THE ENTHALPY OF SOLUTION FOR SOLID BINARY
ALLOYS OF TWO 4d-TRANSITION METALS

A.R. Miedema and A.K. Niessen
Philips Research Laboratories, 5600 MD Eindhoven
The Netherlands

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ABSTRACT: A demonstration is given how to derive the enthalpy of solid solu-
tion of alloys of two 4d transition metals for the three main
crystallographic structures, fcc, hcp and bcc.
Because of two additional terms the enthalpy of solution for solid
phases differs from that in the corresponding liquid alloys. The
first of these, accounting for elastic mismatch, can be estimated
from Eshelby/Friedel-type elastic continuum theory. In our case we
correct the atomic size mismatch for volume changes that accompany
the formation of alloys.
The second term accounts for the variation of structure dependent
energies (i.e. the preference for either the fcc, bcc or hcp type
of crystal structure) with the average number of electrons per atom.
We derive an empirical curve for these structure dependent enthalpy
terms, which is essentially based on theoretical results and gives
a fair account of binary phase diagram characteristics.

1. Introduction

The enthalpy of solution in solid binary alloys of two transition metals
is more complicated than that of the corresponding liquid alloys. There are
two additional terms :

$$\Delta H^O(\text{solid solution}) = \Delta H^O(\text{liq.}) + \Delta H^O(\text{elast.}) + \Delta H^O(\text{struct.}) \qquad (1)$$

The first term is assumed to be known, either from experiment or from
predictions based on empirical model calculations. For alloys of two 4d metals
the amount of experimental information is very limited. Hence, in this paper,
we rely on predictions from the atomic (interface) model. For the sake of
convenience we reproduce for alloys of 4d metals the relevant predictions in
table I. For alloys containing Zr or Nb the predictions are slightly different
from those given in reference [1]. For details see a forthcoming paper in this
journal.
The second term accounts for the elastic energy which is bound to be
present when a matrix atom is replaced by a solute atom of a different size.
Elastic mismatch energies, derived within the Eshelby, Friedel [2, 3] elastic
continuum theory, depend on the bulk modulus of the solute metal, the shear
modulus of the matrix metal and the difference in molar volume of the two
metals. In calculating elastic terms we first correct the volume differences
by including volume changes that accompany alloying. For details we refer to
reference [4]. The results for solid solutions of two 4d transition metals
are given in table II.

TABLE I

Model predictions for the heat of
solution in the liquid state (alloys of two
4d metals, S at infinite dilution in H, units
kJ/mol).

H / S	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Y		+ 34	+101	+81	- 96	-113	-181	-286
Zr	+ 42		+ 15	-23	-195	-212	-260	-338
Nb	+138	+ 17		-22	-139	-156	-176	-208
Mo	+114	- 27	- 23		- 45	- 56	- 59	- 59
Tc	-132	-232	-146	-45		- 1	+ 1	+ 17
Ru	-157	-260	-168	-58	- 1		+ 5	+ 25
Rh	-252	-315	-188	-61	+ 1	+ 5		+ 8
Pd	-378	-390	-211	-57	+ 17	+ 24	+ 7	

TABLE II

The elastic term[xx] in the
enthalpy of solution of alloys of two
4d transition metals (S at infinite
dilution in H, units kJ/mol, substitu-
tional[x] solutions).

H / S	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Y		+27	+84	+131	·+164	+177	+168	+147
Zr	+22		+20	+ 51	+ 77	+ 90	+ 81	+ 60
Nb	+44	+12		+ 5	+ 13	+ 19	+ 16	+ 7
Mo	+56	+33	+ 7		+ 4	+ 9	+ 6	+ 1
Tc	+51	+39	+18	+ 4		+ 2	+ 1	0
Ru	+55	+49	+29	+ 11	+ 2		0	+ 3
Rh	+59	+50	+27	+ 8	+ 1	0		+ 2
Pd	+49	+31	+11	+ 2	0	+ 2	+ 1	

x) For Pd, Rh, Ru and Tc in Y, inter-
stitial rather than substitutional
solubility is to be expected.
xx) Values calculated including volume
contractions and a recent collection
of elastic constants.

