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PHASE TRANSFORMATIONS IN SOME HAFNIUM-TANTALUM-TITANIUM-ZIRCONIUM ALLOYS

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ABSTRACT

Phase transformations in hafnium alloys are of interest as a means of achieving a material which exhibits flow softening and high localized strains during deformation at high strain rates. Hafnium transforms from a body-centered-cubic beta phase to a hexagonal alpha phase upon cooling below 1749°C. Hafnium-based alloys containing up to 17.5% Ti, up to 17.5% Ta, and up to 7.3% Zr by weight were button-arc melted and, in some cases, hot extruded to obtain a refined grain size. A number of alloys were shown to have beta solvus temperatures in the range of 1100 to 1300°C and showed evidence of a shear transformation upon water quenching. The Vickers microhardness of the quenched materials are typically above 350 HV as compared to 300 HV or less for materials with an alpha plus beta structure. Quenching dilatometry indicates a martensite start temperature of about 750°C for the Hf-7.5 Ta-10 Ti-1 Zr alloy and 800°C or more for the Hf-7.5 Ta-7.5 Ti-1 Zr alloy. Tensile tests at 1 s^{-1} strain rate show a constant ultimate tensile strength for temperatures up to 600°C for the above two alloys and a rapid decrease in strength with a further increase in temperature.

INTRODUCTION

Currently, there is interest in materials which exhibit flow softening and high localized strains during deformation at high strain rates [1]. Materials which are susceptible to flow softening are characterized by a rapid decrease in flow stress with increasing temperature or with increasing strain rate. Materials which show a large decrease in flow stress with increased temperature are likely to be found among those which undergo an athermal phase transformation during the adiabatic heating which accompanies localized flow. The athermal phase transformations include the martensitic and massive phase transformations. In contrast, diffusional phase transformations such as precipitation can occur only on time scales which are much longer than that of adiabatic shear deformation at high strain rates.

Hafnium alloys are candidate matrix materials for high-density tungsten-based composites [2-5]. Hafnium has a density of 13.1 g/cc, which is higher than any of the other candidate materials. The mechanical properties of pure hafnium have been characterized [6,7]. Pure hafnium does not show signficant softening at elevated strain rates and exhibits localized shear only after true strains of 0.35 or greater [8]. Hafnium alloys are potentially capable of substantial localized shear deformation at lower strains through an athermal phase transformation. Hafnium does undergo a phase transformation from the low-temperature alpha phase with a hexagonal-close-packed (HCP) structure, to the

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high-temperature beta phase with a body-centered-cubic (BCC) structure, at 1743°C. However, this temperature is too high to play any role in high strain rate shear deformation under the conditions of temperature and strain rate of interest. Alloying of hafnium can substantially lower the transformation temperature to obtain a material with the desired deformation behavior. On the basis of published phase diagrams, titanium, tantalum, zirconium, and manganese were selected for investigation as alloying elements.

MATERIALS AND PROCEDURE

The materials used consisted of hafnium crystal, titanium rod, commercial tantalum foil, and zirconium foil. The hafnium generally contained 1.5% Zr as impurity. The alloys were produced as nonconsumable arc-melted buttons of 50 or 100 g. The buttons were melted four or more times in argon and turned after each melt. Weight changes during melting were recorded. The nominal compositions of the alloys are listed in Table I. There was typically no measurable weight change during melting with the exception of the manganese-containing alloy. Weight losses were usually less than 0.01%. The nominal 1% Zr in all of the materials results from the zirconium impurity in the hafnium.

Table I. Nominal Chemical Compositions for Hafnium Alloys

	Alloy (Weight Percent)				
Identification	Hafnium	Titanium	Tantalum	Zirconium	Manganese
HA1	84	15	--	1	--
HA2	84	--	15	1	--
HA3	84	7.5	7.5	1	--
HB1	84	5	10	1	--
HB2	81.5	5	12.5	1	--
HB3	81.5	7.5	10	1	--
HB4	79	7.5	12.5	1	--
HB5	81.5	10	7.5	1	--
HB6	79	10	10	1	--
HB7	79	12.5	7.5	1	--
HB8	76.5	12.5	10	1	--
HB9	71.2	4	17.5	7.3	--

The arc-melted buttons were sectioned, and the sections were sealed in evacuated quartz tubes and heated at temperatures in the range of 900 to 1400°C prior to quenching in water. Samples of some alloys were also furnace cooled. The as-cast and heat-treated samples were examined by optical metallography. The polished surfaces were viewed with polarized light at 200×. Microhardness measurements were made using a Vickers diamond-pyramid indentor with a 500-g load. In all cases, the hardness is reported as an average of five individual indentations.

