II. DEVELOPMENT OF HIGH STRENGTH TANTALUM BASE ALLOYS*

R. W. Buckman, Jr.,[†] and R. R. Begley**

This paper describes the development of tantalum base alloys intended for application in advanced space power systems. For components such as piping in alkali metal Rankine cycle systems, radioisotope capsules, and fuel claddings in nuclear reactors, critical property criteria include excellent fabricability, good welding characteristics, long time thermal stability, and high creep strength. Tantalum base alloys which successfully meet these criteria were achieved by a balanced combination of solid solution and dispersed phase strengthening, as typified by the alloy ASTAR-811C (Ta-8W-1Re-0.7Hf-0.025C). This alloy has creep strength significantly superior to T-111 (Ta-8W-2Hf) at temperatures up to 2600° F, without sacrifice of fabricability or welding characteristics. The DBTT of TIG welds is of the order of -250° F, and that of recrystallized base metal is below -320° F. Data are presented for tensile and long time creep properties of this alloy, and the role of carbide precipitates in improving high temperature strength is discussed.

Greatly improved high temperature tensile and creep properties can be achieved by an increase in tungsten level and by a substitution of nitrogen for carbon. While this strength increase is obtained with some sacrifice in fabricability, the alloys of increased solute level are attractive for high temperature applications where weldability is not a critical design requirement.

INTRODUCTION

In 1963 the Lewis Research Center of NASA initiated a program at the Westinghouse Astronuclear Laboratory to develop tantalum base alloys for application in advanced space power systems. The intent of the program was to develop alloy(s) which would have improved properties in the 2000° to 3000° F temperature range,

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[†]Westinghouse Astronuclear Laboratory, Pittsburgh, Pennsylvania.

**Westinghouse Research Laboratory, Pittsburgh, Pennsylvania.

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with the major emphasis on application in Rankine cycle nuclear electric power systems which would operate at 2000° to 2600° F. The extended operational life of the systems (>10 000 hr) dictated that resistance to creep deformation be the principal strength criterion. An additional requirement was that the alloys developed be compatible with alkali metals, the intended working fluids in these systems. Since the material would be used in complex heat transfer systems, good fabricability and welding characteristics were also essential.

The intent of this paper is to review the development of a series of fabricable, creep resistant tantalum base alloys which resulted from this program and summarize the properties achieved, rather than treat in detail any specific aspect of the investigation.

EXPERIMENTAL DESIGN

The alloy base selected for evaluation was the tantalum rich corner of the Ta-W-Hf-C system. This system was selected as the most promising based upon earlier work at Westinghouse which led to the development of the alloys T-111 (Ta-8W-2Hf)¹ and T-222 (Ta-10W-2.5Hf-0.01C) (ref. 1). The alloys investigated were of the basic type

$$M + M_{S.S.} + M_{R.E.} + M_1 = \text{Alloy}$$

where

M	Ta
M _{S.S.}	substitutional solute(s)
M _{R.E.}	reactive element solute(s)
M ₁	interstitial solute(s)

This type of alloy derives its strength from a combination of solution and dispersed phase strengthening, the latter arising from the precipitation of an interstitial compound. The Ta-W-Hf-C alloy base was modified by the addition and/or substitution of rhenium and molybdenum for tungsten, zirconium for hafnium, and nitrogen for carbon. The presence of a reactive element (zirconium and/or hafnium) significantly affects the alkali metal corrosion resistance of tantalum and columbium alloys by reducing the oxygen solubility of the matrix, tying up oxygen

¹Composition given in weight percent.

as a HfO_2 or ZrO_2 precipitate (ref. 2). Thus all of the alloys contained a minimum of 1 atomic percent reactive element to assure adequate corrosion resistance.

The reactive elements were also intended to provide precipitation strengthening by reacting with the interstitial elements to form stable carbide and/or nitride phases. However, as will be shown, strengthening by carbides can be achieved in alloys of this type without the reactive element entering into the precipitation reaction. Several alloys were prepared without intentional carbon and nitrogen additions to establish the properties of the solid solution matrix.