The third term indicates the preference for a given crystal structure which,
for combinations of 4d metals in dilute solute solutions, means either the
fcc, the hcp of the bcc crystal structure. From a theoretical point of view
it seems reasonable to assume that structure dependent energies in transi-
tion metal solid solutions will vary systematically with the average number
of conduction electrons per atom, Z, as long as the two metals form a common
band of d-type electronic states. As we shall demonstrate below this
approach gives a quantitative description of ΔH(struct.) in alloys of 4d
metals that agrees closely with experimental information from binary phase
diagrams. Since in this paper we are interested in enthalpy effects at zero
temperature we do not have to distinguish energy effects from enthalpy
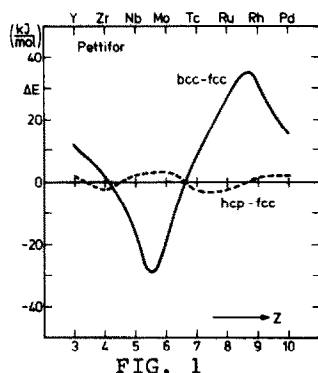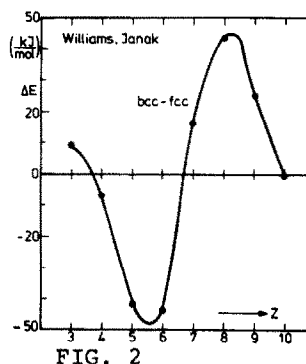effects.

FIG. 1   FIG. 2

Theoretical predictions for energy differences between different crystal structures versus Z, the number of valence electrons for transition metals. Fig. 1, according to Pettifor [5], contains energy differences between bcc and fcc and hcp and fcc structures, respectively, that are derived by summing one-electron energies. Fig. 2 gives the energy difference between bcc and fcc metals derived by Janak and Williams [6] by means of self-consistent ASW calculations.

2. The Structure Dependent Term

Pettifor [5] derived theoretical estimates for the difference in energy for pure transition metals in the fcc, hcp or bcc crystal structures. Pettifor's results are shown in fig. 1, where the energy of hcp and bcc metals is given relative to the fcc structure as the reference state. Then the bcc phase has a value of ΔE below zero for $Z = 5$ (Nb in the 4d series) and $Z = 6$ (Mo), whereas its energy lies clearly above that of the fcc phase for $Z = 8$ (Ru) and $Z = 9$ (Rh).

Results obtained by Williams and Janak [6] given in fig. 2 show a similar trend. It is generally agreed that the theoretical curves as shown in figs. 1 and 2 tend to overestimate the actual differences. As stated by Williams [6] this has to do with the fact that the theoretical curves are based on integration of one electron energies, while the effect of repulsive core interactions is ignored.

We have used the theoretical curves of figs. 1 and 2 as starting values in constructing an empirical curve, fig. 3, using additional information. This includes experimental information about solid solubilities in binary phase diagrams, and the experimentally known enthalpy differences between the bcc and hcp phases in the case of Y(Z=3) and Zr(Z=4).

The next step is the conversion of energy differences into absolute stability values, or rather the variation of the stability of a given crystal structure type with Z. We assume that the reference state in discussing energy to be the average of that of the two closed packed structures (fcc and hcp) on the one hand and that of bcc phases on the other. In formula form

$$\{E(hcp) + E(fcc)\}/2 + E(bcc) = 0. \tag{2}$$

Using equation (2) it is easy to convert the relative stabilities ΔE of fig. 3 into absolute stabilities. For the pure 4d metals the positions of the three phases in the energy scale have been tabulated in table III, and have been plotted in fig. 4.
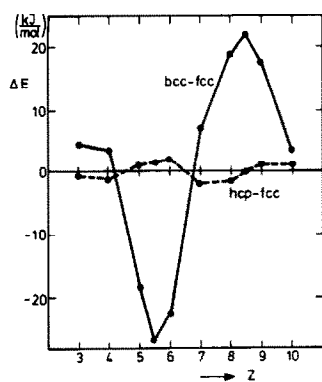
FIG. 3

