

# The Hf-Zr (Hafnium-Zirconium) System

178.49

91.22

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## Stable Equilibrium States

### Phase Diagram at Zero Pressure

There is general agreement [Hansen, Elliott, 69Rud, 76Kub, 81Kub] regarding the main features of the Zr-Hf phase diagram (see Fig. 1). In the liquid phase (L), there is complete miscibility. In the solid state, there exist: (a) a high-temperature bcc ( $\beta$ ) phase, and (b) a low-temperature cph ( $\alpha$ ) phase. Both phases extend from 0 to 100% Hf. Ordering reactions have not been reported in the solid state. The  $\alpha \rightleftharpoons \beta$  and  $\beta \rightleftharpoons L$  equilibrium transformations are incongruent for every alloy composition. It is normally accepted [62Kub, 70Hay, 76Kub, 81Spe] that the phase diagram of the Zr-Hf system corresponds to the situation of nearly ideal solutions.

**The Two-Phase ( $\alpha + \beta$ ) Field.** The temperatures accepted here for the  $\alpha/\beta$  equilibrium in pure Zr and pure Hf are 863 °C [76Alc] and 1743 °C [81Spe], respectively. The ( $\alpha + \beta$ ) boundaries shown in Fig. 1 are a compromise between the indicated allotropic transformation temperatures of the pure metals and the alloy experimental data of [57Hay] and [66Dom]. These data are not sufficient to establish approximate experimental values for the temperature width,  $\Delta\theta$ , of the ( $\alpha + \beta$ ) region; hence, it is provisionally accepted here that this compromise must render a value for  $\Delta\theta$  at 50 at.% Hf very close to that

corresponding to the situation of ideal mixing between Zr and Hf. This condition on  $\Delta\theta$  can be conveniently satisfied by using, as done here, expressions cubic in temperature for the composition of the ( $\alpha + \beta$ ) boundaries, subject to van't Hoff's relation. The resulting numerical expressions for the  $\alpha/(\alpha + \beta)$  and  $\beta/(\alpha + \beta)$  boundaries, which we consider to give the best possible fit (see Fig. 2) to the combined experimental data of [57Hay] and [66Dom] under the indicated constraints, are given below. A check on this simple construction of the ( $\alpha + \beta$ ) region, based on the theoretical work of [54Wag], is mentioned at the end of the section on thermodynamic considerations. At this point, it should also be noted that the errors we ascribe to the ( $\alpha + \beta$ ) region in Fig. 1 are important (see text below).

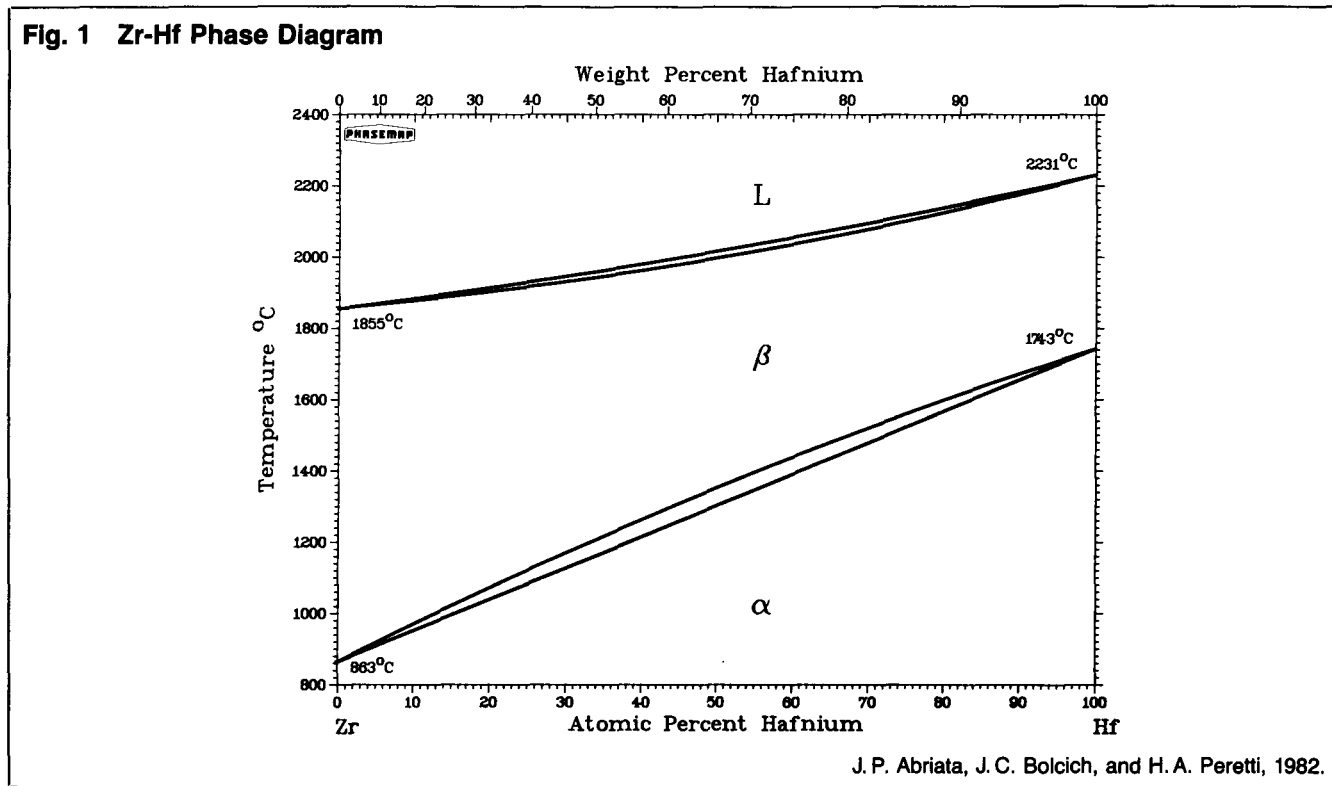
The  $\alpha/(\alpha + \beta)$  curve in Fig. 1 can be represented by the equation:

