number of intermediate phases: $MnAl_6$ ($D2_h$-type orthorhombic), λ (16.8-19 at.%), $MnAl_4$ (denoted μ, hexagonal, $P6_3/mmc$), Mn_4Al_{11} (a high-temperature (HT) orthorhombic form and a low-temperature (LT) triclinic form), γ-MnAl (34.5-51.3 at.% Mn; bcc), γ_1 (30-38.2 at.% Mn) and γ_2 (31.4-47 at.% Mn; $D8_{10}$, Cr_5Al_8-type rhombohedral) and ε-Mn_3Al_2 (53.2-60 at.% Mn; cph). The Al-Pd phase diagram [2001Yur] depicts the following intermediate phases: $PdAl_4$ (hexagonal, space group $P6_322$), $PdAl_3$ (denoted ε_6, orthorhombic), ε_{28} (∼$PdAl_3$, orthorhombic), Pd_8Al_{21} (Pt_8Al_{21}-type tetragonal), Pd_2Al_3 (denoted δ, $D5_{13}$, Ni_2Al_3-type hexagonal), PdAl ($B2$-type cubic and two low-temperature forms: rhombohedral and $B20$-type cubic), Pd_5Al_3 (Rh_5Ge_3-type orthorhombic), Pd_2Al ($C23$, Co_2Si-type orthorhombic), and Pd_5Al_2 (Pd_5Ga_2-type orthorhombic). A partial phase diagram of the Mn-Pd system in the solid state was recently determined by [2004Mii] for the Pd range of 60-76 at.% and for temperatures between 400 and 800 °C. It depicts the following intermediate phases: Pd_3Mn ($D0_{23}$, Al_3Zr-type tetragonal), Pd_2Mn, Pd_5Mn_3, and PdMn ($L1_0$, AuCu-type tetragonal). The high temperature form of PdMn (38-66 at.% Pd) has the cubic CsCl-type structure [Massalski2].

Ternary Phases

An icosahedral phase I is stable in this system with a 6-D hyper cubic cell parameter a_{6D} = 0.645 nm. Also, a decagonal phase D with a parameter of a_{5D} = 0.577 nm is stable. In addition, several quasicrystal approximants T, R, ξ, and ξ′, all of orthorhombic symmetry, have been reported. For the structural characteristics of these phases, see [1993Aud, 2000Kle].

Ternary Phase Equilibria

The early studies of [1991Yok, 1992Yok] were concerned with the production of single crystals of the icosahedral phase I. [1992Yok] reported results on the liquid-solid (I) equilibria and grew large single crystals of I by the Czochralski method. The partial isothermal section depicting the liquid-I equilibria at 870 °C is shown in Fig. 1 from [1992Yok].

[1995God] reported a detailed investigation of the phase equilibria of this system. They did not distinguish between a decagonal phase and phases with a decagonal morphology formed by approximants. With starting metals of >99.998% Al, 99.985% Mn and >99.998% Pd, [1995God] induction-melted under Ar atm a number of alloys in the Al-rich region of this system. Differential thermal analysis was performed at heating/cooling rates of 2-10 °C per min. Measurements of the magnetic susceptibility were also done as a function of temperature on several alloys. For isothermal studies, alloy samples were annealed at 875 °C for 4 days, at 840 °C for 6 days, or at 600 °C for 18 days. The heat treated samples were studied by metallography and energy dispersive x-ray analysis.

The liquidus projection constructed by [1995God] is redrawn in Fig. 2. The phases of primary crystallization are marked in the figure. The I phase forms through the ternary peritectic reaction P_1 at 894 °C. The second ternary peritectic reaction P_2 at 850 °C was attributed by [1995God] to the formation in the ternary region of the binary phase $PdAl_3$ (marked ε in Fig. 2). The primary crystallization regions of PdAl ($B2$) and γMnAl (bcc) are continuous in Fig. 2, as no distinction could be made by [1995God] between the ordered and disordered forms of bcc.

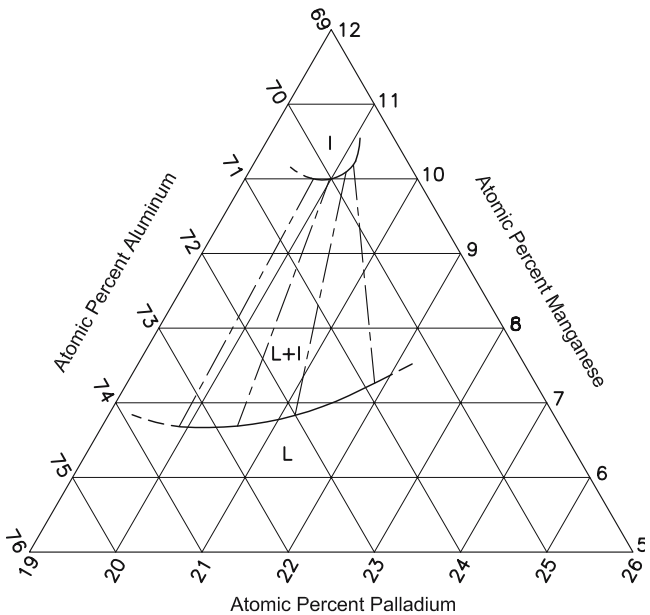

Fig. 1 Al-Mn-Pd liquid-solid equilibria at 870 °C [1992Yok]

