

Increase in the Superconducting Transition Temperature in Zr–Hf Alloys Due To s – d Electron Transfer under Pressure

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The superconducting transition temperatures T_c of Zr–Hf alloys are measured as a function of pressure up to 47.4 GPa. It is found that the value of T_c experiences jumps due to the transition of the hexagonal ω phase to the bcc β phase: T_c of the $Zr_{80}Hf_{20}$ alloy increases from 3.2 to 11 K at $P = 35.0$ GPa, and a jump in T_c from 3.4 to 10 K is observed for the $Zr_{67}Hf_{33}$ alloy at $P = 40.9$ GPa. The isobars of the concentration dependence $T_c(c)$ of the bcc Zr–Hf alloys are qualitatively similar to the $T_c(c)$ curves for the bcc phases in the systems of Vb – IVb subgroup elements at $P = 1$ atm. The data obtained indicate that, because of the s – d electron transition, the IVb subgroup metals become similar in their crystal structure and superconducting properties to the Vb subgroup metals. © 2003 MAIK “Nauka/Interperiodica”.

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1. INTRODUCTION

The development of methods for band-structure calculations of metals in the last three decades has opened the way for the estimation of the stability of crystal structures as a function of their electronic configuration and volume (see, for example, [1–3]). For the metals located early in the periods of the periodic table, it was shown [2] that s electrons must be transferred to the d band upon compression, because the narrow d band is displaced with respect to the bottom of the sp band. Hexagonal ω to bcc β phase transitions in Zr and Hf at high pressures due to an increase in the stability of the bcc structure with increasing d -band occupancy were predicted theoretically virtually simultaneously with their experimental discovery [5–9]. The agreement between calculation and experiment stimulated interest in the problem of s – d electron transitions under pressure. The pressure of the ω → β transformation at 20°C equals ~30 GPa for Zr and ~71 GPa for Hf. Titanium at room temperature transforms to phases with the orthorhombic structure only under pressures of 116–140 GPa, and the β phase does not form up to 220 GPa [10–12]. As the accuracy of calculations increased, it became possible to theoretically describe the entire sequence of α → ω → β phase transformations in Zr and Hf under pressure, starting from the hcp α phase stable at $P = 1$ atm [13–15]. Thus, Zr and Hf at high pressures become analogous in the occupancy of the d band and in their crystal structures to the Vb group metals (Nb and Ta).

Akahama *et al.* [7, 8] extended this analogy to superconducting properties as well, finding that bcc Zr at $P = 30$ GPa has approximately the same T_c as bcc Nb at atmospheric pressure, whereas the starting hcp Zr and Hf phases have low superconducting transition temperatures T_c equal to 0.7 and 0.35 K, respectively. On the other hand, bcc Ta and Nb are characterized by significantly higher values of T_c (5.4 and 9.25 K, respectively).

The change in the electronic configuration and the resemblance of the Ti subgroup metals to the Vb group metals must lead to bright effects under pressure and in their alloys, because doping itself is a factor that affects the mutual arrangement of the Fermi level and the d -band features [1]. Upon doping vanadium, niobium, and tantalum with IVb group metals, the values of T_c appreciably increase. It should be expected that the concentration dependence of T_c in IVb –Zr alloys will also be similar in shape after transition to the β phase under pressure. However, the studies of phase transitions and superconductivity in binary IVb – IVb alloys under pressure are restricted to the Ti–Zr system. For Ti–Zr alloys, it was shown that the parameters of the triple α → ω → β equilibrium point in the T – P diagram strongly decrease as compared to the pure metals [16] and, after the transition of the alloys to the β phase, the superconducting transition temperature increases with increasing concentration of titanium, reaching 15 K in the TiZr alloy of equiatomic composition at 47 GPa [17].

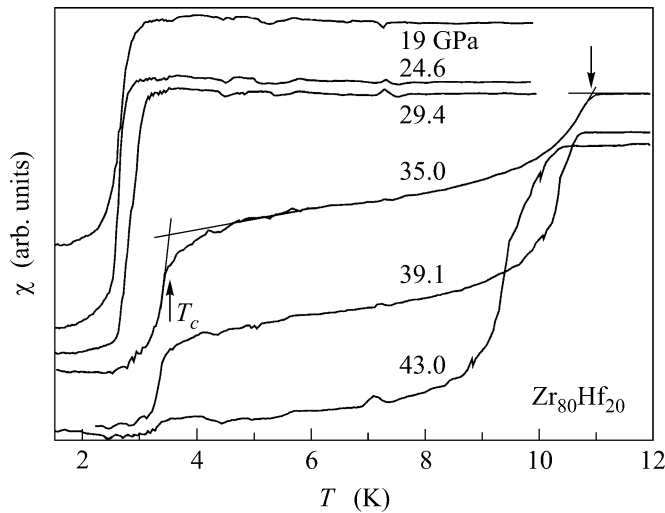


Fig. 1. Curves of the magnetic susceptibility $\chi(T)$ of the $\text{Zr}_{80}\text{Hf}_{20}$ alloy measured in the process of heating at the indicated values of pressure. The graphical determination of T_c is explained using the isobar at 35 GPa as an example.

