Alloying and Strengthening Effects of Rare Earths in Palladium

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The effect of adding small amounts of rare earth elements to palladium is to strengthen the palladium. These strengthening effects are discussed here, based on known phase diagrams of palladium-rare earths, palladium-rare earth alloying behaviour and atomic (or ionic) size effects. The solid solubilities of the rare earths in palladium, transition temperatures of various intermediate phases and eutectic temperature in these systems are influenced by the ionic (or atomic) size of the rare earth elements. A parameter, H_S, the product of the relative difference in atomic weights and the relative difference in atomic radii, between a rare earth and palladium is used to examine the solid solution strengthening effects caused by dilute rare earths. The alloying behaviours of palladium with the rare earths are very analogous, and could perhaps be used to predict alloying behaviour in some unexamined palladium systems.

As rare earths additives have an obvious influence on the structures and properties of platinum group metals and their alloys, increasing attention is being given to developing platinum group metal alloys modified by rare earths (1). Therefore, it is important to summarise and review the alloying behaviour between the rare earths and the platinum group metals. Palladium (Pd) is an important industrial metal and research on phase diagrams between Pd and the rare earths has been very successful. Based on available data, this paper briefly summarises the alloying behaviour of Pd and the strengthening effects when dilute rare earth elements are the solutes.

Phase Diagrams of Pd-RE Systems

A summary of simplified phase diagrams of Pd with 17 rare earth (RE) metals from scandium (Sc) to lutetium (Lu) is given in Figure 1. The Figure is a concise display of the available phase diagram data of these Pd-RE systems (2–13). Limited information has been reported for the Pd-La (lanthanum) (3, 5, 11, 12), Pd-Tm (thulium) (3, 12) and Pd-Lu (2–4) systems. Partial phase diagrams have been established for the Pd-Ce (cerium), Pd-Pr (praseodymium) and Pd-Nd (neodymium) systems in Pd-rich regions (50–100 atomic per cent (at.%) Pd) (2, 7–10). Phase diagrams for other

Pd-RE systems are basically complete and have been evaluated (2–5), except for the Pd-Pm (promethium) system for which no information has yet been published. In Figure 1, solid solubilities, intermediate phases, eutectic and peritectic reactions, as well as solid state reactions are shown. The numbers on the map are: eutectic temperatures, melting points for fusion-type compounds and decomposition temperatures for decomposition-type compounds formed by peritectic reactions. However, these temperatures have not yet been determined in alloy systems such as Pd-La, Pd-Tm and Pd-Lu. Details of these will now be discussed.

Solid Solubilities of Rare Earths in Palladium

The maximum solid solubilities of rare earths in Pd in the equilibrium state are listed in the Table. The value of the solid solubility is 10 at.% for europium (Eu) and greater than 10 at.% for other rare earths (except La, Pr and Nd). However, quite large contrary values have been reported for the solid solubilities of the light rare earths (La, Ce, Pr, Nd) in Pd. Some early research indicated that La and Pr were virtually insoluble in Pd (14–16). Later work by Savitsky (3, 4) showed that the solid solubilities of La and Nd were not higher than 1.5 at.%,

Fig. 1 Sketch map of simplified phase diagrams of the palladium-rare earth systems (the numbers are temperatures in °C; Z = atomic number)
[1] Solid solution
[2] Eutectic reactions
[3] Decomposition-type compounds formed by peritectic reaction
[4] Compounds formed from a melt and containing a homogeneous phase field
[5] Congruent compounds
[6] A low temperature ordered phase formed from solid state reactions

and although no new data has been reported for the solid solubility of La, Zhang *et al.* have reached values of around 9 and 4 at.% for the solid solubilities of Pr and Nd, respectively (9, 10). For Ce, a value for its solid solubility as high as 12–13 at.% Ce, based on the nominal composition of Ce in Pd alloy, was reported (3, 4, 8), but was revised to 7 at.% Ce after experimental data obtained by Bretschneider *et al.* (7).

