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Prediction of the metatectic reaction: application to hafnium alloys

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The metatectic reaction $\beta \xrightarrow{\text{cooling}} \alpha + \mathrm{L}$ is one of the most disadvantageous in relation to high temperature properties of alloys. Assuming the regular solution approximations, the occurrence of this reaction in binary systems where one constituent is subjected to an allotropic transformation is studied. It is shown that the occurrence of the metatectic reaction is strongly related to the difference between the melting and transformation temperatures of the solvent element and to the strain energy contribution of the interaction parameters. It appears that the metatectic reaction is probably more common than is generally assumed.

1. Introduction

The metatectic reaction may be written as

$$\text{solid 1} \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \text{solid 2} + \text{liquid.}$$

This reaction shows that a high temperature solid phase decomposes on cooling into a liquid and another solid phase, i.e. a solid is partly melted when the temperature is lowered and it solidifies again when the temperature is raised. This peculiar behaviour is thermodynamically allowed and it has been observed in some metallic systems [1–3], most frequently there is an allotropic transformation in the solvent element.

From a practical point of view, this transformation can cause excessive segregations during solidification, welding or heat treatments. Moreover, when there is not complete solubility between the low temperature phases, a eutectic or peritectic reaction is brought about at much lower temperatures. This requirement reduces the ability of alloys to be used at high temperature.

This phenomenon is observed for hafnium–copper alloys which have been developed because of their good oxidation resistance [4, 5]. The presence of a metatectic reaction at 1540 ± 20° C and a eutectic reaction at 1295 ± 10° C [6] makes the use of these alloys at high temperatures impossible. However, hafnium has attractive high temperature properties (high melting and phase transformation temperatures, high thermodynamic and structural stability of its oxide) and it should therefore be possible to develop heat-resistant hafnium-based alloys.

The purpose of the present study is to define and predict the conditions leading to the event of a metatectic reaction in binary systems of which one constituent has two allotropic forms. The approach developed by Kaufman and co-workers [7–9] for binary phase diagram prediction provides a suitable basis for such a study. It allows the determination of a simple test which may be used to predict the presence of a metatectic reaction in any binary alloy system. This simple test has been applied to numerous hafnium and zirconium alloys.

2. Conditions for the existence of a metatectic reaction

For an i–j system, Fig. 1 shows a metatectic phase diagram based on the allotropic transformation of i; α denotes the low temperature solid solution, β the high temperature solid solution, $T_i^{\alpha\beta}$ and $T_i^{\beta L}$ the transformation and melting temperatures of pure i respectively, $T_i^{\alpha L}$ is the hypothetical melting temperature of

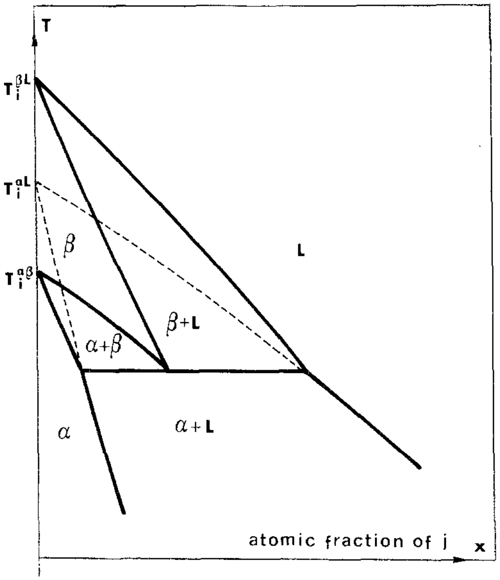

Figure 1 Partial metatectic phase diagram for an i–j system.

the α-phase deduced from its lattice stability parameters.

Each two-phase equilibrium α–β, β–L or α–L can be described from its (x_0, T_0) curve. For a given two-phase equilibrium, the (x_0, T_0) curve defines the locus of points along which the free energy of each phase has the same value. This curve must lie within the corresponding two-phase field of the phase diagram. The type of three-phase equilibrium which can occur between α, β and L phases may be related to the relative position of the (x_0, T_0) curves of each two-phase equilibrium α–β, β–L or α–L. Fig. 2 shows the different cases which can be considered according to the position of the intersection point (x_R, T_R) of the (x_0, T_0) curves. Furthermore, this figure clearly shows that the metatectic reaction is the least advantageous one (Fig. 2d).

