

# Hydrogen in Disordered and Ordered Palladium Alloys

By Ted B. Flanagan

Chemistry Department, University of Vermont, Burlington, U.S.A.

and Y. Sakamoto

Department of Materials Science and Engineering, Nagasaki University, Japan

The solution of hydrogen in palladium-rich substitutional alloys has been of continuing interest since the pioneering studies of Thomas Graham on palladium-silver alloys, in the nineteenth century. The various palladium alloys exhibit different characteristics of hydrogen absorption compared with palladium (1, 2). Graham demonstrated considerable prescience in selecting the palladium-silver alloy system for his investigation of hydrogen absorption by a palladium alloy, since this alloy has subsequently proven to be the alloy of most interest.

A comprehensive account of the solubility of hydrogen in ordered and disordered alloys of palladium is now presented, and the results are interpreted where possible.

## Substantially Disordered Palladium Alloy-Hydrogen Systems

It was established in the early days of neutron diffraction that hydrogen occupies octahedral interstices in palladium (3). It seemed reasonable to assume that this was also the case for those palladium-rich alloys having face centred cubic (f.c.c.) structure. Inelastic neutron scattering has been a valuable tool for the investigation of metal-hydrogen systems (4). The hydrogen vibrations are well separated from the lattice modes and therefore the assumption that the hydrogen atoms behave as independent oscillators is a good one. Thermal neutrons exchange energy with interstitial hydrogen atoms leading to changes in their vibrational energies, and their vibrational frequencies can be determined from analysis of the energies of the scattered neutrons. It was shown by Ross and co-workers (5) that hydrogen vibration frequencies are significantly

lower for octahedral interstices compared to tetrahedral interstices (4) and therefore the optic mode vibrational frequency can serve as a guide for the type of interstice occupied. The optical mode of hydrogen is 69 meV in the dilute phase (6) and 58 meV in the hydride phase of palladium (7) and it is of similar magnitude for hydrogen in palladium alloys (8, 9), which strongly suggests that the octahedral interstices are also occupied in palladium alloys. Despite several claims, there is no convincing evidence for the occupation of interstices other than octahedral ones in palladium and its f.c.c. alloys. It is noteworthy that the vibrational frequencies of the interstitial hydrogen atoms appear largely unchanged upon alloying, at least, for relatively low atom fraction of solute,  $X_M$ .

When hydrogen dissolves in palladium at below the critical temperature,  $T_c$ , of 563 K, a dilute phase of hydrogen forms and then, when further hydrogen dissolves, a hydride phase appears at a hydrogen concentration which is referred to as the terminal solubility of hydrogen (10). The dilute  $\alpha$ -phase co-exists with the hydride,  $\alpha'$ , which is also known as the  $\beta$ -phase, and as further hydrogen is added the fraction of the hydride phase increases. In this two phase region a constant hydrogen pressure is required by the phase rule. This invariant pressure region is referred to as the plateau. At 303 K the dilute phase boundary which co-exists with the hydride phase is (H: Pd) = 0.009 and the hydride phase boundary is (H: Pd) = 0.608 (11) but near the critical concentration both phase compositions approach the critical one of 0.29 (10). Thus the description of the  $\alpha$ -phase as the "dilute" phase is applicable only at moderate temperatures. Finally when the

dilute phase is fully converted to the hydride phase, further addition of hydrogen leads to a rapid increase of hydrogen pressure (and chemical potential), as the hydrogen concentration increases in the non-stoichiometric hydride phase (11).

Hysteresis is observed in the isotherms of palladium and its alloys in the phase transition, that is, the hydride formation pressure is greater than the decomposition pressure. Recently it has been observed that hysteresis in some palladium alloys differs qualitatively from hysteresis in palladium, and this is discussed below.

### Recent Results on Disordered Palladium Alloys

The solubility of hydrogen in palladium alloys has been reviewed here, by Lewis (2) and we will therefore summarise only those features needed as background material for this review, and discuss the results since then in more detail. Almost all of these hydrogen solubility studies concern substantially disordered f.c.c. palladium-rich alloys. For a substitutional alloy whose unit cell is larger than that of palladium, more hydrogen dissolves at a given low pressure than in palladium, and its plateau pressure is smaller than that of palladium-hydrogen. For substitutional metals with a smaller unit cell than palladium the opposite behaviour holds; the dilute phase solubility is smaller at low pressures than for palladium and the plateau pressures are greater than that of palladium. There are some exceptions to this classification, however. For example, in palladium-platinum (12, 13), palladium-niobium (14–16), palladium-tantalum (16) and palladium-zirconium (17, 18) the lattice expands with  $X_M$ , but the alloys behave as contracted alloys with regard to hydrogen absorption; for the latter alloy system the low pressure solubility increases, while the plateau pressure increases slightly, whereas it would normally be expected that the dilute phase solubility would decrease. For these exceptional cases the lattice changes with substituted metal are small but, on the other hand, the changes in the lattice parameter with  $X_{Rh}$  are also small, and the effect of rhodium on the plateau pressures is quite significant. For both types of alloys the extent

of the plateau region is smaller than that for palladium itself. The only exception to this appears to be palladium-rhodium alloys where the plateau region increases with  $X_{Rh}$  (2, 19–23).

Palladium-hydrogen and palladium alloy-hydrogen systems have the great experimental advantage that the chemical potential of hydrogen,  $\Delta\mu_H$ , relative to  $H_2$  (1 atmosphere) can be determined from a measurement of the hydrogen pressure in equilibrium with the hydrogen-containing alloy. Thus

$$\frac{1}{2}RT \ln p_{H_2} = \Delta\mu_H = \mu_H - \frac{1}{2}\mu_{H_2} (1 \text{ atmosphere})$$

From the temperature dependence of  $\Delta\mu_H$ ,  $\Delta H_H$  and  $\Delta S_H$  can be obtained at a given hydrogen content—which is the usual way that thermodynamic data are obtained for palladium-hydrogen and palladium alloy-hydrogen systems.  $\Delta H_H$  and  $\Delta S_H$  are the relative partial molar enthalpy and entropy which are defined analogously to  $\Delta\mu_H$  shown above. In the plateau region the values of  $\Delta H$ , the relative enthalpy and  $\Delta S$ , the relative entropy, are constant across the two phase co-existence region and may be called  $\Delta H_{plat}$  and  $\Delta S_{plat}$ . Thermodynamic parameters can also be determined from calorimetric measurements. This technique has been extensively employed for palladium alloys at high temperatures by Kleppa and his co-workers from about 1975 to 1983 when their research work was summarised by Kleppa (24). Although their combined technique of reaction calorimetry and equilibrium  $p_{H_2}$ -hydrogen content measurements had been previously employed, (25), Kleppa and co-workers applied it in a systematic fashion thereby demonstrating its power for determining thermodynamic data for gas/solid systems. They determined thermodynamic properties for  $H_2$  solution in the dilute phase region in the temperature range from about 555 to 700 K for the following alloys: palladium-silver (26), -gold (27), -copper (28), -manganese (29, 30), -nickel (31), -cobalt (31) and -iron (31).

