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L1₂ DO₂₂ competition in the pseudo binary (Pt, Rh)₃V and (Pd, Rh)₃V alloys

A. LOISEAU^{*,**} and E. CABET^{*}

^{*} *Laboratoire de Physique du Solide, ONERA, BP. 72, 92322 Châtillon cedex, France*

^{**} *LEM/CNRS, ONERA, BP. 72, 92322 Châtillon cedex, France*

INTRODUCTION

The Pt₃V and Pd₃V alloys, which are ordered at low temperature on the FCC lattice, have the particular feature of exhibiting different local order in the disordered and ordered states. In the disordered state, the local order which is characterized by maxima of diffuse intensity at positions of 100 type is that of the cubic L1₂ structure [1,2]. The ordered ground state has the DO₂₂ structure of quadratic symmetry, which can be obtained by introducing each L1₂ cube an antiphase boundary (APB) in the (001) planes. This ordering produces superstructure reflections of 101/2 type. It has been shown from neutron diffraction measurements of the diffuse intensity in Pd₃V that the energy of these APB is very low, or in other words that the atomic interactions are such that L1₂ and DO₂₂ are quasi-degenerate and competitive [1].

Such a situation is propitious to the existence of intermediate structures which can be stabilized at high temperature through effective interactions between APB. Actually the <211> structure to be defined below is stable at high temperature in Pt₃V in a narrow temperature range close to the order-disorder transition [3]. These structures are the so-called long period structures (LPS) obtained from L1₂ by introducing a modulation of APB and which are characterized by the mean distance M (in L1₂ cube units) between APB. In this scheme, M is maximum in L1₂ (M = ∞) and minimum in DO₂₂ (M=1).

In this paper, we show that it is possible to stabilize the L1₂ structure and other simple intermediate long period structures, by varying slightly the atomic interactions, which has been achieved by playing with the electronic structure of the alloys. A particular attention has been paid to the characterization of the stability domain of each phase, by studying the transitions between the different phases.

ELECTRONIC STRUCTURE ARGUMENTS

The experimental electronic structure maps established for the transition metal alloys indicate that DO₂₂ is stabilized for high values of the mean electron concentration, N_e, and that L1₂, on the other hand, is stabilized for low values of this parameter [4]. We recall that N_e is equal to 10 for platinum and palladium (T¹⁰ elements) and equal to 5 for vanadium (T⁵ elements). So all of the compounds of the type T¹⁰₃T⁵ (N_e = 8.75) order according to a structure of the DO₂₂ type. On the other hand, the T⁹₃T⁵ compounds (N_e = 8.00) and T¹⁰₃T⁴ compounds (N_e = 8.50) have the L1₂ structure. More precisely, electronic structure calculations in the tight binding approximation indicate that the energy difference between L1₂ and DO₂₂, ΔE_{stab} = E^{L1₂} - E^{DO₂₂} is negative for N_e below around 8.5 and positive above [5]. More refined LMTO calculations confirm this behaviour and show that ΔE_{stab} is very small for T¹⁰₃T⁵ elements [6,7,8].

These calculations clearly indicate to decrease the mean electron concentration. Experimentally this can be obtained by substituting either Pd and Pt by T⁹ elements (Co, Rh, Ir) or V by T⁴ elements (Ti, Zr, Hf). Ordered compounds with T⁴ elements being frequently hexagonal, the first solution has been preferred and rhodium has been chosen as the substituting element.

DETERMINATION OF THE PHASE DIAGRAMS OF THE $(\text{Pt,Rh})_3\text{V}$ AND $(\text{Pd,Rh})_3\text{V}$ ALLOYS

Different alloys $(\text{Pt}_{1-x}\text{Rh}_x)_3\text{V}$ and $(\text{Pd}_{1-x}\text{Rh}_x)_3\text{V}$ with x ranging from 0 to 0.33 have been characterized at different temperatures, using transmission electron microscopy (diffraction and high resolution imaging). The observations allow us to draw the phase diagrams shown in Fig 1.

Figure 1. Schematic phase diagrams as a function of the total rhodium concentration; a) $(\text{Pt,Rh})_3\text{V}$, b) $(\text{Pd,Rh})_3\text{V}$.

In the $(\text{Pt}_{1-x}\text{Rh}_x)_3\text{V}$ alloys, different LPS are stabilized depending on the rhodium concentration and on the temperature: $M = 1$ or $\langle 1 \rangle$, $M = 4/3$ or $\langle 211 \rangle$, $M = 3/2$ or $\langle 21 \rangle$ and $M = 2$ or $\langle 2 \rangle$. The notation in brackets indicates the APB spacing sequence. For example, in the $M = 3/2$ structure, APB spacings are alternatively two and one cubes, hence the notation $\langle 21 \rangle$. The APB distribution can be determined directly from high resolution images of perfect LPS as shown in Fig 2. Finally, the $L1_2$ or $\langle \infty \rangle$ structure is obtained for x values larger than 0.13.

