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Structural and constitutional studies of some cerium-praseodymium alloys

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Room temperature X-ray diffraction studies on some powdered Ce–Pr alloys indicate that the face-centred-cubic (f c c) structure extends from 0 to 65% Pr* and the double hexagonal (d h c p) structure from 66 to 100% Pr, after a heat treatment of 600° C for 2 h and quickly cooling to room temperature. Variations of atomic volume with composition in both ranges indicate that the volume difference between the f c c form of praseodymium and the d h c p form is similar to that observed for α(d h c p) and β(f c c) lanthanum, whereas extrapolation to 100% Ce from the d h c p range gave an atomic volume for the d h c p Ce appreciably in excess of the atomic volume of fcc γ-Ce. This volume expansion is consistent with a slight change of the effective valency of the cerium atoms in the d h c p solid solutions when compared with the γ-Ce but there is uncertainty as to the precise atomic volume of d h c p β-Ce. The DTA studies indicate a narrow liquidus/solidus separation and the electrical resistivity and DTA measurements indicate a regular change with composition in the transition temperature of the high temperature b c c phase. For the d h c p $\rightleftarrows$ f c c transition there is a marked variation in the width of the hysteresis loop across the Ce–Pr system which can be correlated with the degree of plastic deformation involved in the transformation. There is a marked increase in the slope of the transition temperature with composition for the Pr-rich alloys and no such transition is observed for the praseodymium samples after one heating cycle. A possible d h c p $\rightleftarrows$ f c c transition, however, is indicated by the DTA traces of the commercially pure praseodymium sample on cycling with temperature and this has been attributed to the influence of interstitial impurities.

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1. Introduction

Intra-rare earth alloy systems are of considerable interest because of their magnetic properties and because of the systematic changes in crystal structure which occur in, for instance, a light-heavy intra-rare earth system such as Ce–Gd [1], i.e. f c c → d h c p → Sm-type → c p h. The various structures occur over the same ranges of mean atomic number (Z_m) for the alloys as for the elements and the axial ratios (c/a) of the hexagonal alloys tend to follow a common curve of c/a with Z_m [2]. A number of theoretical models have been proposed to explain the closely similar stacking modifications which occur in the rare earth metals and alloys and some of these have been reviewed by Johansson [3]. Exceptional behaviour is often observed in the atomic volume variations of the intra-rare earth alloy systems involving cerium and this has been attributed to the variable electronic state of this metal in different alloying environments [1, 4]. The early work indicated that the atomic volumes of γ-cerium (f c c) and β-cerium

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* This praseodymium was kindly loaned by Dr D. Fort of the Centre of Materials Science, University of Birmingham, and the metal had been purified by solid state electrolysis to give a resistance ratio of ~ 200.

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(dhcp) lie significantly below the general lanthanide contraction and Gschneidner and Smoluchowski [5] have attributed these and other effects to an effective valency of about 3.1 for these forms of cerium, compared with the normal trivalent state for most of the other rare earth metals. The atomic volume variations of the dhcp alloys in the systems Ce–Gd, Ce–Y [1], Ce–Nd, Ce–Sm and Ce–Tb [4] compared with the corresponding Pr systems have, therefore, been interpreted in terms of a slight change in the valency state of the cerium atoms in solution in the alloys from the value of 3.1 characteristic of γ- and β-Ce to a value of 3.0. Extrapolation of the atomic volume variations to 100% Ce gave an atomic volume of 34.896 ± 0.025 Å^3 for a hypothetical trivalent dhcp form of cerium, which was in very good agreement with the value obtained by extrapolation of the atomic volume versus atomic number variation in the rare earth period [4].

Praseodymium has the dhcp structure over a wide temperature range and the high pressure–high temperature phase diagram of Klement and Jayaraman [6] indicated a high temperature dhcp $\rightleftarrows$ bcc transition at atmospheric pressure. The splat cooling experiments of Bucher *et al.* [7] however, indicated that a fcc form of praseodymium could be produced by this means and this phase was partially retransformed to the dhcp structure by annealing at 560° C. Klemm and Bommer [8] have reported an fcc form of praseodymium. The Th–Pr phase diagram [9], however, did not show a high temperature fcc form of praseodymium whereas the lattice spacing measurements of Norman *et al.* [10] indicated that, if such a phase existed at high temperatures, then a continuous series of solid solutions should exist between fcc Th and fcc Pr.

