ANTIPHASE BOUNDARIES AND INTERFACES IN THE PHASE TRANSFORMATIONS OCCURRING IN CO-PT ALLOYS

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1 - INTRODUCTION

The Co-Pt phase diagram displays phases built on the FCC lattice. At low temperature, the phases are ordered according to the cubic $L1_2$ -type structure for the CoPt_3 and Co_3Pt stoichiometries and the tetragonal $L1_0$ -type structure for the CoPt stoichiometry. At high temperature, the Co-Pt alloys are disordered (FCC solid solution). Only a few phase diagrams of binary alloys display $L1_2$ and $L1_0$ as single ordered states. The peculiarity of these systems, the most famous one being Cu-Au, lies in the fact that $L1_0$ and $L1_2$ are the single ordered structures built on the FCC lattice with only concentration waves of vector $2\pi/a$ [100] and equivalent ones $/1/$. In other words, considering the usual decomposition of the FCC lattice into four simple cubic sublattices, $L1_0$ and $L1_2$ are obtained by occupying differently these sublattices: for $L1_0$ two of them are occupied by A atoms and the two others by B atoms whereas for $L1_2$ only one is occupied by A atoms and the others by B atoms (Fig. 1). All other ordered structures based on the FCC lattice involve other concentration waves.

The study of phase transitions in such systems is therefore of particular interest. The order-disorder transitions are found of first order as expected from Landau-type arguments. The similarity of the ordered structures raises many questions on the nature of the transformation processes, on the resulting microstructures and on the role of the domains walls (or interfaces) in the transformations. For example, the transition $L1_0 \rightarrow L1_2$ is very intriguing. One could imagine a continuous transition, one structure transforming progressively into the other by changing the alloy concentration, without clear region of coexistence. Alternatively, if both structures effectively coexist, how do the interfaces look like? To our knowledge, no study has been done to characterize precisely this transition and the two-phase domain $L1_0 + L1_2$.

In the present work, the Pt-Co system has been chosen to study in detail different phase transformations and the resulting microstructures using transmission electron microscopy. The observations have been performed on the JEOL 200CX (ONERA) for conventional imaging and on the JEOL 4000EX (RUCA) for high resolution imaging. The different phase limits have been determined from the investigation of numerous alloys

ranging from 58 to 75 %at Pt, annealed between 530 and 900°C $/2 - 5/$. The resulting phase diagram is shown in Fig. 1. As a major result, an eutectoid transformation $A1 = \text{disordered state} \rightarrow L1_0 + L1_2$ has been found to arise at 59.5% Pt and at 725°C, whereas a two phase domain $L1_0 + L1_2$ has been shown to extend from 59.5 to 61.5%Pt at the eutectoid plateau and from 59.5 to 63%Pt at low temperature.

Different kinds of transformation have been characterized $/2 - 5/$. Two principal types of phenomena are described below. First, the antiphase boundaries (APB) of the CoPt_3 phase have a remarkable behaviour near a phase transition: they are completely transformed before the transition and wet by the new phase ($L1_0$ or disorder). Secondly the $L1_0 + L1_2$ microstructure formed through the eutectoid reaction exhibits fascinating features which have been characterized in detail.

2 - WETTING OF THE ANTIPHASE BOUNDARIES OF THE CoPt_3 PHASE

This effect has been first studied near the order-disorder transition occurring at $T_D = 755^\circ\text{C}$, by heating in the microscope samples initially highly ordered $/2,5,6/$. The concentration of the alloy $\text{Co}_{30}\text{Pt}_{70}$ has been chosen to be close to the congruent point D (Fig. 1). In the ordered state at low temperature, the alloy displays a microstructure of large domains (translation domains) separated by antiphase boundaries (APB). APB's are characterized by antiphase vectors of type $1/2 \langle 110 \rangle$ which are easily determined in conventional microscopy, by comparing the APB contrast in three dark field images (DF) realized in a two beam geometry with the superstructure reflections (100), (010) and (110) of a (001) zone axis $/2,5/$. A given APB should be out of contrast for one DF over three. Samples were then observed in an orientation close to (001) and APB's followed in DF (110) and (010). Starting from room temperature, the sample is heated step by step and annealed at different temperatures up to T_D , phenomena being recorded with a video-recorder $/7/$.

Fig. 1 - The Co - Pt phase diagram after [2]. The structures of the $L1_0$ and $L1_2$ phases are given in the insets.

Fig.2 - Evolution with temperature of the APB's in $Co_{30}Pt_{70}$ observed in DF (110) :
a) at room temperature : arrows indicate the APB's out of contrast in this DF
b) at $T_D = 17^\circ C$: the previously out of contrast APB's are now slightly visible
c) at $T_D = 9^\circ C$: APB's are transformed into macroscopic layers of disordered phase.