Figure 2. High resolution images of the different long period structures observed in the $(\text{Pt}_{1-x}\text{Rh}_x)_3\text{V}$ alloys: $\langle 211 \rangle$ in a), $\langle 21 \rangle$ in b), $\langle 2 \rangle$ in c) and $\langle \infty \rangle$ in d). The structures are projected along a cubic 100 direction and are based on the $L1_2$ structure which consists in a stacking along a cube direction of alternatively pure Pt planes and mixed PtV planes. The white dots represent the V columns located at positions $+$ or $-$ in cubic (001) mixed planes. Each shift $+$ to $-$ is due to an APB, hence the determination of the APB distribution.

A similar behaviour has been found for the $(\text{Pd}_{1-x}\text{Rh}_x)_3\text{V}$ alloys, where the same LPS have been observed, but for slightly higher rhodium contents. Instead, the $M = 1$ LPS, for instance is stable up to 5% Rh whereas it is only observed in Pt_3V alloy. As a consequence, the $L1_2$ structure has not yet been observed. Investigation of alloys with higher rhodium content is in progress.

A particular attention has been paid to the transitions between the different phases in order to determine either if they can coexist at equilibrium or if intermediate structures can be stabilized in narrow temperature ranges.

Alloys ranging from 10 to 15%Rh are actually clearly two phased $L1_2 + \langle 2 \rangle$: the microstructures consist of large domains of each phase characterized by very sharp and perfectly coherent interfaces which excludes the existence of any other intermediate LPS between $\langle \infty \rangle$ and $\langle 2 \rangle$ (Fig3a).

Figure 3: High resolution images of the microstructure of a two-phased $\langle 2 \rangle + \langle \infty \rangle$ alloy in a) and of a two-phased $\langle 2 \rangle + \langle 211 \rangle$ alloy in b).

The situation is more subtil for other LPS. For instance, the microstructure observed in the $(\text{Pt}_{98}\text{Rh}_2)_3\text{V}$ at 920°C is analysed in Fig4. The diffraction patterns of Fig4a,c correspond to the LPS $\langle 21 \rangle$ ($M=3/2$) observed at high temperature and to the LPS $\langle 211 \rangle$ ($M=4/3$) observed at low temperature.

Figure 4: Diffraction patterns showing the APB modulation satellites of the perfect LPS $\langle 21 \rangle$ in a), the LPS $\langle 211 \rangle$ in c) and of a two-phase $\langle 21 \rangle + \langle 211 \rangle$ alloy in b): the distance between the most intense reflections, is equal to $1/Ma$, M being the average APB spacing and a the parameter of the underlying cubic lattice.

Figure 5 : Evolution of the microstructure of the $(\text{Pt}_{98}\text{Rh}_2)_3\text{V}$ alloy when decreasing the aging temperature within the two-phase field $\langle 21 \rangle + \langle 211 \rangle$. Fringes between white arrows define sequences $\langle 21 \rangle$ and those between dark arrows sequences $\langle 211 \rangle$.

One can recognize satellites due to the APB modulation at definite and rational positions, such as the most intense ones (first order harmonics) are related to the mean distance between APB, M , [9]. At 920°C (Fig4b), the diffraction pattern exhibits elongated reflections at incommensurate positions defining an average APB spacing intermediate between $3/2$ and $4/3$. This could suggest the existence of an intermediate LPS. In fact, high resolution image such as Fig3b reveals a chaotic mixture of various sequences 21, 211, 2111, 21211,.... However, the only periodic sequences, i.e. those that are repeating at least three times, are 21 and 211. This means that no intermediate structure between the structure $\langle 21 \rangle$ and $\langle 211 \rangle$ is stable. Other sequences are in fact defects corresponding to an APB in excess or lacking with respect to the perfect sequences 21 and 211 [9]. Only the mean structure of this chaotic mixture is revealed in the diffraction pattern, where the reflection positions evolve between those of the LPS $\langle 21 \rangle$ and those of the LPS $\langle 211 \rangle$, when decreasing the aging temperature.