FIG. 4

The energy difference between transition metals in different crystal structures as figs. 1 and 2, but now fitted to experimental information. In fig. 4 the energy differences are plotted in a different way : the zero in the energy scale corresponds to the average value of the energy of the bcc structure on the one hand and the two closed packed structures on the other.
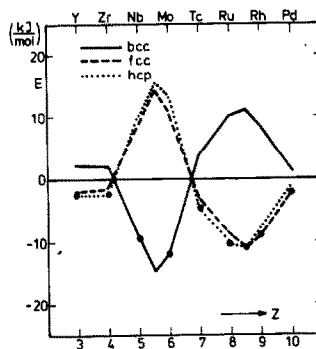
TABLE III
Enthalpy differences between hcp, bcc
and fcc phases of 4d transition metals in a scale
for which $\Delta H(bcc) + \{\Delta H(hcp) + \Delta H(fcc)\}/2=0$ as a
function of Z. Units kJ/mol.

Z	3	4	5	5.5	6	7	8	8.5	9	10
hcp	-2.5	-2.5	+10	+15	+13	-5	-10.5	-11	-8	-1
fcc	-2	-1.5	+9	+14	+11	-3	- 9.5	-11	-9	-2
bcc	+2.2	+2	-9.5	-14.5	-12	+4	+10	+11	+8.5	+1.5

The introduction of absolute stabilities instead of relative stabilities may seem trivial, but they do have important implications, as can be seen from the following example. Starting from Pd(Z=10) and reducing the average number of electrons per atom by alloying, the bcc structure acquires a considerably higher energy (figs. 1-4) and consequently the fcc structure becomes more stable (fig. 4). For a solute metal whose difference in valence, ΔZ, is large, this can make a major contribution to the enthalpy of solution, i.e. ΔZ times the slope of the E versus Z relation for the fcc structure going from Pd(Z=10) to Rh(Z=9). In this way one can understand why solute metals like Y, Zr or Nb lead to a large solid solubility in Pd in spite of the fact that there is an appreciable size mismatch and/or a strong tendency towards compound formation (large and negative heats of alloying in the liquid state). In the general case that the host metal H with crystal structure (h) and the solvent metal S with crystal structure (s) are of a different structure, the structure related contribution contains two terms. First the solute metal is transformed into the crystal structure of the host metal for which the energy change $E_S(h)-E_S(s)$ can be derived from Table III. Then atom is transferred to the lattice of the host metal with an energy effect

$$E_H(h) - E_S(h) + (Z_S-Z_H)(dE_H(h)/dZ)$$

Taking the two terms together we obtain

$$\Delta H^O(\text{struct.}, \text{ S in H}) = -E_S(s) + E_H(h) + (Z_S-Z_H)(dE_H(h)/dZ) \qquad (3)$$

For the above example of hcp Zr as a solute in fcc Pd the formula reads

$$\Delta H^O(\text{struct.}, \text{ hcp Zr in fcc Pd}) =$$

$$-E_{Zr}(hcp) + E_{Pd}(fcc) + 6(E_{Rh}(fcc) - E_{Pd}(fcc)) \qquad (3a)$$

In this example we take as a value of $dE_{Pd}(fcc)/dZ$ the difference between energy of Pd and that of its nearest neighbour in the Periodic Table, Rh, in the fcc structure. From Table III it appears that for Rh and Ru (and for Mo and Nb) the situation is somewhat more complicated because there is an extremum in the lattice stability values in between Ru and Rh and Mo and Nb; at Z=8.5 and Z=5.5, respectively.

In relation (3) we use values of $dE_H(h)/dZ$ that can be different for solute metals increasing or decreasing the number of valence electrons per atom, Z. As a matter of fact this is artificial and a consequence of the "unphysical" discontinuities in the energy derivatives present in figs. 3 and 4. We note, however, that in alloys the average number of valence electrons per atom is a locally defined quantity, being determined by a solute atom with its nearest neighbour atoms. Because of this the smallest value of dZ one can think of (solute and host neighbours in the Periodic Table) is still of the order of 0.1 el/atom. Consequently, for solute and host metals far apart in the Periodic Table a change to lower Z values can well be different from a change to higher average Z values.

