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MECHANICAL PROPERTIES AND STRUCTURE OF OXYGEN-DOPED TANTALUM-BASE ALLOY

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C. T. Liu, H. Inouye, and R. W. Carpenter

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MECHANICAL PROPERTIES AND STRUCTURE OF OXYGEN-DOPED TANTALUM-BASE ALLOY

C. T. Liu, H. Inouye, and R. W. Carpenter

ABSTRACT

Effects of oxygen doping on the mechanical properties and structure of Ta-8% W-2% Hf (T-111) alloy were studied. Internal oxidation treatments were performed on 0.02-in.-thick sheet material at 1000°C and 1 to 2×10^{-5} torr dynamic oxygen pressure. After being doped, the specimens were heat treated at various temperatures. Calculations based on the lattice parameter measurement indicate that the oxygen solubility in T-111 is low and equal to 100 ppm at 1700°C. The tensile properties of oxygen-contaminated specimens were determined in vacuum at temperatures to 1316°C (2400°F). Specimens heat treated at 1700°C varied little in mechanical properties with oxygen content up to 3500 ppm. Beyond this level, the strength increased and ductility decreased abruptly with oxygen contamination. Heat treated T-111 lost its ductility completely when the oxygen content reached 4200 ppm; in contrast, the as-doped T-111 was brittle at an oxygen level of only 800 ppm. An extremely fine coherent precipitate was observed in electron micrographs of as-doped specimens. It coarsened upon annealing at or above 1400°C and eventually formed discrete HfO_2 particles. The structure and mechanical properties are correlated.

INTRODUCTION

The high melting point, proven fabricability and weldability, and excellent strength at elevated temperatures have contributed to the selection of T-111, a tantalum-base alloy containing 8 wt % W and 2 wt % Hf, as an encapsulating strength member for the isotopic fuel in a thermoelectric generator. The basic requirement is that it contain the radioisotopic fuel, $^{238}\text{PuO}_2$, for a normal service life of several years and also survive severe earth impact on reentry from space. Unfortunately, T-111 and other tantalum- and niobium-base alloys readily pick up interstitial elements from low-pressure active gases,¹⁻⁴ and contamination in the part per million (ppm) range markedly degrades their physical and

mechanical properties.^{2,3,5-7} In this application, the contamination can come from decomposition of the oxide fuel and/or release of gaseous impurities from graphite and the insulator materials, such as Min-K 1301, contained in the system. The effect of oxygen contamination is of most concern among the interstitial species, since mockup tests of heat sources showed an increase in the oxygen content in T-111 after exposure to the heat-source environment. This is because T-111 readily reacts with oxygen, even at extremely low partial pressures encountered in these tests.

A literature survey revealed little information^{5,6} on the mechanical properties of oxygen-contaminated T-111. More recent partial studies in this area have resulted in a confusing and to some degree inconsistent picture. This has resulted from a failure to appreciate the effect of thermal history, which Stoner⁵ found to be very significant in oxygen-contaminated welds.

As part of a general research and development project in support of radioisotope heat source programs, we studied in detail the effect of oxygen contamination on the mechanical properties of T-111. An oxygen doping temperature of 1000°C was chosen since it represents one of the possible operating temperatures. To simulate the reentry heat pulse, a set of specimens was heat treated 15 min at 1700°C after oxygen doping and tested at potential impact temperatures up to 1316°C (2400°F).

EXPERIMENTAL

The T-111 alloy plate 1/8 in. thick, whose chemical composition is listed in Table 1, was annealed 1 hr at 1650°C and cold rolled to 20-mil-thick sheet, from which tensile specimens with a gage section of $1 \times 1/8$ in. were stamped. After recrystallization for 1 hr at 1500°C, the specimens were suspended on a platinum fixture inside the furnace and doped with oxygen at a pressure of 1 to 2×10^{-5} torr at 1000°C. The system is capable of producing a vacuum of 1×10^{-7} torr. The reaction time was used to control the degree of oxygen doping, and the oxygen content was determined by both chemical analysis and weight gain of the specimens.