The purposes of the present work were to study the effect of alloying cerium with praseodymium on the valency state of the cerium atoms and to study the structural changes in the Ce–Pr system in an attempt to clarify the situation with respect to praseodymium itself. This is a useful system since cerium has a dhcp $\rightleftarrows$ fcc ($\gamma \rightleftarrows \beta$) transition close to room temperature and hence a progressive rise in the transition temperature would be anticipated on alloying with praseodymium. Thus a systematic study of this variation might provide evidence for or against such a transition in praseodymium itself. In addition, the X-ray diffraction, electrical resistivity and DTA studies will provide constitutional information on the Ce–Pr system.

2. Materials and experimental method

The Ce–Pr alloys used for the resistivity, X-ray and DTA studies were prepared from standard commercial material. The praseodymium was obtained from Rare Earth Products Ltd, and the cerium from Koch-Light Laboratories Ltd. In addition, some relatively pure praseodymium* has been investigated by DTA measurements in order to examine the effect of impurities on the solid state transitions in this metal.

The alloys were produced by arc melting the appropriate weights of the component metals (total weight of about 5 g) in pure argon at 300 Torr. The resultant alloy buttons were turned and melted several times and then vacuum annealed for 7 days at 600° C followed by cooling to room temperature over a period of 2 days.

All the samples used in this work were polycrystalline in nature and details of the specimen preparation for the electrical resistivity measurements and X-ray diffraction studies have been given elsewhere [11, 12]. The resistivity data are accurate to within ± 2% and the atomic volume data to within ± 0.05%.

In the case of the DTA investigations, the samples were in the bulk form and of about 0.03 g in weight; platinum was used as the reference material. A modified Linseis L62 DTA unit together with a Stanton-Redcroft linear temperature programmer were employed for the detection of the solid state transitions and melting temperatures. PtRh–Pt thermocouples were used in the DTA head and the crucibles were made of tantalum. Prior to each experiment the DTA sample chamber was evacuated to a pressure of $\sim 10^{-5}$ Torr and then flushed with ultra pure argon from a BOC Rare Gas Purifier Mk. 3. The DTA runs were conducted under a static atmosphere of purified argon and the transition temperatures were recorded using heating and cooling rates of 2 or 10° C min^{-1}. The measured transition temperatures were not found to be affected by the particular heating or cooling rate employed but the faster rate was more effective in revealing the peaks due to the dhcp $\rightleftarrows$ fcc transitions which

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* All compositions are in at.%.

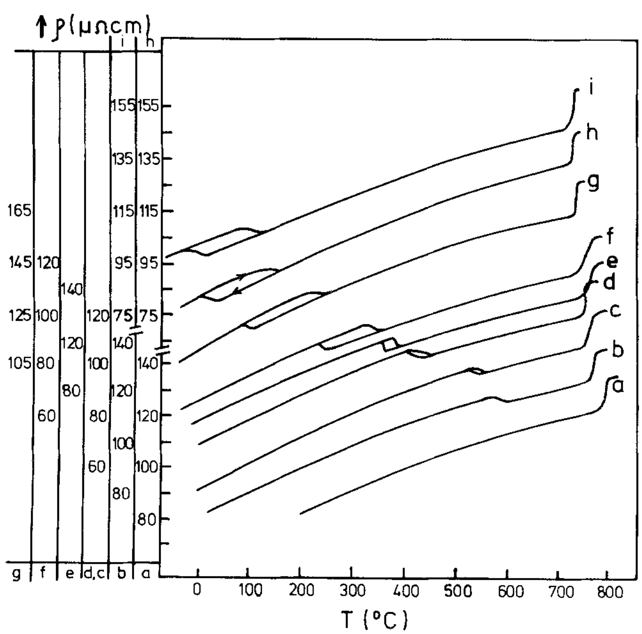

Figure 1 The resistivity versus temperature variations for some Ce-Pr alloys. Note that the resistivity scales have been arranged so that the sequential change in the $\gamma \rightleftarrows \beta$ hysteresis loops can be clearly illustrated. (a) Pr, (b) 90% Pr, (c) 85% Pr, (d) 70% Pr, (e) 60% Pr, (f) 50% Pr, (g) 20% Pr, (h) 5% Pr, (i) Ce.