The palladium-ruthenium-hydrogen system has been examined by Wicke and co-workers (32). This system is a contracted alloy which exhibits larger plateau pressures than palladium.

Recently Sakamoto and co-workers have

re-examined some of these systems and examined some new palladium alloy-hydrogen systems at moderate temperatures where hydride phases form. The systems which they examined were: palladium-yttrium (33), -nickel (34), -vanadium (35), -tantalum and -niobium (16), -gadolinium (36), -titanium and -zirconium (18), -lithium (37), -ytterbium (38) and -scandium (39). In all these studies thermodynamic parameters were determined for the dilute phase and for the hydride phase region from pressure-composition-temperature (p-c-T) measurements near ambient temperature.

Griessen and co-workers determined isotherms for palladium-uranium and palladium-cobalt alloys at moderate temperatures (40). The absorption capacity of the only palladium-uranium disordered alloy which was examined,  $\text{Pd}_{0.95}\text{U}_{0.05}$ , was tremendously reduced compared with palladium. They have also examined the solubility and diffusion of hydrogen in a  $\text{Pd}_{0.8}\text{Cu}_{0.2}$  alloy (41). They conclude, purely on the basis of the lattice gas model applied to their diffusion data, that only the  $\text{Pd}_6$  and  $\text{Pd}_6\text{Cu}$  interstices are occupied, where  $\text{Pd}_6$  refers to those octahedral interstices surrounded exclusively by nearest neighbour palladium atoms, etc.

Recently Weiss and co-workers have determined thermodynamic data at elevated temperatures,  $473\text{K} \leq T \leq 873\text{K}$ , from p-c-T methods for palladium-niobium (42), -tantalum (42), -erbium (42, 43), and  $\text{Pd}_{1-x}\text{RE}_x$  (RE = dysprosium, gadolinium, samarium and yttrium;  $x = 0.05$  and  $0.08$ ) (44) and  $\text{Pd}_{1-x}\text{Th}_x$  and  $\text{Pd}_{1-x}\text{Zr}_x$  ( $x = 0.05$  and  $0.08$ ) (45). All of the alloys were substantially disordered f.c.c. solid solution alloys.

Data for other palladium alloys, for example, for palladium-scandium (46), palladium-niobium (15) and palladium-zirconium (17) systems have been determined recently by Lewis and co-workers. Electrical resistance versus  $r = \text{hydrogen to metal, atom ratio}$ , relationships were determined together with hysteresis. These data were obtained using a combined electrochemical-gas phase method, that is  $\Delta\mu_{\text{H}}$  was established from the electrode potential, and hydrogen introduction was via  $\text{H}_2(\text{g})$ . Lewis and co-workers have been especially concerned with supercritical

behaviour in these alloy-hydrogen systems.

Besides substitutional palladium alloys, interstitial palladium alloys have also been examined, for example palladium-boron alloys (47–50). In this case the lattice expansion is rather large and the resulting alloy acts as an expanded alloy having smaller plateau pressures than pure palladium; the two phase region decreases in breadth considerably with  $X_{\text{B}}$ . Although lithium is also a small species it forms a substitutional rather than an interstitial alloy (37).

Sakamoto and colleagues have recently examined a ternary palladium-rich alloy, namely, palladium-copper-gold (51, 52). The thermodynamic parameters for hydrogen absorption for these alloys appear to be nearly mean values between those for the constituent alloys: palladium-gold and palladium-copper. For example, the  $\text{Pd}_{0.8}\text{Au}_{0.1}\text{Cu}_{0.1}$  is similar to the mean of  $\text{Pd}_{0.9}\text{Au}_{0.1}$  and  $\text{Pd}_{0.9}\text{Cu}_{0.1}$ .

One important result from these relatively recent investigations is that substituted metals in palladium, such as the rare earths, uranium, zirconium, titanium, niobium and tantalum, which absorb  $\text{H}_2(\text{g})$  very exothermically and to a large extent in their pure forms, act in the opposite manner when substituted in the f.c.c. palladium lattice. Pure uranium forms  $\text{UH}_3$ , an extremely stable hydride, but when small amounts of it are substituted in palladium it drastically reduces the uptake of hydrogen by palladium and there is no indication of any trapping of hydrogen by the uranium (40). In the case of palladium-niobium, Wicke and Frölich have shown that the amount of absorption of hydrogen by an alloy containing only a few atomic per cent niobium is quite small, even at pressures up to 100 atmospheres (14). This behaviour seems to point to a global effect of the substituted metal, because even small amounts of some of these substituted metals markedly reduce the hydrogen solubility. This general behaviour may have an explanation in terms of Miedema's model for hydride formation (53). If the palladium-M bonding is very strong, the resultant hydrogen-palladium(M) bonding will be weak. The thermodynamics of mixing palladium and the metal (M) to be substituted in the lattice have not been determined

for very many of these palladium-exothermic, hydrogen absorbing metals, but the palladium-niobium system has been investigated recently and there is indeed a very strong attractive interaction between palladium and niobium atoms (54). For example,  $\Delta H_{Pd}$  in  $Pd_{0.8}Nb_{0.2}$  is  $-7.8$  kJ/mol palladium (54) compared to  $-1.7$  kJ/mol palladium for  $Pd_{0.8}Cu_{0.2}$  (55). The enthalpies of formation of the compounds: PdTi, PdZr and PdHf have been determined by Topor and Kleppa (56, 57); these are intermetallic compounds and not disordered alloys, but their enthalpies of formation will, nonetheless, give an indication of the strength of the palladium-M bonding. The enthalpies of formation of these compounds are:  $-103.1$  kJ/mol PdTi,  $-122.6$  kJ/mol PdZr and  $-134.8$  kJ/mol PdHf, and by comparison the enthalpy of formation for PdCu is  $-6.3$  kJ/mol (55). This shows that the attraction between the Group IVB elements, zirconium, hafnium and titanium, and palladium is quite strong and apparently does not like to be disrupted by hydrogen.

Most commonly the palladium-rich alloys whose hydrogen solubilities have been investigated are considered to be substantially disordered. The interpretation of these solubilities has been based on several simple ideas. Brodowsky and co-workers (20, 58), following Wagner (59), interpreted palladium alloy-hydrogen systems, such as palladium-silver and palladium-tin, using a model in which both the substituted metal and the hydrogen atom donate electrons to the *d*-band of palladium and their expanded lattices allow the insertion of hydrogen to occur more readily than in palladium itself. This global model did not consider the different nearest neighbour environments of the various interstices available to the hydrogen. At the opposite end of the spectrum is the localised model—the simple local environment model (60, 61)—which considers the nearest neighbour interstice environment to be the decisive factor in determining the energy of an interstice and the energy of hydrogen solution. The fractions of the different types of interstices are calculated assuming a completely random distribution of atoms using the binomial theorem. The energy of a given type of interstice,

such as Pd<sub>6</sub> or Pd<sub>5</sub>M, is treated as a fitting parameter. It was found, for example, that only the Pd<sub>6</sub> and Pd<sub>5</sub>Ag interstices were occupied in palladium-rich palladium-silver alloys (60).