After oxygen doping, the specimens were heat treated in a vacuum of 1×10^{-6} torr in an induction furnace held at temperatures of 1400

Table 1. Chemical Composition of
As-Recrystallized T-111^a

Element	Content (wt %)	Element	Content (ppm)
W	7.98	O	25
Hf	2.02	C	25
Nb	0.02	N	8
Mo	0.04	H	1

^aBalance, tantalum.

and 1700°C. The anneal was ended by dropping the specimens out of the hot susceptor. The microstructure of the specimens was examined by both optical and electron microscopy. Disk specimens for electron transmission were first electrolytically dimpled on each side in a solution of 950 cm³ methyl alcohol, 50 cm³ H₂SO₄, and 2 cm³ HF. Final electrothinning was carried out in a cold (-5°C) electrolyte of one part H₂SO₄ in 5 parts methyl alcohol, using a platinum cathode and a current of 0.5 A. Suitable foil was examined by use of a Hitachi electron microscope operating at 650 kV. The metallographic specimens were prepared by vibratory polishing and were etched with a solution of 10 cm³ lactic acid, 2 cm³ HF, and 2 cm³ HNO₃.

The microhardness at room temperature was measured on the mounted specimens with a load of 75 g. Each reported DPH value is an average of 2 to 3 hardness indentations. X-ray diffraction was used for accurately measuring the lattice parameter of the bcc solid solution and for identifying the oxide phase. The diffraction patterns of needle specimens were made with filtered copper radiation and a 114.6-mm Debye-Scherrer camera.

To perform the tensile test at elevated temperatures, a quartz-tube vacuum system was attached to the Instron machine and the specimens were heated by radiation from an inductively heated tantalum susceptor under vacuum below 10⁻⁵ torr. The temperature was controlled with a current-adjusting device and measured with a Pt vs Pt-10 wt % Rh

thermocouple located on the center of the specimen. The load-time curve was recorded automatically on the Instron chart, from which the stress-strain curves were calculated. An extensometer was also used to obtain the accurate room-temperature strain of the specimens isothermally annealed at 1400°C. For minimizing the annealing effect during tensile testing, the specimens were heated rapidly when the temperature exceeded 900°C. For instance, to heat from 900°C to 1316°C took less than 5 min, and the testing was finished within 2 min.

The fracture surfaces of the tensile specimens were examined with a JEOL-U3 scanning electron microscope operated at 25 kV. The fractographs were taken in the magnification range of 100 to 10,000×

RESULTS

Oxygen Doping Rate

The oxygen level in the doped specimens was determined primarily from the weight gain. A few specimens were analyzed chemically, and the weight gain correlated well with chemical analysis. There was no apparent change in concentration of nitrogen, carbon, and hydrogen.

The oxygen content in the specimens doped at 1000°C and 1×10^{-5} torr oxygen pressure increased linearly with time at an average rate of 80 ppm/hr. A few tests run at different temperatures and oxygen pressures showed that the doping rate was not sensitive to temperature between 825 and 1200°C but was proportional to the oxygen pressure and inversely proportional to the specimen thickness. These results clearly indicate that the rate of internal oxidation in T-111 is governed by the kinetics of gas-metal interaction^{4,8} at the metal surface and is not controlled by volume diffusion in the solid, whose rate is strongly temperature dependent.

X-Ray Data

The lattice parameter (a_{β}) of the bcc phase in specimens annealed 15 min at 1700°C after oxygen doping is presented in Fig. 1. The straight

line with a positive slope indicates what would happen to a_β if all the oxygen is retained in solution. Actually, the data points show that after a small increase (almost unobservable) a_β decreases with oxygen content. This decrease is apparently due to the removal of hafnium atoms (which are larger than tantalum and tungsten atoms) from bcc solution by the formation of hafnium-oxygen clusters, which precipitate as HfO_2 particles on high-temperature annealing. The HfO_2 , which has a high-temperature tetragonal structure,⁹ was detected in specimens containing greater than 3 at. % O. The reflection lines from the oxide phase were too weak to be detected at lower oxygen concentrations. This is possibly due to an insufficient volume of diffracting hafnium oxide. A minimum a_β value of 3.291 Å is reached when almost all the hafnium atoms are removed from the solution. Further oxygen doping causes the oxygen to go into interstitial positions and increases the parameter of the tantalum-tungsten-base solution. A detailed discussion of this and the calculation of the two curves in Fig. 1 will be presented later.

The microstructure of internally oxidized T-111 varies with thermal treatment. Fig. 2 compares microstructures of specimens after recrystallization and after doping with 300 ppm O. Both specimens have the typical recrystallized structure with no precipitation within the grains or along grain boundaries. However, a high density of extremely fine Hf-O zones of

Fig. 2. Optical Micrographs of the Specimens. (a) As recrystallized, and (b) as doped with 800 ppm O.

about 50 Å is observed in the TEM (Fig. 3). These zones are coherent with the matrix and distributed uniformly throughout the grains. Figure 3(b) shows the formation of a thin layer of PFZ (precipitation-free zone) adjacent to a grain boundary. No apparent precipitate is observed along the grain boundary.