It appears that the existence of a metatectic reaction necessitates the condition

$$T_R < T_i^{\alpha\beta}.$$

However, this relation may also be true for the eutectoid reaction (Fig. 2e), but the equilibrium of β-phase with an intermetallic compound or pure j constituent cannot occur if x_R is small enough to fulfil the condition

$$x_R < \tfrac{1}{2}x_c \quad \text{or} \quad 0.5. \qquad (1)$$

x_c is the j concentration in the most i-rich compound. Moreover, it has already been noticed that the metatectic reaction involved the existence of a eutectic or peritectic reaction at much lower temperatures, thus a small value of T_R will give rise to the positioning of this second isothermal transformation at too low a temperature.

A survey of the phase diagrams [1–3] shows that the difference between the melting temperature of an element and the lowest eutectic or peritectic reaction in any of its systems does not exceed about 1000° C to 1200° C. Consequently, T_R must fulfil the condition

$$T_i^{\beta L} - 1200 < T_R < T_i^{\alpha\beta}. \qquad (2)$$

The existence of a metatectic reaction is likely if Conditions 1 and 2 are simultaneously fulfilled. For a given element i this condition can be easily represented on an (x, T) plot.

3. Calculation of the (x_R, T_R) co-ordinates

In the regular solution approximation, the equation of the (x_0, T_0) curves corresponding to the α–L, β–L and α–β equilibria are

$$(1-x)\Delta G_i^{\alpha\to L} + x\Delta G_j^{\alpha\to L} + x(1-x)(L-A) = 0$$

$$(1-x)\Delta G_i^{\beta\to L} + x\Delta G_j^{\beta\to L} + x(1-x)(L-B) = 0$$

$$(1-x)\Delta G_i^{\alpha\to\beta} + x\Delta G_j^{\alpha\to\beta} + x(1-x)(B-A) = 0.$$

In these equations x is the atomic fraction of j, and $\Delta G_i^{\alpha\to L}$, $\Delta G_i^{\beta\to L}$ and $\Delta G_i^{\alpha\to\beta}$ are the lattice stability parameters of element i, they are equal to the free energy of melting or transformation and can be written, for example,

$$\begin{aligned}\Delta G_i^{\alpha\to L} &= \Delta H_i^{\alpha\to L} - T\Delta S_i^{\alpha\to L}\\ &= \Delta H_i^{\alpha\to L}(1 - T/T_i^{\alpha L})\end{aligned}$$

where $T_i^{\alpha L}$ is the melting temperature of the α-phase of i. $\Delta G_j^{\alpha\to L}$, $\Delta G_j^{\beta\to L}$ and $\Delta G_j^{\alpha\to\beta}$ are the lattice stability parameters of element j defined for phases having the same structural features as those of element i, for element j; these phases may be stable or unstable. L, A and B are the regular solution interaction parameters for the liquid phase and the α and β phases in the i–j system.

The (x_R, T_R) co-ordinates may be calculated from two of these equations, this calculation leads to the solution of a cubic equation. However, it is not always necessary to solve this equation. The existence of the metatectic reaction being related to a small value of x_R, it is more convenient to consider that the (x_0, T_0) curves coincide