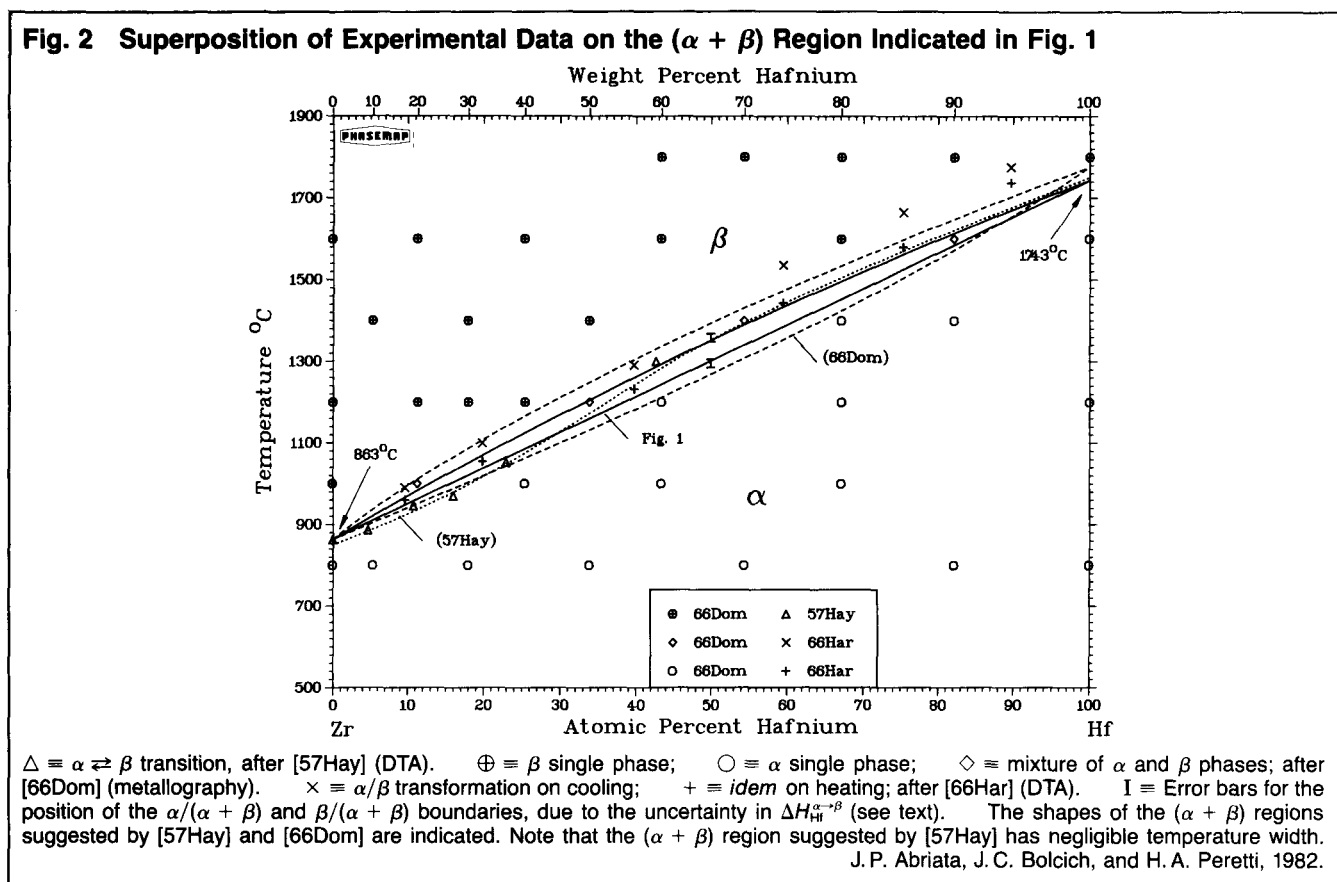
$$\text{at.}\% \text{ Hf} = 1.308 \times 10^{-1}(T-863) - 5.456 \times 10^{-5}(T-863)^2 + 3.974 \times 10^{-8}(T-863)^3 \quad (T \text{ in } ^\circ\text{C})$$