Upon annealing at 1400°C, the fine Hf-O zones shown in Fig. 4(a) coarsen and eventually grow into discrete precipitate particles with a rectangular cross section, as shown in Fig. 4(b). The noncoherent particles have already begun to appear along grain boundaries after a 5-min anneal [Fig. 4(a)]. It is interesting to note that the precipitate near the grain boundary in Fig. 4(a) is finer than that away from it.

Three specimens containing increasing amounts of oxygen were annealed 15 min at 1700°C and the microstructures are shown in Fig. 5. No variation in structure is obvious across the entire specimen. Note that the coarse precipitate is located essentially along grain boundaries. At an oxygen level above 4000 ppm, the particles are almost connected into a network along the boundaries [Fig. 5(c)]. The TEM in Fig. 6(a) shows that the globular grain boundary particles are about 0.5 μm, much larger than those within the grains. At a high magnification, Fig. 6(b) shows many intragranular precipitate particles associated with dislocations.

Microhardness

The oxygen concentration gradient in the as-doped specimens can be detected from the measurement of microhardness across the polished sample. Figure 7 shows the results of such a measurement. The as-recrystallized hardness is low and is equal to 208 DPH. No sharp drop in hardness was observed near the surface of doped specimens; instead, the hardness decreased linearly with the distance. Nevertheless, without doubt oxygen has penetrated deeply into the specimen because the hardness at the center is much higher than that of the as-recrystallized material. Note that the two curves in Fig. 7 have the same slope, -0.34 DPH/μm.

No variation in hardness was observed across the specimens annealed 15 min at 1700°C. Figure 8 shows the average DPH value as a function of

Fig. 3. Electron Micrographs of the Specimens Doped With 3000 ppm O. (a) View with grain boundaries tilted, and (b) view with grain boundary perpendicular to surface, so PFZ is not hidden.

Fig. 4. Electron Micrographs of the Specimens Isothermally Annealed (a) 5 min, and (b) 4 hr at 1400°C After Doping With 3000 ppm O.

Fig. 5. Optical Micrographs of the Specimens Heat Treated 15 min at 1700°C After Doping With (a) 810 ppm, (b) 1640 ppm, and (c) 4430 ppm O.

Fig. 6. Electron Micrographs of Specimens Heat Treated 15 min at 1700°C After Doping With 3000 ppm O.

Fig. 7. Variation of Microhardness Across the Specimens Doped With 732 and 2010 ppm O.

Fig. 8. Variation of Microhardness With Oxygen Content of the Specimens Heat Treated 15 min at 1700°C.

oxygen content of the homogenized specimens. At low oxygen concentrations, there is a very small linear increase in hardness (15.8 DPH/1000 ppm O) with increasing oxygen content up to about 3500 ppm. Above this concentration the slope of the plot abruptly increases, but again the rate is linear, at about 200 DPH/1000 ppm O. The 3500 ppm is equivalent to approximately 3.35 at. %; comparing Fig. 8 with Fig. 1 shows clearly that the abrupt change in lattice parameter also occurs at this composition.

Mechanical Properties

The mechanical properties of internally oxidized T-111 were sensitive to the thermal treatment. The results are presented in three thermal

conditions: (1) as doped at 1000°C, (2) homogenized 15 min at 1700°C, and (3) aged at 1400°C.

As-Doped Condition

The tensile properties of T-111 specimens as doped with various levels of oxygen were determined at temperatures up to 1316°C (2400°F). The results in Fig. 9 show that the yield and tensile strengths both increase with oxygen content up to about 800 ppm. The tensile-strength curves begin to drop when the specimens fracture before yielding. The elongation decreases continuously with oxygen content at room temperature, 1093 (2000°F), and 1316°C (2400°F) but is not sensitive to oxygen up to 500 ppm at 760°C (1400°F). The as-doped specimens lose their ductility completely when doped with 800 ppm O. It is surprising that the increase in testing temperature does not improve the ductility at all even in tests above the doping temperature.