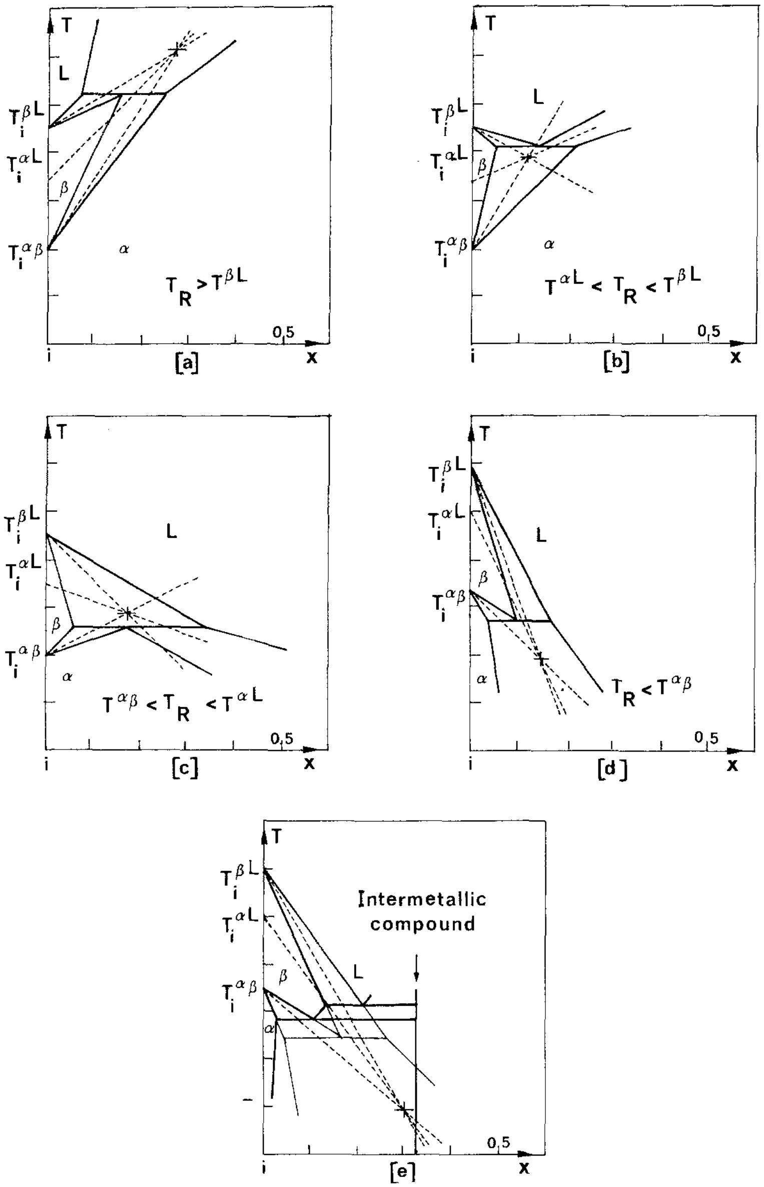

Figure 2 Different types of three-phase equilibrium between α, β and L phases in relationship to the position of the intersection point of the (x_0, T_0) curves.

with their tangent at $x = 0$. For the α–L two-phase equilibrium, the slope of this tangent is expressed by

$$p^{\alpha L} = \left[\frac{dT_0}{dx_0}\right]^{\alpha L}_{x=0}$$

$$= \frac{1}{\Delta S_i^{\alpha\to L}}\left[\Delta H_j^{\alpha\to L}\left(1 - \frac{T_i^{\alpha L}}{T_j^{\alpha L}}\right) + L - A\right].$$

Similar equations can be generated for $p^{\beta L}$ and $p^{\alpha\beta}$. Then, it is easy to calculate the (x_R, T_R) co-ordinates. According to the system under consideration x_R is given by

$$x_R = \frac{T_i^{\beta L} - T_i^{\alpha L}}{p^{\alpha L} - p^{\beta L}} \quad \text{or} \quad \frac{T_i^{\alpha L} - T_i^{\alpha\beta}}{p^{\alpha\beta} - p^{\alpha L}}$$

$$\text{or} \quad \frac{T_i^{\beta L} - T_i^{\alpha\beta}}{p^{\alpha\beta} - p^{\beta L}}. \qquad (3)$$

The above approximation cannot introduce important errors unless one of the (x_0, T_0) curves reaches an extreme for a small value of x. From the derivative of the (x_0, T_0) functions, it can be shown that this is achieved only if

$$0.8 < \frac{\Delta S_i^{\alpha\to L}(T_i^{\alpha L} - T_i^{\alpha L})}{(L - A)} < 1.2. \qquad (4)$$

Similar relationships can be generated for α–L and α–β equilibria.

4. Application to hafnium and zirconium alloys

These calculations have been applied to hafnium and zirconium alloys. Both have two allotropic varieties, the low temperature α-form is hcp, the high temperature β-form is bcc. Table I shows the lattice stability parameters which were used for this study. They were either taken from the work of Kaufman and co-workers [7–9] or they were derived from the procedure described by these authors [7] from the thermodynamic data collected by Kubaschewski and co-workers [10].