For the sake of convenience the values of $dE_H(h)/dZ$ for the pure 4d metals have been collected in Table IV, for three crystal structures and for both increasing and decreasing Z. The value of $E_S(s)$ and $E_H(h)$ to be used in applying (3) are the lowest values at a given Z value to be found in table III.

TABLE IV

Values of the change of the structure dependent energy contribution with the average number of valence electrons per atom Z (i.e. dE_H/dZ) at integral values of Z and three crystal structures. Units are kJ/mol per electron.

Z		3	4	5	6	7	8	9	10
hcp	Z<0	–	0	+13	– 4	–18	–6	+6	+7
	Z>0	0	+13	+10	–18	– 6	–1	+7	–
fcc	Z<0	–	+ 1	+11	– 6	–14	–7	+4	+7
	Z>0	+1	+11	+10	–14	– 7	–3	+7	–
bcc	Z<0	–	0	–12	+ 5	+16	+6	–5	–7
	Z>0	0	–12	–10	+16	+ 6	+2	–7	–

TABLE V

The structure dependent term in the enthalpy of solution for solid alloys of two 4d metals, Units kJ/mol; standard reference states; S is solute metal, H is solvent metal.

H / S	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Zr(hcp)	0		+19	+34	+40	+58	+69	+74
Nb	+16	+ 4		0	–25	–29	–41	–58
Mo	–25	–20	– 8		+9	+32	+45	+54
Tc	+69	+46	+40	+25		0	– 7	–19
Ru	+19	+14	+15	+10	0		– 2	–11
Rh	–30	–26	–15	– 9	–12	– 2		0
Pd	–48	–41	–27	–18	–18	– 7	0	
Zr(bcc)	+ 5	+ 5	0	– 9	–28	–35	–47	–65

In table V we have collected calculated values for ΔH(struct.) for com-
binations of 4d metals with reference to pure metals in their standard
states. In addition we include values with bcc Zr as the solvent metal.
Y is left out as a solvent, because in many cases interstitial alloys
are likely to be formed.

3. Comparison with Experiment

The total heat of solution (at infinite dilution) for solid alloys of
two 4d metals can be obtained by adding the three contributions from tables
I, II and V, respectively. Since there is very little quantitative experi-
mental information to compare with, we will make use of indirect information
about solid solubility limits in binary systems as published in handbooks
on phase diagrams.

In case where there is a positive heat of mixing in the liquid state
the situation is relatively simple. For transition metal combinations a
positive heat of mixing in the liquid corresponds with an absence of ordered
intermediate phases for the solid alloys. Solid solubilities are correlated
with the value of the total enthalpy effect (Eqn. 1). In the range of small
solubilities one can estimate solubility limits from the approximate relation

$$C = \exp(-\Delta H^o(\text{solid solution S in H})/RT) \qquad (4)$$

For the combinations of 4d metals for which this situation applies, we
compare experimentally observed solid solubilities with calculated values of
the total enthalpy of solution in table VI. It is clearly demonstrated that
for negative or slightly positive values of ΔH^o (sol) the solubility is
larger than 5 a/o or even continuous, while for the pronounced positive
values the solubility is small. The agreement would be perfect without the
two examples with bcc Zr. However, the calculated elastic contribution for
bcc Zr could be largely overestimated since due to the lack of experimental
values we have used the same elastic constants for HCP Zr and this high
temperature bcc phase.

TABLE VI

Experimental information on solid solubilities in binary alloys
of 4d transition metals. Here the model prediction of the heat
of mixing has the positive sign. For comparison we include the
sum   of the three contributions to the enthalpy of solution,
relation (1).

