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The Allotropic Transformation of Hafnium

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The existence of an allotropic transformation in hafnium, suggested by Zwicker in 1926, has been confirmed. The transformation temperature is $1310 \pm 10^\circ$C. The high temperature beta-form is probably body-centered cubic.

INTRODUCTION

In a paper published in 1926, Zwicker\textsuperscript{1} reported for the first time the existence of an allotropic transformation in zirconium and in hafnium. His conclusions were based on anomalies found in the variation of electrical resistivity with temperature. In the case of zirconium, Zwicker's measurements indicated a maximum around $877^\circ$C followed by a minimum at $1157^\circ$C and he concluded that a transformation was taking place between these temperatures. It has been shown since\textsuperscript{2} that the allotropic transformation in zirconium takes place with little or no hysteresis at $862\pm 5^\circ$C. From the maximum and minimum observed in the hafnium electrical resistance curves, Zwicker concluded that a transformation occurred between 1327 and 1527$^\circ$C. No further reference to work on the transformation of hafnium has been found in the literature.

The results of the present investigation prove that an allotropic transformation takes place in hafnium at $1310 \pm 10^\circ$C. In addition, a study of the hafnium-columbium system led to the conclusion that these two metals form a complete series of solid solutions at high temperature. This result is interpreted as an indirect proof that the high temperature form of hafnium is body-centered cubic.

THERMAL ANALYSIS MEASUREMENTS

The hafnium metal used for this investigation was prepared by the Van Arkel process by the Foote Mineral Company (bar No. 778). The lattice parameters were measured from a powder pattern obtained with a 14.32 cm camera and copper $K\alpha_1$ radiation. The Cohen least-squares method was applied to lines (123), (302), (006), (205), and (220) in the back reflection range. These parameters are $a = 3.1952A$, $c = 5.0569A$, and $c/a = 1.5827$.

It was inferred that if a transformation existed in hafnium, it would be of the same type as that found in titanium and zirconium. The transformation of the hexagonal close-packed to the body-centered cubic high temperature form of these two metals is diffusionless and practically independent of the rate of cooling.\textsuperscript{3} The technique used for the study of titanium and zirconium was therefore applied to hafnium.

This technique, described by Greninger in a study of the martensite transformation in steels,\textsuperscript{4} consists of heating a very small specimen of metal to which fine thermocouples are spot welded and quenching it by means of a blast of helium. From the temperature vs time curve recorded on an oscillograph, the transformation temperature and the rate of cooling may be determined. The results of measurements at various rates of heating and cooling are given in Table I. It appears that the transformation temperature is not affected by the rate of cooling. The transformation is therefore of the diffusionless type similar to that found in titanium and zirconium.\textsuperscript{5}

CRYSTAL STRUCTURE OF THE HIGH TEMPERATURE FORM OF HAFNIUM

Because of the difficulties involved in obtaining diffraction patterns at high temperature without contamination of the specimen, an indirect method was used to establish the crystal structure of beta-hafnium.

\textsuperscript{1} C. Zwicker, Physica 6, 361–365 (1926).
\textsuperscript{2} W. G. Burgers, Physica 1, 561 (1934).
\textsuperscript{3} P. Duwez (to be published).
On the basis of the Hume-Rothery rules governing alloy formation, it can be predicted that if beta-hafnium is body-centered cubic, alloys of hafnium with either columbium or tantalum should form a continuous series of solid solutions at high temperature. A series of hafnium-columbium alloys were prepared by melting in a helium arc furnace similar to that described in reference 5. Since the total amount of hafnium available was less than 5 grams, the weight of each alloy sample was limited to approximately 0.5 gram. After melting, the alloys were sealed in evacuated fused silica tubes, homogenized for 48 hours at 1000°C, and quenched from that temperature.

Nine compositions were investigated: 10, 20, 23.5, 30, 43.5, 47, 55, 66, and 77 atomic percent columbium in hafnium. The x-ray diffraction patterns of the alloys containing more than 30 percent columbium were readily indexed on the basis of a body-centered cubic structure. The patterns of the three alloys having less than 30 atomic percent columbium contained reflections of hexagonal hafnium, in addition to the reflections of a body-centered cube. The plot of lattice parameter of the body-centered cubic phase vs composition is shown in Fig. 1. The diagram clearly demonstrates that at 1000°C a solid solution exists between hafnium and columbium from 30 to 100 percent columbium, and a two-phase region (hexagonal hafnium plus cubic solid solution) extends from an undetermined concentration up to about 30 percent columbium.

The extensive solid solubility of hafnium in columbium at 1000°C suggests that at temperatures above the transformation of hafnium the two metals are completely soluble in each other. This statement, however, cannot be checked by room temperature x-ray diffraction measurements because the high temperature body-centered cubic phase in the alloys rich in hafnium cannot be retained by quenching. It was observed that when the alloys containing 10 and 20 atomic percent columbium were rapidly cooled from the melt, the resulting structure was a mixture of hexagonal close-packed and body-centered cubic phases. This behavior is exactly the same as that observed in the titanium-molybdenum system, in which there is complete solubility at high temperature, but the body-centered cubic structure cannot be retained by quenching unless the molybdenum concentration is greater than about 6 atomic percent. For concentrations smaller than 6 percent, the transformation into an hexagonal super-saturated solid solution always takes place, at least partially, through a martensitic type of transformation. By extrapolating the curve of Fig. 1 to zero columbium concentration, the lattice parameter obtained is 3.50A, which represents approximately the edge of the unit cell of the body-centered cubic modification of hafnium if it would be measured at room temperature.