The behavior of the structure and superconducting properties of Zr–Hf alloys under pressure is of special interest. Because both elements are prone to a change in their electronic configuration, it might be expected from the phenomenological point of view that, as the pressure grows, a transition from the IVb–IVb system to an analogue of the IVb–Vb system will take place after the electronic and structural rearrangement in zirconium and further to an analogue of the Vb–Vb system after the rearrangement in hafnium. This work is devoted to an experimental investigation into the superconductivity of Zr–Hf alloys containing up to 33 at % Hf at pressures of up to 47 GPa to the point of their transition to the β phase.

2. PROCEDURE

The alloys to be studied were prepared from rods of iodide Zr and Hf remelted in a vacuum by zone melting. The purity of the starting metals was higher than 99.95 at %, including interstitial impurities. Chips cut from the starting metals were mechanically mixed in the required proportions and were pressed in the form of cylinders. Rods composed of ten separate cylinders were subjected to repeated remeltings in a vacuum. The final composition of the alloys was determined with the use of a JXA-5 local x-ray microanalyzer and comprised 20.6 ± 0.5 and 33.6 ± 0.2 at % Hf.

Superconducting transitions were detected as anomalies in the temperature dependence of the magnetic susceptibility $\chi(T)$ measured by an alternate current. The press was made of nonmagnetic materials and was equipped with diamond anvils. As well as other details of measurements, it was described previously [17]. In order to exclude the effects of the mechanical relax-

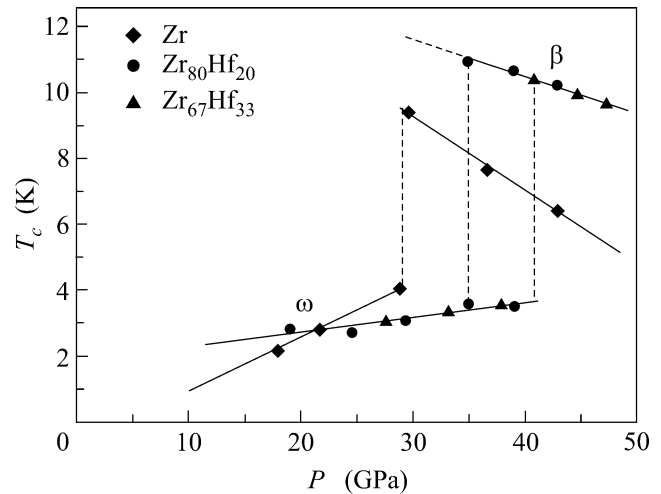


Fig. 2. Pressure effect on the superconducting transition temperature in Zr [17], $\text{Zr}_{80}\text{Hf}_{20}$, and $\text{Zr}_{67}\text{Hf}_{33}$.

ation of the press upon cooling, the pressure was determined by the shift of the ruby luminescence line after heating the press up to room temperature at the end of a cycle of cooling and heating.

3. RESULTS

The isobaric curves $\chi(T)$ for the $\text{Zr}_{80}\text{Hf}_{20}$ alloy measured on heating the samples are shown in Fig. 1. The $\chi(T)$ curves for pure Zr and the $\text{Zr}_{67}\text{Hf}_{33}$ alloy are of the same shape. Jumps in the $\chi(T)$ curves are due to superconducting transitions in the ω phase ($2.5 < T_c < 3.5$ K) and in the β phase ($T_c > 9$ K). The jumps in the isobars at 19.0, 24.6, and 29.4 GPa for the single-phase states of the alloy with the ω structure are steep. The jumps corresponding to the two-phase $\omega + \beta$ states of the alloy at pressures of 35.0, 39.1, and 43.0 GPa are more diffuse because of microstresses and the proximity effect. The values of T_c were determined as the points of intersection between the tangent to the segment of the steep drop in the $\chi(T)$ curve and the extension of its high-temperature horizontal portion, as shown by arrows in Fig. 1.