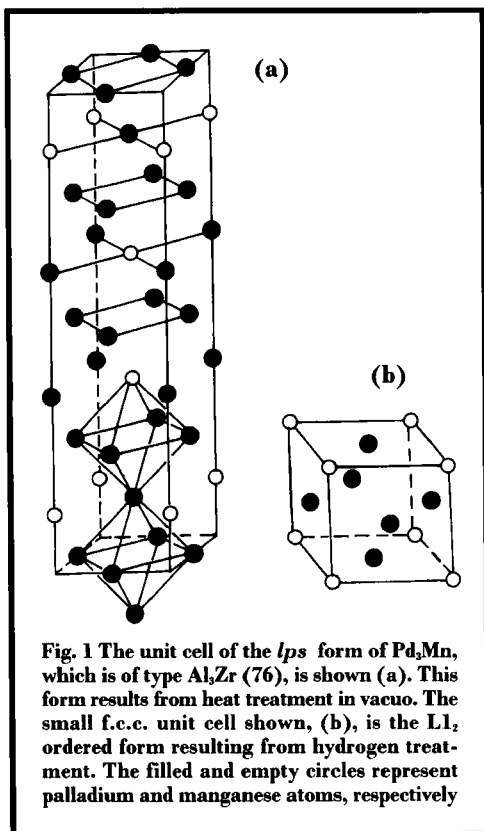
Although both of these models managed to fit experimental data with the aid of adjustable parameters, unsatisfactory features remained. The global model uses the unrealistic assumption that all of the interstices are equivalent, whereas there is evidence from the values of the entropy changes at infinite dilution of hydrogen that there must be some selective occupation of interstices, at least at low hydrogen contents (24). The local model suffers from a complete neglect of any rôle for the electronic structure of the alloys. The site energies are treated as adjustable parameters; the presence of such parameters is an unsatisfactory feature of both of the simple models.

Since these two models having opposite viewpoints were proposed and applied to the palladium-silver-hydrogen system, additional, more sophisticated models have appeared incorporating features of both models and in which the interstice site energies have been calculated using semi-empirical models (62, 63). A good review of these more recent models is given by Salomons, Hemmes, and Griessen (64). While these recent models are more successful, the question arises as to whether they have been carried too far considering the absence of any independent evidence establishing the validity of the assumptions. The only direct support seems to be their ability to fit the experimental hydrogen solubility data and, since this is accomplished using adjustable parameters, it is not fully convincing.

A recent paper by Oates and Mika considers the effects of short range order on the fraction of the various interstice sites using the cluster variation method (65). They find that the fractions can differ markedly from those for a completely random distribution.

### Hydrogen Solution in Ordered Palladium Alloys

In contrast to disordered palladium alloys, the fraction and spacial distribution of each type of interstice is known for ordered alloys. Hydrogen solubility results in such alloys may provide some



insight into the validity of the assumptions employed in the models used to interpret hydrogen solution in the disordered alloys, for example, is it correct to assume that the  $\text{Pd}_6$  interstices are the preferred sites?

The first investigation of hydrogen solution in an order-disordered alloy was that of the  $\text{Pd}_3\text{Fe}$  system which can be prepared in a disordered or in a  $\text{L1}_2$  ordered form. Neither form of this alloy absorbs appreciable hydrogen at 1 atmosphere, and therefore solubility studies had to be carried out at elevated pressures (66). At comparable conditions of temperature and pressure the hydrogen solubility was 4.5 to 9 times greater in the ordered form. No thermodynamic parameters were determined because of the uncertainties of such determinations in the moderately high pressure range using pressure changes; but, nonetheless, this was a rather remarkable result which showed that the solubility was very

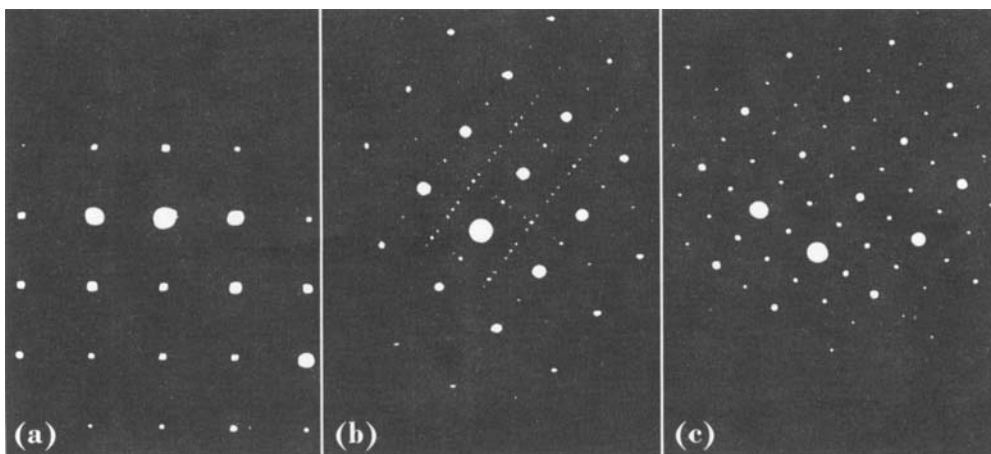
dependent upon the structure of stoichiometrically identical f.c.c. alloys.

The use of palladium-rare earth alloys for hydrogen gas purification has been investigated by Harris and co-workers (67). They found in the course of these studies that a superlattice formed at the stoichiometry:  $\text{Pd}_3\text{Ce}$  and although the hydrogen solubility was small for each form, it was greater for the disordered form (68). They attributed the greater solubility in the disordered form to defects in this material. Sakamoto and colleagues confirmed these results and demonstrated with this alloy system how hydrogen solubilities, measured at various temperatures during the heating of an initially disordered alloy, could be employed to follow the progress of the ordering process (69). In the ordered form of the alloy 0.25 of the interstices are of the type  $\text{Pd}_6$ , and in the completely disordered form there are 0.448. This difference can qualitatively account for the solubility differences. Doyle and Harris have found in the analogous  $\text{Pd}_3\text{Y}$  alloy that the disordered form also dissolves more hydrogen than the ordered form, under comparable conditions (70). They also found that the solubility decreases with increase in size of the domains in the ordered material, and they point to the necessity of considering the rôle of the antiphase boundaries in the solubility.

$\text{Pd}_3\text{Mn}$  was found by Watanabe to form a long period superstructure of the type  $\text{Ag}_3\text{Mg}$  when annealed in vacuo (71). The critical temperature for this ordering was reported to be about 800 K. These results were confirmed by Cable and colleagues by neutron diffraction (72). Structural studies of the non-stoichiometric alloys (73-75) followed studies of the stoichiometric alloy. There is disagreement about the type of order in the substoichiometric range.

Recently Ahlzen and colleagues reclassified the long period ordered superstructure of  $\text{Pd}_3\text{Mn}$  as type  $\text{Al}_3\text{Zr}$  rather than as type  $\text{Ag}_3\text{Mg}$  (76). The unit cell is shown in Figure 1. Here this  $\text{Al}_3\text{Zr}$  type structure will be referred to as the *lps* (long period superstructure) structure.