Similarly, for  $\beta/(\alpha + \beta)$  the corresponding equation is:

$$\text{at.}\% \text{ Hf} = 9.461 \times 10^{-2}(T-863) + 8.161 \times 10^{-6}(T-863)^2 + 1.529 \times 10^{-8}(T-863)^3 \quad (T \text{ in } ^\circ\text{C})$$

These numerical expressions conform with the van't Hoff's equation, in which the values for the heats of the  $\alpha \rightarrow \beta$





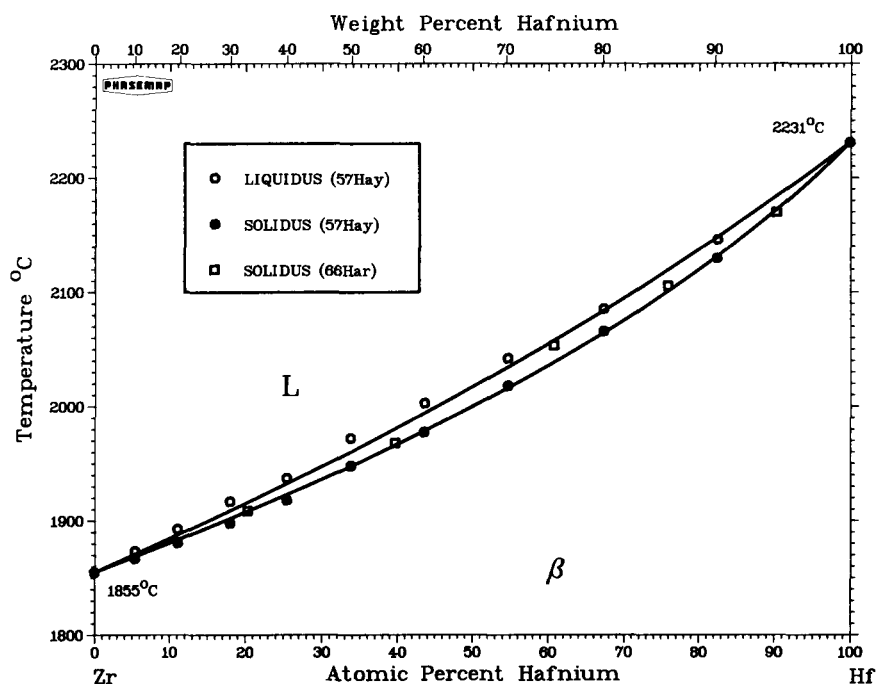
transformations in pure Zr and pure Hf are assumed to be 930 cal/mol [76Alc] and 1400 cal/mol [76Cez, 81Spe], respectively. [57Hay] worked in the range 0 to 43 at.% Hf, determining the  $\alpha \rightleftharpoons \beta$  transformation by differential thermal analysis. The temperature width suggested by [57Hay] for the  $(\alpha + \beta)$  region (see Fig. 2) is negligible and definitely narrower than that of Fig. 1. This can be attributed to insufficient sensitivity of the experimental technique used to determine this region [Elliott].