The pressure dependences of T_c for the ω and β phases of pure Zr and the $\text{Zr}_{80}\text{Hf}_{20}$ and $\text{Zr}_{67}\text{Hf}_{33}$ alloys are shown in Fig. 2. As for zirconium, the lower segment of the $T_c(P)$ curve before the jump corresponds to the ω phase and the upper part corresponds to the β phase. This was determined by structural measurements *in situ*, whose results will be published later. It is evident in Fig. 2 that the superconducting transition temperatures of the ω and β phases of both the alloys studied in this work coincide within the limits of the experimental error. The $T_c(P)$ lines are straight with the

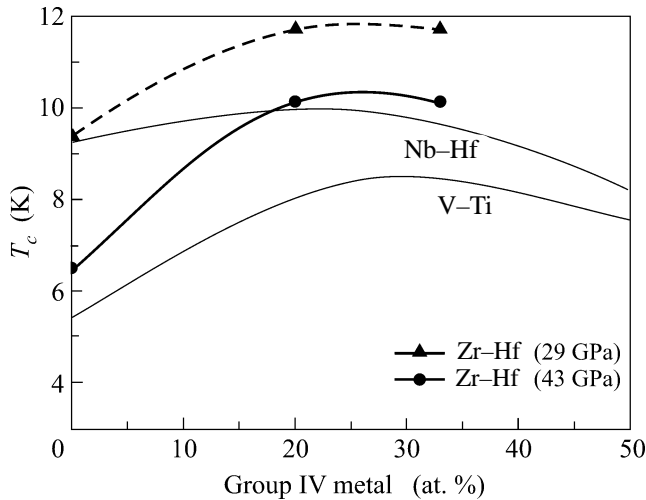


Fig. 3. Dependence of the values of T_c on the Hf or Ti content for the β phases of Zr–Hf alloys at pressures of 29 and 43 GPa and Nb–Hf and V–Ti alloys [18] at atmospheric pressure.

slopes to the pressure axis dT_c/dP equal to $+0.042$ K/GPa for the ω phase and -0.122 K/GPa for the β phase. The pressures at the beginning of the $\omega \rightarrow \beta$ phase transition, which were assigned to the appearance of the jumps in $\chi(T)$ corresponding to the β phase, comprise 29 GPa for pure Zr, 35 GPa for the $Zr_{80}Hf_{20}$ alloy, and 40.9 GPa for the $Zr_{67}Hf_{33}$ alloy. Assuming that the pressure of the $\omega \rightarrow \beta$ transition in the Zr–Hf system is a linear function of concentration and extrapolating this function to pure Hf, we obtain a value of ~ 65 GPa, which is close to the published value of 71 GPa [9].

Figure 3 displays the isobaric concentration dependences of T_c at two pressures for the β phase of the Zr–Hf alloys studied in this work. Analogous dependences of T_c for two solid β solutions of Vb and IVb group elements, namely, Nb–Hf and V–Ti alloys [18], are plotted in the figure for comparison. The isobaric curve for $P = 43$ GPa is constructed by the experimental dependence $T_c(P)$ shown in Fig. 2 and is depicted by a solid line. The isobaric curve for $P = 29$ GPa is constructed by the experimental value of T_c for pure zirconium and the points obtained by a linear extrapolation of the experimental lines $T_c(P)$ for the $Zr_{80}Hf_{20}$ and $Zr_{67}Hf_{33}$ alloys. It is shown by a dashed line. Note that T_c for β -Zr at $P = 29$ GPa virtually coincides with T_c for pure niobium at atmospheric pressure.

Figure 3 demonstrates that all four curves of the isobaric dependence of T_c on the concentration of the IVb group metal (Hf or Ti, respectively) are qualitatively similar. Both in bcc solid solutions of IVb – Vb systems at atmospheric pressure and in solid β solutions of the Zr–Hf system (that is, IVb – IVb) at high pressures, T_c first increases and then passes through a shallow maxi-

mum as the concentration of the IVb group element (Hf for the Zr–Hf system) increases. At the chosen values of pressure (29 and 43 GPa), all the four curves are similar not only in shape but also in the position of the maximum located in the concentration range 25–30 at % Hf or Ti.

Because no direct methods are available for determining the degree of band occupancy under pressure, the occupancy can be judged only in an indirect way by experimental data. The experimental data obtained for alloys clearly confirm the ideas of s – d electron transition in Zr and Hf under the action of pressure. The isobaric curves $T_c(c)$ for the bcc phase at high pressure in the system in hand are close in shape to the analogous curves for the IVb – Vb system (for example, Ti–V or Zr–Nb) at atmospheric pressure. That is, Zr–Hf alloys under pressures above the formation of the bcc phase, with which s – d electron transition is associated, behave as though they transform from IVb – IVb alloys to IVb – Vb alloys. It is essential that the total number of $s + d$ valence electrons remains unchanged and only their redistribution among subbands takes place. This fact clearly indicates that it is the degree of d -band occupancy rather than the total number of valence electrons that plays a determining role in the formation of the crystal structure and superconducting properties of metals of the IVb and Vb subgroups of the periodic system of elements.

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