The substitutional solutes investigated were selected on the basis of their solubility in tantalum and their effects on matrix elastic modulus and diffusivity as discussed in a recent review of creep of refractory metals by Begley, Harrod, and Gold (ref. 3). The alloying behavior of tantalum with particular reference to those factors which affect high temperature mechanical properties and low temperature ductility has been described by Buckman and Goodspeed (ref. 4); hence a detailed discussion of the considerations involved in defining the experimental program will not be presented here.

EXPERIMENTAL PROCEDURES

Ta and Ta-10W produced by electron beam melting and containing less than 100 ppm total interstitials was used as the base material. Alloys for initial studies were prepared in the form of $1\frac{3}{4}$ pound buttons by nonconsumable arc melting in a high purity argon atmosphere. Alloys for more detailed evaluations were prepared as 2-inch-diameter ingots weighing 7 pounds by double vacuum arc melting, using ac power. Finally, the optimized compositions were scaled up to 4-inch-diameter 80-pound ingots which were also prepared by vacuum arc melting.

Ingot breakdown was achieved by high energy rate forging and/or extrusion in the temperature range of 2200° to 3100° F, depending on alloy composition. The as-cast ingot material was coated with either a Al-12Si alloy or plasma sprayed Mo to reduce contamination during high temperature processing. Following careful conditioning, material was produced in the form of sheet by a combination of warm (800° F) and cold rolling. Bar stock of a number alloys was prepared by hot and cold swaging, with the specific processing schedule varying depending on alloy composition.

All intermediate and final annealing was performed on material which was conditioned and chemically cleaned to remove any contaminated surface layers and then wrapped in tantalum foil to prevent contamination during annealing. Heat treatments were conducted in a tantalum resistance heated furnace at pressures $\leq 1 \times 10^{-5}$ torr.

Specimens were generally annealed 1 hour at 3000⁰ F prior to evaluation. Elevated temperature tensile tests were also carried out in vacuum at pressures $\leq 1 \times 10^{-5}$ torr with the specimen gage length wrapped in tantalum foil. Creep tests were performed in sputter ion pumped vacuum systems of the type described by Buckman and Hetherington (ref. 5) at pressures below 1×10^{-8} torr. The low pressures achieved in these units are required to prevent test environment interactions which would lead to spurious creep test results (refs. 6 and 7).

Alloy sheet specimens 0.04 inch thick were evaluated by both TIG and electron beam welding. Automatic TIG welding was performed in a vacuum purged weld chamber back-filled with He containing less than 1 ppm total active impurities. The chamber was equipped with instrumentation to continuously monitor oxygen and water vapor concentrations in the welding atmosphere. The welding procedures used have been described by Lessmann (ref. 8). Electron beam welds were made in a 100-kilovolt Hamilton Zeiss unit evacuated to less than 5×10^{-6} torr prior to welding. Welds were evaluated primarily by bend tests to establish the ductile-brittle bend transition temperature. Bend deflection rate was 1 inch per minute and a 1.8 t bend radius was used.

During all phases of alloy preparation, processing, and evaluation, particular care was devoted to achieving homogeneity and freedom from contamination, and extensive chemical analyses were performed to monitor the effectiveness of the techniques used. A more detailed description of the experimental procedures is reported by Buckman and Goodspeed (ref. 9).

RESULTS

The effects of compositional and structural variations were evaluated on the basis of their effect on fabricability, weldability, ductile to brittle transition temperature, and high temperature creep strength. The initial studies were largely directed at establishing the boundaries for satisfactory fabricating characteristics.

Fabricability

The combined effect of tungsten, hafnium, and carbon content on as-cast hardness is illustrated in figure II-1. The dashed line approximates the composition beyond which fabricability was impaired, this being defined as the onset of edge cracking with a 50-percent reduction in billet height resulting from a single blow of a Dynapak high energy rate forging unit. Forging temperature was 2200⁰ to 2300⁰ F

for those alloys having an as-cast hardness of less than 300 DPH and 2700° F for those over 300 DPH. The forging results could be correlated with microstructure. At carbon levels where a continuous grain boundary carbide phase formed, edge cracking was encountered. The carbon level at which the continuous carbide phase formed decreased as the W + Hf content was increased. At W + Hf levels in excess of 12 percent and carbon levels greater than 0.1 percent, a subboundary network decorated with a continuous carbide phase was observed. As-cast ingots exhibiting this characteristic microstructure had very poor forgeability.