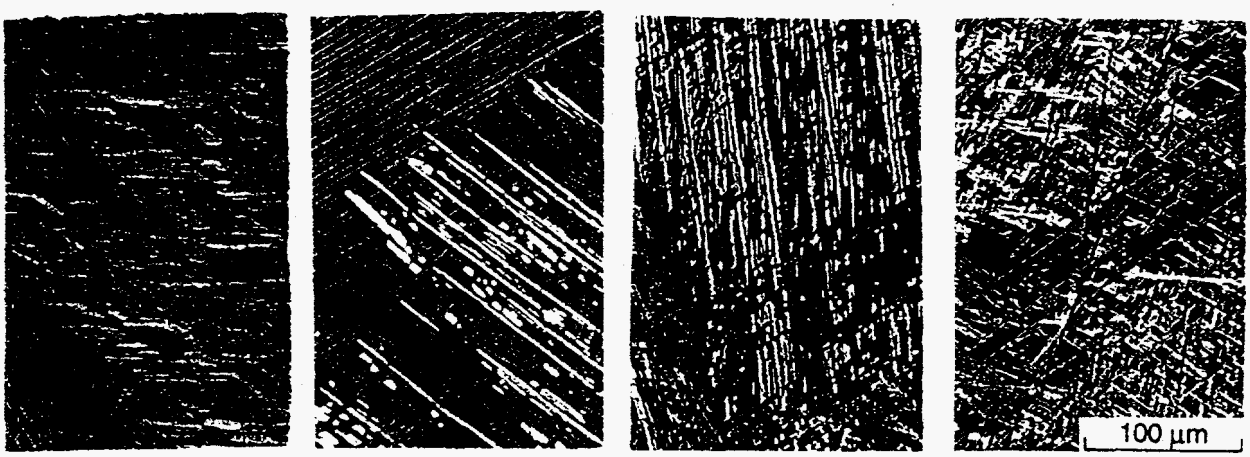
Two of the alloy compositions (HB3 and HB6) were selected for further study. Arc-melted buttons weighing 700 g each were produced and drop cast into a 25-mm-diam copper mold. For each composition, two lengths of bar totaling about 150 mm were placed into the cavity of a Type 316 stainless steel can of 50 mm OD, which was lined with 0.13-mm-thick tantalum foil. Each can was evacuated and sealed by electron-beam welding. The cans were preheated for 1 h at 1100 or 1200°C for HB6 or HB3, respectively, and extruded through a die with an opening of 21 mm diam for an extrusion ratio of 6:1. The extruded bars were then reheated to 1125 and 1225°C, respectively, for 30 min and water quenched. Sections of each extrusion were machined to produce tensile test specimens, dilatometry specimens, and metallographic specimens.

Tensile tests were performed on a Gleeble testing machine using 6.4-mm-gauge-length by 2.5-mm-diam specimens. The specimens were resistance heated for 2 s to the test temperature and held at the test temperature for an additional 2 s. The resistance heating remained on during the test except for the tests at 1200°C, for which the power was programmed to shut off at the initiation of loading. This was done after localized melting was observed at the point of the cone fracture site for tests performed with the heating power on. The test was performed at a strain rate of 1 s^{-1}. The 0.2% offset yield strength, the ultimate tensile strength, and the total elongation were determined from the load versus displacement data.

Analyses of the HB3 and HB6 alloys were performed using a quenching dilatometer. The 3-mm-diam by 8-mm-length specimens were heated to a temperature of 1200°C for HB6 and 1300°C for HB3 at a rate of 30 to 100°C/s, held at temperature for 10 s, and then gas quenched to room temperature at more than 100°C/s. The temperature was measured by means of a Type S thermocouple welded to the specimen and the length change measured by means of the displacement of quartz rods contacting the sample.

Results

The microstructure of the HB3 alloy quenched from various temperatures as well as in the as-cast condition are shown in Figure 1. This alloy shows clear evidence of shear transformation at the 1300°C temperature and a Widmanstatten structure at the 1100°C temperature. The other alloys show similar behavior, however, the change in microstructures is observed at different quenching temperatures. At the higher quenching temperatures, the microstructures exhibit evidence of a shear or twinning deformation and have an appearance similar to the acicular martensites seen in some titanium alloys. At the lower temperatures, there are numerous parallel platelets which appear to have a Widmanstatten alpha plus beta structure. In some cases, at intermediate temperatures, there appears to be a mix of these microstructures. The minimum temperature for which evidence of the shear transformation is observed in quenched samples is shown in Table II. This temperature is expected to be approximately that of the solvus temperature for the high-temperature beta phase.