It is well known that the solid solubilities of alloys are related to factors such as the crystal structure, atomic size, electronegativity and valence, etc. However, for rare earths these factors are not always favourable for indicating that their solid solubilities in Pd could be high. For instance, the differences in the atomic radii (parameter B in the Table) between Pd and the rare earths: 20% (Sc) to 49% (Eu) and the differences in electronegativity between Pd and the rare earths from 0.93 (Sc) to 1.03 (La) are over the limits (proposed by Hume-Rothery and Darken-Gurry) of atomic size criterion (15%) and electronegativity difference criterion (0.4), respectively, for forming extensive solid solubilities (17, 18). Despite this, the solid solubilities of rare earths are still affected by atomic size and electronegativity. In general, the solid solubility of a rare earth in Pd can reach and exceed 10 at.% when the difference in atomic radii < 30% and the difference in electronegativity < 1.0. Clearly, these differences are beyond the Hume-Rothery and Darken-Gurry criteria (17, 18).
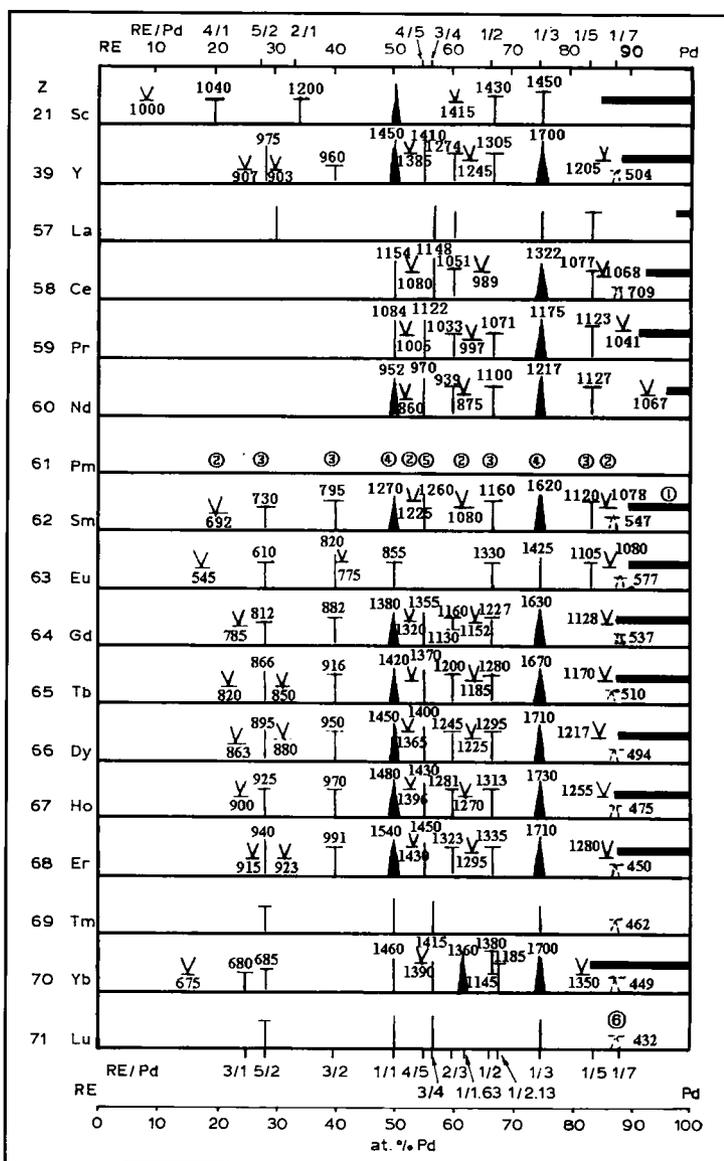
Table

Maximum Solid Solubilities (C_{max}) of Rare Earths in Palladium and Some Related Parameters