were much less pronounced than those due to the high temperature bcc transitions. The transition temperatures were taken to be the point of deviation of the ΔT (temperature difference between standard and sample) trace from the base line and have been estimated to be correct to within ± 5° C.

3. Experimental results and discussion

3.1. Resistivity studies

Measurements of the electrical resistivity (ρ) of a range of Ce–Pr alloys have been carried out in the temperature range 20 to 800° C and a selection of the ρ versus T results (after an initial heating and cooling cycle) are shown in Fig. 1. These curves indicate that, apart from the Pr sample, there are three types of anomaly on heating, the negative step in $\rho(T)$ (dhcp → fcc), the positive step in $\rho(T)$ (fcc → bcc) and a general non-linearity in the curves (convex upwards). Similar departures from linearity have been observed for other light rare earth metals and have been explained by anomalous variations of the phonon resistivity [13]. The non-linearity in the curves shown in Fig. 2 was only apparent after the initial heating run.

It is clear from Fig. 1 that the praseodymium sample only exhibited one solid state phase transformation (dhcp ⇄ bcc) whereas the other alloys and cerium exhibited two transitions, namely dhcp ⇄ fcc and fcc ⇄ bcc, with an increasing hysteresis loop width for the dhcp ⇄ fcc transition as the cerium concentration increased. In every case the resistivity decreased by

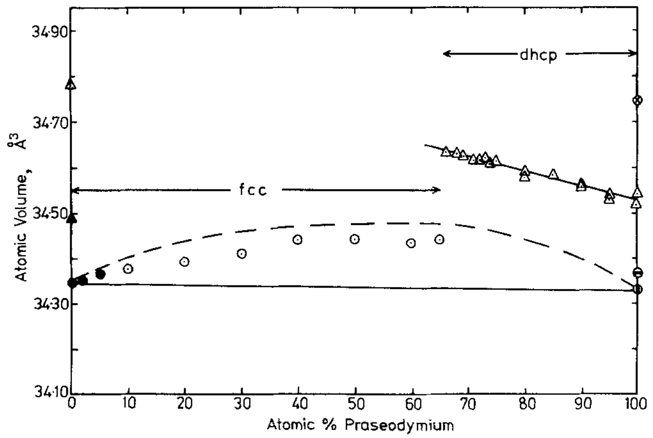

Figure 2 The variation of atomic volume with composition for the Ce-Pr alloys at room temperature (after quickly cooling the powders from 600° C). ○ fcc alloys, ● fcc alloys [10], △ dhcp alloys, ▲ β-Ce [15], ⧋ β-Ce [19], ⦶ fcc Pr [10], ⊖ fcc Pr [8], ⊗ fcc Pr [7].

TABLE I A comparison of some $\gamma \rightleftarrows \beta$ transformation temperatures in cerium

$\gamma \to \beta$ (° C)	$\beta \to \gamma$ (° C)	Width of hysteresis ΔT	Purity (at.%)	Reference
− 23 ± 3	168 ± 7	191	99.53	[15]
1 ± 3	81 ± 7	80	96.41	[15]
− 10	100	110	98.97	[16]
10 ± 5	110 ± 5	100	−	Present work

A reliable value for the purity of the commercial grade cerium investigated in this work is not available. However, Gschneidner *et al.* [15] suggested that the higher is the purity of the cerium, the larger is the hysteresis between $\beta \to \gamma$ and $\gamma \to \beta$ and on this basis, the present results would indicate that the cerium employed in this work has a similar purity to that used by McHargue and Yakel [16].

about 3% for dhcp → fcc and increased by about 10% for fcc → bcc (or dhcp → bcc in the case of praseodymium), i.e. the magnitudes of the steps for the two transitions did not vary significantly across the alloy system. The resistivity data on praseodymium are in good agreement with those of Spedding *et al.* [14].

