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EQUILIBRIUM PHASE DIAGRAM FOR THE Pr–Fe SYSTEM BELOW THE EUTECTIC POINT CONSTRUCTED FROM ELECTRON DIFFRACTION DATA

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Electron diffraction data revealed the presence of equilibrium Pr_2Fe_{17} and α-Pr phases in annealed Pr–25 at.% Fe and Pr–77 at.% Fe alloys, respectively. The phase formation was verified by analysis based on structure-orientation relationships and matrix equations relating the equilibrium Pr_2Fe_{17} phase with the coherent metastable $PrFe_2$ phases of the $C14$ and $C15$ types. It is concluded that the equilibrium phase diagram of the Pr–Fe system has a single two-phase region of α-Pr + Pr_2Fe_{17} on the Pr side below the eutectic point.

Up to now, the equilibrium phase diagram of the Pr–Fe system has not been conclusively established. The equilibrium diagram presented in [1] contains two two-phase regions (α-Pr + $PrFe_2$ and $PrFe_2 + Pr_2Fe_{17}$) on the Pr side below the eutectic point. According to our X-ray diffraction data [2], there exists a single two-phase region of α-Pr + Pr_2Fe_{17} in the equilibrium state, while the $PrFe_2$ phases of the $C14$ and $C15$ Laves types are nonequilibrium phases with a very long-term metastability. X-ray diffraction gives a diffraction pattern that is statistically averaged over the entire sample, including all phases present in a multiphase sample. Therefore, it is advisable to use an electron diffraction technique employing a thin primary beam of a micron cross section, which would allow a point diffraction pattern to be obtained separately from each phase. The purpose of this work was to determine, by the electron diffraction method, the type of the two-phase region in the phase diagram of the Pr–Fe system in the equilibrium state below the eutectic point.

Experiments were performed on Pr–25 at.% Fe and Pr–77 at.% Fe alloys. These alloys belong, respectively, to the two-phase regions α-Pr + $PrFe_2$ and $PrFe_2$ + Pr_2Fe_{17}, according to [1], and to the two-phase region α-Pr + Pr_2Fe_{17}, according to [2].

The Pr–Fe alloys were obtained by melting in an argon atmosphere in an arc furnace with nonconsumable tungsten electrode and a water-cooled copper tray. The alloys were synthesized from carbonyl iron and vacuum-distilled praseodymium with an impurity content from 10^{-7} to 10^{-2} at.%. The alloys were annealed in quartz tubes evacuated to high vacuum. The samples were studied in a Tesla BS-613 electron microscope with an accelerating voltage of 80 keV and a constant $\lambda L = 21$ Å mm. The samples for the electron diffraction analysis were prepared by deposition of fine powders onto a base copper grid, which allowed only part of the full diffraction pattern to be obtained. Another disadvantage of these samples were difficulties, related to random arrangement of crystalline grains, in obtaining electron microdiffraction patterns corresponding to the base planes of the reciprocal lattices.

In the analysis of the microdiffraction patterns, we have taken into account that there are definite structure-orientation correlations [3] between the stable Pr_2Fe_{17} phase and the coherent metastable $PrFe_2$ phases of the $C14$ and $C15$ type. This results in similar arrangements of sites in some zero cross sections (particularly in the coherence planes) of the reciprocal lattices of these phases. The Pr_2Fe_{17} phase has a rhombohedral lattice with the parameters $a = 8.585$ Å, $c = 12.464$ Å (in a hexagonal setting) and the space group $R3m$ [4]. The $PrFe_2$ phase with the structure of the $C14$ Laves type has a hexagonal lattice with the parameters $a = 5.26$ Å, $c = 8.62$ Å and the space group $P6_3/mmc$ [2]. The $PrFe_2$ phase of the $C15$ Laves

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type has an fcc lattice with the parameters $a = 6.78$ Å and the space group $Fd3m$ [3]. Despite the dissimilar structures of Pr_2Fe_{17} and $PrFe_2$ $C14$ (different symmetry types, lattice parameters, and space groups), the arrangement of lattice sites and their separations in the coherence plane are much alike for the two phases, differing only by a 30° rotation about the c axis. This similarity hinders an unambiguous phase identification from respective electron microdiffraction patterns. For this reason, each electron microdiffraction pattern was compared with all parallel sections of reciprocal lattices of coherent phases.

The orientation relationships for the phases Pr_2Fe_{17} and $PrFe_2$ $C14$, and also for Pr_2Fe_{17} and $PrFe_2$ $C15$ can be written in the form

$$[100]^*_{2:17} \parallel [2\bar{1}0]^*_{C14}, \quad [010]^*_{2:17} \parallel [110]^*_{C14}, \quad [001]^*_{2:17} \parallel [001]^*_{C14}, \tag{1}$$

$$[100]^*_{2:17} \parallel [01\bar{1}]^*_{C15}, \quad [010]^*_{2:17} \parallel [\bar{1}10]^*_{C15}, \quad [001]^*_{2:17} \parallel [111]^*_{C15}. \tag{2}$$

Then, the matrix equations are as follows:

$$\begin{vmatrix} h \\ k \\ l \end{vmatrix}^*_{C14} = \begin{vmatrix} 0.7 & 0.35 & 0 \\ -0.35 & 0.35 & 0 \\ 0 & 0 & 0.35 \end{vmatrix} \cdot \begin{vmatrix} h \\ k \\ l \end{vmatrix}^*_{2:17}, \tag{3}$$

$$\begin{vmatrix} h \\ k \\ l \end{vmatrix}_{C15} = \begin{vmatrix} 0 & -0.32 & 0.32 \\ 0.32 & 0.32 & 0.32 \\ -0.32 & 0 & 0.32 \end{vmatrix} \cdot \begin{vmatrix} h \\ k \\ l \end{vmatrix}^*_{2:17}. \tag{4}$$