Substitution of nitrogen for carbon resulted in degradation of forgeability as the nitrogen level was increased above 400 ppm. Substitution of 1.5 percent Re and 0.85 percent Mo in an alloy of 9 percent total solute level and 0.07 C did not result in any decrease in fabricability.

The same general trends observed for primary working applied to the secondary working of the alloys. Alloys containing up to 10 percent W + Hf and 0.1 percent carbon could be cold rolled to good quality strip.

Weldability

Experimental compositions exhibiting marginal fabricating characteristics were readily identified during the primary and secondary working operations. However, the changes in ductile-brittle bend transition temperature (DBTT) resulting from fusion welding provided a much more sensitive fabricability index. Material annealed 1 hour at 3000° F to provide a fully recrystallized microstructure was TIG welded and the ductile-brittle transition temperature determined. The transition temperature is defined as the lowest temperature at which a full 90° bend (1.8 t bend radius) was obtained without any indication of cracking. As shown in figure II-2, the addition of carbon to the Ta-W-Hf matrix results in a significant increase in the as-TIG welded transition temperature. At a W + Hf content of 9 to 10 percent, the addition of 400 ppm carbon raises the DBTT to approximately room temperature. Recrystallized base metal of the same composition has a DBTT below -320° F. Metallographic examination of welds in alloys containing up to 0.05 C revealed an essentially single phase fusion and heat affected zone, while the adjacent base metal showed characteristic carbide precipitates. During welding, the carbides are dissolved and largely retained in solution on cooling. Hardness measurements taken across the welds showed a significant increase in the hardness of the fusion and heat affected zone areas as compared to the base metal, thus confirming the retention of carbon in solution (or as a very fine precipitate which forms on cooling). The increase in DBTT of the as-welded material is readily explained on this basis.

Postweld annealing at temperatures of 2600° to 2700° F was found to be effective in reducing the transition temperature by permitting carbide precipitation to occur. The minimum temperature for satisfactory recovery of bend ductility was not established in this study, however.

Nitrogen additions were found to raise the DBTT of weld material, the effect being significantly greater than for equivalent carbon additions.

Creep Behavior

High temperature creep strength increased with increasing tungsten level, as expected. The substitution of small amounts of rhenium for tungsten had an unexpectedly potent effect in increasing the creep strength of Ta-W-Hf and Ta-W-Hf-C alloys, as shown in figure II-3. Additions of the order of 1 percent conferred significantly improved properties while larger amounts had no additional effect. This behavior cannot be rationalized in terms of simple solution strengthening, nor does it appear to be related to effects on precipitate morphology or stability since it is observed in alloys having no interstitial addition. Buckman and Goodspeed (ref. 4) have suggested that it may be due to an electronic contribution.

The effect of carbon additions on the 2400° F creep properties of Ta-W-Hf alloys is summarized in figure II-4. These results show that the strength of the matrix increases appreciably with increasing carbon content, reaching a maximum at about 250 to 300 ppm C, and decreasing thereafter. However, all of these alloys were annealed 1 hour at 3000° F prior to testing. It is presumed that the carbide phase is coarser in the alloys of higher carbon content, providing a poorer structure for creep resistance. The carbon solubility in the Ta-W-Hf matrix at 3000° F is approximately 100 ppm; thus only a small fraction of the carbon in the alloys of higher carbon content was dissolved during the 3000° F anneal. The carbon not in solution at this temperature would tend to agglomerate as coarse carbide precipitates. It would be expected that if the annealing temperature were raised above the carbon solvus, and the cooling rate from the solution anneal sufficiently rapidly to precipitate a fine carbide phase, then strength would continue to increase with increasing carbon content. Studies of Cb alloys and results to be discussed later in this paper show that best creep results for carbide hardened alloys are achieved by annealing above the carbon solvus.