Alloy	Solub. at T (a/o); (°C)	ΔH^o(calc.) (kJ/mol)	Alloy	Solub. at T (a/o); (°C)	ΔH^o(sol.) (kJ/mol)
hcp			Tc Rh	70; 1000	−5
Zr Y	0.5 ; 886	+64	Tc Pd	50; 1500	−2
Zr Nb	0.6 ; 610	+54			
bcc			Ru Rh	>20; 1000	+3
Zr Y	≈2 ; 1363	+69	Ru Pd	9; 1200	+17
Zr Nb	cont.; >970	+35			
			Rh Pd	cont.; >845	+10
Nb Y	<0.1 ; 1400	+198			
			Pd Rh	cont.; >845	+8
Mo Y	0.04; 1400	+145			

For clearly negative values of the heat of mixing in the liquid state
the situation is different. As a rule one can expect a lot of intermediate
phases to be present, so that solid solubility is determined by thermo-
dynamic equilibrium between a dilute solution and its neighbouring compound.
We suggest that in this situation solid solubilities tend to correlate with
the sum of ΔH^o(elast.) and ΔH^o(struct.) rather than with the total enthalpy
of solution.

Here we use the picture of a competing ordered phase in which the minority
solute metal atoms are completely surrounded by majority host metal atoms.
As far as the first, liquid like, term in the enthalpy of solution is con-
cerned, there is no difference [7] between the ordered phase and a highly

diluted alloy. Only at higher concentrations a clearly negative ΔH^O(liq.) will oppose solid solubility because configurations with similar nearest neighbours do occur.

For three reasons the solid solubilities calculated from the sum of ΔH^O(elast.) and ΔH^O(struct.) are crude estimates only. An ordered compound rich in the host metal may well be non-existing 1), a possible extra structure contribution for the ordered compound is not taken into account 2) and at atomic concentrations above 5 a.o. excess entropy effects could be quite important too 3).

A comparison with experimental information on solid solubilities is made in Table VII. Only binary combinations with a negative value of ΔH^O(liq.), Table I, are included.

TABLE VII

As Table VI but now for binary systems with the negative sign for the heat of mixing in the liquid state. For comparison we include the sum of the elastic and the structure dependent term in the enthalpy of solution, ΔH^O(eff.).

Alloy	Solub. at T (a.o.);(^{O}C)	ΔH^O(eff.) (kJ/mol)	Alloy	Solub. at T (a.o.);(^{O}C)	ΔH^O(eff.) (kJ/mol)
hcp			Tc Y	no info.	+120
Zr Mo	small	+85	Tc Zr	no info.	+ 85
Zr Tc	no info.	+117	Tc Nb	no info.	+ 58
Zr Ru	<0.5 ; 650	+148	Tc Mo	≈10	+ 29
Zr Rh	small	+150	Tc Ru	cont.	+ 2
Zr Pd	small	+134			
bcc			Ru Y	no info.	+ 74
Zr Mo	23 ; 1550	+ 42	Ru Zr	2 ; 1600	+ 63
Zr Tc	no info.	+ 49	Ru Nb	29 ; 1774 / 19 ; 1000	+ 44
Zr Ru	11 ; 1740	+ 55			
Zr Rh	9 ; 1065	+ 34	Ru Mo	50 ; 1850	+ 21
Zr Pd	12 ; 1030	− 5	Ru Tc	cont.	+ 2
Nb Mo	cont.	+ 5	Rh Y	no info.	+ 29
Nb Tc	no info.	− 12	Rh Zr	10 ; 1700	+ 24
Nb Ru	55 ; 1400	− 10	Rh Nb	16 ; 1900	+ 12
Nb Rh	20 ; 1660	− 25	Rh Mo	15 ; 2000 / 12 ; 1000	− 1
Nb Pd	35 ; 1255	− 51			
Mo Zr	23 ; 1550	+ 13	Pd Y	13 ; 1200	+ 1
Mo Nb	cont.	− 1	Pd Zr	14 ; 1600	− 10
Mo Tc	large	+ 13	Pd Nb	18 ; 1500	− 16
Mo Ru	30 ; 1550 / 10 ; 1400	+ 41	Pd Mo	40 ; 1400	− 16
Mo Rh	20 ; 1940 / 4 ; 1200	+ 51			
Mo Pd	3 ; 1425	+ 55			

One can see that there is quite good agreement. In case the value of ΔH^O(eff.) (which is the sum of elastic and structure terms) is large and positive the solid solubility is small at reasonably low temperatures. If ΔH^O(eff.) is negative or only weakly positive there is always appreciable solid solubility.

