Fcc⇌Fct Martensitic Transformation in Pt_3Al and Pt_3Ga

Yoshihiro OYA, Tomoyuki ISHII***

Abstracts

Based on the platinum rich side of Pt-Al and Pt-Ga binary equilibrium phase diagrams recently revised, the phase transformations of intermetallic compounds Pt_3Al and Pt_3Ga are investigated. It has been shown that in between the high temperature form of $L1_2$, γ' and the low temperature form of $D0_c'$, γ_2', there exists an intermediate phase, $D0_c$, γ_1' in both Pt_3Al and Pt_3Ga. It is shown that the consecutive transitions of these phases are found to be martensitic in nature and transmission electron microscopy provides an evidence that $L1_2 \rightleftarrows D0_c$ transition is one of structural transformations analogous to that from fcc to fct crystal structure.

Introduction

Many of $L1_2$ intermetallic compounds such as Ni_3Al are well known to exhibit anomalous positive temperature dependence of strength [1]. Research interest on the $L1_2$ compounds has recently expanded because not only of this mechanical anomaly but also of the fact that several compounds such as Pt_3Al and Pt_3Ga exhibit a distinct negative temperature dependence of strength below ambient temperature [2, 3]. In platinum based $L1_2$ compounds Pt_3Al, for example, the 0.2% compressive flow stress in Pt_3Al is over 1400 MPa at 77 K while that at room temperature is about 800 MPa [2]. Such strong negative temperature dependence is generally observed only in bcc alloys and the mechanism for the unusal mechanical behavior in certain $L1_2$ compounds at low temperatures has yet been understood.

In view of the revised phase diagrams for Pt-Al and Pt-Ga systems [4] reproduced in Fig. 1 and 2, the existence of intermediate and low temperature forms of $L1_2$ (γ') and $D0_c$(γ_1') and $D0_c'$(γ_2'), is commonly characteristic to both alloy systems. By a thorough investigation of the binary phase diagrams having $L1_2$ compounds, it is suggested that the appearance of a modified $L1_2$ phase would be relevant to the unusual low temperature mechanical behavior of the compound. It is therefore important to investigate the relative phase stability between $L1_2$ and $D0_c$ or $D0_c'$ crystal structure to examine the possible correlation with the characteristic plastic behavior of the compound.

* 高分解能分析電子顕微鏡センター助手　金属材料学
** 理工学部機械工学科教授　金属材料学

The present investigation concerns the transformation behavior from $L1_2$ to $D0_c$ and to $D0_c'$ in Pt_3Al and Pt_3Ga. Of particular interest is that the phase stability range of $D0_c$ differs by over 1000 K in between the previous works [5, 11] and the recent work [4] on the equilibrium phase diagrams of both Pt-Al and Pt-Ga, systems, and that the appearance of the optical micrographs of a transformed Pt_3Ga (25.5 at % Ga) alloy indicated the transformation to be martensitic [4]. It is shown here an evidence that the phase transition from the $L1_2$ to the distorted $L1_2$ would be basically the srtuctural transformation from fcc to fct, which is martensitic in nature.

Experimental Procedure

Pt_3Al and Pt_3Ga alloys were prepared by arc-melting under an argon atmosphere using platinum sheet of 99.9%, aluminum of 99.99% and gallium pellet of 99.999% in purities. As the weight loss after the melting was within 0.05 mass %, the nominal compositions are accepted. All ingots were homogenized at 1273 K for 0.6 Ms followed by water quenching.

Specimens for optical metallography were prepared by etching with aqua regia after mechanical polishing and those for transmission electron microscopy by the atom milling technique. Transmission electron microscopy on the transformation product $D0_c(\gamma_1')$ in a Pt-26.5 at % Ga alloy was carried out with a JEM-200CX microscope at an accelerating voltage of 200 kV using a specimen cooling holder to avoid the reverse transformation to $L1_2$ structure.

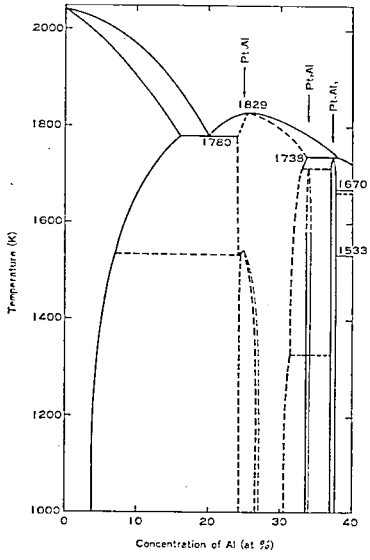

Fig. 1 The Pt-Al phase diagram recently revised [2].

