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THERMODYNAMICS OF FORMATION AND MELTING BEHAVIOUR OF RARE EARTH–PALLADIUM COMPOUNDS ($RE_{68}Pd_{28}$)

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ABSTRACT

Using the dynamic differential calorimetric method (DDC), heats of formation, heats and entropies of fusion have been measured for $RE_{68}Pd_{28}$ compounds where RE = Tb, Dy, Ho, Er, Tm and Lu. The apparent anomalous change in the thermodynamic properties of these phases is confirmed by similar changes in other physical and mechanical properties such as density and microhardness. In this case the thermodynamic data, beyond their essential meaning, make it possible to evidence crystallographic details not yet known.

INTRODUCTION

As part of an investigation dealing with the determination of some thermodynamic properties of the intermetallic compounds formed by the rare earths (RE) with the group VIII elements, we have examined the so-called RE_5Pd_2 phases and report here the results obtained for the heats of formation, heats and entropies of fusion and some mechanical properties.

The existence of the RE_5Pd_2 compounds was already known[1,2] but recently they have been studied in this laboratory from a crystallographic point of view determining their structure[3]. As a result of single crystal X-ray diffraction analysis supported by differential thermal and micrographic investigations, we have found that all these phases which are isomorphous and exist for Tb, Dy, Ho, Er, Tm and Lu, crystallize with a cubic symmetry in the Fd3m space group and their correct stoichiometry corresponds to the $RE_{68}Pd_{28}$ formula. The structure adopted by these phases is not a simple one, due both to the unusual unit cell atomic content and to three partially filled atomic sets which allows atomic rearrangements or deviations from the actual stoichiometry.

EXPERIMENTAL

During the preparation of the samples for our crystallographic research it was observed that a strongly exothermic reaction takes place between RE and Pd in the temperature range 800–1000°C. The heat evolved in this reaction was sufficient to melt the samples and the alloys so obtained were single phase; this is in accord with the phase diagrams reported by Loebich and Raub[2] for the Dy–Pd and Er–Pd systems where these compounds appear to have congruent melting points. Contrary to these findings[2], also for Ho_5Pd_2, we found a congruent melting point as observed in the differential thermal analysis curves. For these reasons such phases were suitable to be studied by the dynamic differential calorimetric method (DDC) previously employed for $RESn_3$[4], $REPb_3$[5], $RETl_3$ and $REIn_3$[6] phases and whose operational details have been reported elsewhere[4].

RE's and Pd metals used in this investigation were obtained from Koch-Light Lab. and Johnson Matthey, England, with a purity of 99.9% and 99.99%, respectively. Proper amounts of powders of the two metals (50 mesh), for a total weight from 1.00 to 1.50 g, were pressed into pellets and then transferred in the Mo containers which were closed by arc-welding is an argon atmosphere. During this operation care was taken to avoid any prereaction in the samples. The thermograms were obtained at heating rates of 10 or 20°C min^{-1} and the magnitude of the thermal effects was evaluated from the corresponding calibration curves.

As the reaction between the RE's and Pd occurs at temperatures close to the melting points of the alloys and ends well above, to evaluate the heats of formation the first exothermic thermal effect due to the reaction must be added to the exothermic thermal effect due to the subsequent solidification of the alloy corresponding to the sequence:

$$\begin{array}{l} 68\,RE(s)+28\,Pd(s) = RE_{68}Pd_{28}(l)+\Delta H_r(T_r) \\ \underline{RE_{68}Pd_{28}(l) = RE_{68}Pd_{28}(s)+\Delta H_m(T_m)} \\ 68\,RE(s)+28\,Pd(s) = RE_{68}Pd_{28}(s)+\Delta H_f(T_r) \end{array}$$

and hence

$$\Delta H_f(T_r) = \Delta H_r(T_r)+\Delta H_m(T_m)$$

neglecting the small difference of temperature between T_r and T_m (see Table 1). A

TABLE 1

THERMODYNAMIC PROPERTIES OF $RE_{68}Pd_{28}$ COMPOUNDS

T_r = temperature at which the reaction starts; ΔH_f = heat of formation; ΔH_m = heat of fusion; ΔS_m = entropy of fusion; T_m = melting temperature.

RE	T_r (°C)	ΔH_f (kcal g-at.$^{-1}$)	T_m (K)	ΔH_m (kcal g-at.$^{-1}$)	ΔS_m (cal deg^{-1} g-at.$^{-1}$)
Tb	810	−8.5	1093	2.4	2.2
Dy	855	−8.1	1123	2.5	2.2
Ho	900	−7.9	1158	2.5	2.2
Er	925	−9.8	1203	3.0	2.5
Tm	940	−9.0	1208	2.9	2.4
Lu	980	−9.5	1228	3.0	2.4

typical example is reported in Fig. 1. Here the heats of formation are given at slightly increasing temperatures, from Tb to Lu, depending on T_r. The standard values (298 K) would require a knowledge of the heat capacities, especially for the compounds. The entropies of fusion were computed from the values of the heats of fusion and melting temperatures.