A more detailed view of the experimental information on phase diagrams supports our predictions of enthalpy effects and in particular, that of a major role played by the structure dependent term.

a) Pd base alloys. The phase diagrams of fig. 5 illustrate the appreciable solid solubility of metals like Y, Zr, Nb, Mo in Pd. In the first instance one should have been surprised because of the large elastic term (Y and Zr) and the large and negative heat of mixing in the liquid (table I). However, the strongly negative values of ΔH^O(struct.) make the large solid solubilities quite understandable. There is also quantitative evidence for a negative term in ΔH^O for Pd with metals reducing Z. Kleykamp [8] has reported on ΔG^{exc} in Pd-Mo alloys, showing the trend to be strongly negative

on the Pd rich side. Ni-Cr solid solutions (isoelectronic with Pd-Mo) are also known [9] to have an enthalpy of mixing in the solid state with more negative values on the Ni rich side of the system.
b) Zr-base alloys. Fig. 4 easily explains the extremely large difference in solid solubility of elements like Mo, Ru, Rh and Pd in bcc and hcp Zr respectively. As can be seen in fig. 4 upon increasing the average number of electrons, the hcp phase becomes less stable at a rate of 12.5 kJ/mol per electrons, while the bcc structure becomes more stable at a rate of 11.5 kJ/mol per electron. For Ru (ΔZ=4), Rh(ΔZ=5) and Pd(ΔZ=6) the difference in ΔH(struct.) becomes very large for the two phases. The experimental situation can be illustrated by fig. 6 for the Zr-Pd system. In table VII we give values for ΔH°(eff.) for both the hcp and bcc structure. The large and positive values of ΔH°(eff.) for Pd, Rh and Ru in hcp Zr correspond to extremely small solid solubilities of the order of ppm at 1000°C. Again the much smaller positive values of ΔH°(eff.) for Pd, Rh, Ru in bcc Zr may be overestimated because elastic energies have been derived from elastic constants of the hcp phase.
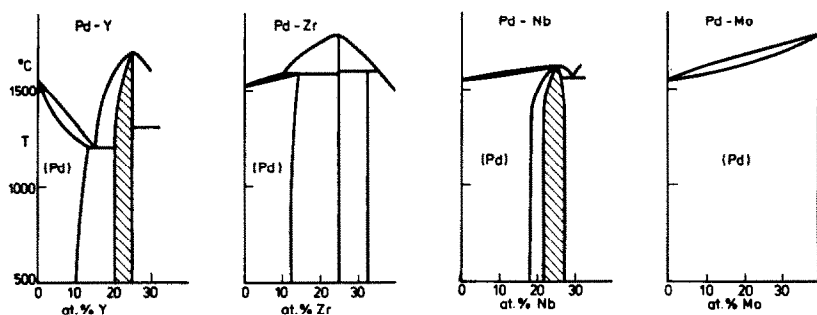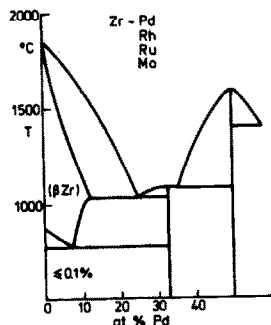

FIG. 5

The Pd-rich side of the binary phase diagrams of Pd alloyed with Y, Zr, Nb and Mo. In spite of an expected strong tendency towards compound formation there is extensive solid solubility in the fcc Pd phase, because of a large and negative structure dependent enthalpy contribution.

FIG. 6.