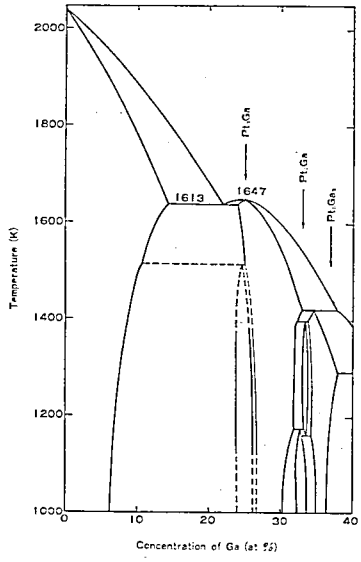

Fig. 2 The Pt-Ga phase diagram recently revised [2].

Results and Discussion

(1) Phase transformations in Pt_3Al and Pt_3Ga alloys

In relation to the revised phase diagrams of both Pt-Al and Pt-Ga systems in Fig. 1 and 2, the phase transformation characteristics of $L1_2$ Pt_3Al (or Pt_3Ga) to the intermediate and low temperature forms are first reviewed. DTA (differential thermal analysis) heating curves and thermal dilatation curves are shown in Fig. 3 and 4 for the Pt-Al and Pt-Ga alloys around stoichiometric composition of Pt_3Al (or Pt_3Ga), which are taken from the recent work [2]. It is apparent that there are two exothermic peaks is Fig. 3 and corresponding two steps of the volume contraction on cooling in Fig. 4 indicating two successive phase transfromations of $L1_2$ phase.

Those transformation temperatures obtained by both DTA and dilatometry are summarized in Figs. 5 and 6 as a function of Al or Ga concentration. In both figures, the transformation temperatures are observed to be nearly constant at platinum rich side where platinum solid solotion, γ, should coexist and hence is the two phase region. The high temperature X-ray powder patterns of 20 at% Al and 22 at% Ga alloys indicate that the $L1_2$ phase is stable at least above 773 K, in accord with the results in Figs. 3 and 4. The intermediate phase denoted here as γ_1' is stable at a narrow composition range and under a small temperature interval in both systems.

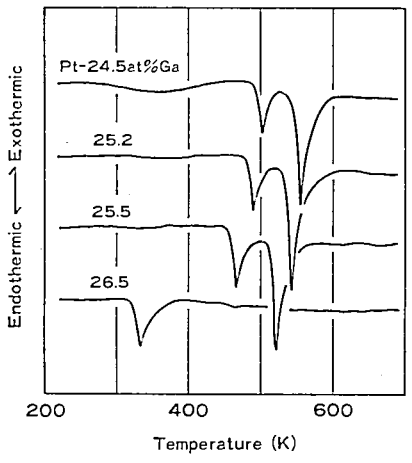

Fig. 3 DTA heating curves of several Pt-Ga alloys [2]. Heating rate is 0.167 k/s.

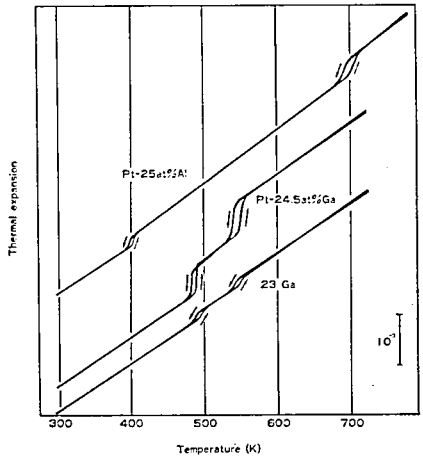

Fig.4 Examples of thermal expansion curves for Pt-Al and Pt-Ga alloys [2]. Heating rate is 0.167 k/s.