The evolution of the microstructure of the $(\text{Pt}_{98}\text{Rh}_2)_3\text{V}$ alloy within the two-phase field $\langle 21 \rangle + \langle 211 \rangle$ is shown in Fig5. Images are dark field fringe images obtained with two satellites of the modulation, such as the fringe spacings are equal to the periods of the different sequences present in the microstructure. This period is three cubes for LPS $\langle 21 \rangle$ and four cubes for LPS $\langle 211 \rangle$. One therefore observes in the images basically two kinds of fringes, A, (LPS $\langle 21 \rangle$) and B, (LPS $\langle 211 \rangle$) in different proportions depending on the temperature, with spacings in the ratio $4/3$. At 1020°C , fringes related to the LPS $\langle 21 \rangle$ are observed without any defect in the APB sequence whereas at 1000°C , isolated fringes of type B can be identified (Fig5a): they correspond to the presence of an APB in excess, with respect to the sequence $\langle 21 \rangle$ giving rise to a sequence $\langle 211 \rangle$. At 950°C , the density of sequences

of type $\langle 211 \rangle$ increases and they can now repeat two or three times. Below 920°C , (Fig5c,d), we can really speak of a two-phase alloy: fringes of kind B can repeat many times. The proportion of sequences $\langle 211 \rangle$ is about 20% at 920°C , 27% at 870°C , and 33% at 820°C . As a matter of fact, this evolution is related to the evolution of the satellites spacing in the diffraction patterns, as explained previously.

A similar behaviour has been found in the $(\text{Pt}_{92}\text{Rh}_8)_3\text{V}$ alloy concerning the two-phase field $\langle 21 \rangle + \langle 2 \rangle$ and the relevant microstructures are shown in Fig6a,b,c. Fringe spacings are now three cubes for $\langle 21 \rangle$ and two cubes for $\langle 2 \rangle$, i.e. in ratio $3/2$.

Figure 6 : Evolution of the microstructure of the $(\text{Pt}_{92}\text{Rh}_8)_3\text{V}$ alloy when decreasing the aging temperature within the two-phase field $\langle 21 \rangle + \langle 2 \rangle$. Fringes between the white arrows define sequences $\langle 21 \rangle$ and those between dark arrows sequences $\langle 2 \rangle$.

It is worth noting that these microstructures are the result of very long aging treatments, about 45 days at 820°C for instance. The small size of the phase domains is certainly due to a very sluggish kinetics and to the fact that the APB are very much pinned to the lattice and move with difficulty. When the aging time is not long enough to reach equilibrium, one can observe, in the $(\text{Pt}_{92}\text{Rh}_8)_3\text{V}$ alloy for example, that the periodic sequences (i.e. repeating more than three times) are not only $\langle 2 \rangle$ and $\langle 21 \rangle$ but also $\langle 221 \rangle$ or $\langle 2221 \rangle$, these later corresponding to the hypothetical LPS $M = 5/3$ and $7/4$. This suggests that metastable intermediate LPS can be formed in kinetic stages. Such a phenomenon has already been shown in Au_{3+x}Zn [10].

CONCLUSION

The substitution of a small amount of Pd and Pt by Rh in Pd_3V and Pt_3V stabilizes a few simple long period structures ($M=3/2, 4/3, \dots$) and, in the $(\text{Pt,Rh})_3\text{V}$ system, the L_{12} structure, which is the stable form of Rh_3V . For the first time, to our knowledge, transitions between LPS as a function of temperature or as a function of time can be studied in detail. The analysis of the mechanism of transformation from one LPS to another as a function of time will be presented in a forthcoming paper.

L_{12} has been shown to appear at 13% Rh in the $(\text{Pt,Rh})_3\text{V}$ system. This result is in very good agreement with electronic structure calculations. In particular, at this concentration, the electronic concentration, N_e is equal to 8.6 which nearly corresponds to the value recently found by Pasturel for which ΔE_{stab} vanishes [7].

On the other hand, the stability of such a set of long period structures which cannot be explained within usual microscopic models such as the ANNNI model is currently under study.

- [1] Solal F., Caudron R., Ducastelle F., Finel A. and Loiseau, A. *Phys. Rev. Lett.* **58** (1987) 2245.
- [2] Cabet E. and Loiseau, A. *Proceedings of the Nato School on 'Statics and Dynamics of phase Transformations in Solids* (Rhodes, 1992) in press.
- [3] Schryvers D. and Amelinckx S., *Acta Metall.* **34** (1985) 43.
Planès, J., Loiseau A., Ducastelle F. and Van Tendeloo G., *Inst. Phys. Conf. Ser.* n°90 (1987) 261.
- [4] Bieber A. and Gautier F., *Acta Metall.* **34** (1986) 2291.
- [5] Bieber A., Ducastelle F., Gautier F., Treglia G. and Turchi P., *Solid State Com.* **45** (1983) 585.
- [6] Pei S., Massalski T.B., Temmerman, W.M., Sterne P.A. and Stocks G.M., *Phys. Rev. B* **39** (1989) 5767.
- [7] Pasturel A., private communication, (1992).
- [8] Wolverton C., Ceder G., de Fontaine D., Dreyss'e H., submitted to *Phys. Rev. B* (1993)
- [9] Loiseau A., Van Tendeloo, G., Portier R., and Ducastelle F., *J. Phys. France* **46** (1985) 595.
- [10] Broddin D., Van Tendeloo G. and Amelinckx S., *J. Phys.:Condens. Matter* **2** (1990) 3459