[66Dom] studied the  $(\alpha + \beta)$  region by means of metallographic examination of heat treated (800 to 1800  $^{\circ}\text{C}$ ) and quenched specimens. On quenching from  $(\alpha + \beta)$ , [66Dom] was able to observe a typical microstructure showing transformed  $\beta$  plus isothermal  $\alpha$ . He remarked that there was no evidence of any retention of the high-temperature bcc ( $\beta$ ) phase upon quenching, but that this was not corroborated by X-ray analysis. The obtained results were judged by [66Dom] to be in substantial agreement with those of [57Hay] but, nevertheless, [66Dom] suggested a much wider  $(\alpha + \beta)$  region than that of [57Hay] (see Fig. 2). Work by [69Dom] on the ternary Zr-Hf-O system gave results that are consistent with those of [66Dom] for Zr-Hf. [69Dom] also showed that oxygen quickly stabilizes the  $\alpha$  phase.

For completeness, Fig. 2 also shows data due to [66Har] obtained by differential thermal analysis; these data appear to deviate toward higher temperatures and, in the instance of the Hf-rich alloys, they are not considered to be compatible with the  $\alpha/\beta$  equilibrium temperature of pure Hf accepted here. Possibly, the samples used in these experiments were contaminated with oxygen.

[59Dea] measured the electrical resistance vs. raising temperature of Hf-rich alloys containing up to 18 at.% Zr. [76Cez], based on the work of [59Dea], adopted the value of 7.2  $^{\circ}\text{C}/\text{at.}\% \text{ Zr}$  for the lowering of the  $\alpha \rightarrow \beta$  (heating) transformation temperature of pure Hf upon alloying with Zr. This value is consistent with Fig. 1, where the average slope of the  $(\alpha + \beta)$  boundaries at pure Hf is  $-7.39 \text{ }^{\circ}\text{C}/\text{at.}\% \text{ Zr}$ . Using thermal analysis and working with alloys up to 6.5 at.% Zr, [64Kri] obtained the (mean) value  $-11.2 \text{ }^{\circ}\text{C}/\text{at.}\% \text{ Zr}$  for the lowering of the  $\beta \rightarrow \alpha$  (cooling) transformation temperature, a value that seems too negative to be directly related to the  $(\alpha + \beta)$  stable-equilibrium region (this deviation could be due to the inadequacy of the experimental technique itself).

It is necessary to remark that a considerable uncertainty still exists regarding the shape (width) of the provisional  $(\alpha + \beta)$  region indicated in Fig. 1. This is related to the uncertainty we must ascribe to the value 1400 cal/mol used here for the heat of the  $\alpha \rightarrow \beta$  transformation in pure Hf ( $\Delta H_{\text{Hf}}^{\alpha \rightarrow \beta}$ ). This value, which is based essentially on only one experimental determination [76Cez], was recently recommended by [81Spe] as the most probable value of  $\Delta H_{\text{Hf}}^{\alpha \rightarrow \beta}$ ; however, this value would be definitely too low to be used in an otherwise successful thermodynamic modeling [80Bre] of the Hf-Mo phase diagram. Thus, although keeping the 1400 cal/mol as the most probable value of  $\Delta H_{\text{Hf}}^{\alpha \rightarrow \beta}$ , we propose here to bracket this quantity between 1260 and 3080 cal/mol, the upper limit being the value necessitated by [80Bre] in his synthesis of the Hf-Mo phase diagram. The uncertainty in the  $(\alpha + \beta)$  region, associated with this bracketing, is graphically represented in Fig. 2 for the equiatomic composition.

Fig. 3 Superposition of Experimental Data on the ( $\beta + L$ ) Region Indicated in Fig. 1

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**The Two-Phase ( $\beta + L$ ) Field.** The ( $\beta + L$ ) region was studied by [57Hay], [66Dom], and [66Har]. [66Dom] reported only a cursory melting point vs. composition study, and, therefore, it is not considered further in this evaluation. The melting points of Zr and Hf are taken to be 1855 and 2231 °C, respectively [81BAP].