The Zr-rich side of the binary phase diagram of Zr and Pd, which may also represent Zr with Mo, Tc, Ru and Rh and corresponding binary systems based on Ti or Hf. Note the extremely large difference in solid solubility for hcp and bcc Zr.

c) Mo and Nb base alloys. Another example supporting the picture of figure 4 is the difference in phase diagrams between Mo and Nb with Ru, Rh and Pd. The experimental situation is illustrated in fig. 7, which depicts the Mo-Pd and Nb-Pd system. Since elastic mismatch energies are small and mixing enthalpies are more ideal for Mo than for Nb, one might have expected that for Mo base alloys solid solubilities exceed those of the Nb ones in this case. However, from fig. 4 and table IV one learns that upon increasing Z from Z=6(Mo) to higher values, the bcc structure is rapidly destabilized,

leading to a significant positive value for ΔH^O(struct.), which is absent
in the corresponding Nb-base alloys.
d) Tc base alloys. Although the experimental information is limited for Tc
one can make a comparison with expectations based on fig. 4. Reducing Z from
that of Tc (Z=7), the hcp structure is clearly destabilized; consequently
one would expect the solid solubilities of Nb and Zr to be small, as is also
illustrated by the large values of ΔH^O(eff.) of +85 and +58 for Nb and Zr in
Tc, respectively, given in table VII. Contrarily, the hcp structure becomes
more stable when going from Z=7 to Z=8. This explains the very extensive
solid solubility of Ru, Rh and Pd in Tc (100%, 70% and 50 at.%, respectively).
e) Alloys based on Ru or Rh. The solubility of 4d metals in Rh and Ru also
reflects the trends derived for ΔH(struct.). The maximum solid solubilities
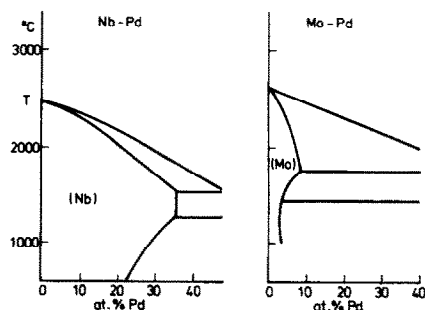

FIG. 7

A comparison of the phase diagram of
Nb and Mo with Pd. In spite of a more
negative enthalpy of alloy formation
the solid solubility of Pd in Nb
considerably exceeds that of Pd in Mo.

of Zr and Nb in Rh are limited to an electron/atom number that corresponds
to the minimum energy of the fcc phase at Z=8.5. The solid solubility of Zr
in Ru is small (smaller than that of Zr in Rh) because, upon reducing Z
starting from Z=8 the hcp structure becomes considerably less stable.

4. Conclusions

    The present results agree with the Calphad group assumptions as far the
approximate magnitude of the structure dependent enthalpies for the pure
metals are concerned. For the enthalpy of mixing in a binary system we have
a liquid like term and an elastic term which for transition metals are not
very different from a regular solution behaviour (although they may be
asymmetrical).
    In our approach the structure dependent term can vary with concentration
in a complicated way while in the Calphad approach [10, 11] this term varies
linearly with atomic concentration. In our case structure dependent energies
can only be linearly dependent on concentration if one deals with neighbou-
ring elements in the Periodic Table. The difference is most clearly illus-
trated by the Zr-Ru system. Since the pure metals Zr and Ru are both hcp
metals, the Calphad approach either implies a value ΔH(struct.) = 0 or a
value of E(hcp) varying linearly with atomic concentration for Zr-Ru alloys.
However, in our case the energy for hcp alloys shows a more complex variation
(fig. 4) when alloying Zr(Z=4) with Ru(Z=8).
    The present approach may present a welcome addition to the information
entering the Calphad type of description of phase diagrams. We present not
only   estimates of the enthalpy differences between fcc, bcc and hcp
phases of pure transition metals, but in principle also a value for the
initial change of the enthalpy with concentration for these three phases
for binary systems. There is a liquid like term to be taken from table I,
an elastic term given in table II and a structure dependent term given in
table II and a structure dependent term to be derived by means of relation
III, using values for lattice stabilities and variations of these with Z
given in tables III and IV.
    As we shall discuss elsewhere, the results can be extended to include
the 5d metals and the weakly magnetic 3d metals. One can make use of a curve
like fig. 4 for other series of transition metals as well, but scaled, for
instance, with the average heat of fusion of 4d metals relative to that of
5d and 3d metals respectively.

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