The transition temperatures for the $\gamma \rightleftarrows \beta$ phase change in cerium are similar to some previously reported values [15, 16] which are summarized in Table I. It can be seen, however, that there is a fairly wide spread of results which can be attributed to the different impurity levels in the cerium samples employed in these measurements. There is doubt as to the precise volume change involved in the $\gamma \rightleftarrows \beta$ transformation (see discussion of the X-ray diffraction data) but the width of the hysteresis observed in the present work and in previous investigations [15, 16] clearly indicates that plastic deformation is associated with this transformation, and this would be consistent with the low transformation temperatures in cerium.

In the case of the CePr alloys, the addition of up to 20% Pr does not significantly change the width of the hysteresis loop but the additions do shift the transformations to higher temperatures (Fig. 1). There is some narrowing of the loop at 50% Pr and at greater praseodymium contents there is a marked reduction of the loop width such that it is not detectable in the 90% Pr alloy which has a $\beta(\alpha) \to \gamma$ transition temperature of 600° C. These data, together with the DTA measurements, will be discussed later in terms of the transformation characteristics of the alloys.

3.2. X-ray diffraction studies

The X-ray diffraction studies indicate that after annealing the powdered alloys at 600° C for 2 h and then quickly cooling to room temperature, the alloys in the range 0 to 65% Pr have the fcc structure and alloys in the range 66 to 100% Pr have the dhcp structure (with weak fcc lines being observed between 66 and 74% Pr inclusively). This behaviour can be compared with that of the Ce–Nd system [4] where the fcc structure occurs in the range 0 to 30% Nd and the dhcp structure from 40 to 100% Nd, after a very similar heat treatment of the powdered material. This observation is consistent with the expected greater stability of the hexagonal structure in neodymium compared with praseodymium.

There is a linear variation of atomic volume with composition within the dhcp range of the Ce–Pr system as shown in Fig. 2, and extrapolation to 100% Ce gives an atomic volume of 34.850 ± 0.025 Å^3. This is close to the mean value of 34.896 ± 0.025 Å^3 obtained from the extrapolation of the linear atomic volume variations of a number of dhcp rare earth–cerium alloys to 100% Ce [1, 4], which corresponded to the expected value for trivalent cerium.

In our earlier interpretation of the atomic volume variations of some dhcp rare earth–cerium systems [1, 4] we used the atomic volume of β-cerium determined by Gschneidner *et al.* [15] which indicated a volume expansion of 0.36% in going from γ- to β-cerium. This appeared to be a realistic value for the volume change as it is similar to the volume difference between α-lanthanum (fcc) and β-lanthanum (dhcp) [17–19]. The more recent work of Beaudry and Palmer [19], however, indicated a significantly bigger volume difference of 1.21% between γ- and β-cerium (see Table II) and the atomic volume of β-cerium (34.784 Å^3) determined by these workers is not far below the extrapolated value of 34.850 Å^3 obtained from the atomic volume variation of the dhcp Ce–Pr alloys. The volume change of 1.21% is much larger than that reported by Gschneidner *et al.* [15] and is much larger than that involved

TABLE II A comparison of the published *a*- and *c*-spacings of β-cerium

a-spacing (Å)	*c*-spacing (Å)	Atomic volume ($Å^3$)	Reference
3.673 ± 0.001	11.802 ± 0.005	34.472	[15]
3.6810 ± 0.0006	11.857 ± 0.001	34.784	[19]

in the α → β transition in lanthanum. These observations could indicate that a purer form of cerium was examined by Beaudry and Palmer [19] and that, in this case, the γ → β transition involved both a change in the crystal structure and a change in the electronic state of the cerium, thus accounting for the significantly larger volume expansion compared with the earlier data. Because of these uncertainties, however, it is not known whether the extrapolated atomic volume for dhcp cerium obtained from the present lattice spacing data for the Ce–Pr alloys represents the volume of β-cerium or a hypothetically expanded trivalent form of dhcp cerium which has an atomic volume in excess of that of β-cerium.