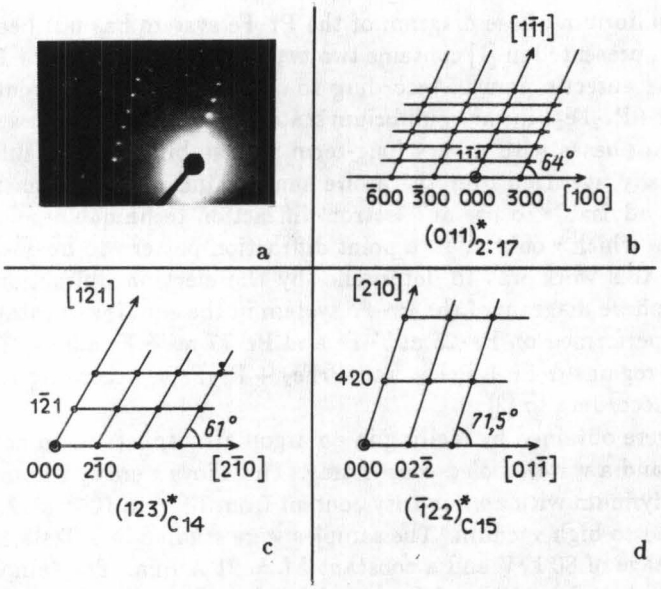

Fig. 1

Figure 1a shows an electron microdiffraction pattern from the Pr–25 at.% Fe alloy after a 30 min annealing at 650°C. This pattern corresponds to the $(011)^*_{2:17}$ plane of the reciprocal lattice (Fig. 1b) (the middle row of reflections is not revealed because of object's peculiarities). Let us examine the patterns for the conjugated planes of the reciprocal lattices of $PrFe_2$ $C14$ and $PrFe_2$ $C15$. Using Eqs. (3) and (4), we obtain

$$[100]^*_{2:17} \parallel [2\bar{1}0]^*_{C14}, \quad [1\bar{1}1]^*_{2:17} \parallel [1\bar{2}1]^*_{C14}, \quad (011)^*_{2:17} \parallel (123)^*_{C14}, \tag{5}$$

$$[100]^*_{2:17} \parallel [01\bar{1}]^*_{C15}, \quad [1\bar{1}1]^*_{2:17} \parallel [210]^*_{C15}, \quad (011)^*_{2:17} \parallel (\bar{1}22)^*_{C15}. \tag{6}$$

Figures 1c and 1d show the corresponding sections of the reciprocal lattices. As is seen, a complete coincidence of the positions of reflections on the electron microdiffraction pattern with the reciprocal lattice sites is

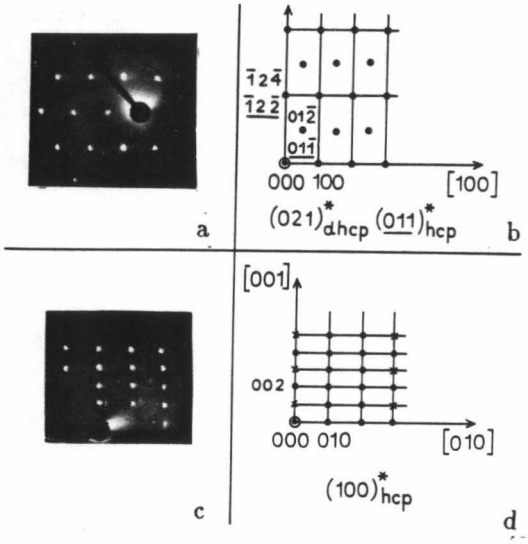

Fig. 2

observed only for the Pr_2Fe_{17} phase. This is an unambiguous evidence that an equilibrium Pr_2Fe_{17} phase forms in the Pr–25 at.% Fe alloy.

Figures 2a and 2c show electron microdiffraction patterns from the Pr–77 at.% Fe alloy annealed at 600°C for 500 h, which are indexed in the α-Pr type structures. The α-Pr structure was initially treated as possessing a hexagonal (*hcp*) lattice with the parameters $a = 3.67$ Å, $c = 5.89$ Å and the space group $P6_3/mmc$ [5]. Eventually, we concluded that the phase had a hexagonal lattice with the parameter c doubled as compared to that in the *hcp* lattice ($a = 3.67$ Å, $c = 11.832$ Å); this structure was called the *dhcp* structure [6]. The matrix equation for the transition from *hcp* to *dhcp* can be written as

$$\begin{vmatrix} h \\ k \\ l \end{vmatrix}^*_{hcp} \cdot \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0.5 \end{vmatrix} \cdot \begin{vmatrix} h \\ k \\ l \end{vmatrix}^*_{dhcp} . \tag{7}$$

In this context, the electron microdiffraction pattern of Fig. 2a can be interpreted either as belonging to a *dhcp* structure and coinciding with $(021)^*_{dhcp}$ (Fig. 2b), or as belonging to an *hcp* structure and coinciding with $(011)^*_{hcp}$ (the indices relating to the *hcp* structure are underlined). However, the electron microdiffraction pattern of Fig. 2c can be interpreted only within an *hcp* structure as coinciding with $(100)^*_{hcp}$ (Fig. 2d; the crosses indicate forbidden reflections that appear due to the double diffraction).

The formation of the equilibrium Pr_2Fe_{17} and α-Pr phases in the Pr–25 at.% Fe and Pr–77 at.% Fe alloys, respectively, prove convincingly that both alloys occur in a two-phase region (α-Pr + Pr_2Fe_{17}) and that the equilibrium phase diagram of the Pr–Fe system indeed has a single two-phase region below the eutectic point.

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