The carbide phases present in the Ta-W-Hf-C alloys were identified as either the dimetal carbide, Ta_2C , or the monocarbide, $(Ta, Hf)C_{1-x}$. Depending on composition, either or both of these carbides were observed in the matrix. The creep behavior of the experimental alloys could be rationalized on the basis of location in

the Ta-W-Hf-C quasi-ternary phase diagram, as illustrated in figure II-5. It is apparent that compositions exhibiting the best creep properties contained only the dimetal carbide as the precipitating phase (curves labeled A in the lower portion of fig. II-5). The compositions having the poorest properties (curves C) contained only the monometal carbide, $(\text{Ta, Hf})\text{C}_{1-x}$, while those containing both carbide phases had intermediate properties. It does not appear to be the identity of the precipitate per se which controls creep resistance, but rather that in order to stabilize the monocarbide phase fairly large additions of hafnium are necessary. In an alloy containing 500 ppm carbon, for example, approximately 3 percent Hf is required to stabilize the monocarbide. This results in a significant hafnium concentration in the matrix which has a deleterious effect on creep resistance (ref. 4). For this reason the best creep properties are achieved in alloys containing the Ta_2C precipitate since these alloys have hafnium concentrations of the order of 1 percent.

The minor compositional variations investigated by substituting different atom species, that is, nitrogen for carbon, molybdenum for tungsten, and zirconium for hafnium, provided a marked improvement in 2400°F creep properties, as shown by the data of figure II-6. This strength improvement is primarily associated with the increased effectiveness of the nitride precipitate in creep strengthening as compared to the carbide, at temperatures up to 2400°F . In the nitrogen containing alloys, the nitrogen is present as a reactive metal mononitride. The remarkable strength properties of the nitride hardened alloys are evidenced by the alloy composition Ta-5.3W-0.65Mo-1.56Re-0.52Zr-0.08N. This composition had a tensile strength in excess of 100 000 psi at 2400°F , as well as excellent 2400°F creep properties. However, as noted previously, the fabricability and weldability of alloys containing moderate nitrogen additions are marginal for alloys intended for use in the form of sheet and tubing. In applications where excellent fabricability and weldability are not critical requirements, the nitride strengthened compositions possess very attractive potential.

ALLOY OPTIMIZATION

Based upon the requirement for excellent fabricability and good as-welded ductility, a substitutional solute level of approximately 9 percent, and a carbon content of 0.025 percent was selected. Hafnium was maintained at the minimum level judged adequate for good alkali metal corrosion resistance, approximately 1 percent. Since significantly enhanced creep resistance was shown to result from small additions of rhenium without loss of fabricability, an addition of 1 percent Re

was selected for the optimized composition. The optimized fabricable alloy thus has the composition Ta-8W-1Re-1Hf-0.025C. This alloy, designated ASTAR-811C was scaled up for rather extensive evaluation of fabricating characteristics, weldability, and mechanical properties. The mechanical properties of ASTAR-811C are compared to those of the tantalum alloys T-111 and T-222 in table II-1. As can be seen, the tensile properties of ASTAR-811C are intermediate between those of T-111 and T-222. All three alloys have ductile-brittle transition temperatures below -320° F. In the as-TIG welded condition, the DBTT of ASTAR-811C is slightly higher than that of T-222, ranging from -250° to -150° F depending upon the welding parameters utilized. However, the major difference between ASTAR-811C and the other two alloys is the markedly superior creep strength of ASTAR-811C. Figure II-7 is a Larson-Miller plot which compares the creep properties of ASTAR-811C to T-111 and shows the significant improvement in properties realized in the creep optimized alloy. Also included in figure II-7 are data for a Ta-8W-1Re-1Hf alloy, which is the matrix composition of ASTAR-811C without the carbon addition. As can be seen, the carbide phase provides a substantial strengthening increment at the lower temperatures. However, at temperatures of the order of 2600° F the carbide phase makes no appreciable contribution to creep strength.

Further improvement in the creep strength of ASTAR-811C can be achieved by proper heat treatment. Generally, annealing at or above the carbon solvus improves creep resistance, as discussed in the paper by Harrod and Buckman in this volume.

Tensile data for ASTAR-811C are plotted as a function of temperature in figure II-8. Moderate strength and excellent ductility are maintained over the entire temperature range from -320° to 3000° F. Similar tensile tests conducted on TIG welded material showed essentially 100 percent joint efficiency and excellent ductility. Initial thermal stability studies of both base and weld metal have not indicated the presence of aging reactions which would result in ductility impairment.

