



# Effects of oxygen and oxidation on tensile behavior of V–4Cr–4Ti alloy

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## Abstract

Vanadium-base alloys are potential candidates for applications such as the first wall and other structural components of fusion reactors, but a good understanding of the oxidation behavior of the alloys intended for elevated-temperature use is essential. We conducted a systematic study to determine the effects of time and temperature of air exposure on the oxidation behavior and microstructure of V–4Cr–4Ti alloy. Uniaxial tensile tests were conducted at room temperature and at 500°C on preoxidized specimens of the alloy to examine the effects of oxidation time and oxygen migration on maximum engineering stress and uniform and total elongation. The effect of preexposure of the specimens to environments with varying oxygen partial pressures on the tensile properties of the alloy was investigated. Extensive microstructural analyses of the oxygen-exposed/tensile-tested specimens were conducted to evaluate the cracking propensity for the alloy. In addition, tensile-property data for the alloy were correlated with oxygen pressure in the exposure environment, test temperature, and exposure time. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Vanadium-base alloys nominally containing 4–5 wt% chromium and 4–5 wt% titanium have been identified as the most viable materials for fusion reactor applications because they have lower long-term activation, lower irradiation afterheat, lower biological hazard potential and thermal stress factor, better creep resistance, compatibility with coolants such as liquid alkali metals, and better mechanical formability. A primary deterrent to the use of vanadium-base alloys at elevated temperatures is their relatively high affinity for interstitial impurities, i.e., oxygen, nitrogen, hydrogen, and carbon. In particular, oxygen (the subject of this paper) may degrade alloy properties during service through dissolution in the matrix or formation of oxide particles in the matrix, along the grain boundaries, and/or on the surface of the alloys. Therefore, a good understanding of the oxidation behavior of the alloys intended for elevated-temperature use is of significant importance.

Recently oxidation studies were conducted on V–5Cr–5Ti (designated as 55) alloy specimens at several temperatures in an air environment [1,2]. The oxidation process followed a parabolic rate law. The oxide scale exhibited a dual layer, with the outer layer predominantly vanadium oxide and the inner layer (V,Ti) oxide. Subsequently, another study was conducted to determine and compare the air-oxidation behavior of V–4Cr–4Ti (designated as 44) and 55 alloys in the temperature range of 300–650°C [3]. Models describing the oxidation kinetics, oxide type and its thickness, alloy grain size, and depth of oxygen diffusion in the substrate alloy were determined for the two alloys and compared. From the results obtained, the following conclusions are drawn:

- The oxide that formed on either alloy was predominantly V<sub>2</sub>O<sub>5</sub> with some VO<sub>2</sub> and/or a complex (V, Cr, Ti) oxide possibly also present.
- Oxide scales on both alloys were continuous and tenacious, and the oxidation kinetics followed a parabolic or a nearly parabolic nonlinear growth rate law.
- The 55 alloys were consistently more oxidation-resistant than the 44 alloys, and the difference in their oxidation resistance increased with increasing temperature above 500°C.

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- Oxygen diffusion was faster in the 44 alloy than in the 55 alloy. However, the activation energies of diffusion of oxygen in both alloys were within 5% of one another.
- The microstructures of both alloys were quite stable, because no measurable grain growth was observed in either after 2100 h at 500°C or after  $\approx 200$  h at 650°C.

The present paper examines the oxidation performance of 44 alloy in environments with various oxygen partial pressures. In addition, the effect of preexposure of the specimens to environments with various oxygen partial pressures on the tensile properties of 44 alloy was investigated. Extensive microstructural analyses of the oxygen-exposed/tensile tested specimens were conducted to evaluate the cracking propensity for the alloys. In addition, tensile-property data for the alloy were correlated with oxygen pressure in the exposure environment, test temperature, and exposure time.

## 2. Experimental procedure

The 44 alloy was obtained as 1-mm-thick cold-rolled sheets. Tensile specimens were fabricated according to ASTM specifications and had a gauge length of  $\approx 19$  mm and a gauge width of  $\approx 4.5$  mm. Before any further treatment or testing, all samples were annealed for 1 h at 1050°C under a pressure of  $\approx 10^{-6}$  Torr. Grain size of the 44 alloy specimens was  $\approx 20$   $\mu\text{m}$ . Coupon specimens of annealed alloy were enclosed in quartz or vycor capsules in vacuum and exposed for several time periods at temperatures between 500°C and 1000°C. After the exposures, the specimens were mounted in cross section and grain sizes were determined by linear and areal analysis methods according to ASTM Standard E112.

The uniaxial tensile specimens were preoxidized in air at 500°C for 24 to 2060 h prior to tensile testing in air at room temperature and at 500°C. The preoxidized specimens were tested at a strain rate of  $1.8 \times 10^{-4} \text{ s}^{-1}$ . Total elongation was measured with a vernier caliper and by using load/elongation chart records. The fracture surfaces, longitudinal and axial cross sections of tested specimens were examined by scanning electron microscopy (SEM).

Tensile samples of the alloy were also exposed to several environments with oxygen partial pressures in a range of  $1 \times 10^{-6}$  to 760 Torr and to 99.999% pure He for 250–275 h at 500°C and were subsequently tensile-tested at a strain rate of  $1.8 \times 10^{-4} \text{ s}^{-1}$  in air at room temperature or 500°C. The oxide scales on the samples were identified by X-ray diffraction (XRD) analysis on the surface of several samples, as well as on the oxides scraped from their surfaces. Longitudinal and transverse cross sections of the tested specimens were examined by SEM.