Homogenized Condition

The stress-strain curves of the homogenized specimens show strain-aging effect or Protevin-Lechatelier effect (serration on the stress-strain curve) for all oxygen contents at elevated temperatures. This effect is most prominent at 760°C. The tensile data are plotted in Fig. 10 as a function of oxygen content. The elongation curves show a sharp drop up to about 100 ppm O. Beyond this level the tensile properties are not strongly sensitive to the oxygen content up to about 3400 ppm. The yield strength slightly decreases at room temperature, but the strength at elevated temperatures increases with the oxygen content. Between 100 and 3000 ppm O the specimens in the homogenized condition show a gradual reduction of ductility at room temperature and 1316°C but not as much change at 760 and 1093°C. This is very different from the as-doped results (see Fig. 9). When the oxygen content is beyond 3400 ppm, the strength increases sharply and the ductility decreases markedly. Note that the increase in strength is more pronounced at low temperatures. The homogenized T-111 loses its ductility completely at an oxygen level of 4000 to 4200 ppm, independent of testing temperature.

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Fig. 9. Tensile Data of As-Doped Specimens.

Fig. 10. Tensile Data of Specimens Heat Treated 15 min at 1700°C After Oxygen Doping.

Isothermally Aged Condition

A series of specimens doped with 3000 ppm O was annealed isothermally at 1400°C. The tensile data are presented in Table 2. Stress-strain curves are plotted in Fig. 11. The as-doped specimen fractured within the elastic limit. Upon annealing at 1400°C, the ductility increased and strength decreased continuously with time. Also the specimen began to fracture in a ductile manner after annealing for 5 min.

Table 2. Effect of Isothermal Anneal at 1400°C on the Room-Temperature Tensile Properties of T-III Doped With 3000 ppm O

Annealing Time (min)	Yield Strength (psi)	Tensile Strength (psi)	Elongation (%)	Fracture Mode
0	a	127,000 ^a	0.4 ^a	brittle
2	225,000	233,000	1.7	brittle
5	203,000	217,000	3.6	ductile
30	153,000	177,000	10.5	ductile
240	107,000	142,000	13.0	ductile

^aFractured within elastic limit.

Fig. 11. Stress-Strain Curves of the Specimens Isothermally Annealed at 1400°C After Doping With 3000 ppm O.

Scanning Electron Microscopy

The tensile specimens that had been fractured at room and elevated temperatures were examined by SEM. Figure 12 shows the typical dimple-type ductile rupture for as-recrystallized specimen. Figure 13 shows the complete fracture surface of the specimen with 8.8% elongation at room temperature as doped with 500 ppm O. The outer region consists of transgranular cleavage and intergranular separation, and a thin ductile region is near the center. With increase of oxygen to 730 ppm, no ductile region was observed, but the frequency of cleavage fracture increased significantly (Fig. 14). Figure 15 shows a remarkable place where the grain boundary separation (region A) and transgranular cleavage (region B) both occurred at the same area and propagated at the same time. The intergranular fracture becomes more active in tests at elevated temperatures. The specimen fractured at 1093°C shows almost all grain boundary separation (Fig. 16). It is surprising that some "precipitate-like" phase appears on the grain boundaries [region A, Fig. 16(b)] and grain boundary areas (region B).

Fig. 12. Fractograph of a Recrystallized Specimen Fractured at Room Temperature.

Fig. 13. Fracture Surface Across the Specimen Doped With 550 ppm O, and Fractured at Room Temperature.

Fig. 14. Fracture Surface Across the Specimen Doped With 730 ppm O, Fractured at Room Temperature.

Fig. 15. Fractograph of the Specimen As Doped With 730 ppm O, fractured at room temperature. A — Grain boundary separation, B — cleavage, and C — slip traces on the grain boundary.

Fig. 16. Fractographs of the Specimen As-Doped With 680 ppm O, Fractured at 1093°C. (a) Representative view of fracture surface, and (b) higher magnification showing precipitate-like phase on grain boundary, A, and grain boundary area, B.

In connection with an increase in ductility by homogenization, the specimen doped with 3640 ppm O shows the dimple-type ductile fracture. In this case, the discrete HfO_2 particles are observed clearly at the valleys of the crests [Fig. 17(a)]. Further increase in oxygen content reduces the roughness of the fracture surface [Fig. 17(b)]. And at an oxygen level of

Fig. 17. Fractographs of the Homogenized Specimens Doped With Oxygen:
(a) 3640 ppm, (b) 4050 ppm, and (c) 5150 ppm.

5150 ppm, the fracture surface shows complete grain boundary separation on which numerous disk-shaped particles are observed [Fig. 17(c)].

DISCUSSION

State of Oxygen in Internally Oxidized T-111

Both x-ray diffraction and TEM indicate that the hafnium oxide begins to form in T-111 when the oxygen level exceeds the solubility limit. The mechanical properties of internally oxidized T-111 depend largely on the amount of oxygen retained in solution and the amount of oxygen precipitated as oxide. The state of oxygen in the alloy is determined from the thermodynamic calculations proposed recently by Liu, Inouye, and Carpenter.¹⁰ This method, originally used to calculate the distribution and solubility limit of interstitials in binary substitutional solid solutions, is now extended to the ternary alloy Ta-W-Hf.