Element	Atomic radius, r, nm	r^{3+}, nm	Electronegativity	$C_{max}^{(1)}$, at.%	$A^{(2)}$	$B^{(3)}$	$H_s^{(4)}$
Pd	0.137	–	2.2	–	–	–	–
Sc	0.164	0.0730	1.27	15	2.37	0.2	0.476
Y	0.180	0.0905	1.2	12.3, 11(6)	1.2	0.31	0.377
La	0.1879	0.1071	1.17	1.5	0.77	0.37	0.286
Ce	0.1825	0.1034	1.21	~7(7), 12.2(8), 13(3,4)	0.76	0.33	0.252
Pr	0.1828	0.1013	1.2	~9(9)	0.75	0.35	0.251
Nd	0.1821	0.0995	1.19	1.5(3,4), ~4(10)	0.74	0.33	0.244
Sm	0.1804	0.0964	1.18	10.3	0.71	0.32	0.227
Eu	0.2042	0.0950	1.2	10	0.70	0.49	0.343
Gd	0.1801	0.0938	1.2	12, 11(6)	0.68	0.32	0.214
Tb	0.1783	0.0923	1.21	–	0.67	0.30	0.202
Dy	0.1774	0.0908	1.21	12.3	0.65	0.295	0.192
Ho	0.1766	0.0894	1.21	12.5	0.64	0.29	0.185
Er	0.1757	0.0881	1.22	13	0.64	0.28	0.181
Tm	0.1746	0.0869	1.22	–	0.63	0.274	0.173
Yb	0.1740	0.0858	1.21	16.5	0.62	0.27	0.167
Lu	0.1735	0.0848	1.21	–	0.61	0.266	0.163

(1) The values of solid solubilities not given sources were taken from References 3 and 4
(2) A = atomic weight of palladium/atomic weight of rare earth
(3) B = ($r_{RE} - r_{Pd}$)/r_{Pd}, the relative atomic radius difference of rare earths to palladium
(4) $H_s = A \cdot B$, the solid solution strengthening parameter

On the other hand, the solid solubilities increase with the lanthanide contraction. The smaller solid solubilities of the light rare earths in Pd should be related to their larger differences in atomic radius and electronegativity. The large differences in electronegativity between the light rare earths and Pd lead to the formation of the Pd_5RE compounds in these systems, and this restricts greater solid solubility. Pd_5RE does not occur in Pd-heavy rare earth systems due to the relatively small difference in electronegativity – one reason why the heavy rare earths have greater solid solubility.