Fig. 3 - a) High resolution image of a wet APB, in a projection along [001]; b) High resolution image of an APB transformed into a disordered layer. A large aperture including the fundamental reflections has been used

Fig. 4 - Antiphase boundaries in $\text{Co}_{37}\text{Pt}_{63}$ aged at 550°C. a) DF (100), b) DF (110), c) DF (010).

Fig. 5 - High resolution image showing a node of three APB's, in a projection along [001]. A large aperture including the fundamental reflections has been used. The APB's are labelled 1, 2, 3 and are respectively wet by the L1_0 variants X, Y, Z

Up to roughly 40°C below T_D , the APB contrast does not change significantly. As shown in Fig. 2a this contrast obeys the rule given above. The APB's are almost isotropic and some edge on parts are clearly seen. 40°C below T_D , some modifications appear and are reinforced as the temperature increases. The APB's now become partially visible in the DF mode where they were previously out of contrast (Fig. 2b). High resolution imaging of these APB's, realized in annealed quenched samples, clearly shows that some disorder takes place in the core of the APB (Fig. 3a). The image is a projection along a [100] direction of an APB seen edge on. On each side of the boundary, the square pattern of white dots corresponds to the Co columns of the $L1_2$ domains in antiphase. At the boundary, this contrast is modified being grey and somewhat diffuse and in the central part of the boundary, a fine square pattern of grey dots having a periodicity half of the first one appears and is related to the FCC disordered lattice. This disorder gives rise to the residual contrast observed in the DF images. At $T_D - 9^\circ\text{C}$, which should roughly correspond to coexistence with the disordered state, all the APB have now the same dark contrast in the three DF (100), (010), (110), which means that they are transformed in thin disordered layers (Fig. 2c). Their atomic structure is shown in Fig. 3b: the $L1_2$ domains are in antiphase and at the boundary a macroscopic layer of disordered phase has taken place, giving rise to two new interfaces $L1_2$ / disorder. It is striking to remark that these interfaces are not well defined and seem to be fractal-like. At this temperature, the thickness of the layer increases with time and reaches an apparent width of 40nm after 30mn (Fig. 2c). Increasing further the temperature up to T_D induces an homogeneous nucleation of the disordered phase inside the domains and the maximum apparent width of the APB's is about 60nm [2,5].

These in situ experiments, coupled with high resolution electron microscopy observations on annealed quenched samples show that APB's are modified *before* reaching the coexistence temperature with the disordered phase, which is typical of an *interfacial wetting behaviour* [5,8]. It was theoretically expected for $L1_2$ [9] but not yet experimentally observed. The results are also in excellent qualitative agreement with more recent calculations [10].

A similar behaviour occurs near the transition $L1_2 \rightarrow L1_2 + L1_0$ (path III in Fig. 1). In that case, the APB's are wet by the $L1_0$ phase. This phenomenon has been studied in the $\text{Co}_{37}\text{Pt}_{63}$ alloy. The alloy was initially annealed in the disordered state, then slowly cooled down to a temperature of interest (between 730 and 530°C), aged a long time and finally quenched. This aging procedure was particularly suited to study the different steps of the ordering processes leading to the final $L1_0 + L1_2$ state [2,4].

Following the path III, the alloy is first ordered according to the $L1_2$ structure and displays the usual microstructure as in Fig. 2a with APB's obeying the extinction rule given above. At 550°C, the APB contrast is modified as shown in Fig. 4. By comparing the three DF (100), (010), (110) of a (001) zone axis, the APB's appear now with a dark contrast in two given DF and with a strong white contrast in the third DF. In addition, their contours, previously smooth, are now well faceted and straight segments are clearly seen edge on. The APB's are no longer perfect walls between $L1_2$ domains but they are decorated by $L1_0$. Let us recall that the $L1_0$ structure, being tetragonal, presents three orientation variants, X, Y and Z, depending on the orientation of the four-fold axis with respect to the cube axis of the FCC lattice. In reciprocal space, $L1_0$ ordering produces superstructure reflections at position (001) for Z, (100) for X and (010) for Y and equivalent ones around each fundamental reflection of the FCC lattice. Thus, using the three DF (100), (010), (110) of the (001) zone axis, a given variant will appear dark in two DF and white in the third DF. APB's seen in Fig. 4 exactly obey this contrast rule.