Let X_{Hf} be the atom fraction of hafnium and X_{M} the atom fraction of tantalum-tungsten solid solution; $X_{\text{M}} + X_{\text{Hf}} = 1$. If one considers that the formation of the interstitial compound, HfO_2 , within the volume of solution is analogous to the chemical reaction,

the thermodynamic equation that describes this reaction can be written¹⁰ as

$$\left[\frac{(1 - X_0)X_{\text{Hf}} - y}{1 - 3y} \right] \left(\frac{X_0 - 2y}{1 - 3y} \right)^2 = X_{\text{Hf}} (1 - X_0^*) X_0^{*2} = K, \quad (2)$$

where X_0 in atom fraction denotes the total amount of oxygen added, y the amount of hafnium taken out of the bcc solution (referred to as β solution), X_0^* the solubility limit of oxygen in T-111; K is a reaction constant related to the chemical equilibrium constant and the activity coefficient. The calculation of X_0^* and K requires y , which can be determined from the expression for the influence of interstitial and

substitutional additions on the lattice parameter as a Taylor's series expansion retaining only the first-order terms:

$$a_{\beta} = a_M + b_{\text{Hf}} \left[\frac{(1 - X_0)X_{\text{Hf}} - y}{1 - 3y} \right] + b_O \left[\frac{X_0 - 2y}{1 - 3y} \right], \quad (3)$$

if the lattice parameter of β solution, a_{β} , is measured from a specimen containing a known level of oxygen, X_0 . Here, a_M is the lattice parameter of the tantalum-tungsten alloy base, and b_{Hf} and b_O are the change of lattice parameter of tantalum-tungsten base per unit atom fraction of hafnium and oxygen, respectively.

The first step in calculating X_0^* and K is to find the proper lattice parameters in Eq. (3). The addition of interstitial oxygen and substitutional hafnium in the tantalum-tungsten alloy base increases the lattice parameter. Based on the literature data of 0.320 Å for hafnium in tungsten¹¹ and 0.230 Å for hafnium in tantalum,¹² an interpolated value of $b_{\text{Hf}} = 0.236$ Å is obtained for Ta-8% W alloy. The oxygen solubility limit in tungsten metal is very low, so no lattice parameter data are available for tungsten-oxygen system. Thus, $b_O = 0.458$ Å for pure tantalum metal¹³ is used for calculations in Eq. (3). For a check, putting the b values and a_{β} for as-recrystallized T-111 in Eq. (3) gives $a_M = 3.2900$ Å for Ta-8% W alloy. This value agrees well with the lattice parameter value reported by Schramm et al.¹⁴ Substituting all the lattice parameters in Eq. (3) gives

$$a_{\beta} = 3.2900 + 0.236 \left[\frac{(1 - X_0)X_{\text{Hf}} - y}{1 - 3y} \right] + 0.458 \left[\frac{X_0 - 2y}{1 - 3y} \right], \quad (4)$$

for T-111 doped with oxygen.

The lattice parameters in Fig. 1 are used to determine the oxygen solubility in T-111 at 1700°C. The X_0^* values calculated by Eqs. (2) and (4) are presented in Table 3; the average value is 0.0008. There is no systematic change of X_0^* with X_0 , so the average value of X_0^* is considered to be independent of X_0 . The calculated X_0^* is much lower than the oxygen solubility in pure tantalum, which has been reported¹³ to be about 5 at. % at 1700°C. The low oxygen solubility in T-111 must be due to the

stronger chemical affinity of oxygen for hafnium than for tantalum or tungsten. This can be verified from the thermodynamic data of oxides:¹⁵ the standard free energy of formation of HfO_2 (-126.1 kcal/g-at. O) is appreciably more negative than that of either WO_2 (-61 kcal/g-at. O) or Ta_2O_5 (-91.3 kcal/g-at. O), the oxides precipitated from the metal-oxygen alloys. It should be noted that the calculated X_0^* value here is in excellent agreement with the reported^{10,16} oxygen solubility limits in niobium-base alloys containing 1 to 5% Hf or Zr. These alloys are chemically similar to T-111. Also, Buckman and Ammon¹⁷ have found almost nil oxygen solubility in Ta-W-Hf alloys.