Figure 2 shows the relationship between the maximum solid solubilities (C_{max}) of rare earths in Pd and their ionic radii (r^{3+}). All data points (except Sc) lie close to a straight line. This observation indicates that solid solutions of rare
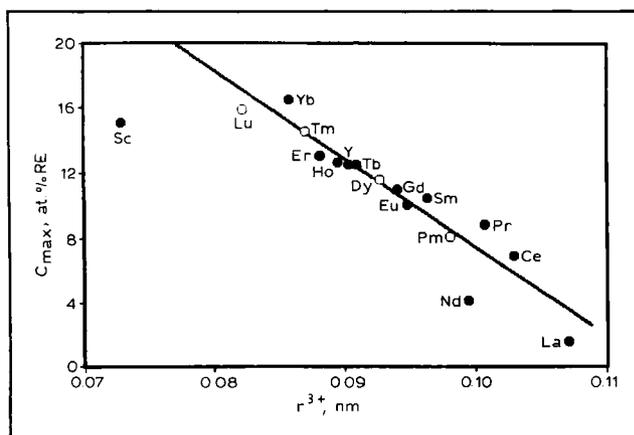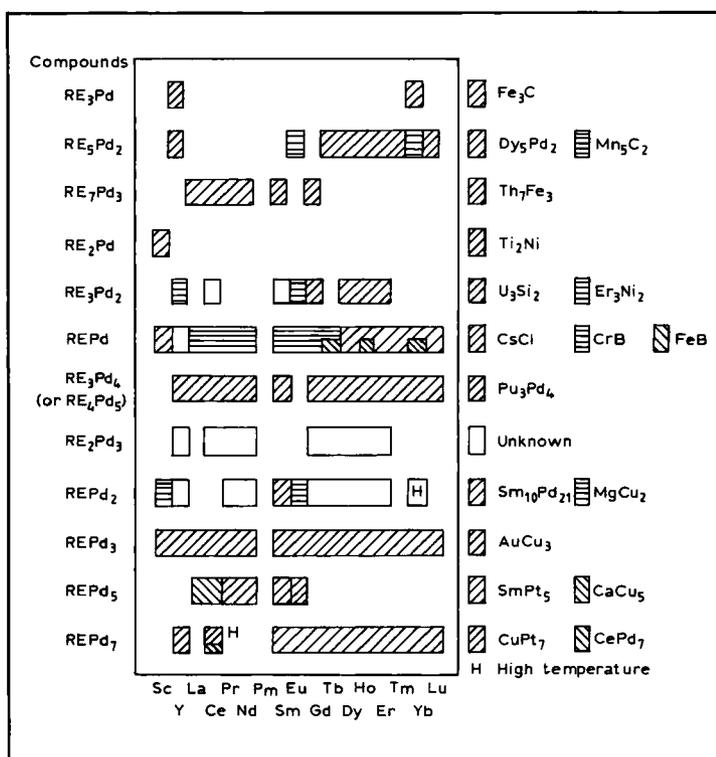

Fig. 2 Dependence of the maximum solid solubilities, C_{max}, of rare earths in palladium on the ionic radii, r^{3+}
● Available data from references listed in the Table
○ Predicted data according to ionic radii

Fig. 3 The crystal structures and distribution of intermediate phases in palladium-rare earth systems (24)

earths in Pd can be regarded as trivalent solutes. In agreement with the ionic radii and the lanthanide partial molar volume contraction, Bretschneider *et al.* (7) confirmed that all rare earths in Pd are trivalent. In general, Ce can be either trivalent or tetravalent, depending on the particular system, but the electronic state of Ce in Pd is identical to those of the other rare earth metals (7). Although Eu has less tendency to become trivalent, and ytterbium (Yb) can be either divalent or trivalent, both are trivalent in Pd solid solutions as well as in some compounds with Pd (13, 19). From Figure 2, it can be predicted that, according to their ionic radii, the solid solubilities of Pm, terbium (Tb), Tm and Lu are about 8, 11, 14 and 16 at.%, respectively, if their data points lie on the straight line. However, because the alloying behaviour of Sc is similar to that of Lu (20), the solid solubility of Lu in Pd should be close to that of Sc.

Large differences in electronegativity can cause electron migration between atoms of solvent and solute during the alloying process. Electron migration in solid solution is proportional to the difference of electronegativity (21). Thus, during alloying the valence electrons transfer from the Fermi level of the rare earth to that of the alloy. The energy change of the binary alloy during alloying contains a positive term due to the difference in the atomic sizes and a negative term caused by the charge transfer (22). According to a continuum elastic model for the Pd (Ce) alloy, the atomic misfit energy in an infinitely dilute Pd (Ce) alloy is $+172$ kJ mol^{-1}, whereas the charge transfer energy is -444 kJ mol^{-1} (7). The negative charge transfer energy will overcompensate for the positive atomic misfit energy, and this should decrease the energy of the alloy and increase the solid solubility. Thus, a large negative charge transfer energy is the main factor for a rare earth element having high solid solubility in Pd. In fact, Pd not only has large solid solubilities for rare earths (much larger than those of rare earths in silver (Ag), gold (Au) and the other platinum group metals) but as a solid solvent it also has the highest solubility for elements in the Periodic Table (23).