(*a*) 1300°C (*b*) 1200°C (*c*) 1100°C (*d*) Arc-Cast

Figure 1. Microstructures of alloy HB3 (Hf-7.5 Ti-10 Ta -1 Zr) heated for 1 h in vacuum and water quenched from various temperatures show evidence of a shear type transformation when quenched from 1300°C and a diffusional Widmanstatten structure at temperatures of 1100°C and below.

The HA2, with no titanium addition, shows a structure of coarse equiaxed precipitates when quenched from 1400°C. The HA1 alloy quenched from 1200°C and the HA3 alloy quenched from 1300°C exhibit shear transformations similar to those seen for the HB3 alloy in Figure 1(*a*).

Table II. Summary of Microstructures and Hardness Results

Alloy	Minimum Temperature (°C)	
	Shear Transformation on Quenching	Hardness Upper Shelf Temperature
HB1	1300	1300
HB2	1300	1250
HB3	1200	1200
HB4	1200	--
HB5	1200	1100
HB6	1100	1100
HB7	1100	--
HB8	1000	1100
HB9	1200	--

The room-temperature microhardness is plotted as a function of heat-treatment temperature for alloys HB1 through HB9 in Figures 2 and 3. The hardness decreases with decreased heat-treatment temperature. For most of the alloys, there is an upper shelf hardness at high temperature and a rapid decrease in hardness with heat-treatment temperature at lower temperatures. This decrease in hardness is generally found over the same range of temperatures for which the microstructure changes from shear transformation to a diffusional transformation. The temperature at which this rapid decrease in hardness begins is shown in Table II and can be compared to the minimum quenching temperature which produces a microstructure with evidence of shear transformations. The hardness plot of alloy HB9 is unusual in that it shows a minimum in hardness at the 1100°C temperature and a large increase in hardness with further decrease in heat-treatment temperature.

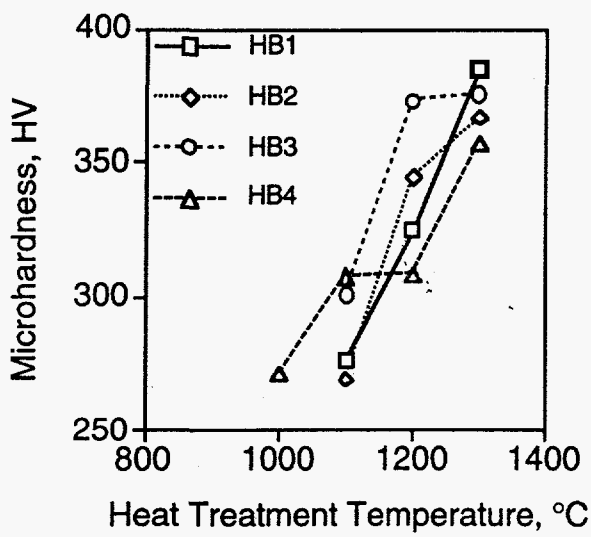


Figure 2. Heat-treatment response of quenched hafnium alloys HB1 through HB4 as measured by microhardness at room temperature.

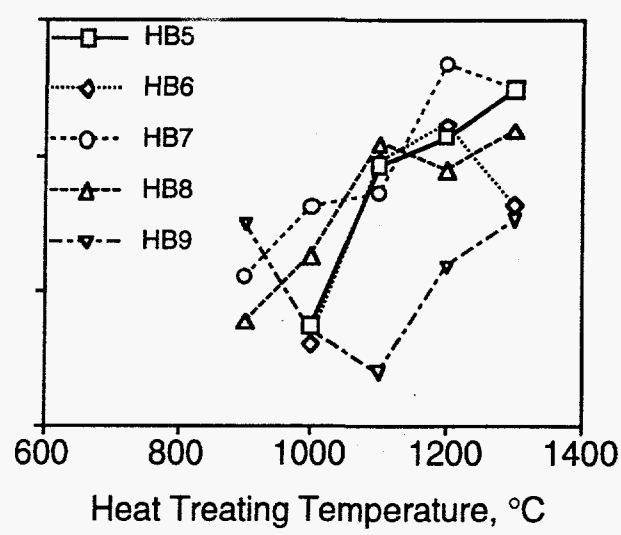


Figure 3. Heat-treatment response of quenched hafnium alloys HB5 through HB9 as measured by microhardness at room temperature.