The solubility of hydrogen gas in the *lps* ordered form, which forms by annealing in vacuo, was studied by Phutela and Kleppa (30). They



**Fig. 2** The electron diffraction patterns are shown along the [001] direction of the three forms of Pd<sub>3</sub>Mn. (a) disordered (b) *lps* (c) *L1*<sub>2</sub>

followed its hydrogen solubilities through the critical temperature,  $\approx 800$  K, during heating and subsequent cooling. They concluded, on the basis of solubility behaviour extrapolated through the critical temperature, that the solubility is greater in the ordered than in the disordered form. This study also demonstrates how hydrogen solubilities can be employed for following the degree of order. They did not compare the solubilities in the ordered and disordered forms at the same temperatures.

More recently Flanagan, Sakamoto and their co-workers have re-investigated this system and they have complemented their hydrogen solubility studies with physical characterisations, especially electron diffraction and electrical resistivity changes (77–85). Because of the depth of results concerning this alloy–hydrogen system, which have not been previously reviewed, the system will be discussed here in detail.

### Recent Results Concerning the Pd<sub>3-x</sub>Mn<sub>1+x</sub> System Structure and Properties

The **disordered alloys** were prepared by heating them in silica tubes to about 1200 K and then quenching them into ice water, while simultaneously breaking the containing quartz vessel. The alloys were not completely disordered—because some very faint superlattice reflections

were observed for the stoichiometric compound – but they are largely disordered. The electron diffraction pattern along the [001] direction is shown, Figure 2(a), for the stoichiometric alloy.

**Long-period superstructure alloys** were prepared by annealing in vacuo at about 700 K or by slowly cooling, at 2 K/h, from above 800 K. The electron diffraction pattern for the stoichiometric alloy is shown in Figure 2(b) where the splitting of the principal reflections is caused by the elongation of the unit cell in the *c*-direction from one to four of the elementary cubes of the disordered alloy.

The **L1<sub>2</sub> structure** was prepared by hydrogen-induced ordering of the disordered alloy (see below). The electron diffraction pattern is shown in Figure 2(c) where extra superlattice reflections appear, but there is an absence of the splitting characteristic of the long period structure. The L1<sub>2</sub> form is stable below about 550 K.

Thus, three different forms of the same alloy can be prepared and investigated at moderate pressures of hydrogen up to about 550 K; this leads to interesting comparisons of the hydrogen solubilities between the three forms.

### Electrical Resistivity Behaviour

The resistivity behaviour of an initially disordered stoichiometric alloy is shown in Figure 3 as it is heated at 2 K/h in the temperature

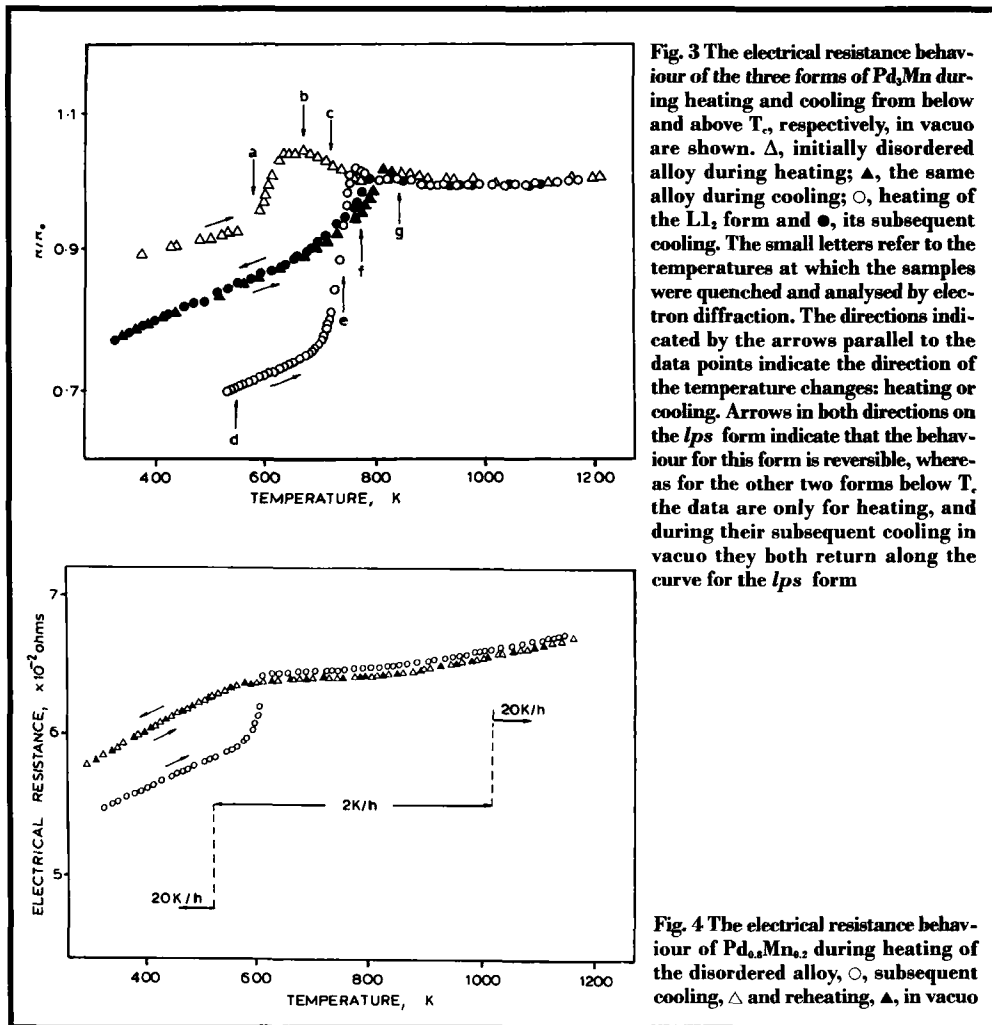


Fig. 3 The electrical resistance behaviour of the three forms of Pd<sub>3</sub>Mn during heating and cooling from below and above T<sub>c</sub>, respectively, in vacuo are shown. Δ, initially disordered alloy during heating; ▲, the same alloy during cooling; ○, heating of the L1<sub>2</sub> form and ●, its subsequent cooling. The small letters refer to the temperatures at which the samples were quenched and analysed by electron diffraction. The directions indicated by the arrows parallel to the data points indicate the direction of the temperature changes: heating or cooling. Arrows in both directions on the *lps* form indicate that the behaviour for this form is reversible, whereas for the other two forms below T<sub>c</sub> the data are only for heating, and during their subsequent cooling in vacuo they both return along the curve for the *lps* form