Intermediate Phase in Palladium-Rare Earths Systems

Because of the large difference of electronegativity between Pd and the rare earths, a series of intermetallic compounds have been found. They form compounds with RE:Pd atomic ratios of: 1:7, 1:5, 1:3, 1:2, 2:3, 3:4 (or 4:5), 1:1, 3:2, 2:1, 7:3, 5:2
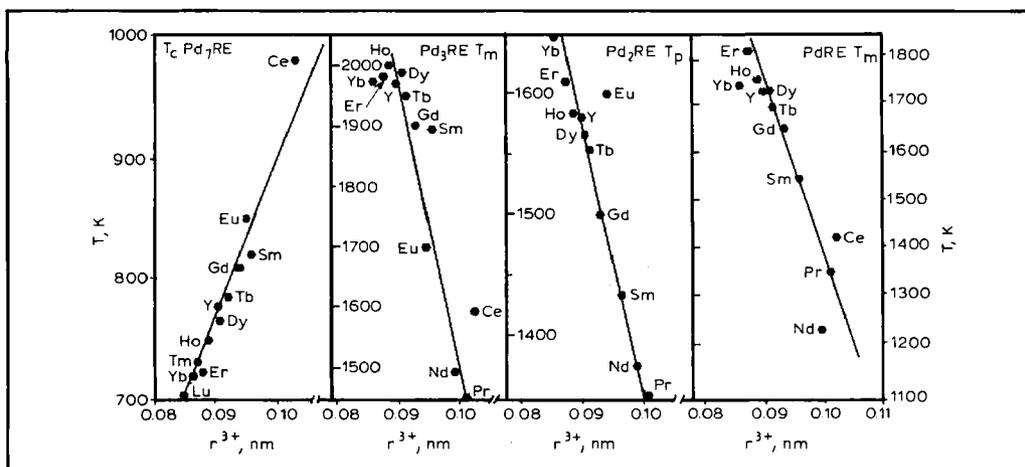
Fig. 4 *The dependence of the critical temperatures of ordered and intermediate phases on the ionic radii, r^{3+}, of the rare earths*

and 3:1. The crystal structures and distribution of the intermediate phases are shown in Figure 3 (24). The Pd_7RE ordered phase occurring at lower temperatures is accompanied by the peritectoid reaction:

$$\alpha(Pd) + Pd_5RE = Pd\text{-}RE$$

for light rare earths, and

$$\alpha(Pd) + Pd_3RE = Pd_7RE$$

for heavy rare earths and yttrium (Y).

Having a large atomic misfit is a favourable indication for the formation of the ordered phase. The Pd_7Ce phase in the PdCe system has two types of ordered structure: Pt_7Cu and Pd_7Ce. The Pd_7Ce phase is a derivative of the Cu_3Au-type Pd_3Ce phase at a lower temperature (20) and transforms into the Pt_7Cu-type ordered phase at higher temperature. The Pd_7RE phase in the other Pd-RE systems has only the Pt_7Cu-type ordered structure.

The Pd_5RE phase is the product of the peritectic reaction:

$$L + Pd_3RE = Pd_5RE$$

where L = liquid phase and exists only in Pd light rare earths systems.

The Pd_3RE phase is formed congruently and possesses homogeneity of 2 to 4.5 at.% RE based on the Pd_3RE stoichiometry, however, only Pd_3Eu is a stoichiometric compound.

In all the Pd-RE systems, the phase regions of Pd_3RE spread toward the Pd-rich end and gradual-ly widen – from Eu (in the middle) to both ends of the light and heavy rare earths. The lattice parameters and unit cell volumes of the stoichiometric Pd_3RE phase decrease gradually with the lanthanide contraction, and no abnormal phenomena are observed, even for Ce, Eu or Yb.