The constant K corresponding to the average X_0^* is 1.3×10^{-8} . Putting this value in Eq. (2), we calculated the curve of lattice parameter vs oxygen content by solving the simultaneous Equations (2) and (4). As shown in Fig. 1, the calculated curve is in good agreement with the data points, and the minimum occurs at 3.85 at. % (3500 ppm) oxygen. The calculations show clearly that beyond X_0^* the drop of a_β with X_0 is due to the precipitation of hafnium oxide from beta solution. The minimum value is reached when the decrease in a_β due to removal of hafnium from solution is balanced by the increase due to retention of interstitial oxygen. Because of the extremely low value of K (which reflects the strong affinity between hafnium and oxygen), the oxygen in beta solution increases significantly only when all the hafnium atoms are scavenged. Thus, the minimum lattice parameter occurs at an oxygen-to-hafnium atom ratio close to 2. Beyond 3.9 at. %, additional oxygen will begin to remain in solution and sharply increase a_β , as shown in Fig. 1.

Table 3. Calculation of Oxygen Solubility Limit X_0^* for T-111 Specimens Homogenized and Quenched From 1700°C After Doping With Different Levels of Oxygen

X_0 (Atom Fraction)	a_β (Å)	y (Atom Fraction)	X_0^* (Atom Fraction)
0.0371	3.2911	0.01816	0.0003
0.0287	3.2919	0.0139	0.0006
0.00995	3.2945	0.00426	0.0013
0.00414	3.2950	0.00147	0.0010

Correlation Between the Structure and Mechanical Properties

The results show that the thermal history alters the nature and morphology of the oxide precipitate and has a large effect on the mechanical properties of internally oxidized T-111. The correlation between the tensile properties and the structures obtained from various thermal treatments is described below.

Embrittlement of As-Doped Specimens

The lattice parameter calculations show that oxygen in excess of the solubility limit reacts with hafnium to form Hf-O zones with an effective composition HfO_2 . These coherent zones in the as-doped condition are extremely fine ($\approx 50 \text{ \AA}$) and are distributed uniformly throughout the grains (Fig. 3). Similar zone structures have been observed² in the internally oxidized Nb-1% Zr alloy. Microhardness measurements (Fig. 7) indicate the presence of an oxygen concentration gradient, but some of the oxygen has already penetrated to the core of the 0.02-in.-thick specimens, even at a level of 700 ppm. Examination by TEM reveals no difference in zone structure across the specimen doped with 3000 ppm O.

The small coherent precipitate particles act as effective barriers to the motion of dislocations; thus the strength of as-doped specimens increases with oxygen content up to a maximum of about 800 ppm (Fig. 9). Beyond this concentration, the ductility of the specimens is almost nil and the specimens fail by brittle fracture, regardless of the test temperature. Transgranular cleavages are observed in the specimen containing 550 ppm O (Fig. 13). The occurrence of this mode of fracture may result from the hardening of grain interior (by numerous coherent zones) to such a degree that the yield strength reaches the level of the cleavage strength of the material. In agreement with this mechanism, the frequency of cleavage increases significantly with oxygen content, as shown in Fig. 14. There is no doubt that intergranular fracture is also an active failure mode in the as-doped specimens (Figs. 13-15). Since no apparent precipitate is observed on the grain boundaries (see Figs. 3 and 13), intergranular fracture is possibly caused by either retention of a high level of oxygen in solution near the grain boundary or the formation of a precipitate-free zone (PFZ) adjacent to the grain boundary. If the embrittlement is due to the first mechanism, we should expect a decrease in frequency and

eventually the disappearance of intergranular fracture with an increase in testing temperature. However, examination of the fracture surface reveals the opposite case (Fig. 16). We thus believe that intergranular fracture is caused by the second mechanism. The following observations and arguments support this assertion.

1. A PFZ is observed in the as-doped specimens [Fig. 3(b)].
2. With an increase in the testing temperature, the PFZ is expected to decrease in strength at a faster rate than the grain interiors, which are full of hard precipitate. This would then concentrate further deformation in the PFZ and promote the intergranular fracture at high temperature, as shown in Fig. 16, and produce slip traces on certain fracture boundaries, as shown in Fig. 15.
3. This fracture mode provides a plausible explanation of the "precipitate-like" phase on the fractured surface in Fig. 16. Thus the "precipitate-like" phase on grain boundaries is actually the PFZ after ductile rupture at high temperatures.