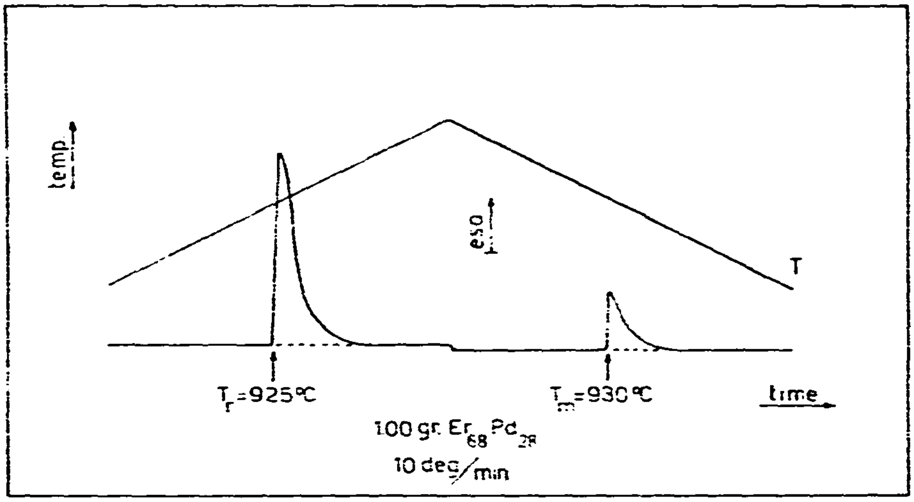

Fig. 1. Typical example of thermograms obtained for $RE_{68}Pd_{28}$ compounds.

The total error which affects these results was estimated to be ±8–10% for the heats of formation and ±5–6% for the heats and entropies of fusion; temperature measurements were correct to within ±5°C.

To ensure reproducibility in the results several samples were prepared (5–6) at different heating rates and, at last, three "good" samples were considered in the evaluation of the thermodynamic data. After the reaction ended the samples were examined micrographically: only alloys which contained a single phase were considered and the subsequent X-ray examination showed only the presence of the

TABLE 2

CRYSTALLOGRAPHIC AND MECHANICAL PROPERTIES OF $RE_{68}Pd_{28}$ COMPOUNDS

RE	a_0 (Å)	$\rho_{calc.}$ ($g\ cm^{-3}$)	$\rho_{obs.}$ ($g\ cm^{-3}$)	*HV* ($kg\ mm^{-2}$)
Tb	13.607	9.09	—	180
Dy	13.529	9.41	9.36	195
Ho	13.450	9.69	9.68	200
Er	13.368	9.98	10.62	335
Tm	13.290	10.23	10.40	340
Lu	13.241	10.64	11.11	345

$RE_{68}Pd_{28}$ phases. The values of the lattice constant agree with those previously determined[3].

Density measurements were made with the pycnometric method using $BrCH_2$–CH_2Br as reference liquid and tests for microhardness were carried out, on the metallographic specimens, with the Vickers method using a 20 and 50 g load; the average values from several tests are reported in Table 2 together with crystallographic and density data.

DISCUSSION

Palladium forms $RE_{68}Pd_{28}$ phases with heavier rare earths, from Tb to Lu, as a result of a highly exothermic reaction which leads to the formation of isomorphous compounds with congruent and relatively low melting points in respect to the other caracteristic temperatures of the corresponding phase diagrams. Ytterbium and europium, being divalent in this composition, give Yb_5Pd_2 and Eu_5Pd_2 phases but with a different monoclinic structure[7,8].

According to the empirical classification given by Robinson and Bever[9], these phases both for the values of the heats of formation and for the heats and entropies of fusion can be ascribed to the metallic type bond compounds.

As observed in most series of isomorphous RE intermetallic compounds the trend in the heats of formation should be a decrease with increasing RE atomic number with only few exceptions such as REH_2 and RE_2O_3[4–6,10], but this seems only partially the case with $RE_{68}Pd_{28}$ phases as Er, Tm and Lu have heats of formation more negative by ~1 kcal/g-at^{-1} in respect to Tb, Dy and Ho. This singular behaviour is again evident in the heats and entropies of fusion where the differences among Tb, Dy, Ho in respect to Er, Tm and Lu are of about 0.5 kcal g-at^{-1} and 0.2 cal deg^{-1} g-at^{-1}, respectively. Moreover, not only the thermodynamic properties but other physical and mechanical properties also confirm the preceding singularity.

Dy and Ho have experimental densities in very good agreement with those obtained from crystallographic data, while Er, Tm and Lu show distinctly higher values; and Vickers microhardness shows again an increase, in the same direction, of about 75%.

As already observed the structure adopted by these phases is not a simple one and it seems disordered as indicated by the entropies of fusion with a slight ordering for Er, Tm and Lu[11]; undoubtedly we assist, at Er, to a bond strenghtening as indicated by the increase in the heat of formation, heat of fusion and microhardness while the increase in density could indicate a unit cell content a little different from the actual $RE_{68}Pd_{28}$ composition with the formation of a little solid solubility range. This seems the most probable explanation for such a behaviour; the structure remains unaltered as results from X-ray powder photographs show but the thermodynamic, physical and mechanical properties evidence crystallographic details not yet known. Another possibility could be an atomic rearrangement especially in the partially filled positions but not such as to destroy the isomorphism observed in these compounds.

Probably a detailed single crystal structure investigation for all these phases could decide for one or both of these assumptions.

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