In X-ray structure-determined Pd_2RE compounds, Pd_2Sm has the $Sm_{10}Pd_{21}$ structure (a = 2.4853 nm, b = 0.5765 nm, c = 1.651 nm, β = 90°88'); Pd_2Sc and Pd_2Eu are $MgCu_2$-type Laves phase. For Pd_2Sc, the ratio of the atomic radii, r_{Sc}/r_{Pd}, equals 1.197, which is close to the atomic radius ratio 1.225 of the ideal Laves phase. For Pd_2Eu, r_{Eu}/r_{Pd} equals 1.49, which deviates from the ideal atomic radius ratio but is still in the range of the permitted maximum deviation value of 1.6 for the Laves phase. For all other rare earths from La to Lu, the r_{RE}/r_{Pd} values lie between 1.37 and 1.266; this size factor is favourable for the formation of the $MgCu_2$-type Laves phase.

The PdRE phase occurs in all the Pd-rare earths systems and these are formed congruently, with PdEu – formed peritectically – being the only exception. The CsCl-type structure is found for Sc and the heavy rare earths from Lu to dysprosium (Dy), which have smaller atomic radii, but the low temperature FeB-type isomer occurs in the Pd-Tb, Pd-Ho and Pd-Yb systems. The CrB-type structure is formed for the rare earths with larger atomic radii – from Tb to La. In other words, the sequence

CsCl-FeB-CrB is found on going from Lu to La. This is also observed in other systems of rare earths with Group VIII metals (13). The structure of the PdY phase should be of CsCl-type because the alloying behaviour of Y is similar to that of Dy (25).

The Pd_5RE_4 and Pd_4RE_3 are actually an identical compound because they have near stoichiometric compositions.

Figure 4 shows the dependence of the critical temperatures of several main intermediate phases on the ionic radii of the rare earths. For the Pd_7RE ordered phases, the critical temperatures, T_c, (7, 26–32) increase with the increase in ionic radii. In contrast to the dependence of T_c on r^{3+}, the melting points, T_m, of the Pd_3RE and PdRE phases, and the decomposition temperature, T_p, of the Pd_2RE phase, decrease linearly with the increase of ionic radii. This dependence on the ionic radii was also observed for other intermediate phases, such as Pd_3RE_2 and Pd_5RE_4, etc.

In general it can be seen that the light rare earths have higher critical temperatures for the Pd_7RE ordered phase and lower melting points or decomposition temperatures for congruent-type or decomposition-type compounds than do heavy rare earths.

Eutectic Reactions and Eutectic Temperature

It can be seen from Figure 1 that four eutectic reactions exist in Pd-rare earth systems (but not in the Pd-Sc system). The distribution region of the eutectic concentration is relatively narrow (Figure 1), while that of the eutectic temperature is quite wide, for each eutectic system (Figure 5). Figure 5 shows the dependence of the eutectic temperatures at the Pd-rich end on the rare earth atomic radii. The same tendency of eutectic temperature could be obtained for the ionic radii (r^{3+}) of the rare earths. The eutectic temperatures decrease linearly with the increase of atomic (or ionic) radii. For the first eutectic systems (in Figure 1 near to RE/Pd = 1/7, from the Pd-rich side) the dependence of the eutectic temperature on the rare earth atomic radius is a broken line with a turning point at samarium (Sm); that is, the eutectic temperature
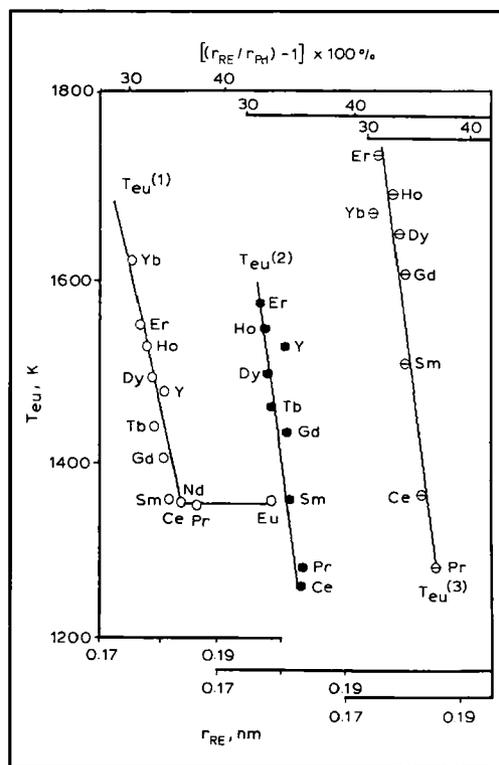