The present work shows that there is an extensive range of fcc solid solutions for the powdered material (0 to 65% Pr) after the heat treatment employed in these studies. The atomic volume of fcc praseodymium can be taken as 34.335 $Å^3$, the value derived from the lattice spacings of the fcc Th–Pr solid solutions [10]. This is a particularly reliable extrapolation since the range of fcc solutions extends to 96% Pr and the extrapolated value gives a difference of 0.60% between the two forms of praseodymium, i.e. similar to the difference observed between the dhcp and fcc forms of lanthanum [19]. If it is assumed that there is a positive departure from ideality for the atomic volume variation in these solutions, identical with that observed in the fcc solid solutions of the La–Ce system [20] then the derived atomic volume variation is shown as the dotted line in Fig. 2; it can be seen that the behaviour is similar to that of the measured atomic volumes in the range 0 to 65% Pr. Previous lattice spacing measurements have been made for the Ce-rich alloys [21] (0 to 5% Pr) and these show good agreement with the present data.

Included in Fig. 2 are the atomic volumes of fcc praseodymium determined by Klemm and Bommer [8] and by Bucher *et al.* [7]. The former was probably an impurity stabilized phase and exhibited an atomic volume close to that derived from the Th–Pr data. The atomic volume of the fcc phase produced by splat cooling is appreciably in excess of that of dhcp praseodymium despite the expected greater packing efficiency of the fcc structure. This could indicate that the sample was in a highly strained condition and this would be consistent with the splat cooling treatment. The phase, in fact, could be strain induced and therefore its presence does not necessarily imply a high temperature fcc phase for praseodymium under equilibrium conditions.

The fact that, in the Ce–Pr alloys, the fcc structure persists up to the 65% Pr composition after quickly cooling the powders from 600° C, indicates that only a small proportion of these alloys undergo the fcc → dhcp transition on cooling from high temperatures. This behaviour is similar to that of cerium [15, 22] and can be correlated with the width of the hysteresis loop, i.e. the degree of plastic deformation involved in the transformation (see the discussion of the transformation studies).

3.3. DTA studies

Ce–Pr alloys containing up to 95% Pr exhibited three high temperature peaks in their DTA traces and, in order of increasing temperature, these have been attributed to the dhcp → fcc, fcc → bcc and melting reactions. The reverse reactions have been observed on cooling and Fig. 3 shows the

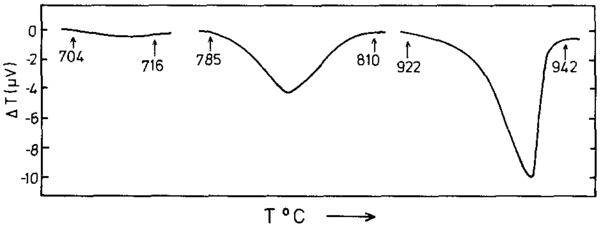

Figure 3 DTA traces of the 95% Pr alloy showing the phase transitions on heating. For the sake of comparison, the traces have been obtained with the same sensitivity factor, and it should be noted that the transition at 704° C can be more clearly resolved by using a more sensitive range on the DTA equipment.