HIGH STRENGTH ALLOYS

In the selection of the ASTAR-811C composition, maintenance of excellent fabricating and welding characteristics was a major consideration. The results of the investigation clearly demonstrated that greatly improved high temperature properties could be realized if the fabricability and weldability constraints could be relaxed. For components such as turbine blades and disks, bolts, etc. these properties can be compromised somewhat to achieve better high temperature strength. Consequently, studies are currently in progress to establish the properties obtain-

able in alloys which have adequate fabricability for use in the form of forgings and bar stock.

Figure II-9 shows the effect of increasing substitutional solute content (W + Re) on the tensile properties of a tantalum alloy base containing 0.7 percent Hf and 0.025 percent C. Elevated temperature tensile strength increases monotonically with increasing solute level. However, room temperature ductility decreases drastically at substitutional solute level over approximately 15 percent. This effectively establishes the upper composition limit for alloys of this type which will have a desirable combination of engineering properties. Creep properties of several of the high strength alloys are plotted in figure II-10. These experimental alloys have creep strength greatly superior to ASTAR-811C, as well as being significantly better than Cb-TZM. Some of these compositions have been satisfactorily welded by electron beam welding techniques. Detailed evaluation of these high strength alloys is currently in progress.

SUMMARY OF RESULTS

A series of tantalum base alloys has been developed which have many potential applications in space power systems. The progress which has been made in improving high temperature creep properties is illustrated in figure II-11, where stress for 1 percent creep in 1000 hours is plotted as a function of temperature. These alloys provide the best combination of strength, fabricability, and weldability available for applications in the 2000° to 2600° F temperature range. The highly fabricable alloy ASTAR-811C appears to have many potential applications in advanced space power systems, including reactor fuel claddings, pressure vessels, and piping; radioisotope fuel capsules, thermionic reactor components, and components in advanced Brayton cycle power systems. Long term creep, thermal stability, weldability, and alkali metal corrosion tests are currently in progress under NASA sponsorship to provide the design data necessary for the successful utilization of this material in a wide variety of space power system applications.

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TABLE II-1. - SUMMARY OF MECHANICAL PROPERTIES OF T-111, T-222, AND ASTAR-811C

Property	T-111 (Ta-8W-2Hf)	T-222 (Ta-10W-2.5Hf-0.01C)	ASTAR-811C (Ta-8W-1Re-1Hf-0.025C)
0.2 Percent offset yield strength, psi			
-320° F	131 000	181 000	147 000
75° F	68 600	109 200	85 000
2000° F	30 000	42 200	35 000
2400° F	26 400	40 200	30 400
Creep strength - time to strain 1 percent at 2400° F and 15 000 psi, hr	20	80	260
Ductile brittle transition temperature, °F			
Base metal	<-320	<-320	<-320
As-TIG welded	<-320	-250	-150 to -250

Figure II-1. - Effect of carbon on as-cast hardness of Ta-W-Hf compositions. (Open symbols, good forgeability; closed symbols, poor forgeability.)

Figure II-2. - Effect of carbon on ductile-brittle transition temperature of As-TIG-welded experimental Ta-W-Hf-C alloy sheet.

Figure II-3. - Effect of rhenium on creep properties of Ta-W-Hf alloys tested at 2400° F and 15 000 psi. Specimens annealed 1 hour at 3000° F prior to test.

Figure II-4. - Effect of carbon on creep behavior of Ta-W-Hf alloys at 2400° F and 15 000 psi.

Figure II-5. - 2400° F creep behavior of Ta-W-Hf-C alloys. Tantalum base 9W 0.5Hf 0.02-0.10C alloy annealed 1 hour at 3000° F prior to testing.

Figure II-6. - Effect of composition on creep behavior of experimental tantalum alloys. Test temperature, 2400° F; stress, 20 000 psi.

Figure II-7. - Larson-Miller plot comparing time to 1 percent elongation for tantalum alloys.

Figure II-8. - Tensile properties of ASTAR-811C.

Figure II-9. - Effect of substitutional solute level on creep properties and room temperature elongation of Ta-8-16W-1-2Re-0.7Hf-0.025C alloy rod. Annealed 1 hour at 3300°F prior to test.

Figure II-10. - Creep properties of experimental tantalum base alloy rod.

Figure II-11. - Creep properties of refractory metal alloys.