The interaction parameters were evaluated in the same way [7]. Using Kaufman's notation, one can write

$$L - B = -(e_1 + e_2)$$

$$L - A = -(e_1 + e_2 + e_3)$$

where e_1 is a strain energy term depending on the size difference between i and j which is always positive. e_2 and e_3 are the "electronic" contributions for the interaction parameters of the β- and α-phases respectively. The values of e_2 and e_3 are the same for elements belonging to the same group. Table II shows the data which are used for the calculation of e_1 and the determined values of e_1, e_2 and e_3, e_1 are given by the formula

$$e_1 = \frac{1}{2}(H_i + H_j)\left(\frac{V_i - V_j}{V_i + V_j}\right)^2$$

where H_i and H_j are the enthalpies of vaporization and V_i and V_j the atomic volumes of elements i and j.

Fig. 3 shows a graphical representation of the results which were obtained. The (x_R, T_R) co-ordinates were calculated from the α–L and β–L equilibria only. The (x_R, T_R) field that the metatectic reaction is expected to occur within depends on the nature of the second solid phase. The field surrounded by a thin line is associated with the elements not forming intermetallic compounds with hafnium or zirconium such as Th, Y and Sc, for example. The thick line defines the (x_R, T_R) field for the systems forming $\mathrm{Hf(Zr)_2M}$ intermetallic compounds. It can be seen that there are no metatectic reactions with zirconium. On the contrary, the metatectic reaction should be observed for the Hf–Co, Hf–Ni and Hf–Cu systems which form $\mathrm{Hf_2M}$ intermetallic compounds and Hf–Y and Hf–Th which do not form intermetallic compounds. Their results are either in agreement with published phase diagrams or they confirm the expected phase diagram [1–3, 6].

In order to test these results, the (x_R, T_R) co-ordinates for the Hf–Co, Hf–Ni and Hf–Cu systems were also calculated by means of interaction parameters obtained from the Zr–Co, Zr–Ni and Zr–Cu phase diagrams. The strain energy term e_1 being kept constant, the e_2 and e_3 components may be calculated from the eutectic and eutectoid positions. The (x_R, T_R) co-ordinates calculated with these values corroborate the

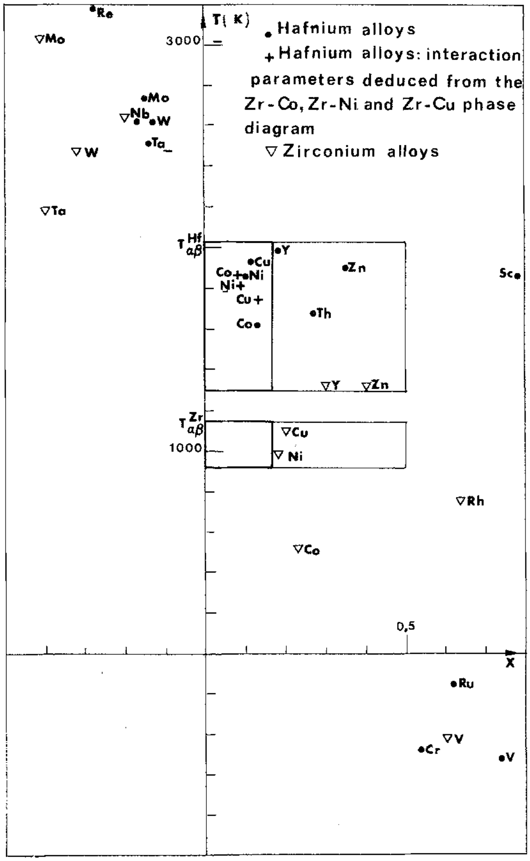

Figure 3 Graphical representation of the position of the (x_R, T_R) point for several zirconium or hafnium binary systems.

TABLE I Enthalpy and entropy differences between the h c p (α) or b c c (β) phases and the liquid phase for several pure metals [7–10]