The microstructures of the extruded materials of HB3 quenched from 1200°C and HB6 quenched from 1100°C are similar to those of cast materials, but do show less evidence of large regions of shear transformation than do the microstructures of similarly heat-treated materials from arc-melted buttons. This could be attributed to a number of possible causes: (1) the smaller grain size of the extruded material, or (2) a more sluggish quench due to the larger size of the extruded bars encased in the steel can.

Tensile yield strength and ultimate tensile strength of the heat-treated extruded materials from HB3 and HB6 are plotted as a function of test temperature in Figure 4. The tensile elongation versus test temperature is plotted in Figure 5. The yield stress decreases nearly linearly with increased test temperature over the entire range of 400 to 1200°C. The ultimate tensile strength decreases most rapidly with temperature in the range of 600 to 1000°C. The tensile elongations are all in the range of about 25 to 50%. The elongation values are lowest at 400°C, highest at 1200°C, and relatively constant in the range of 600 to 1000°C.

The results of the analysis by dilatometry for the HB6 material are shown in Figures 6 and 7. The length changes during initial heating at 30°C/s and gas quenching at more than 100°C/s are seen in Figure 6. The heating curve indicates a large negative deviation from linearity starting at about 750°C and reaching a maximum deviation at 900°C. The cooling curve shows a positive deviation from linearity, indicative of a transformation producing an increase in volume, at 740°C. The heating curve for the second thermal cycle (in this case, at 100°C/s) of the same sample is shown in Figure 7(*a*). This shows only a small negative deviation from linearity at about 1000°C. The portion of the cooling curve from 850 to 600°C in Figure 7(*b*) shows a positive deviation at 720°C. The results from the cooling curves can be interpreted to indicate a martensite start temperature of 720 to 740°C. The initial heating curve indicates that the extruded bar material, which was heated at 1125°C and water quenched, did not achieve a fully martensitic structure. The gas quenching of the small dilatometer specimen from 1200°C achieves a more fully martensitic structure. The microstructure of the gas-quenched specimen in Figure 7 appears almost featureless as compared to the microstructure of the water-quenched bar material. The dilatometry results for the HB3 alloy material show similar behavior. The positive deviation upon cooling corresponding to a martensite start temperature occurs at higher temperatures than for HB6. A temperature of 790 to 800°C was obtained for the first three thermal cycles to 1300°C. Three subsequent runs showed a similar event only at 925°C. The reason for the change in the measured transfomation start temperature is not known.

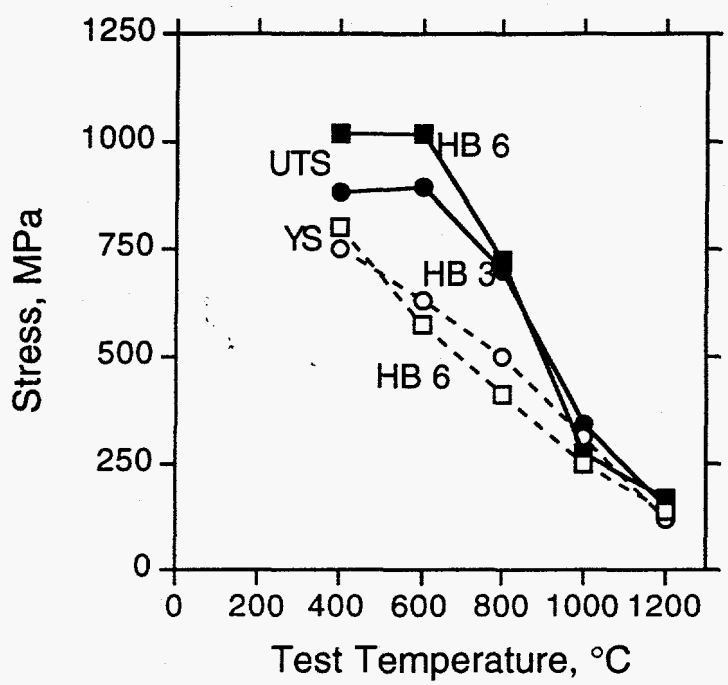


Figure 4. Effect of test temperature on ultimate tensile strength and 0.2% offset yield stress of quenched alloys HB3 and HB6 tested at a strain rate of 1 s^{-1}.