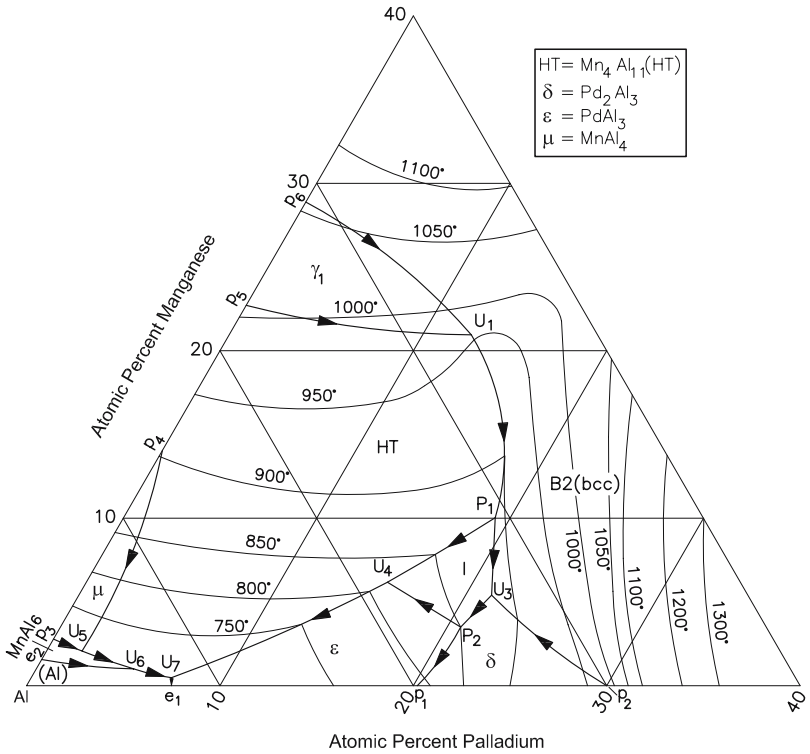

Fig. 2 Al-Mn-Pd liquidus projection for Al-rich alloys [1995God]

The isothermal sections for the Al-rich region at 875, 840, and 600 °C are shown in Fig. 3-5. These correspond to the stable distribution of phases. At 875 °C (Fig. 3), the liquid phase extends up to 10 at.% Mn. The I phase has a range of 7.5-10 at.% Mn. The three-phase equilibrium of (HT + γ_2 + *B*2) results from the eutectoidal decomposition of γ_1 at 923 °C. The decagonal phase D is present. At 840 °C (Fig. 4), $PdAl_3$(ε), which forms through the ternary peritectic reaction P_2 at 850 °C, is present. The low-temperature form of Mn_4Al_{11} is marked LT in Fig. 4. At 600 °C (Fig. 5), the homogeneity region of I has decreased. The liquid phase at the Al-corner is replaced with (Al). The binary phase λ was not found by [1995God] at 600 °C. A reaction scheme consistent with the liquidus projection in Fig. 2 and the isothermal sections in Fig. 3 to 5 was given by [1995God].

The liquidus projection shown in Fig. 2 corresponds to the thermal arrests observed during cooling. The heating experiments of [1995God], however, showed that the D phase takes part in the liquid-solid equilibrium and decomposes peritectically at 896 °C. The formation of D during cooling through the ternary peritectoid reaction HT + I + B2 ↔ D at ∼770 °C is to be considered as a metastable reaction [1995God]. Four vertical sections (corresponding to stable reactions) at 10Pd, 20Pd, 70Al and 6Mn (atomic %) respectively were also constructed by [1995God].

[1999Gru] induction-melted 33 alloys in the Al-rich region and annealed them at 880-850 °C for 65-70 h, at 790 °C for 590 h, or at 710 °C for 1450 h. The phase equilibria were studied with optical, scanning and transmission electron metallography, x-ray powder diffraction and energy dispersive x-ray analysis. The isothermal sections constructed by [1999Gru] are similar to those of [1995God]. The transition reaction (U_3): $L + B2 \leftrightarrow I + Pd_2Al_3$, reported at 867 °C by [1995God], was found to occur between 880 and 870 °C by [1999Gru]. The ternary phase ξ′ reported by [1993Aud] was taken to be the binary extension of $PdAl_3$ by [1999Gru]. [1999Gru] did not find the occurrence of any quasicrystalline approximants.