Element	$\Delta H^{\alpha\to L}$ (cal mol^{-1})	$\Delta S^{\alpha\to L}$ (cal mol^{-1} K^{-1}	$T^{\alpha L}$ (K)	$\Delta H^{\beta\to L}$ (cal mol^{-1})	$\Delta S^{\beta\to L}$ (cal mol K^{-1})	$T^{\beta L}$ (K)
Sc	4327	2.46	1759	3369	1.86	1812
Y	3917	2.19	1785	2724	1.51	1799
Th	3823	2.50	1529	3853	1.9	2028
Zr	5280	2.90	1820	4250	2.00	2125
Hf	6820	2.90	2351	4990	2.00	2495
V	2860	2.80	1020	4360	2.00	2180
Nb	3980	2.80	1420	5480	2.00	2740
Ta	5040	2.80	1800	6540	2.00	3270
Cr	2350	2.00	1175	4350	2.00	2175
Mo	3800	2.00	1900	5800	2.00	2900
W	5300	2.00	2650	7300	2.00	3650
Re	6900	2.00	3450	6500	2.40	2710
Ru	5100	2.00	2550	3980	2.80	1420
Os	6600	2.00	3300	5480	2.80	1960
Co	3980	2.34	1701	3310	2.19	1511
Rh	5674	2.75	2063	5264	2.60	2025
Ir	7000	2.75	2545	6590	2.60	2535
Ni	3958	2.74	1445	2879	2.19	1315
Pd	3845	2.55	1508	2766	2.00	1383
Pt	4442	2.60	1708	3363	2.05	1640
Cu	2970	2.60	1142	2270	2.10	1081
Ag	2552	2.49	1025	1852	1.99	931
Au	2843	2.54	1119	2143	2.04	1050
Zn	1750	2.53	693	1060	1.93	549

TABLE II Enthalpy of vaporization (H_V), atomic volume (V) and component of the interaction parameters for the zirconium and hafnium systems

Element	H_V	V	$e_{1\,Zr}$	$e_{1\,Hf}$	e_2	e_3
Be	− 78 040	4.88	26 257	25 117	–	–
Sc	− 79 000	15.04	133	334	0	0
Y	−101 700	19.89	3 682	4 612	0	0
La	−100 180	22.60	6 718	7 955	–	–
Th	−137 500	19.80	4 106	5 143	0	0
V	−123 000	8.37	8 610	754	0	0
Nb	−173 000	10.84	2 634	1 929	0	0
Ta	−187 000	10.91	2 620	1 897	0	0
Cr	− 94 000	7.23	12 301	11 161	− 900	2430
Mo*	−157 000	9.40	5 937	4 920	− 900	2430
W*	−202 000	9.58	6 204	5 077	− 900	2430
Mn	− 67 060	7.62	9 359	8 413	–	–
Re*	−186 000	8.86	8 494	7 234	−1900	5330
Fe	− 99 550	7.09	13 282	12 080	–	–
Ru*	−155 000	8.19	10 422	9 140	−3700	6550
Os*	−162 000	8.43	9 599	8 338	−3700	6550
Co	−102 000	6.69	15 588	14 335	−2850	3530
Rh*	−133 000	8.31	9169	8 013	−2850	3530
Ir*	−160 000	8.56	8 996	7 773	−2850	3530
Ni	−103 000	6.57	16 355	15 082	−4400	1710
Pd*	− 91 000	8.86	6 063	5 189	−4400	1710
Pt*	−135 000	9.10	6 403	5 401	−4400	1710
Cu	− 81 000	7.11	12 185	11 103	−4010	610
Ag*	− 66 800	10.27	2 559	2 002	−4010	610
Au*	− 90 500	10.19	2 985	2 348	−4010	610
Zn	− 31 245	9.17	3 902	3 314	−3725	− 120

preceeding results. It can be noticed that, except for the Hf–Ta system, the approximation of the (x_0, T_0) curves to their tangent is always valid according to Equation 4.

5. Discussion

These results clearly show that the difference between the zirconium and hafnium binary systems is related to the difference ΔT between the melting and transformation temperatures

$$\Delta T = T_{\mathrm{i}}^{\beta \mathrm{L}} - T_{\mathrm{i}}^{\alpha \mathrm{L}}.$$

The magnitude of ΔT strongly affects the position and the extent of the $(x_{\mathrm{R}}, T_{\mathrm{R}})$ field corresponding to the existence of the metatectic reaction. Furthermore, it can be seen from Equation 3 that the value of x_{R} calculated by means of the α–β and β–L (x_0, T_0) equations is directly proportional to ΔT.