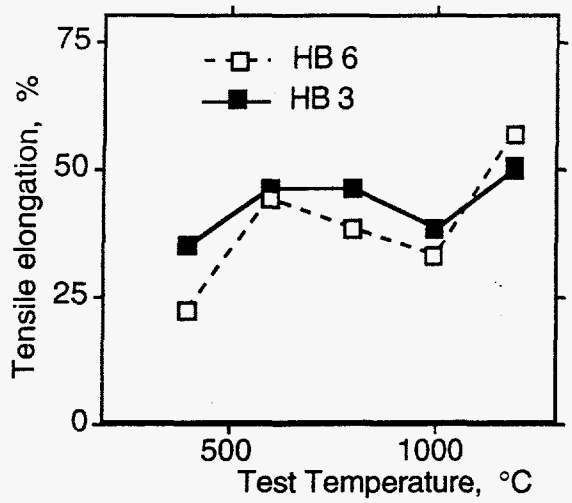


Figure 5. Effect of test temperature on tensile elongation of quenched alloys HB3 and HB6 tested at a strain rate of 1/s.

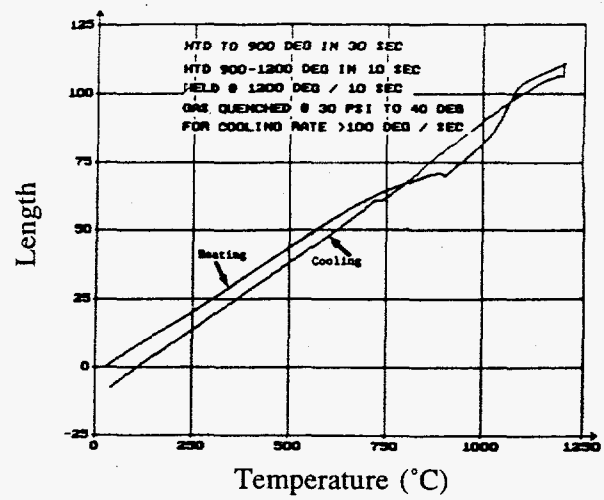


Figure 6. Heating and cooling curves obtained from quenching dilatometer during first thermal cycle of HB6 alloy specimen.

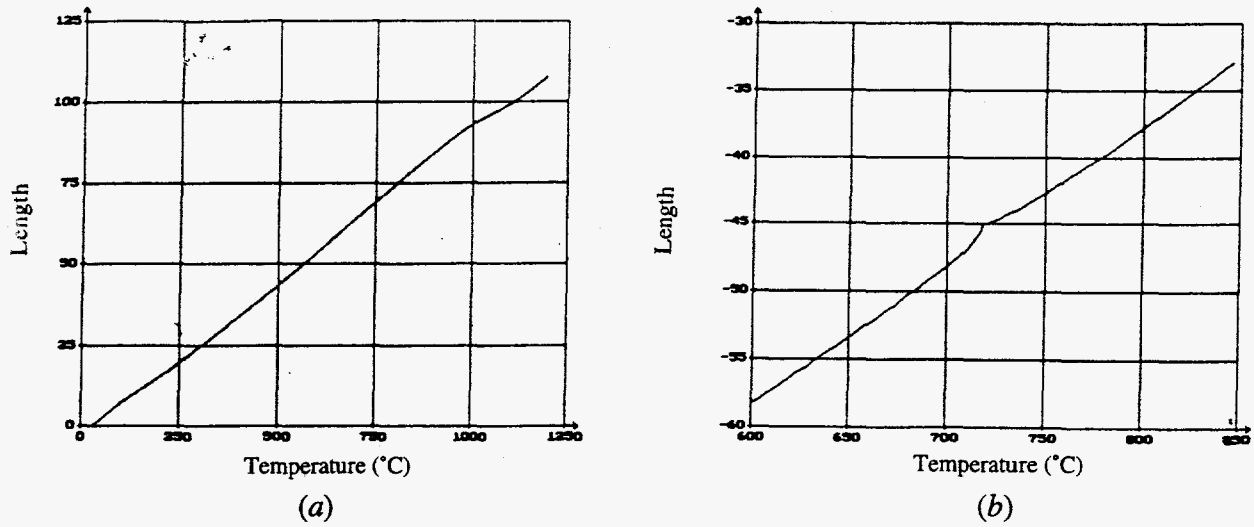


Figure 7. Heating curve (*a*) and portion of cooling curve (*b*) obtained from quenching dilatometer during second thermal cycle of HB6 alloy specimen.