Fig. 5 The dependence of eutectic temperatures in palladium-rich palladium-rare earth systems on the atomic radii of the rare earths. $T_{eu}^{(n)}$ (n = 1, 2, 3) is the eutectic temperature of the nth eutectic system from the palladium-rich side

no longer falls, instead it remains essentially constant when the atomic radius of the rare earths reaches about 0.18 nm and the atomic size difference between Pd and the rare earths is about 31%. This is similar to the dependence of the first eutectic temperatures on the atomic radii of rare earths in the Ag-RE and Au-RE systems (33–35). The difference is only that the turning points on the plots of the Ag-RE and Au-RE systems are located at about 0.175 nm (about 21% atomic size difference), which is lower than in the Pd-RE systems. It is not certain whether there are also turning points on plots of the eutectic temperatures of the three other eutectic reactions in the Pd-RE systems (see Figure 1) because these eutectic systems have not occurred or been established in Pd alloy systems containing rare earths with large atomic radii (such as Pd-Eu or Pd-light rare earths systems).
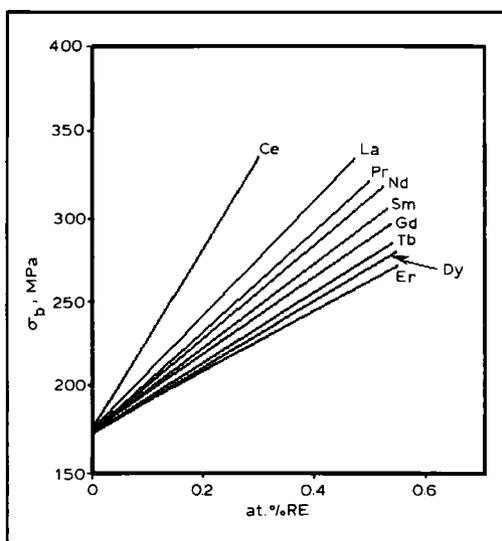
Fig. 6 The dependence of the tensile strength of some palladium-rare earth alloys annealed at 900°C on the rare earth concentration

Hume-Rothery *et al.* (17) pointed out that liquid drop formation from out of a simple alloy system depended on the atomic size difference between solvent and solute. The larger the difference, the more liquid drops form from the solid solution. As liquid drop formation leads to a lowering of the eutectic temperature, the Hume-Rothery rule also applies to the eutectic temperature.

In fact, the dependence of the eutectic temperature in Pd-rare earth systems on the rare earth atomic radii has extended the Hume-Rothery rule to more complicated alloy systems.

Solid Solution Strengthening of Palladium by Dilute Rare Earths

The solid solution strengthening effect of dilute rare earths in Pd is related to two factors. The first factor is the ratio of the atomic weights of Pd to the rare earth = A (see the Table). This value is approximately directly proportional to the ratio of the numbers of atoms of Pd and rare earths at a certain weight per cent. The second factor is the relative difference in atomic size of rare earth to Pd, parameter B, where $B = (r_{RE} - r_{Pd})/r_{Pd}$. This is related to the extent that the Pd lattice is distorted by the rare earth solute. The solid solution strengthening effect of rare earths on Pd can be

roughly expressed using the parameter $H_s = A \cdot B$. The Table lists parameters A and B as well as the strengthening parameter, H_s, of each rare earth solute to Pd. The H_s values have the order:

$$H_s \text{ (Sc, Y, Eu)} > H_s \text{ (light RE from La to Sm)}$$
$$> H_s \text{ (heavy RE from Gd to Lu)}$$

Generally speaking, the strengthening effect of rare earths on Pd should follow the same order as the H_s values. The large strengthening effect from Sc, Y, Eu and light rare earths is attributed mainly, for Sc and Y, to the relatively light atomic weights or the relatively large values of A, and, for Eu and the light rare earths, to the larger difference in atomic radii between the rare earth and Pd.