The solidus curve indicated in Fig. 1 has been adjusted to the values given by [57Hay] (see Fig. 3) who determined the solidus and liquidus by optical measurements. The numerical description of the solidus in Fig. 1 is given by:

$$\begin{aligned} \text{at.\% Hf} = & 3.774 \times 10^{-1}(T-1855) - 2.279 \\ & \times 10^{-4}(T-1855)^2 \\ & - 1.817 \times 10^{-7}(T-1855)^3 \end{aligned} \quad (T \text{ in } ^\circ\text{C})$$

which is also in general agreement with the incipient melting data by [66Har] (see Fig. 3) and the solidus evaluated by [69Rud].

The liquidus shown in Fig. 1 is represented by:

$$\begin{aligned} \text{at.\% Hf} = & 3.274 \times 10^{-1}(T-1855) - 1.007 \\ & \times 10^{-4}(T-1855)^2 \\ & - 1.665 \times 10^{-7}(T-1855)^3 \end{aligned} \quad (T \text{ in } ^\circ\text{C})$$

This numerical expression has been determined considering both the previously given expression for the solidus curve and the van't Hoff's equation, computed using for the heats of melting of pure Zr, and pure Hf, the values of 4500 ( $\pm 500$ ) cal/mol [76Alc] and 6500 ( $\pm 1000$ ) cal/mol [81Spe], respectively.

This construction of the ( $\beta + L$ ) boundaries is rather similar to that made above for the situation of the ( $\alpha + \beta$ ) boundaries. Accordingly, the fact that the liquidus pro-

posed here agrees well with the corresponding data due to [57Hay] (we consider that the existing small differences shown in Fig. 3 are within the uncertainty produced by the stated error in the estimation of the heats of melting of Zr and Hf, plus the experimental errors themselves) suggests that the width  $\Delta\theta$  of the ( $\beta + L$ ) region at 50 at.% Hf should be very close to the width calculated for the instance of ideal mixing between Zr and Hf. This proved to be true (see also the comment on  $\Delta\theta$  of the ( $\beta + L$ ) field at the end of the section on thermodynamic considerations). For completeness, let us mention that the liquidus curve evaluated by [69Rud] lies about 35 °C higher in temperature at the equiatomic composition than that of Fig. 1.

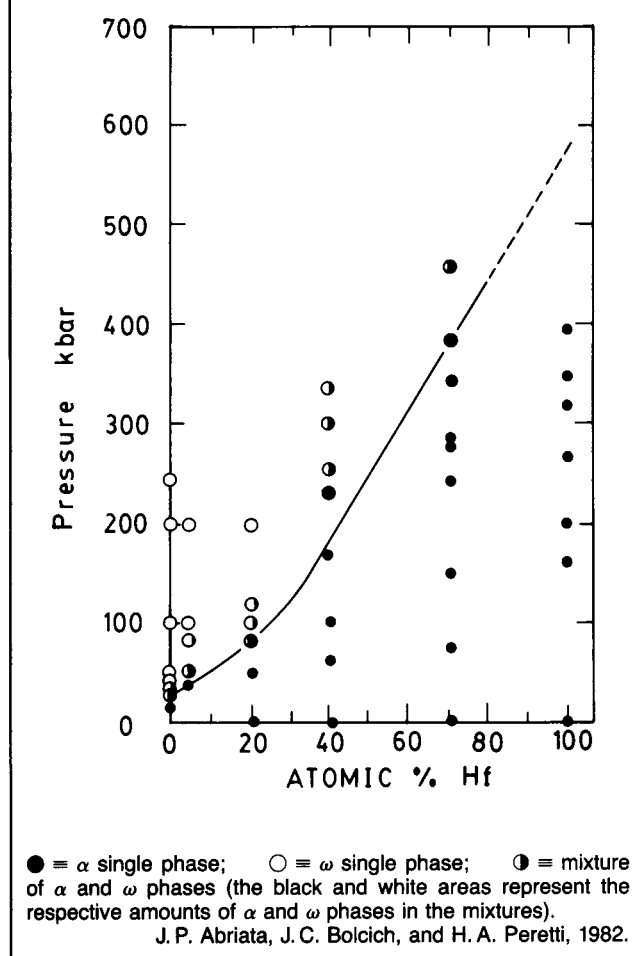
### Phase Diagram Under Pressure

Three allotropic solid phases have been shown to exist in pure Zr and Zr-Hf alloys under pressure:  $\alpha$ ,  $\beta$ , and (hexagonal)  $\omega$ . The same seems to be true for pure Hf [75Kut, 81Min].