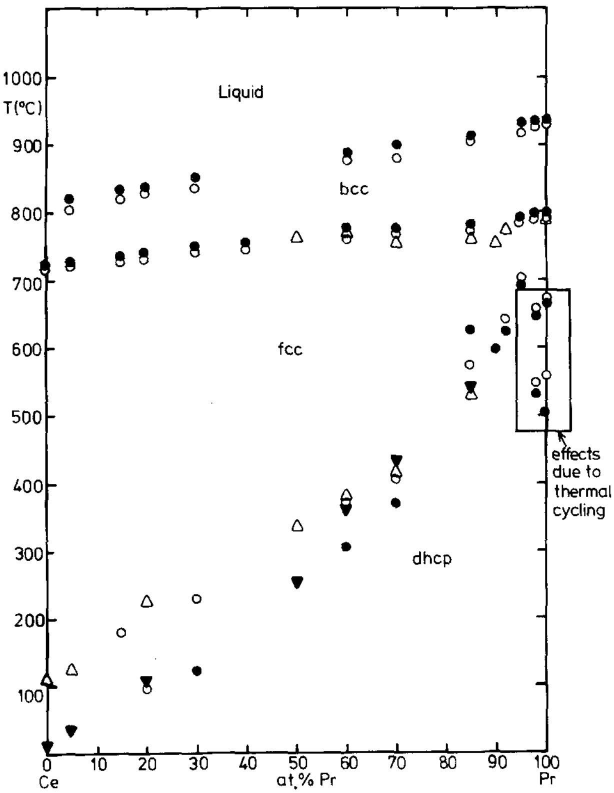

Figure 4 The ce-Pr phase diagram as determined by resistivity and DTA measurements. Phase transitions detected by resistivity on △ heating and ▼ on cooling. Phase transitions detected by DTA on ○ heating and ● on cooling. The inset shows the DTA transitions of 95% Pr and Pr after thermal cycling in a static argon environment.

shapes and relative magnitudes of the DTA peaks (on heating) for the 95% Pr alloy, which are typical of the effects exhibited by most of the alloys studied in this work (note the much larger effect associated with the bcc transition when compared with that for the dhcp → fcc change). The solid state transition temperatures together with the melting and solidification temperatures are plotted as a function of composition in Fig. 4 together with the information obtained from the electrical resistivity measurements. Variations of the heating and cooling rates for the DTA runs had little effect on the transition temperatures and in most cases good agreement was obtained between the transition temperatures determined from both techniques. The alloys at 92% and 95% Pr, however, did not exhibit a dhcp ⇄ fcc transformation in the electrical resistivity data, but did show effects consistent with this transformation in the DTA measurements (see for instance Fig. 3). As there is no evidence from the resistivity studies of a progressive diminution in the resistivity step associated with the dhcp → fcc change with increasing praseodymium content, the discrepancy between these two sets of data could be due to variations in the thermal history of the samples employed in these studies (e.g. cooling rates) which effect their transformation characteristics.

The DTA measurements for the 98% Pr and commercially pure praseodymium samples were initially consistent with the resistivity studies, in that these materials only exhibited two DTA peaks on initial heating, the temperatures of which corresponded to the dhcp → bcc and melting reactions. These effects occurred at the same temperatures on the second and third heating cycles (carried out under the same static atmosphere of argon) but two additional peaks occurred in both samples at lower temperatures; these observations are shown in the inset in Fig. 4. The DTA measurements on the purified praseodymium sample, however, did not indicate any solid state transformations other than dhcp → bcc, even after heating the sample for the third time in the same static argon atmosphere. Thus the transformation characteristics of the two types of praseodymium are distinctly different after the first heating cycle in the DTA equipment, even though the measurements were made under a closely similar argon environment.

The melting point data obtained from the DTA studies indicates a narrow liquidus–solidus separation in the Ce–Pr alloy system (see Fig. 4) and this is consistent with melting point observations on other intra-rare earth alloy systems such as Pr–Nd [23].

4. Solid state transformation characteristics of the Ce–Pr alloys

A number of features of the solid state transformation characteristics of the Ce–Pr alloys have been revealed by the electrical resistivity, X-ray diffraction and DTA measurements carried out in this investigation, and these are now discussed.

The extent of the hysteresis in the dhcp ⇄ fcc transition diminishes with increasing praseodymium content and hence increasing transformation temperature, such that, at the 90% Pr composition the hysteresis was so narrow that it could not be detected by the resistivity measurements (see Fig. 1). These observations are consistent with the extent of the hysteresis being associated with the degree of plastic deformation involved in the phase transformation. Thus at those temperatures where the dhcp ⇄ fcc transformation is purely martensitic in character, the plastic deformation associated with the transformation would be expected to produce a wide hysteresis loop. As the transformation temperature increases, however, the nature of the transformation would be expected to change to a mixture of martensitic and diffusion-controlled processes and eventually to a completely diffusion-controlled process. These changes would result in a diminution and eventual disappearance of the plastic deformation associated with the transformation. This would explain the change in hysteresis loop behaviour in the Ce–Pr system and the change in character of the dhcp ⇄ fcc transformation occurs when the transformation temperature reaches about $0.5\,T_\mathrm{m}$, where T_m is the absolute melting point of the alloy.