As shown in Fig. 9, the ductility at 760°C is not sensitive to the oxygen level up to 500 ppm, but the ductility at the other three temperatures decreases continuously. This difference in behavior can be rationalized from examination of the fracture process and deformation character of T-111. On plastic deformation, macroscopic cracks formed on the edges and surfaces, which contain a higher level of oxygen and are therefore more brittle. The propagation of these cracks through the ductile core reduces the overall ductility at room temperature, 1093, and 1316°C. The strain-hardening exponent and difference in ultimate and yield strength, reported by Sheffler et al.,¹⁸ are plotted as functions of testing temperature in Fig. 18. Both curves have a maximum value at around 800°C. This indicates that surface cracks formed at low stress levels do not readily propagate at 760°C because the ductile core can absorb the stress increment resulting from the formation of macroscopic surface cracks. To demonstrate this, we doped three specimens with 300 ppm O at 825°C* and tested them at various temperatures. Figure 19 shows numerous cracks on the specimen fractured at 825°C and very few at room temperature and 1093°C.

*The low doping temperature was chosen because it produces a sharp oxygen gradient on the surface.

Fig. 18. Strain Hardening Exponent and Difference in Ultimate and Yield Strength as Functions of Testing Temperature.

Fig. 19. Appearance of the Specimens Doped With 300 ppm O at 825°C, Fractured at: A, Room Temperature; B, 825°C; C, 1093°C.

Mechanical Properties of Homogenized Specimens

Annealing the oxygen-doped alloy 15 min at 1700°C homogenizes the oxygen in the specimen and coarsens the oxide precipitate. The microstructure in Fig. 5 and the microhardness measurement across the specimen both prove that the oxygen gradient is eliminated by this treatment.

The plot of tensile data in Fig. 10 shows three distinct sections on the curves; the correlation between the mechanical properties and structural feature for each section is discussed in terms of oxygen content.

Oxygen content within 100 ppm. — The theoretical calculations and lattice parameter measurements indicate that the oxygen solubility in T-111 is extremely low. Thus, the sharp drop in ductility up to 100 ppm is due to the retention of a small amount of oxygen in solution.

Oxygen content between 100 and 3400 ppm. — As shown in Fig. 10, the tensile properties of T-111 vary little with the oxygen content between 100 and 3400 ppm. In this range because the oxygen reacts with hafnium to form HfO_2 and very little is retained in bcc solution, the mechanical properties are affected by both precipitation of oxide and scavenging of hafnium from solution. The precipitates in the homogenized specimens are coarse and noncoherent; therefore their strengthening effect is small. It seems that the solid-solution strengthening is more pronounced at room temperature, and the yield strength shows a small drop with oxygen content (Fig. 10). At elevated temperatures the particle-strengthening becomes prominent, and the yield strength increases with oxygen content. Note that this decrease in room-temperature yield strength does not contradict the increase in hardness shown in Fig. 8, since the hardness corresponds to the flow stress at 8% strain.¹⁹

In contrast with the as-doped results, the homogenized specimens show only little or no reduction of ductility with oxygen content. This is because the matrix of each grain is "ductilized" by coarsening of the precipitate within the grains. These large, noncoherent particles do not inhibit the dislocation movement during deformation as do the smaller ones; this eliminates the brittle cleavage fracture. The large globular grain boundary particles [Fig. 6(a)] do not seriously embrittle the grain boundary. Examination of the fracture surface shows that the fracture process in the

internally oxidized T-111 is similar to that in alloys containing rigid particles;^{20,21} that is, the fracture initiates by nucleation of cracks around the oxide particles, on further deformation the cracks grow into cavities containing the particle, and finally the cavities link to create the unique structural feature shown in Fig. 17(a), where each HfO_2 particle is located in a dimple.

Oxygen content above 3400 ppm. — The strength increases sharply and the ductility decreases seriously with oxygen content above 3400 ppm. A sharp change in hardness is also observed at 3500 ppm (i.e. 3.85 at. %) as shown in Fig. 8. These results are in excellent agreement with the lattice parameter calculations, which show that at this composition essentially all of the hafnium has been precipitated as HfO_2 , leaving a Ta-8% W solid solution. Beyond this concentration level, the oxygen remains in interstitial positions of the bcc lattice, rapidly increasing the lattice parameter and sharply changing mechanical properties. In general, solid-solution strengthening is most significant at low temperatures, which is consistent with the results in Fig. 10.

