

on heating. [81Tay] determined the Rh-S phase diagram (0 to 60 at.% S) by DTA and the thermobalance method under pressures sufficiently high to suppress boiling of the compounds (Fig. 1). [81Tay] observed the L  $\leftrightarrow$  (Rh) + Rh<sub>17</sub>S<sub>15</sub> eutectic point at 35.4 and 940 °C, whereas [71Zwi] observed it at 37.5 at.% S and 925 °C.

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# U-Zr (Uranium-Zirconium)

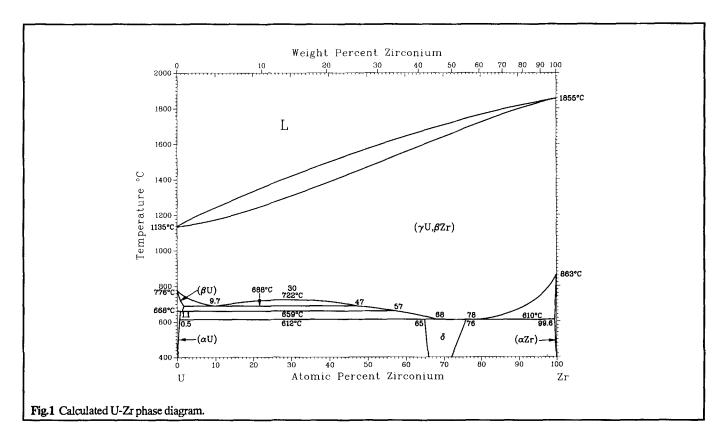
## H. Okamoto

The U-Zr phase diagram in [Massalski2] was adopted from [89She]. According to [91Oka2], the initial slope of  $(\gamma U,\beta Zr)/[(\gamma U,\beta Zr) + (\alpha Zr)]$  was too flat, considering that the solid solubility of U in  $(\alpha Zr)$  is small and that the enthalpy of  $\beta Zr/Zr$  transformation is small (~4 kJ/mol). The  $(\gamma U,\beta Zr)/[(U,\beta Zr) + (\beta U)]$  boundary also showed the same difficulty. In this regard, the phase diagram calculated by [91Oga] (Fig. 1) is thermodynamically more appropriate. [91Oga] used the phase diagram of [89She] as the primary input data. However, the excess Gibbs energies of the liquid and the bcc phases obtained by [91Oga] included enthalpy and excess entropy parts with unusual magni-

tudes [910ka1]. This problem is caused by the existence of a miscibility gap (positive enthalpy of mixing is required) in the solid phase at temperatures not much below the liquidus and solidus boundaries that appear to require negative enthalpies of mixing for both liquid and solid phases. The difficulty in thermodynamic modeling may indicate that the entire phase boundaries of this system must be reexamined experimentally.

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