The width of the hysteresis loop can be taken as an indication of the extent to which the high temperature fcc phase transforms to the dhcp phase on cooling. Thus the wider is the loop, the greater is the plastic deformation associated with the transformation and the more incomplete is the fcc → dhcp transition due to the inhibiting effect of the plastic distortion. This effect has been discussed in relation to the fcc → dhcp transformation in cerium [22]. The variation of the fcc → dhcp transformation temperatures with composition (Fig. 4) indicates that, for a 100% transformation, all the alloys in the range 100 to 5% Pr should have the dhcp structure after cooling from 600° C. The X-ray diffraction measurements, however, indicated that only the alloys from 100 to 65% Pr exhibited the dhcp structure after cooling from 600° C and the more Ce-rich alloys were predominantly fcc in character. This behaviour can be correlated with the hysteresis characteristics of the alloys and the predominance of the fcc structure in the alloys corresponds with the widening of the hysteresis loop, indicating an incomplete fcc → dhcp change at the transformation temperature (even at transformation temperatures around 300° C). The extent to which these alloys transform from one structure to the other would be expected to be very dependent on the thermal and mechanical history of the samples and this is the subject of some dilatometric studies on these materials [24].

The DTA results for the 85% Pr alloy indicate a reversal of the heating and cooling transformation behaviour for this alloy so that the transformation temperature on heating is significantly *below* that on cooling. A similar reversal has also been observed in the resistivity behaviour of the 70% Pr alloy but not in the DTA behaviour which exhibited the expected effects. These variations in behaviour are probably due to the dependence of the transformation characteristics of these alloys on the precise therman and mechanical history of the samples.

The dhcp ⇄ fcc transition temperatures exhibit a regular, approximately linear increase with praseodymium content up to about 70% Pr composition and there is then a more rapid, nonlinear increase with composition. Because of this variation for the Pr-rich alloys, it is difficult to reliably extrapolate the transition temperature/composition curve but the indications are that, either the dhcp + fcc phase field meets the bcc + fcc phase field just before 100% Pr to give a high temperature eutectoid or peritectoid reaction close to 100% Pr, or the dhcp ⇄ fcc transition does occur in praseodymium (commercial grade) just below a bcc ⇄ fcc transition and the resistivity and DTA effects associated with the dhcp ⇄ fcc change merge with the pronounced changes due to the bcc ⇄ fcc transformation. The latter interpretation is more likely since Fig. 4 shows that the bcc transition temperatures vary more or less linearly across the Ce–Pr system (apart from the dip around the 90% Pr composition) and there is no obvious indication of a high temperature eutectoid or peritectoid reaction.