Furthermore, an high resolution image of a node of three decorated APB's, is shown in Fig. 5. Co columns are seen as white dots. In the $L1_2$ domains, dots form square patterns, which are in antiphase each other, according to the vectors $1/2[110]$, $1/2[011]$, $1/2[011]$. Each boundary is decorated by a given $L1_0$ orientation variant, depending on the nature of the antiphase vector. For example, a square dot pattern rotated by 45° with respect to that of $L1_2$ takes place at the APB $1/2[110]$ (APB labelled 3 in Fig. 5). It corresponds to the Co columns of $L1_0$ projected along [001], which defines the variant Z. For the two other APB's, dot patterns correspond to the projection of $L1_0$ along [100] and [010], which let us identify the variants X and Y. Note that the thickness of the $L1_0$ layers does not exceed 3-4 periods and that the transition between $L1_0$ and $L1_2$ - type orderings seems to be abrupt. Furthermore, the new interfaces $L1_0$ / $L1_2$ tend to be located in (110) types of planes.

These observations show that, near the transition $L1_2 \rightarrow L1_2 + L1_0$, the APB's of the $L1_2$ phase are transformed, being decorated by $L1_0$. When reaching the temperature of coexistence, the decorated APB's become progressively thin $L1_0$ layers which grow to form thick platelets as shown in Fig. 6. The evolution of the APB's *before* the formation of the thick platelets is again typical of an *interfacial wetting* phenomenon.

In addition, let us mention that a similar wetting behaviour has been observed near the transition $L1_0 \rightarrow L1_2 + L1_0$ (path I in Fig. 1). In that case, the interfaces separating two orientation variants of $L1_0$, say X and Y, are progressively wet by the $L1_2$

Fig. 6 - Thick platelets of $L1_0$ in the $L1_2$ matrix in $Co_{38.5}Pt_{61.5}$ aged at $700^\circ C$: a) DF (010), b) DF (110), c) DF (100).

Fig. 7 - High resolution image along [001] involving the variants X and Y of the $L1_0$ phase.

Fig. 8 - a) a typical microstructure involving the variants X and Y in DF (110). b) Schematic drawing of the tiling of domains.

phase, giving rise to two new interfaces according to the sequence $X/L1_2/Y, /2,4/$.

3 - DESCRIPTION OF THE $L1_0 + L1_2$ MICROSTRUCTURE

Different $L1_0 + L1_2$ microstructures have been observed as a function of temperature and of concentration, depending on the phase transformations the alloy has undergone during the aging procedure explained above. Examining the phase diagram, three sequences of transformation leading to $L1_0 + L1_2$ state can be depicted and are indicated in Fig. 1 as paths I, II, III. Processes I and III are in two steps and we just have seen that the second step involves wetting of domain walls of the ordered structure, formed in the first step. The microstructure formed through the process II appears as archetypal of the $L1_0 + L1_2$ microstructure and is now described in detail.

The microstructure is a patchwork of large areas, which consist, each, of a tiling formed by $L1_2$ domains and by two given orientation variants of $L1_0$. Fig. 7 shows a high resolution image of a typical area involving the variants X and Y, projected along [001] such that all the interfaces are seen edge on. The $L1_0$ domains are seen as rhombi surrounded by the $L1_2$ phase.

The tiling has remarkable topological properties emphasized in Fig. 8. Fig. 8a shows a DF (110) image of an area involving X and Y in an orientation near [001]. In these conditions, the $L1_2$ domains are the only visible domains, which clearly reveals their distribution in the tiling. The mosaic consists of zig zag bands of domains aligned along [110] and [1-10]. In each band $L1_2$ domains regularly alternate with a given $L1_0$ variant (see Fig. 8b). The interfaces are only of type $L1_0/L1_2$, and have definite orientations, which are close to $\langle 110 \rangle$. There is however a systematic angular deviation from the perfect crystallographic position of $\pm 11^\circ (\pm 3)$ in magnitude as shown in Fig. 8b. On the other hand, diagonals of $L1_0$ domains are roughly along $\langle 100 \rangle$ directions. Furthermore, high resolution images show that the interfaces are perfectly coherent. Optical diffraction measurements performed on the high resolution images have shown that in $L1_0$ the ratio c/a is equal to 0.99 while in the stoichiometric alloy it is equal to 0.96.

The regularity and the scale of the tiling are very striking: some areas display almost perfectly periodic patterns and one can define locally a square lattice with a parameter equal to 20nm. In spite of a certain dispersion, the size of the domains is always very small, being around 20 - 30 nm.

The mechanism of formation of this microstructure raises many questions and is currently under study. The topological properties, we have pointed out, have close similarities with those of the microstructure of $L1_0$ germs embedded in the disordered matrix observed in CoPt /11/. This let us suggest that

the formation of the two-phase microstructure is driven by long range *elastic interactions* between $L1_0$ germs, which have been shown to control the growth of $L1_0$ domains in CoPt /12/. The absence of any APB either in $L1_2$ nor in $L1_0$ let us think that the mosaic of domains is the *direct image* of the superlattice formed by the germs in the early stages of growth.

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