[2000Kle] extended the earlier study of [1993Aud] on the occurrence of quasicrystalline approximants in this system. With starting metals of 99.999% Al, 99.9% Mn and 99.9% Pd, [2000Kle] induction-melted under Ar atm 16 ternary alloys in the Al-rich region. The liquid-solid equilibria were studied by holding isothermally partially-molten samples at 952, 945, 920, 840, 730, or 685 °C for 45 min and quenching rapidly in water. The composition of the first phase to form was determined approximately first with energy dispersive x-ray spectroscopy and then more accurately with x-ray wavelength spectroscopy. The composition of the solid area close to the solid-liquid interface was measured to minimize the effect of coring in the solid. Compositions of tie-lines and tie-triangles were determined and listed. The crystallographic structures of the different phases were identified by electron diffraction and high resolution imaging in a transmission electron microscope. The quasicrystalline approximants T, R, and ξ′ were found among the solid phases in equilibrium with the liquid. A liquidus projection incorporating the quasicrystalline

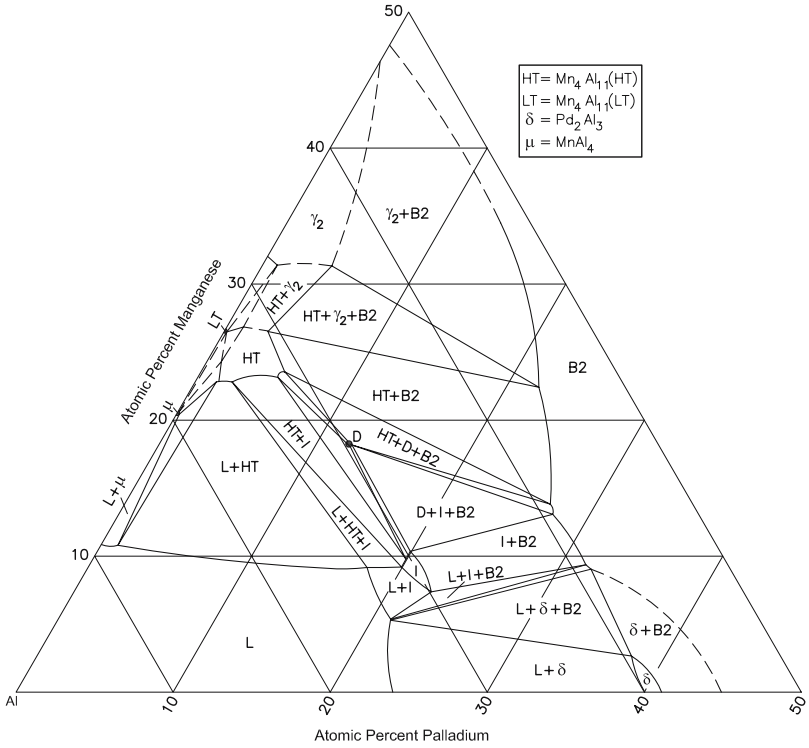

Fig. 3 Al-Mn-Pd isothermal section at 875 °C for Al-rich alloys [1995God]

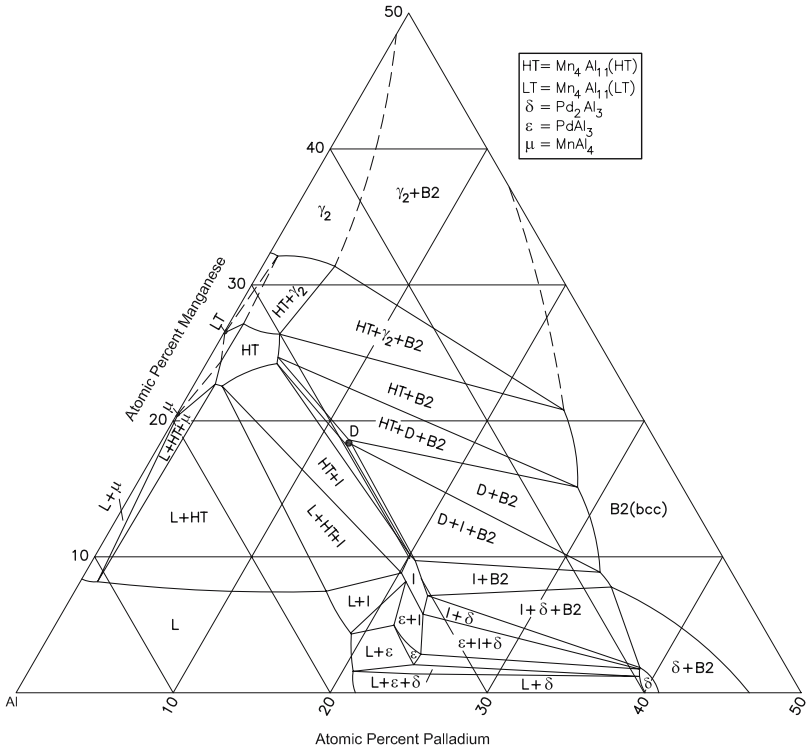

Fig. 4 Al-Mn-Pd isothermal section at 840 °C for Al-rich alloys [1995God]