(2) Crystallography of the intermediate and low temperature phases

According to the careful examinations on X-ray powder diffraction patterns, it is most likely that the crystal structure of intermediate phase γ_1' and that of γ_2' appearing in Pt_3Al and Pt_3Ga are both the distorted $L1_2$ structures being $D0_c$

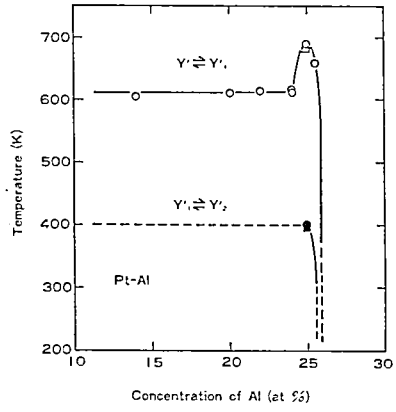

Fig. 5 Composition dependence of the transformation temperatures for $\gamma' \rightarrow \gamma_1'$ and $\gamma_1' \rightarrow \gamma_2'$ in Pt-Al alloys. Circles obtained by DTA and squares by dilatation.

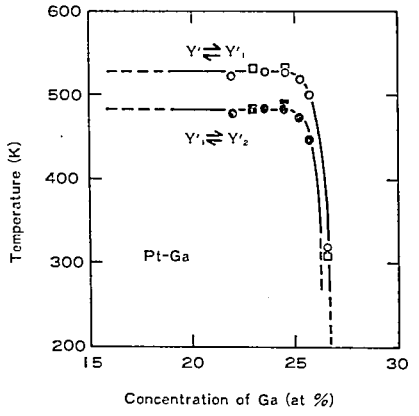

Fig. 6 Composition dependence of the transformation temperature for $\gamma' \rightarrow \gamma_1'$ and $\gamma_1' \rightarrow \gamma_2'$ in Pt-Ga alloys. Circles obtained by DTA and squares by dilatation.

and $D0_c'$, respectively [4]. The former crystal structure is an isotype of U_3Si, while the latter is resembling to U_3Si denoted by Kimmel [12]. The pictorial view and the atomic arrangement in each crystal structure is shown in Fig. 7b and 7c together with those in $L1_2$ (Fig. 7a). To be noted in Fig. 7 is that the atomic arragement is shown as a prejection along $\langle 001 \rangle$ of tetragonal unit cell having four times the volume of the $L1_2$ unit cell. The characteristic of the atomic arrangement in $D0_c$ or $D0_c'$ is a systematic displacement of platinum atoms on the planes at $z=1/4$ and 3/4, being different in manner in each crystal structure but yielding tetragonality along $\langle 001 \rangle$ of the unit cell in both cases. The parameter to express the amount of displacement, u, in $D0_c'$ Pt_3Ga (24.3 at%) has been given as 0.020 [10] and in $D0_c$ Pt_3Ga (26.5 at%) as 0.009 [13] with c/a of 1.441 and 1.425, respectively. Note that c/a for the tetragonal unit cell of $L1_2$ is 1.414.

(3) Martensitic transformation from $L1_2$ to the distorted $L1_2$ phase

The phase transformation from $L1_2(\gamma)$ to $D0_c(\gamma_1')$ or to $D0_c'(\gamma_2')$ should basically be the one from fcc with $c/a=1$ to fct with $c/a>1$, when the unit cell is converted to fcc. The microstructural characterization of each transformation product, however, is difficult to make seperately because of the very narrow compositional as well as temperature range for γ_1' to be stable at ambient temperature. Actually it has been pointed out that γ' becomes stable at even etching temperature in a Pt-Ga alloy with 26.5 at%Ga.

In Fig. 8 the optical micrographs are shown of Pt-25.5 at%Ga and Pt-27.0 at%Ga alloys exhibiting single phase structure of γ' and γ_2'. The structure for the latter alloy should be resulted through both $L1_2 \rightarrow D0_c'$ and $D0_c \rightarrow D0_c'$ phase transformations. Together with the results on dilatometry shown in Fig. 4, both transformations to