The main features of the temperature-pressure phase diagram of pure Zr are given in an evaluation in this issue [82Abr]. For Hf we have: the temperature 1743 °C [81Spe] for the  $\alpha/\beta$  equilibrium at zero pressure and, as tentatively estimated by [75Kut], the pressure  $\sim 210$  kbar for the  $\alpha/\omega$  equilibrium at room temperature, the coordinates  $\sim 1527$  °C and  $\sim 300$  kbar for the  $\alpha/\beta/\omega$  triple point, and the slope  $(dT/dp)^{\beta/\omega} \approx 7$  °C/kbar.

Using *in situ* high-pressure X-ray diffraction techniques, [81Min] studied the  $\alpha \rightarrow \omega$  transformation in Zr-Hf alloys (up to 71.3 at.% Hf) as a function of increasing pressure, at room temperature. Due to the strong hysteresis expected in this transformation [75Kut, 78Voh, 81Min], the experimentally observed pressures at which the transformation

**Fig. 4**  $\alpha \rightarrow \omega$  Transformation in Zr-Hf Alloys as a Function of Increasing Pressure, at Room Temperature



appears to take place (see Fig. 4) are conjectured to be significantly higher than the true equilibrium values. Consistent with this, the  $\alpha \rightarrow \omega$  transition pressure for pure Hf, estimated by [81Min], is about 600 kbar at room temperature, which is substantially higher than the stable-equilibrium value ( $\sim 210$  kbar) estimated by [75Kut].

## Thermodynamic Considerations

**Experimental Data.** No high-temperature thermodynamic data are reported in the literature for the Zr-Hf system. Low temperature specific heats between 1.1 and 4.2 K have been measured in the  $\alpha$  phase by [68Bet] for several alloy compositions between pure Zr and pure Hf.

**Modeling.** The phenomenological modeling of the Zr-Hf phase diagram has been most frequently based on the assumption of ideal behavior of the phases involved [62Kub, 76Kub, 79Kau, 81Spe]. This assumption is consistent with the fact that the volume of formation of Zr-Hf alloys can be assessed to be essentially zero for all compositions [81Min] and, more generally, with the observation that there are very close similarities between the physico-chemical properties of the Group IV transition elements Zr and Hf. In particular, various relevant physical parameters, in the

**Table 1** Zr-Hf Physical Parameters

| Parameter   | Zr    | Hf    | Reference         |
|---|-------|-------|-------------------|
| Metallic valence .....  | 4     | 4     | [62Uy]<br>[73Pan] |
| Metallic radius (nm) .....  | 0.160 | 0.159 | [70Dic]           |
| Electronegativity (Miedema's scale, in volts) .....   | 3.15  | 3.30  | [73Mie]           |
| Ionic radius for valence state +4 (nm) .....  | 0.079 | 0.079 | [70Dic]           |
| Solubility (the square root of the cohesive energy density, in $(\text{cal}/\text{cm}^3)^{1/2}$ ) ..... | 102   | 105   | [70Kau]           |
| Density of electrons at the boundary of the Wigner-Seitz cell (in atomic units) .....                   | 0.023 | 0.026 | [73Mie]           |
| Axial ratio of the $\alpha$ phase .....   | 1.595 | 1.587 | [81Min]           |

sense that they are commonly related to important contributions to the excess free energy of metallic alloys, have very close values for Zr and Hf (see Table 1).

In the  $\alpha$  phase, the assumption of an ideal behavior also is consistent with the fact that the measured electronic specific heat coefficient ( $\gamma$ ) changes nearly linearly with composition between the values for pure Zr and pure Hf [68Bet]. Additionally, according to our estimates, the vibrational contribution to the  $\alpha$ -phase entropy of formation, calculated within the harmonic approximation and using the experimental low-temperature Debye temperature ( $\theta$ ) reported by [68Bet] for several compositions between 0 and 100% Hf, is negligible. Similar  $\gamma$  and  $\theta$  values for the  $\beta$  phase are not available.

Based on microscopic arguments, and without taking into consideration structural effects, [76Mie] and [81Wat] attempted to predict the heat of formation ( $\Delta H$ ) of equiatomic Zr-Hf alloys. They obtained the values  $\Delta H = 0$  and  $\Delta H = -0.005$  eV/atom, respectively. These two results are essentially consistent with the assumption of ideal behavior, but one should remark that the corresponding calculations are based on apparently completely different approaches: [76Mie] used a "macroscopic atom" model of alloys, where the metallic atom is characterized by its electronegativity and electron density at the boundary of the Wigner-Seitz cell, whereas, in turn, the [81Wat] calculation is based on the rectangular electron-band model used previously by [69Fri] to explain the general parabolic trend of the cohesive energy across a transition metal row of the Periodic Table.