approximants constructed by [2000Kle] is shown in Fig. 6. Primary crystallization areas of T, R and ξ' are seen. [2000Kle] pointed out the difficulties of such studies due to the very small differences in composition and in the Gibbs energy of the phases, which results in very long (practically infinite) time to achieve equilibrium.

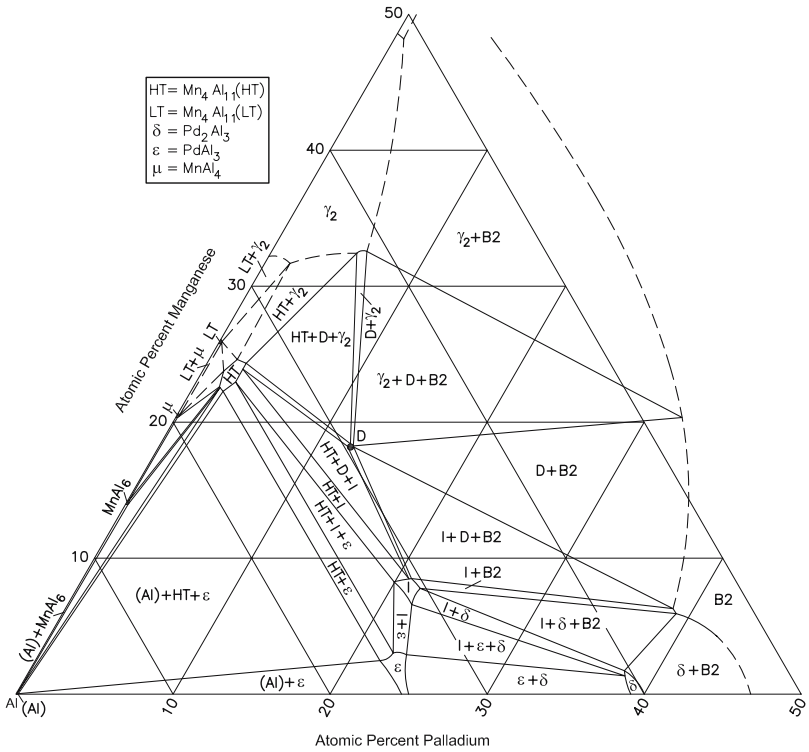

Fig. 5 Al-Mn-Pd isothermal section at 600 °C for Al-rich alloys [1995God]

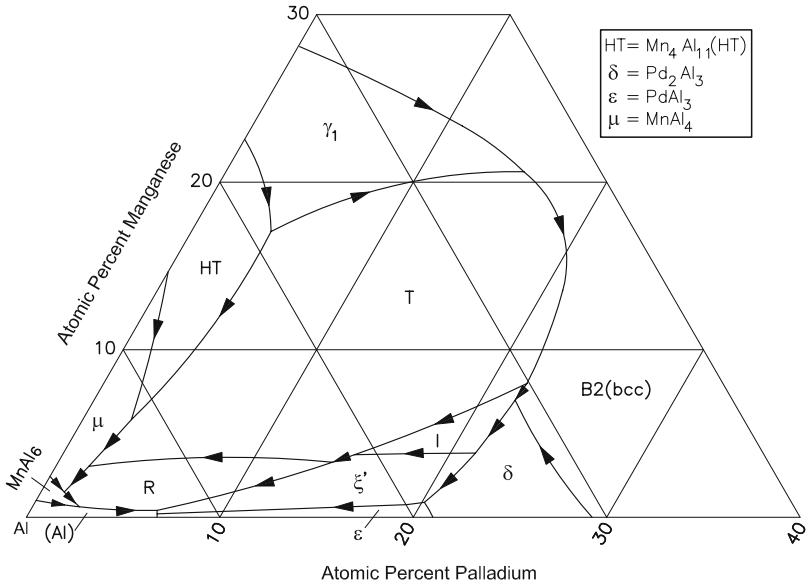

Fig. 6 Al-Mn-Pd liquidus projection incorporating quasicrystalline approximants T, R, and ξ′ [2000Kle]

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