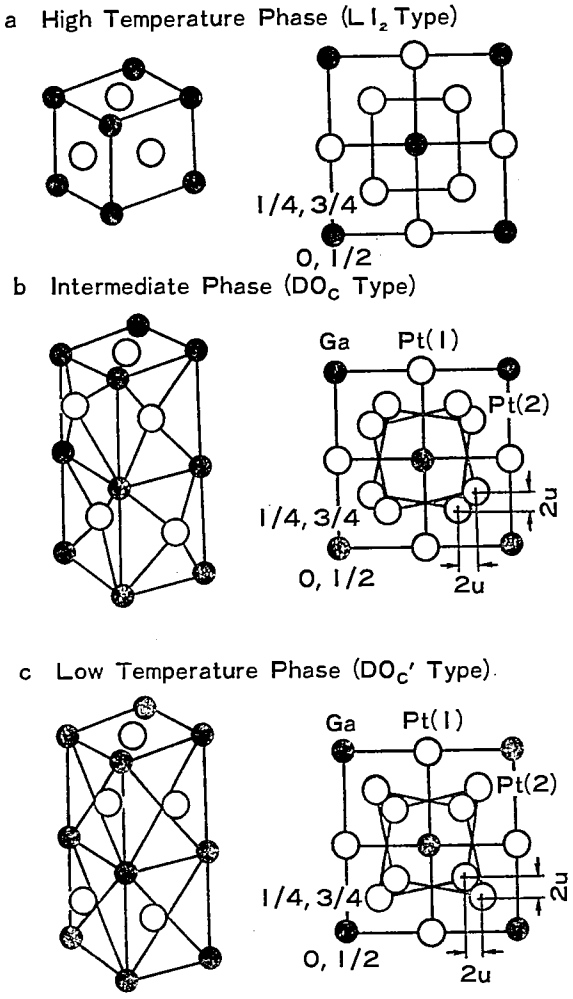

Fig. 7 Atomic arrangement in the modified $L1_2$ structures.

yield the microstructure of Fig. 8b must be martensitic in nature. The microstructure consists of sets of large plates of 20 to 30 in width and much finer substure is visible in each plate. The macroscopic appearance is similar to that of surface relief resulted from martensitic or bainitic transformation. A facet containing unidirectional plates is nearly the same in size as a grain observed in the $L1_2$ single phase alloy (Fig. 8a).

Transmission electron microscopy was only successful for examining the transformation product in a Pt-26.5 at%Ga alloy at under 170 K using specimen cooling holder. Both Pt_3Al and Pt_3Ga alloys for a range of compositions are generally extremely brittle and therefore preparation and handling of thin foils needs careful and skilled procedure. It was fortunate for us, however, that the alloy being examined would be the only possible composition for the observation of single phase γ_1'. The micro-

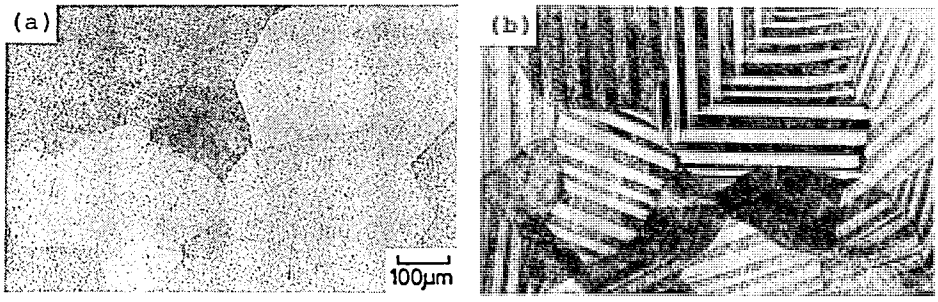

Fig. 8 Optical micrographs of a) Pt-27.0 at%Ga with γ' and b) Pt-25.5 at%Ga with γ_2' single phase structure.

structure of the alloy before cooling the specimen with liquid nitrogen is a single phase $L1_2$ judged by both the bright field image and selected area diffraction pattern giving only the superlattice spots for the $L1_2$ ordered structure. As the specimen is cooled down, characteristic strength features analogous to the lath martensite in steels start appearing at monitoring temperature around 220 K.

Bright and dark field electron micrographs at an arbitrary but constant monitoring temperature of 160 K is shown in Fig. 9. A banded structure with two sets of fine straight laths are visible and each set is found mutually perpendicular. The foil orientation is (110) based on the cubic indices and as is shown in the selected area diffraction pattern the longitudinal direction of laths are parallel to either of $\langle\bar{1}10\rangle$ or $(\bar{1}10)$ trace. The dark field electron micrograph taken with (002) diffraction spot in Fig. 9b shows that the contrast in a set of laths is reversed. These evidences