Fig. 4 The electrical resistance behaviour of Pd<sub>31</sub>Mn<sub>69</sub> during heating of the disordered alloy, ○, subsequent cooling, Δ and reheating, ▲, in vacuo

range where changes occur due to ordering. The alloy commences to change to the ordered *lps* form at about 550 K; at ≈ 800 K it re-disorders. In contrast to other order-disorder systems, the resistivity of an initially disordered alloy increases during ordering and then decreases, which leads to a pronounced maximum below the critical temperature, T<sub>c</sub> = 800 K. Electron diffraction patterns of quenched samples taken during this heating of the initially disordered alloy revealed that ordering takes place during the increase of resistance. For example at point **a** the alloy was still in the disordered form, but at **b** the superlattice reflections characteristic of the

*lps* form appeared, and at **c** they are quite strong. A maximum similar to that shown in Figure 3 is also found in resistivity curves for alloys of composition: Pd<sub>0.77</sub>Mn<sub>0.23</sub>, Pd<sub>0.73</sub>Mn<sub>0.27</sub>, Pd<sub>0.71</sub>Mn<sub>0.29</sub> and Pd<sub>0.69</sub>Mn<sub>0.31</sub> (85). The maximum is greatest for the stoichiometric alloy, see Figure 3. During subsequent cooling a different resistance pathway is followed as the alloy orders, below the critical temperature, to the *lps* form. On subsequent reheating it follows this same pathway again except that a small hysteresis appears in T<sub>c</sub>, which is characteristic of a first order transition.

The *lps* form is the stable form in the absence of dissolved hydrogen, and therefore if the L1<sub>2</sub>

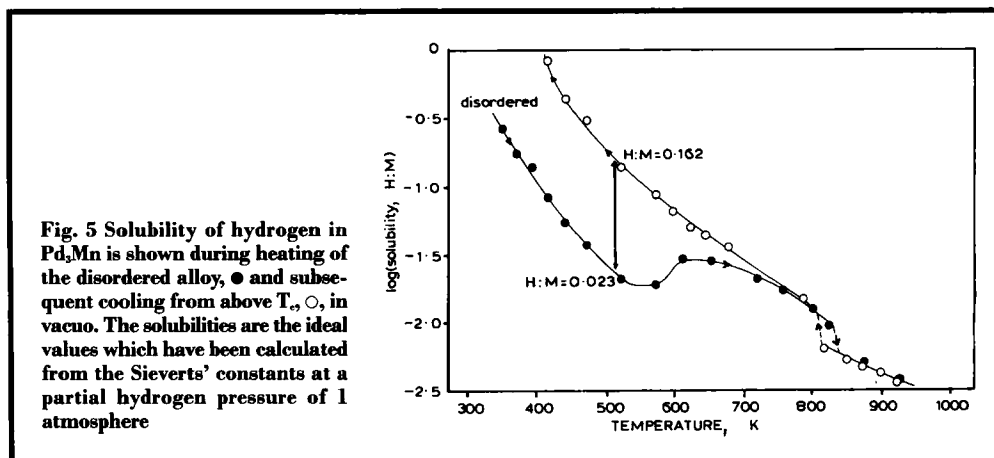
form is heated in vacuo, it should transform to the *lps* form. The resistivity behaviour of the  $L1_2$  form as it is heated and then subsequently cooled in vacuo is also shown in Figure 3. The resistivity of the  $L1_2$  ordered alloy is lower than that of the *lps* ordered alloy. This is because it has a simple ordered structure without the antiphase domain boundaries which occur in the *lps* form and presumably cause the maximum in the resistance relationship. The resistance of the  $L1_2$  form commences to show a non-linear increase starting at about 700 K, a higher temperature than that at which the disordered alloy starts to order, indicating that the  $L1_2$  form is more stable with respect to the *lps* form than is the disordered structure. Electron diffraction patterns of quenched samples taken at various temperatures during heating revealed that at **d** the alloy was still  $L1_2$  but at **e** and **f** the order was *lps* (Figure 3); at **g** the alloy was mainly disordered.

Resistivity data for the  $Pd_{0.8}Mn_{0.2}$  alloy are shown in Figure 4 during heating of the disordered alloy, where a transition to higher resistivities starts at about the same temperature as in the stoichiometric alloy. On the other hand, it seems that  $T_c$  occurs at a lower temperature for this non-stoichiometric alloy. This alloy does not show a maximum of resistance during the ordering of the disordered alloy (Figure 4). For the  $Pd_{0.85}Mn_{0.15}$  alloy the disorder  $\rightarrow$  order transition is not apparent from the resistivity (85).

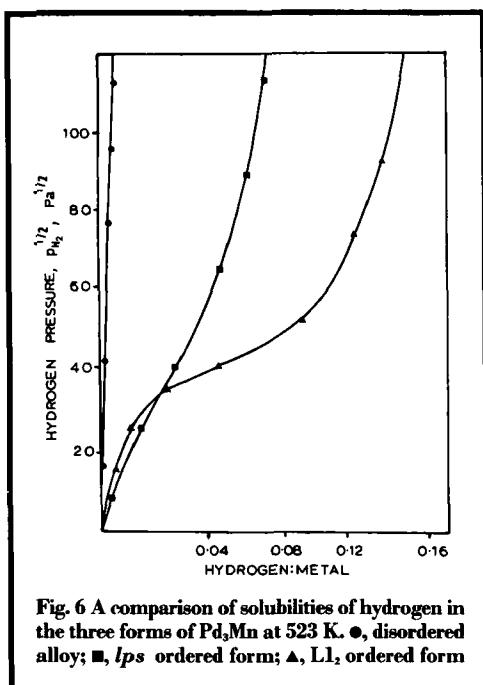
Hydrogen solubility is much greater in the *lps*

ordered form than in the disordered form, and therefore the hydrogen solubilities can also be employed to follow ordering in this system, as in the Pd,Ce system (69). In these experiments for following ordering in the Pd<sub>3</sub>Mn alloy, hydrogen solubilities of the initially disordered alloy are measured at relatively low hydrogen pressures at progressively increasing temperatures. The hydrogen solubility versus temperature relationships are shown in Figure 5. The overall heating and cooling rate was approximately 2 K per hour, that is, intentionally the same as during the resistivity studies. During the initial heating of the disordered alloy a linear van't Hoff plot is found until about 430 K, and thereafter the solubility can be seen to increase because of the onset of ordering at about 575 K. Ordering proceeds until the alloy is fully ordered and then the solubilities follow another linear van't Hoff relation until disordering commences near the critical temperature. Upon cooling, the solubility follows linear van't Hoff plots above  $T_c$  for the disordered alloy and below it for the re-ordered alloy. (The linear van't Hoff plots may be seen in a plot of  $\log(\text{solubility})$  against  $T^{-1}$ ).

The hydrogen solubilities in the  $Pd_{0.8}Mn_{0.2}$  and  $Pd_{0.85}Mn_{0.15}$  alloys also show transitions to the ordered phase during heating and a second transition above  $T_c$  to the disordered phase; on cooling a transition to the ordered state occurs followed by a single linear van't Hoff relation (83). A hysteresis is seen in the  $T_c$  values during







heating and cooling, just as for the resistivity data (Figures 3 and 4).

The ordering transitions are more sensitively reflected by these hydrogen solubility data than they are by the resistivity changes. Therefore, for this system this is a superior technique for following the ordering-disordering process.