The homogenized specimens lose their ductility completely at an oxygen level of 4000 to 4200 ppm. At this point we might conclude that about 800 ppm O occupies interstitial positions and could possibly account for the observed embrittlement. However, we rule out this possibility because an increase in testing temperature does not improve the ductility (Fig. 10); that is, for the oxygen-doped T-111 there is no "ductile-to-brittle transition temperature" as is generally observed for the interstitially embrittled refractory metals and alloys.^{22,23} Based on the microstructure in Figs. 5(c) and 17(c), we believe that the brittle fracture of homogenized T-111 is due to the fact that a significant fraction of the grain boundary area is occupied by oxide particles.

Ductilization by Isothermal Treatment

To study the effect of precipitation growth on the mechanical properties, the specimens doped with 3000 ppm O were annealed isothermally at 1400°C. The small zones initially formed in as-doped specimens coarsen upon annealing at this temperature (Fig. 4). The strain contrast in TEM

indicates that the precipitates become partially coherent with the matrix after 5 min and completely lose their coherency around 4 hr. These changes are responsible for the decrease in strength with time, as shown in Fig. 11. The as-doped specimen fractured within the elastic limit. The ductility recovers gradually as the precipitate coarsens and the PFZ widens upon annealing. Embrittlement due to the PFZ should be reduced when its width is comparable to the interparticle spacing. Tensile elongation and particle size seem to correlate. The specimen begins to show ductile fracture with 3.6% elongation upon annealing 5 min, which gives particle sizes about $1.5 \times 10^{-2} \mu\text{m}$. The ductility is 13% at a particle size of about $4 \times 10^{-2} \mu\text{m}$. And the ductility further increases to 19% when the particle size in the homogenized specimen is about $8 \times 10^{-2} \mu\text{m}$.

SUMMARY AND CONCLUSIONS

1. The 0.02-in.-thick sheet specimens of T-111 were doped with different levels of oxygen up to 5000 ppm at 1000°C in a dynamic oxygen pressure of 1 to 2×10^{-5} torr.
2. The oxygen doping rate was not sensitive to the doping temperature but was proportional to the gas pressure and doping time and inversely proportional to the thickness of the specimen. These results indicate that the rate of oxygen uptake in T-111 is governed by the kinetics of gas-metal interaction at the metal surface, and is not controlled by the diffusion of oxygen in the solid, which has a strongly temperature-dependent rate.
3. The tensile properties of internally oxidized T-111 were very sensitive to thermal treatment that alters the nature and distribution of the oxide (HfO_2) precipitates.
4. Extremely fine oxide zones about $50 \text{ \AA}$ wide, uniformly distributed throughout the grains, formed in the as-doped specimen.
5. Upon annealing at or above 1400°C, these zones coarsened and eventually grew into discrete rectangular particles of HfO_2 .
6. The mechanical properties of as-doped specimens were sensitive to the oxygen contamination level. The strength increased and ductility decreased with oxygen content. The alloy T-111 completely lost its ductility at about 800 ppm O, and an increase in testing temperature up

to 1316°C (2400°F) did not improve the ductility. The as-doped embrittlement was due to the formation of PFZ near the grain boundaries and the hardening of the grain volume by numerous tiny coherent zones. Both intergranular fracture and transgranular cleavage were observed on the surface of the brittle-fractured specimen. Intergranular fracture became the dominant mode of fracture at elevated temperatures.

7. Both microstructural examination and microhardness measurement indicated that the oxygen gradient formed in the as-doped condition was eliminated by annealing 15 min at 1700°C.

8. The mechanical properties of homogenized specimens depend on the amount of oxygen retained in solution and the amount of oxygen precipitated out as oxide.

9. Calculations based on lattice parameter measurements show that the oxygen solubility in T-111 is low and equal to 100 ppm at 1700°C. Beyond the solubility limit, the oxygen reacts with hafnium to form an oxide with an effective composition HfO_2 . When almost all the hafnium atoms are scavenged out of solution by doping with 3500 ppm (3.85 at. %) O, any additional oxygen doped will remain in solution, which causes a sharp increase in the lattice parameter of the remaining Ta-8% W base.

10. In contrast to the as-doped results, the tensile properties of homogenized specimens were not sensitive to the oxygen content up to 3500 ppm. This is because precipitates coarsen by this treatment. In agreement with the lattice parameter calculations, the strength increased sharply and ductility decreased markedly beyond 3500 ppm because additional oxygen was retained in solution. The homogenized T-111 lost its ductility completely at about 4200 ppm O.

11. To study the growth kinetics of the oxide precipitate, a series of specimens doped with 3000 ppm O was annealed isothermally at 1400°C. The specimen, which is extremely brittle in the as-doped condition, can be ductilized by a 5-min anneal at 1400°C. An increase in the room-temperature ductility with increasing oxide particle size was observed.

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