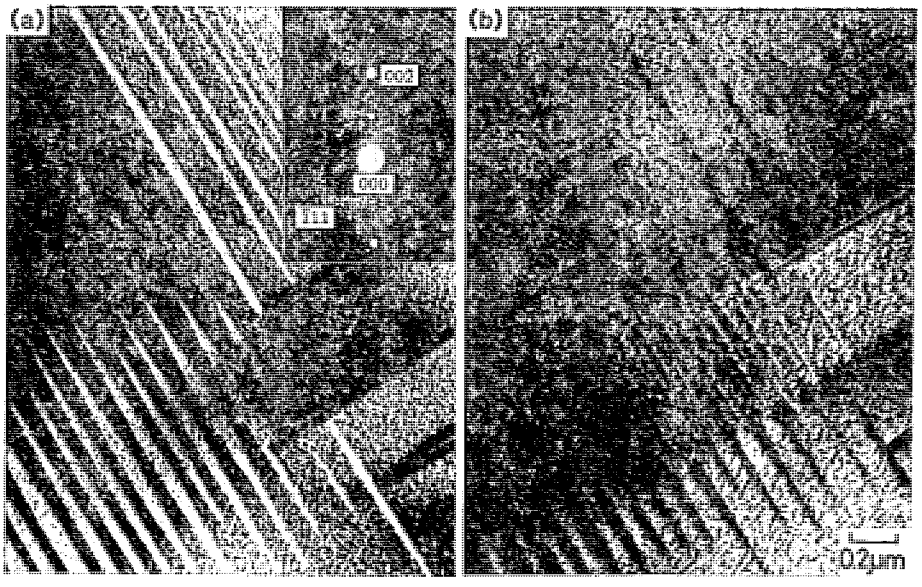

Fig. 9 a) Bright and b) dark field electron micrographs of Pt-26.5 at%Ga alloy. Incident beam direction is normal to (100) and the dark field micrograph is taken using (002) fundamental reflection.

suggest that neighboring laths are twin related with (110) habit plane. Such situation is quite similar as what have been observed in martensitic transformation from fcc to fct crystal structure in several In-rich alloys [14-16]. In In-Pb alloys, for example, the transformation is reversible and the mechanism is shown to be associated with cooperative atomic rearrangement and transformation strain is reduced by the formation of transformation twinns on (110) planes. This would be exactly the case for the mechanism of martensitic transformation from $L1_2$ to $D0_c$ and it is therefore likely to be a type of structural transformation.

Acknowledgement

This report is a part of systematic work on the orderd alloys organized by professor T. Suzuki.

We appreciate very much for his support, advice and discussion, also for the financial support of Special Grant by Meisei University.

References

[1] Y. Mishima, Y. Oya and T. Suzuki: High-Temperature Ordered Intermetallic Alloys, Ed. by C.C. Koch, C.T. Liu and N.S. Stoloff, Materials Research Society, Pittsburgh, 1985, p. 263.
[2] D.M. Wee, O. Noguchi, Y. Oya and T. Suzuki: Trans. Japan Inst. Metals, **21** (1980), 237.
[3] D.M. Wee, D.P. Pope and V. Vitek: Acta Met., **32** (1984), 829.
[4] Y. Oya, Y. Mishima and T. Suzuki: Z. Metallk., submitted.
[5] P. Guex and P. Feschotte: J. Less Common Metals, **46** (1976), 101.
[6] R. Huch and W. Klemm: Z. Anorg. Allge. Chem., **329** (1964), 123.
[7] W. Bronger and W. Klemm: Z. Anorg. Allge. Chem, **319** (1962), 58.
[8] S. Bhan and K. Schubert: Z. Metallk., **51** (1960), 327.
[9] S. Bhan and K. Schubert: J. Less Common Metals, **17** (1969), 73.
[10] T. Chattopadhyay and K. Schubert: ibid., **41** (1975), 19.
[11] T. Chattopadhyay, K. Khalaff and K. Schubert: Metall, **28** (1974), 1160.
[12] G. Kimmel: J. Less Common Metals, **59** (1978), 83.
[13] Y. Oya, Y. Mishima and T. Suzuki: To be published.
[14] O. Nittono and Y. Koyama: Trans. Japan Inst. Metals, **23** (1982), 285.
[15] Y. Koyama, T. Ukena and O. Nittono: ibid., **23** (1982), 518.
[16] Y. Koyama and O. Nittono: ibid., **23** (1982), 736.
[17] T. Suzuki and Y. Oya: J. Mater. Sci., **16** (1982), 2737.