### Hydrogen Solubilities in the Different Forms of Pd<sub>3</sub>Mn

Hydrogen solubilities in the three forms of the Pd<sub>3</sub>Mn alloy can be compared at the same temperatures and over a range of hydrogen pressures. Some results are shown in Figure 6 where it can be seen that very different hydrogen solubilities are found (79). In co-operation with Andersson and her co-workers, the deuterium atoms were located, by neutron diffraction, in Pd<sub>3</sub>MnD<sub>0.61</sub>, the *lps* form, at about 85 per cent in the Pd<sub>6</sub> and 15 per cent in the Pd<sub>3</sub>Mn interstice (76); in the L1<sub>2</sub> form 100 per cent of the deuterium was located in the Pd<sub>6</sub> interstice (86). This is a significant result because it was the first time that deuterium atoms had been located in a palladium alloy. It was previously intuitively believed

by most workers that the palladium-rich sites would be the favoured ones, but hitherto this had not been demonstrated. It can, of course, be safely assumed that the hydrogen isotope favours the same sites.

### Hydrogen-Induced Ordering

In the above studies the disorder → order transitions were carried out in vacuo (Figures 3, 4 and 5) and the ordered phase which formed was *lps*. It has been found that in the presence of a small amount of dissolved hydrogen a largely disordered Pd<sub>3</sub>Mn alloy orders at temperatures where there was no ordering in vacuo; interestingly, the hydrogen-ordered form was found to differ from that resulting from annealing in vacuo (77). The two ordered forms can be interconverted by adding or removing hydrogen at about 700 K (79, 81).

The disorder → order transition was carried out at moderately high hydrogen pressures (1.0 to 5.0 MPa) under which the disordered alloy was found to order to the L1<sub>2</sub> form at temperatures as low as 423 K (in  $p_{H_2} \geq 1$  MPa); ordering did not occur in the absence of hydrogen at these temperatures (77, 84). The ordering at low temperatures was incomplete and more complete ordering to the L1<sub>2</sub> form took place at higher hydrogen pressures and temperatures, for example, an almost completely L1<sub>2</sub> ordered alloy formed from the disordered alloy at 5.0 MPa and 723 K (84).

The non-stoichiometric alloys also ordered to an L1<sub>2</sub> form in the presence of hydrogen at moderately high pressures (82). An electron diffraction pattern of the Pd<sub>0.8</sub>Mn<sub>0.2</sub> alloy which had been exposed to 5 MPa of hydrogen at 523 K for 67 hours showed a strong L1<sub>2</sub> pattern, but the *lps* pattern was not so clear after cooling the same alloy slowly in vacuo from above  $T_c$ .

### Suppression of Ordering by Dissolved Hydrogen

It has recently been proposed by Griessen and co-workers, on the basis of hydrogen solubility studies, that dissolved hydrogen suppresses the short range ordering of Pd<sub>0.9</sub>Y<sub>0.09</sub> alloys (87). This was confirmed and its occurrence was shown to

be broader by Sakamoto and co-workers (88). The presence of dissolved hydrogen was found to suppress the long range ordering in a series of Pd<sub>7</sub>RE (RE = rare earth metal) alloys and in Pd<sub>7</sub>Li. The amounts of hydrogen dissolved are relatively small but exert a decisive influence on the stability of the structure. The energies of the ordered and disordered forms of some alloys must differ by only small amounts and the presence of a perturbation, such as dissolved hydrogen, can cause a reversal of the stability of the disordered with respect to the ordered forms. The dissolved hydrogen weakens the M-palladium bonding, thus stabilising the disordered form.

### Hydrogen-Induced Acceleration of Phase Separation

In the GPa range of hydrogen pressures Ponyatovski and co-workers have observed interesting changes in initially homogeneous f.c.c. palladium alloys (89–92). They found that disordered Pd<sub>0.6</sub>Cu<sub>0.4</sub> (89) and Pd<sub>0.5</sub>Ag<sub>0.5</sub> (92) order in the presence of very high hydrogen pressures at temperatures  $\geq 493$  K; the hydrogen atoms form a part of these ordered structures. They found that palladium-nickel alloys segregate when exposed to ultra high pressures ( $\geq 5$  kbar) at  $T \geq 493$  K. Segregation was proven by the existence of two sets of f.c.c. X-ray diffraction reflections (89). They also found that f.c.c. homogeneous palladium-platinum alloys with  $X_{Pt} \geq 0.15$  segregate into palladium- and platinum-rich phases at 2 to 6 GPa and 623 K (90); all the Pd-Pt alloys but the Pd<sub>0.75</sub>Pt<sub>0.25</sub> alloy reverted to their homogeneous states at atmospheric pressure and  $T \geq 573$  K.

The palladium-rhodium binary f.c.c. alloy system has a miscibility gap, but normally the alloys

are prepared and kept in a homogeneous, metastable state at ambient temperatures. In fact, it is quite difficult to determine the phase diagram, and Raub and co-workers annealed a Pd<sub>0.40</sub>Rh<sub>0.51</sub> alloy for 6 months at 873 K in order to obtain two sets of f.c.c. lattice parameters indicative of the separated phases (93). In contrast to the results of Ponyatovski and colleagues, it has recently been found that dissolved hydrogen can accelerate the phase separation at moderate pressures of hydrogen (94). For example, after heating a Pd<sub>0.8</sub>Rh<sub>0.2</sub> alloy for 4 hours in 5.5 MPa hydrogen at 873 K, there was evidence for a greater degree of phase separation than that resulting from an identical treatment without hydrogen (94). Evidence for hydrogen-induced phase separation has been observed for a Pd<sub>0.8</sub>-Rh<sub>0.2</sub> alloy after storage at 473 K at H:M = 0.4.

### Conclusions

The investigation of the absorption of hydrogen by palladium alloys, starting from Graham's investigation of palladium-silver in the middle of the last century until very recently, has been principally concerned with the measurement of isotherms and other properties of substantially disordered, "frozen" palladium-rich alloys. Laterly the investigation seems to be moving to a more sophisticated stage of development where hydrogen-induced lattice mobility can be a factor, and where the rôles of long- and short-range order are considered. The understanding of the interaction of hydrogen with palladium alloys encompasses some challenging problems in statistical mechanics.

### Acknowledgement

The authors wish to thank Professor W. A. Oates (KFA, Jülich) for valuable discussions.