The microhardness measurements obtained from the extruded bars after various heat treatments are listed in Table III. The values for HB3 show relatively good agreement to those for the arc-melted buttons of the same composition. The value for HB6 bar material heated at 1125°C and water quenched is comparable to that for the HB6 button material. The gas-quenched sample shows higher hardness, possibly indicative of a greater quantity of martensitic phase.

DISCUSSION

In selecting alloys for investigation, the density of the material is one consideration. The other major consideration is the phase transformation response. The alloys, unlike pure hafnium, have a two-phase field of alpha plus beta. Ideally, the alloy can be heated in the beta field and then rapidly cooled to form alpha phase or some metastable phase by a diffusionless phase transformation, either a massive or martensitic. The material in the as-quenched condition during high-strain-rate deformation would undergo a local rise in temperature, causing the material to revert to the beta

Table III. Summary of Microhardness of Samples of Extruded Bar Material

Alloy	Heating Conditions	Cooling Method	Microhardness (HV)
HB3	1225°C/30 min	Water Quench	349
	1000°C/1 h	Furnace Cool	295
HB6	1125°C/30 min	Water Quench	369
	1300°C/10 s	Gas Quench	399
	1000°C/1 h	Furnace Cool	337

phase. This would also occur by a diffusionless shear transformation and result in a phase with lower flow stress than the bulk of the material. This would then cause further localization of the shear and a further increase in temperature locally to propagate the shear band. It is desirable that the reversion to the higher temperature phase occur at not too high a temperature, possibly in the range of 600 to 1200°C. During quenching to room temperature, it is desirable to be able to produce a fully martensitic phase at reasonable quench rates. Further, the temperature from which the material is quenched should be in the beta region, and this temperature should be as low as practical to avoid the need to heat to very high temperatures prior to quenching.

The results of this study indicate that the primary goal of obtaining a hafnium alloy with suitable heat-treatment characteristics has been achieved. Apparent shear transformation products are obtained by quenching from as low as 1100°C, as compared to the hafnium transformation temperature of 1750°C. However, due to the limited extent of this study, the actual transformations and products of those transformations are not known. Further work including X-ray diffraction, transmission electron microscopy, and additional dilatometry studies are needed to determine the actual phase transformations. The transformation, believed to be martensitic, does cause a modest increase in hardness, as shown by the effect of heat-treatment temperature on the hardness. The dilatometer studies performed so far do show an indication of a martensite start temperature in the range of about 700 to 900°C. This would appear to be sufficiently high to avoid retained beta phase during quenching. There is no appearance of any feature on the heating curve which could definitively be associated with the reverse transformation from martensite to beta phase during heating, which is the reaction expected during high strain rate deformation.

The results of tensile testing using the Gleeble tester also appear encouraging. The material should exhibit a rapid decrease in flow stress with increasing temperature, to promote adiabatic shear deformation during ballistic impact. The Gleeble test is run under conditions of maximum strain rate and minimum time at temperature to approach as closely as practical the conditions of impact. The ultimate tensile strength can be used as an approximation of the flow stress under compression in ballistic impact deformation. The ultimate tensile strength of both HB3 and HB6 show a rather rapid decrease in ultimate tensile strength over the temperature range of 600 to 1000°C. The material shows good ductility over the entire range of test temperatures.

Preliminary results of high strain rate (3700 to 6100 s^{-1}) compression testing of the quenched HB3 and HB6 alloys show visible shear banding at strains of approximately 0.2 [9]. Thus, these alloys develop shear instabilites well before pure hafnium, which exhibits shear localization only at a strain of 0.35 or more.

CONCLUSIONS

The following conclusions can be drawn from this investigation of hafnium alloys with titanium contents of 4 to 7.5%, tantalum contents of 7.5 to 17.5%, and zirconium contents of 1 to 7.3%:

1. The alloys can be beta-solution treated at temperatures in the range of 1100 to 1300°C and water quenched to produce a martensitic microstructure.

2. The microhardness (HV) of the quenched alloys is typically above 350 as compared to 300 or less for slow-cooled alloys with an alpha plus beta structure.

3. Quenching dilatometry indicates a martensite start temperature of about 750°C for the Hf-7.5 Ta-10 Ti-1 Zr alloy and 800°C or more for the Hf-7.5 Ta-7.5 Ti-1 Zr alloy.

4. Tensile tests at a strain rate of 1 s^{-1} shows a constant ultimate tensile strength for temperatures up to 600°C for the above two alloys and a rapid decrease in strength with a further increase in temperature.

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