Moreover, the influence of the value of ΔT may be also analysed from the cubic equation which allows the calculation of the exact value of the $(x_{\mathrm{R}}, T_{\mathrm{R}})$ co-ordinates. If this equation is written

$$ax^3 + bx^2 + ex + d = 0$$

it may be noticed that the constant term d is independent of element j. Its numerical value is also independent as are all the coefficients of this equation of the pair of (x_0, T_0) equations which were considered, and thus it may be given by

$$d = -\Delta S_{\mathrm{i}}^{\beta \to \mathrm{L}} \, \Delta S_{\mathrm{i}}^{\alpha \to \beta} \, \Delta T$$

Its numerical value is always negative, consequently the existence of a solution of the cubic equation with a small positive value is related to the conditions

$$c > 0 \quad \text{and} \quad d \ll c$$

where c is the coefficient for the first degree term. For a given positive value of c, this last condition will be more easily fulfilled if d is small, or if ΔT is small.

On the other hand, the expression of c may be given by

$$c = \Delta S_{\mathrm{i}}^{\beta \to \mathrm{L}}(B - A) - \Delta S_{\mathrm{i}}^{\alpha \to \beta}(L - B) + F(\Delta S, \Delta H)_{\mathrm{i,j}}^{\alpha\beta,\, \beta \mathrm{L}}.$$

F is a term dependent only on the lattice stability parameters of i and j, and it may be positive or negative. Thus, the condition $c > 0$ necessarily involves

$$\Delta S_{\mathrm{i}}^{\beta \to \mathrm{L}}(B - A) - \Delta S_{\mathrm{i}}^{\alpha \to \beta}(L - B) > 0.$$

Using Kaufman's notation, this condition leads to

$$e_3 < \frac{\Delta S_{\mathrm{i}}^{\alpha \to \beta}}{\Delta S_{\mathrm{i}}^{\beta \to \mathrm{L}}}(e_1 + e_2). \tag{5}$$

TABLE III Data on the allotropic transformation of pure metals

Element	Transformation	$T^{\alpha\beta}$	$T^{\beta \mathrm{L}}$	ΔT	Metatectics
Co	h c p → c.f.c.	420	1495	1075	
Zr	h c p → c.c.	862	1852	990	
Ti	h c p → c.c.	882	1677	795	
Hf	h c p → c.c.	1750	2222	472	Hf–Co, Hf–Th
U	quad → c.c.	775	1132	357	
Th	c.f.c. → c.c.	1400	1750	350	Th–Ce
Sc	h c p → c.f.c.	1350	1539	189	
Nd	h c p → c.c.	855	1016	161	
Pu	quad → c.c.	490	650	160	Pu–Co, Pu–Fe
Sm	rhomb → c.c.	924	1073	149	
Fe	c.f.c. → c.c.	1390	1536	146	Fe–Nb, Fe–Ta, Fe–Zr, Fe–Hf, Fe–Zn, Fe–B, Fe–S
Pr	h c p → c.c.	795	931	136	
Mn	c.f.c. → c.c.	1126	1244	118	Mn–Cu, Mn–Zn, Mn–Gd, Mn–Y
Ce	c.f.c. → c.c.	726	798	72	Ce–Mn, Ce–Cu
Tb	h c p → c.c.	1287	1357	70	
La	c.f.c. → c.c.	861	920	59	
Gd	h c p → c.c.	1260	1312	52	
Y	h c p → c.c.	1479	1526	47	
Ho	h c p → c.c.	1428	1470	42	
Dy	h c p → c.c.	1384	1409	25	
Yb	c.f.c. → c.c.	792	816	24	

This relation shows that a high value of the strain energy component e_1 favours the occurrence of the metatectic reactions. This led us to think that a metatectic reaction may be expected in the binary systems of hafnium with Be, Fe, La and Mn for which a high value of e_1 is found. Also, this explains that the greatest proportion of elements leading to a metatectic reaction in the hafnium binary system belong to the first long period.

On the other hand it would appear that a high electronic component for the α-phase tends to stabilize α with respect to β and disfavours the metatectic reaction. This relationship (Equation 5) may be used as a first test for selecting the alloy elements which do not lead to a metatectic reaction. In Table II, the elements which do not verify Equation 5 are noted by an asterisk; it is easy to see that any of them can lead to a metatectic reaction.

Allotropic transformation data for numerous metallic elements are shown in Table III. It may be noticed that the value of ΔT for hafnium is one of the largest; only Ti, Zr and Co have ΔT values greater than that of Hf. This leads us to think that the metatectic reaction is probably more common than is generally assumed and it can occur in many binary phase diagrams of which one constituent has two allotropic forms.

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