### References

- 1 F. A. Lewis, "The Palladium Hydrogen System", Academic Press, New York, 1967
- 2 F. A. Lewis, *Platinum Metals Rev.*, 1982, **26**, (3), 121
- 3 J. E. Worsham, M. K. Wilkinson and C. G. Shull, *J. Phys. Chem. Solids*, 1957, **3**, 303
- 4 T. Springer, in "Hydrogen in Metals", I; ed. G. Alefeld and J. Völkl, Springer-Verlag, Berlin, 1978
- 5 D. Ross, P. Martin, W. Oates and R. K. Bakhsh, *Z. Phys. Chem. Neue Folge.*, 1979, **114**, 221
- 6 J. J. Rush, J. M. Rowe and D. Richter, *Z. Phys. B. Cond. Matter*, 1984, 283
- 7 J. Bergsma and J. A. Goedkoop, *Physica*, 1960, **26**, 744
- 8 A. J. Maeland, *Can. J. Phys.*, 1968, **46**, 121
- 9 M. R. Choudhury and D. K. Ross, *Solid State Commun.*, 1973, **13**, 229
- 10 E. Wicke and J. Blaurock, *J. Less-Common. Met.*, 1987, **130**, 351

- 11 E. Wicke and G. Nernst, *Ber. Bunsenges. Phys. Chem.*, 1964, **68**, 224
- 12 A. W. Carson, T. B. Flanagan and F. A. Lewis, *Trans. Faraday Soc.*, 1960, **56**, 1332
- 13 A. J. Macland and T. B. Flanagan, *J. Phys. Chem.*, 1964, **69**, 3575
- 14 E. Wicke and K. Frölich, *Z. Phys. Chem. Neue Folge*, 1989, **163**, 35
- 15 K. Kandasamy, F. A. Lewis, W. McFall and R.-A. McNicholl, *Z. Phys. Chem. Neue Folge*, 1989, **163**, 41
- 16 Y. Sakamoto, K. Kajihara, T. Kikumura and T. Flanagan, *J. Chem. Soc., Faraday Trans. I*, 1990, **86**, 377
- 17 K. Kandasamy and F. A. Lewis, *Z. Phys. Chem. Neue Folge*, 1988, **158**, 253
- 18 Y. Sakamoto, U. Miyagawa, E. Hamamoto, F. Chen, T. Flanagan and R.-A. McNicholl, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 1457
- 19 J. C. Barton, J. A. S. Greene and F. A. Lewis, *Trans. Faraday Soc.*, 1966, **62**, 960
- 20 H. Brodowsky and H. Husemann, *Ber. Bunsenges. Phys. Chem.*, 1966, **70**, 626
- 21 B. Baranowski, S. Majchrzak and T. B. Flanagan, *J. Phys. Chem.*, 1973, **77**, 35
- 22 J. D. Clewley, J. F. Lynch and T. B. Flanagan, *J. Chem. Soc., Faraday Trans. I*, 1977, **73**, 494
- 23 Y. Sakamoto, K. Baba and T. B. Flanagan, *Z. Phys. Chem. Neue Folge*, 1988, **158**, 223
- 24 O. J. Kleppa, *Ber. Bunsenges. Phys. Chem.*, 1983, **87**, 741
- 25 J. F. Lynch and T. B. Flanagan, *J. Chem. Soc., Faraday Trans. I*, 1974, **70**, 814
- 26 C. Picard, O. Kleppa and G. Boureau, *J. Chem. Phys.*, 1979, **70**, 2710
- 27 M. Shamsuddin and O. Kleppa, *J. Chem. Phys.*, 1979, **71**, 5154
- 28 O. Kleppa, M. Shamsuddin and C. Picard, *J. Chem. Phys.*, 1979, **71**, 1656
- 29 R. Phutela and O. Kleppa, *J. Chem. Phys.*, 1981, **75**, 4095
- 30 R. Phutela and O. Kleppa, *J. Chem. Phys.*, 1982, **76**, 1525
- 31 M. Shamsuddin and O. Kleppa, *J. Chem. Phys.*, 1984, **80**, 3760
- 32 K. Frölich, H. Severin, R. Hempelmann and E. Wicke, *Z. Phys. Chem. Neue Folge*, 1980, **119**, 33
- 33 Y. Sakamoto, K. Kajihara, Y. Fukusaki and T. Flanagan, *Z. Phys. Chem. Neue Folge*, 1988, **159**, 61
- 34 Y. Sakamoto, T. Matsuo, H. Sakai and T. Flanagan, *Z. Phys. Chem. N. F.*, 1989, **162**, 83
- 35 Y. Sakamoto, K. Kajihara, E. Ono, K. Baba and T. Flanagan, *Z. Phys. Chem. Neue Folge*, 1989, **165**, 67
- 36 Y. Sakamoto, F. Chen, M. Furukawa and T. Flanagan, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 190
- 37 Y. Sakamoto, F. Chen, J. Muto and T. Flanagan, *Z. Phys. Chem. Neue Folge*, 1991, **173**, 235
- 38 F. Chen, M. Furukawa and Y. Sakamoto, *J. Less-Common Met.*, 1991, **172–174**, 56
- 39 Y. Sakamoto, F. Chen and R.-A. McNicholl, *J. Alloys Compd.*, in press
- 40 R. Feenstra, D. de Groot, R. Griessen, J. Burger and A. Menovski, *J. Less-Common Met.*, 1987, **130**, 375
- 41 E. Salomons, U. Ljungblad and R. Griessen, *Defect and Diffusion Forum*, 1989, **66 – 69**, 327
- 42 S. Ramaprabhu, R. Leiberich and A. Weiss, *Z. Phys. Chem. Neue Folge*, 1989, **161**, 83
- 43 S. Ramaprabhu and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 146
- 44 S. Ramaprabhu, N. Rajalakshmi and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 686
- 45 S. Ramaprabhu, N. Rajalakshmi and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 490
- 46 R.-A. McNicholl and F. A. Lewis, *J. Less-Common Met.*, 1991, **172–174**, 160
- 47 A. Sieverts and K. Brüning, *Z. Phys. Chem.*, 1934, **A168**, 411
- 48 R. Burch and F. A. Lewis, *Trans. Faraday Soc.*, 1970, **66**, 727
- 49 H. Husemann and H. Brodowsky, *Z. Naturforsch.*, 1968, **23a**, 1693
- 50 Y. Sakamoto, Y. Tanaka, K. Baba and T. B. Flanagan, *Z. Phys. Chem. Neue Folge*, 1988, **158**, 237
- 51 Y. Sakamoto, N. Ishimaru and Y. Mukai, *Int. J. Phys. Chem.*, 1991, **95**, 680
- 52 Y. Sakamoto, N. Ishimaru and Y. Inoue, *Int. J. Phys. Chem.*, 1992, **96**, 128
- 53 P. Boutin and A. Miedema, *J. Less-Common Met.*, 1980, **71**, 147
- 54 M. J. Stickney, M. S. Chandrasekharaiah, K. Gingerich and J. Speed, *Met. Trans.*, 1991, **22A**, 1937
- 55 K. Myles and J. Darby, *Acta Metall.*, 1968, **16**, 485
- 56 L. Topor and O. Kleppa, *Z. Metallkd.*, 1986, **77**, 633
- 57 L. Topor and O. Kleppa, *Met. Trans.*, 1987, **18A**, 1989
- 58 H. Brodowsky and E. Poeschel, *Z. Phys. Chem. Neue Folge*, 1964, **44**, 143
- 59 C. Wagner, *Z. Phys. Chem.*, 1944, **A193**, 407
- 60 W. Oates and R. Ramanathan, *Hydrogen in Metals*, Proc. 2nd Intl. Congress, Pergamon Press, Paris, 1977
- 61 G. Boureau, O. Kleppa and K. Hong, *J. Chem. Phys.*, 1977, **67**, 3437
- 62 R. Griessen and A. Driessen, *J. Less-Common Met.*, 1984, **245**
- 63 R. Griessen, in "Hydrogen in Amorphous and Disordered Solids", ed. G. Bambakikis and R. Bowman, Plenum Press, New York, 1986, p.153
- 64 E. Salomons, H. Hemmes and R. Griessen, *J. Phys. Condens. Matter*, 1990, **2**, 817
- 65 W. A. Oates and K. Mika, *Z. Phys. Chem. Neue Folge*, to be published
- 66 T. B. Flanagan, S. Majchrzak and B. Baranowski, *Philos. Mag.*, 1972, **25**, 257