Figure 6 shows the dependence of the tensile strength of some Pd-RE alloys annealed at 900°C on the rare earth concentrations (36). There is a linear relationship between the tensile strength and the rare earth concentration which is valid for dilute concentration up to 0.6 at.% RE. Therefore, values of the tensile strength could be normalised on 0.1 at.% RE. Figure 7 shows the dependence of $\Delta\sigma_b$, which are the corresponding increments of tensile strengths of the Pd–0.1 at.% RE alloys to that of Pd, on the solid solution strengthening parameter H_s. The $\Delta\sigma_b$ values increase with the H_s values; only Ce has a large deviation. Obviously, the light rare earths have a stronger effect on the strength properties of Pd at ambient temperature than heavy rare earths.
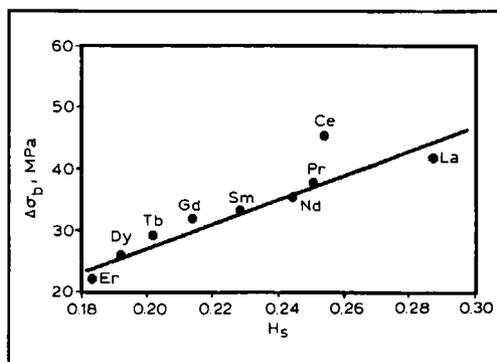

Fig. 7 The dependence of increments (Δσb) on the tensile strength of palladium-0.1 at.% rare earth to that of palladium on the solid solution strengthening parameter, Hs

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Yuantao Ning is a Professor of Physical Metallurgy at Kunming Institute of Precious Metals, China. His main research interests are related to the principles of alloying and new materials based on precious metals, particularly platinum metals and their alloys, including ones modified by the rare earth metals. He has published around 200 papers in national and international periodicals and won national prizes for his scientific achievements.

Platinum Nanoparticle Catalysts

Supported catalysts are usually prepared by impregnating water soluble metal salts on a porous support, followed by drying, calcining and reduction. This produces well-dispersed catalysts with particles in the nm range having high activity and good thermal stability. However, the particle size distribution is wide and only limited control is achievable, making size-linked interpretation of catalytic mechanisms difficult. Therefore, for better control, different methods of preparation are under investigation.

Researchers in Sweden have examined the deposition of Pt nanoparticles, prepared in water-in-oil microemulsions, on γ-Al$_2$O$_3$ (H. H. Ingelsten, J.-C. Béziat, K. Bergkvist, A. Palmqvist, M. Skoglundh, H. Qiuhong, L. K. L. Falk and K. Holmberg, *Langmuir*, 2002, 18, (5), 1811–1818). In one method, based on work by Boutonnet *et al.*, the γ-Al$_2$O$_3$ was added to the Pt particle suspension and the microemulsion was then destabilised by adding tetrahydrofuran (THF), which deposited the Pt particles onto the support. In a second method, Pt nanoparticles were transferred to an aqueous solution and stabilised by a surfactant prior to adding γ-Al$_2$O$_3$. Both catalysts had high activity for CO oxidation by oxygen, but some particle agglomeration had occurred. This was due to a too-rapid addition of THF, and inefficient redispersion of the primary Pt particles on transfer to the aqueous phase, respectively. Further work is suggested on the choice of pH, surfactant and control of the electrostatic interaction between the Pt particles and the γ-Al$_2$O$_3$.