The phase diagram of the Zr-Hf system also has been modeled considering nearly-ideal behavior of the phases involved [71Cha, 80Bal]. [71Cha] assumed equal deviation from ideality in the  $\beta$  and L phases and, using known thermochemical data for the melting of pure Zr and pure Hf, calculated the solidus curve from the experimental liquidus determined by [57Hay]. The solidus obtained in this way shows excellent agreement with the corresponding experimental data of [57Hay]. The ( $\beta + L$ ) region suggested by [71Cha] is in substantial agreement with that indicated in Fig. 1.

[80Bal] used the regular solution model for the liquid and solid phases, and fitted in detail the Zr-Hf phase diagram given in [Metals Handbook] (this diagram shows ( $\alpha + \beta$ ) and ( $\beta + L$ ) fields that are significantly wider than those given in Fig. 1). The values used for the interaction pa-

## Zr-Hf Crystal Structure Data

| Phase          | Composition, at.% Hf | Pearson symbol | Prototype(a)        | a      | c      | Lattice parameters, nm<br>c/a | Comments   | References |
|----------------|----------------------|----------------|---------------------|--------|--------|-------------------------------|--|------------|
| $\alpha$ ..... | 0                    | <i>hP2</i>     | Mg                  | 0.3232 | 0.5147 | 1.593                         | All values measured at room temperature and zero pressure.   | [81Rab]    |
|                | 0                    |                |                     | 0.3226 | 0.5146 | 1.595                         | The molar volume $V_0(\alpha)$ , as a  | [81Min]    |
|                | 5.2                  |                |                     | 0.3231 | 0.5134 | 1.589                         | function of composition, can be  |            |
|                | 21.1                 |                |                     | 0.3219 | 0.5115 | 1.589                         | well represented by the equation   |            |
|                | 42.9                 |                |                     | 0.3209 | 0.5126 | 1.597                         | [81 Min] (in $\text{cm}^3/\text{mol}$ )  |            |
|                | 71.3                 |                |                     | 0.3202 | 0.5106 | 1.595                         | $V_0(\alpha) = 14.01 - 0.005 \times (\text{at.}\% \text{ Hf})$ .   |            |
|                | 100                  |                |                     | 0.3190 | 0.5067 | 1.587                         |  |            |
|                | 0                    |                |                     | 0.3231 | 0.5148 | 1.593                         |  | [53Rus]    |
|                | 1.2                  |                |                     | 0.3231 | 0.5146 | 1.593                         |  |            |
|                | 61.8                 |                |                     | 0.3211 | 0.5094 | 1.586                         |  |            |
|                | 96.5                 |                |                     | 0.3199 | 0.5060 | 1.581                         |  |            |
|                | 100                  |                |                     | 0.3195 | 0.5051 | 1.581                         |  |            |
| $\omega$ ..... | 0                    | <i>hP3</i>     | $\omega\text{CrTi}$ | 0.5039 | 0.3136 | 0.622                         | All values measured in the metastable $\omega$ phase, at room temperature and zero pressure; $\omega$ retained after high pressure treatment at room temperature.  | [81Rab]    |
|                | 0                    |                |                     | 0.5035 | 0.3141 | 0.624                         | The molar volume $V_0(\omega)$ , at  | [81Min]    |
|                | 5.2                  |                |                     | 0.5021 | 0.3119 | 0.621                         | least up to 42.9 at.% Hf, can  |            |
|                | 21.1                 |                |                     | 0.5008 | 0.3107 | 0.620                         | be well represented by the   |            |
|                | 42.9                 |                |                     | 0.4991 | 0.3093 | 0.620                         | equation [81Min] (in $\text{cm}^3/\text{mol}$ )  |            |
|                |                      |                |                     |        |        |                               | $V_0(\omega) = 13.76 - 0.009 \times (\text{at.}\% \text{ Hf})$ .   |            |
| $\beta$ .....  | ...                  | <i>cI2</i>     | W                   | ...    | ...    | ...                           | No lattice parameter data are available for the $\beta$ phase. It appears that it is not possible to retain the $\beta$ phase by quenching from its stable-equilibrium field [66Dom] (see also comments in text under "The two-phase ( $\alpha + \beta$ ) field"). | ...        |

(a) From [Pearson].

parameters were (in cal/mol)  $A = 152$ ,  $B = 152$ , and  $L = 96$ , where  $A$ ,  $B$  and  $L$  refer to the  $\alpha$ ,  $\beta$ , and L phase, respectively.