- 67 D. T. Hughes and I. R. Harris, *Z. Phys. Chem. Neue Folge*, 1979, **117**, 185
- 68 D. A. Smith, I. P. Jones and I. R. Harris, *J. Less-Common Met.*, 1984, **103**, 33
- 69 Y. Sakamoto, T. B. Flanagan and T. Kuji, *Z. Phys. Chem. Neue Folge.*, 1985, **143**, 61
- 70 M. L. Doyle and I. R. Harris, *Z. Phys. Chem. Neue Folge*, 1989, **163**, 59
- 71 D. Watanabe, *Trans. Jpn. Inst. Met.*, 1962, **3**, 234
- 72 J. W. Cable, E. O. Wollan, W. C. Koehler and H. R. Child, *Phys. Rev.*, 1962, **128**, 2118
- 73 H. Sato and R. S. Toth, *Phys. Rev.*, 1965, **139**, 1581
- 74 H. Iwasaki, K. Okamura and S. Ogawa, *J. Phys. Soc. Jpn.*, 1971, **31**, 497
- 75 J. Gjønnes and A. Olsen, *Phys. Status Solidi (a)*, 1973, **17**
- 76 P. J. Ahlzén, Y. Andersson, R. Tellgren, D. Rodic, T. B. Flanagan and Y. Sakamoto, *Z. Phys. Chem. Neue Folge.*, 1989, **163**, 213
- 77 T. B. Flanagan, A. P. Craft, T. Kuji, K. Baba and Y. Sakamoto, *Scr. Metall.*, 1986, **20**, 1745
- 78 K. Baba, Y. Sakamoto, T. B. Flanagan, T. Kuji and A. Craft, *Scr. Metall.*, 1987, **21**, 299
- 79 K. Baba, Y. Niki, Y. Sakamoto, T. B. Flanagan and A. Craft, *Scr. Metall.*, 1987, **21**, 1147
- 80 A. P. Craft, R. Foley, T. B. Flanagan, K. Baba, Y. Niki and Y. Sakamoto, *Scr. Metall.*, 1988, **22**, 511
- 81 K. Baba, Y. Niki, Y. Sakamoto, A. P. Craft and T. B. Flanagan, *J. Mater. Sci. Lett.*, 1988, **7**, 1160
- 82 K. Baba, Y. Niki, Y. Sakamoto and T. B. Flanagan, *J. Less-Common Met.*, 1991, **172-174**, 246
- 83 T. B. Flanagan, A. Craft, Y. Niki, K. Baba and Y. Sakamoto, *J. Alloys Compd.*, 1992, **184**, 69
- 84 Y. Sakamoto, K. Baba, Y. Niki, Y. Ishibashi and T. B. Flanagan, *J. Alloys Compd.*, 1992, **184**, 57
- 85 K. Baba, Y. Niki, Y. Sakamoto and T. B. Flanagan, *J. Alloys Compd.*, 1992, **179**, 321
- 86 P. Ahlzén, Y. Andersson, R. Tellgren, T. B. Flanagan and Y. Sakamoto, to be published
- 87 E. Salomons, N. Koeman, J. Rector and R. Griessen, *J. Phys. Condens. Matter*, 1990, **2**, 835
- 88 Y. Sakamoto, K. Takao and T. B. Flanagan to be published
- 89 V. Degtyareva, V. Antonova, I. Belash and E. Ponyatovski, *Phys. Status Solidi (a)*, 1981, **66**, 77
- 90 V. Antonov, V. Antonova, I. Belash, E. Ponyatovski and V. Rashuptkin, *Phys. Status Solidi (a)*, 1983, **78**, 137
- 91 V. Antonov, V. Antonova, I. Belash and E. Ponyatovski, *Phys. Met. Metall.*, 1984, **57**, 671
- 92 A. Irodova, V. Glazkov, V. Somenkov, T. Kurchatov, V. Antonov and E. Ponyatovski, *Z. Phys. Chem. Neue Folge*, 1989, **163**, 53
- 93 E. Raub, H. Beeskow and D. Menzel, *Z. Metallkd.*, 1959, **50**, 428
- 94 H. Noh, T. B. Flanagan and M. Ransick, *Scr. Metall. Mater.*, 1992, **26**, 353

## Rhodium Alloys for Magnetocooling Devices

It appears that the efficiency of the traditional methods of thermomechanical refrigeration cannot be improved further, and therefore there is a need to find alternatives. One such method could be magnetocaloric refrigeration, which is based on the reversible heating and cooling of a medium when its magnetisation is changed. However, this requires the use of suitable magnetic materials which display good field-induced entropy changes over a wide temperature range.

Although the antiferromagnetic-ferromagnetic phase transition in rhodium-iron alloys has been investigated previously, there have not been many experimental determinations of the thermomagnetic properties of these alloys. Now researchers at Moscow State University, Russia, and at Turkmen State University, Turkmenia, have reported the results of their studies. They investigated the temperature dependence of initial magnetic permeability, specific heat capacity and the magnetocaloric effect in both annealed and quenched samples of 49 iron-51 rhodium alloys near to the antiferromagnetic-ferromagnetic first-order transition, (M. P. Annaorazov, K. A. Asatryan, G. Myalikgulyev,

S. A. Nikitin, A. M. Tishin and A. L. Tyurin, *Cryogenics*, 1992, **32**, (10), 867-872).

Polycrystalline samples made by induction melting rhodium and iron in argon were homogenised by annealing for 72 hours at 1300 K under vacuum, followed by slow cooling to room temperature. A temperature drop of 12.9 K occurred under adiabatic conditions when a magnetic field of about 2 T was applied to a quenched sample at 308.2 K. The behaviour and the value of the magnetocaloric effect were very sensitive both to heat treatment and to the applied field. The value of the refrigerant capacity of a quenched sample of the alloy at a field of 1.95 T, determined from magnetocaloric temperature changes combined with zero-field specific heat data, was 135.22 J/kg T. This is significantly greater than the refrigerant capacity of gadolinium, which is regarded as a useful material for magnetocaloric refrigeration. Therefore rhodium-iron alloys are considered to be suitable materials for use in stage magnetic refrigerators. The transition temperature of this binary system may be changed by dilution with 3d, 4d and 5d transition elements.