The apparent change in the transformation characteristics of the 98% Pr alloy and the praseodymium sample (commercial grade) after thermal cycling in the DTA equipment could indicate that, although these samples do not exhibit a clearly defined dhcp → fcc transition on the initial heating run, sufficient interstitial impurities are absorbed from the static argon environment in the DTA sample chamber, to stabilize the fcc phase on the subsequent heating and cooling cycles. Distinct effects were then observed in the DTA measurements and these observations would indicate that, initially the dhcp ⇄ fcc transition was just below the bcc transition (and could not therefore be distinguished by resistivity or DTA studies from the bcc transition) and the effect of the interstitial impurities was to lower the dhcp ⇄ fcc transition temperature. As the samples were heated in a carefully purified argon atmosphere, it would appear that a low level of interstitial impurities was responsible for the appreciable reduction of the transition temperature. Two additional DTA peaks were observed in both samples after the initial heating treatment and the lowest temperature peak (559° C on heating Pr) can be ascribed to the crossing of a solubility boundary corresponding to the dissolution of an interstitial impurity (or impurities) in the dhcp phase. The phase relationships could be similar to those observed in the Sm–H system [25], and the stabilization of the fcc structure in 98% Pr and Pr could be due to the introduction of hydrogen into these materials as a consequence of the reaction between the samples and residual water vapour in the argon. Additional DTA peaks have not been observed for the purified praseodymium even after three heating cycles in a static argon environment closely similar in character to that used in the other measurements. The difference in behaviour can be attributed to a significantly lower initial level of interstitial impurities in the purified praseodymium so that a higher level of impurities would have to be introduced by metal–gas reactions before there would be any significant effect on the phase stabilities. Thus, it is possible that the purified praseodymium sample would eventually behave in a similar manner to the commercial sample, providing the sample was held at high temperatures for a sufficient period of time. The accumulation of impurities (such as hydrogen) however, would depend on the purity of the argon atmosphere and it might be necessary to replace the argon before there is any change in the transformation characteristics of the purified praseodymium sample. A lowering of the dhcp ⇄ fcc transformation temperature for the other Ce–Pr alloys would be anticipated as a result of thermal cycling in the argon atmosphere and the magnitude of the change would depend on the solubility relationships in the alloy–interstitial systems. If the effects reported above are largely due to the presence of interstitial hydrogen then it should be possible to restore the original transformation behaviour by heating the samples in a high vacuum at high temperatures.

The present work indicates that if the Ce–Pr alloys could be prepared from purified constituents instead of the normal commercially pure materials, then there should be a significant shift of the fcc + dhcp phase field to lower Pr contents and a phase diagram similar in form to that of La–Nd [16] would be anticipated.

5. Conclusions

The main conclusions of this investigation can be summarized as follows.

(1) In the Ce–Pr alloys there is an increase in the dhcp ⇄ fcc transformation temperature with increasing Pr content and extrapolation of this variation to 100% Pr indicates that, in the Pr sample of commercial purity, this transformation probably occurs immediately below the bcc transition. If this was the case then it would not be possible to resolve the resistivity and DTA effects associated with this change.

(2) The DTA measurements indicate that interstitials absorbed from the static argon atmosphere appear to stabilize the fcc phase in the commercial Pr sample and the 98% Pr alloy. The purified Pr sample did not behave in this fashion and this was attributed to the lower initial level of interstitial impurities in this material.

(3) The width of the hysteresis loop associated with the dhcp ⇄ fcc transformation exhibits a pronounced narrowing for the Pr-rich alloys, and this has been attributed to the change in the character of the transformation due to the increase in the transformation temperature, i.e. from a martensitic to a diffusion-controlled process. The incomplete transitions from fcc to dhcp observed for the alloys in the range 0 to 65% Pr can be attributed to the inhibiting effect of plastic

distortion and hence can be correlated with the hysteresis width of the transformation.

(4) The linear variation of atomic volume with composition for the dhcp alloys (100 to 66% Pr) extrapolates to an atomic volume at 100% Ce which is close to the expected value for trivalent cerium. This value is appreciably in excess of the atomic volume of β-Ce obtained by Gschneidner *et al.* [15] but is close to the volume of β-Ce obtained by Beaudry and Palmer [19]. Because of the discrepancy in the published values of the atomic volume of β-Ce (which is probably due to different impurity concentrations), it is not clear whether the present studies of the atomic volume variation in the dhcp Ce–Pr alloys represent the ideal variation between α-Pr and β-Ce or indicate a slight change of valency for the cerium atoms in the Pr-rich solid solutions.

(5) The atomic volume variation of the fcc Ce–Pr solid solutions is consistent with (a) the atomic volume of fcc Pr being that derived from the fcc Th–Pr lattice spacing variation, and (b) a positive departure from ideality similar to that observed in the atomic volume variation of the fcc solid solutions in the La–Ce system.

(6) The DTA melting and solidification data indicate a narrow liquidus/solidus separation, as expected in an intra-rare earth alloy system of this kind.

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