It is of some interest to estimate the excess free energy change between the  $\alpha$  and  $\beta$  phases,  $F_E^{\alpha \rightarrow \beta}$ , by means of the provisional phase diagram given in Fig. 1. For this purpose we assume that:

$$F_E^{\alpha \rightarrow \beta} \approx (T_0 - T_0^{\text{ideal}})((1-x)\Delta S_{\text{Zr}}^{\alpha \rightarrow \beta} + x\Delta S_{\text{Hf}}^{\alpha \rightarrow \beta})$$

where  $(T_0, x)$  are the coordinates of the equal free energy curve for the  $\alpha$  and  $\beta$  phases,  $T_0^{\text{ideal}}$  are the corresponding  $T_0$  values for the hypothetical situation of  $\alpha$  and  $\beta$  being ideal solutions,  $x$  is the atomic fraction of Hf, and  $\Delta S_{\text{Zr,Hf}}^{\alpha \rightarrow \beta}$  are the entropy changes for the equilibrium  $\alpha \rightleftharpoons \beta$  transformation in pure Zr and pure Hf, respectively. Thus, using the thermochemical data accepted in this evaluation, we conclude  $0 < F_E^{\alpha \rightarrow \beta} \approx 180x(1-x)$  (in cal/mol), which is in line with the assumption of nearly-ideal behavior of the  $\alpha$  and  $\beta$  phases.

The temperature width  $\Delta\theta$  of the  $(\alpha + \beta)$  region in the Zr-Hf system could be estimated using the theoretical analysis of nearly-ideal solutions by [54Wag] (see also [76Kub]): it results in  $\Delta\theta \approx 49^\circ\text{C}$  at the equiatomic composition, which compares well to the value  $\Delta\theta = 52^\circ\text{C}$  in Fig. 1. This agreement supports our procedure for establishing the  $(\alpha + \beta)$  boundaries in the section "Phase Diagram at Zero Pressure".

The  $(\beta + \text{L})$  region can be discussed in a way similar to that of  $(\alpha + \beta)$  above. From this, it follows  $0 > F_E^{\beta \rightarrow \text{L}} \approx -530x(1-x)$  (in cal/mol), which is in line with the assumption of nearly-ideal behavior of the  $\beta$  and L phases; also, from [54Wag] we obtain  $\Delta\theta \approx 16^\circ\text{C}$  at 50 at.% Hf, in good agreement with the value  $\Delta\theta = 17^\circ\text{C}$  in Fig. 1.

## Metastable Equilibrium States

We were unable to find reports of metastable equilibrium states for the Zr-Hf system in the literature.

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Hf evaluation contributed by J. P. Abriata, J. C. Bolcich, and H. A. Peretti, Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400-S. C. de Bariloche, Rio Negro, Argentina. Literature searched through 1981. Dr. Abriata is the ASM/NBS Data Program Category Editor for binary zirconium alloys.

## The Nb-Zr (Niobium-Zirconium) System

92.9064

91.22

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### Stable Equilibrium

#### Temperature-Composition Phase Diagram

There is general agreement [Hansen, Elliott, Shunk] regarding the qualitative features of the Zr-Nb equilibrium phase diagram (see Fig. 1). In the solid state there exist ( $\alpha$ ) a bcc ( $\beta$ ) phase which, at sufficiently high temperatures, extends from 0 to 100 at.% Nb, whereas at lower temp-

eratures it exhibits a critical solution point (see Table 1) and a corresponding ( $\beta$ Zr) + ( $\beta$ Nb) miscibility gap; and ( $b$ ) a monotectoid reaction ( $\beta$ Zr)  $\rightleftharpoons$  ( $\alpha$ Zr) + ( $\beta$ Nb), which results in the coexistence of cph ( $\alpha$ Zr) with ( $\beta$ Nb) down to low temperatures. In the liquid state there is complete miscibility, and the liquidus and solidus show a minimum point where the  $\beta$  phase melts congruently.