## 3. Results and discussion

### 3.1. Grain size measurements

The grain size of a material and the grain growth rate for the material as a function of temperature and exposure time can influence the mechanical properties of the material, as well as the transport of interstitial elements such as O, C, N, and H. A finer grain size can lead to increased diffusion of interstitials via grain boundaries, with a resultant increase in total concentration of the interstitial elements. On the other hand, grain boundary diffusion of these elements can also result in fine precipitates of second-phase particles that can pin the grain boundaries and thereby stabilize the microstructure over extended periods of time.

Fig. 1 shows the measured grain size values as a function of exposure time for 44 alloy after exposure at 500°C, 650°C, 800°C, and 1000°C. Grain size measurements showed virtual absence of grain growth at 500°C, 650°C, and 800°C after  $\approx 5000$  h. The initial grain size of the alloy was in the range of 18–20  $\mu\text{m}$  and changed little with exposure. At 1000°C, the alloy showed no grain growth after 100 h and 600 h but showed an increase to 62–84  $\mu\text{m}$  after 2000 h. Preliminary examination of the specimens exposed at 650°C for 5000 h by transmission electron microscopy indicated a distribution of fine precipitates of vanadium–nitrogen [ $\approx(\text{Ti},\text{V})_3\text{N}$ ] phase along either side of grain boundary, which probably makes the boundary immobile.

### 3.2. Effect of oxidation in air on tensile properties

To evaluate the effect of oxide scale formation and oxygen penetration into the substrate alloy, the tensile behavior of the alloy was examined as a function of oxygen ingress and oxide scale formation. Tensile-test

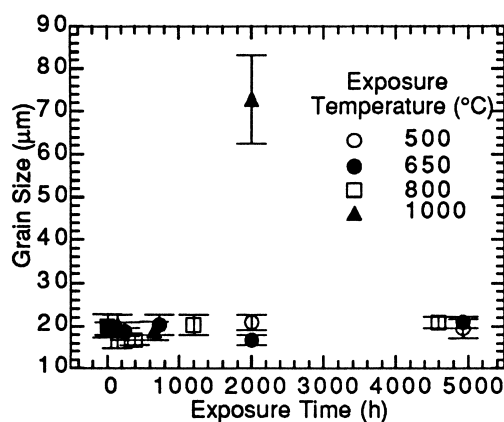


Fig. 1. Grain size variation in 44 alloy as a function of time and temperature.

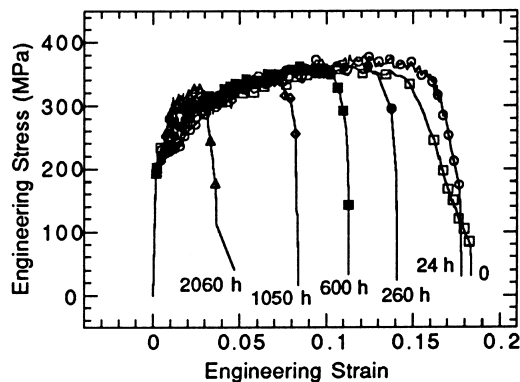


Fig. 2. Effect of preoxidation at 500°C on stress-strain behavior of 44 alloy tested at 500°C in air at a strain rate of  $1.8 \times 10^{-4} \text{ s}^{-1}$ .

data were reported earlier for 55 alloy specimens exposed to air for 24–2060 h at 500°C and then tensile-tested in air at either room temperature or at 500°C [1,2]. Similar exposures to air were made for tensile specimens of 44 alloy and subsequently tensile tested at 500°C in air.

Fig. 2 shows the engineering stress/engineering strain curves at 500°C for specimens after oxidation for several exposure times in the range of 0–2060 h. The maximum engineering stress, uniform elongation, and total elongation for specimens with various treatments are listed in Table 1. The data indicate that the stress/strain behavior of 44 alloy is virtually unaffected by 24 h exposure in air at 500°C. As the exposure time increases to 260 h, the tensile ductility of the alloy decreases. The ductility reduction continues as the exposure time increases further to 600, 1050, and 2060 h at 500°C.

A comparison of the tensile properties of the 44 alloy with those of the 55 alloy published earlier [2] shows that for the same pretreatment, the 55 alloy exhibits 10–25% higher ultimate tensile strength at both 500°C and at room temperature. Further for the same pretreatment, the uniform and total elongation values for the 44 alloy were lower than that for the 55 alloy. For example, the

uniform elongation values at 500°C were 0.048 and 0.016 for 55 and 44 alloy specimens after 2060-h exposure to air at 500°C.

Fig. 3 shows the variations in maximum engineering stress and uniform and total elongation as a function of preoxidation time in air at 500°C for tests conducted at room temperature and 500°C. The results show that 44 alloy is inherently weaker than the 55 alloy even without oxidation, and that the influence of oxygen ingress follows the same trend in both alloys. The tensile elongation values for the two alloys at a test temperature of 500°C follows the similar decreasing trend with increasing time of oxidation. The uniform and total elongation values at room temperature are almost zero for 55 alloy oxidized for longer than  $\approx 500$  h in air at 500°C. Such data were not developed for 44 alloy, but the behavior of 44 alloy is expected to be similar, based on the similarities in oxidation kinetics for the two alloys.

### 3.3. Effect of oxidation in low $p_{\text{O}_2}$ on tensile properties

A test program is underway to evaluate the effect of partial pressure of oxygen in the exposure environment on the oxygen ingress into the V alloys and its effect on tensile properties. Specimens of 44 alloy, initially in annealed condition, were exposed for 250–275 h at 500°C in environments with various  $p_{\text{O}_2}$  levels and subsequently tensile-tested at either room temperature or 500°C. Fig. 4 shows the engineering stress/engineering strain curves at 500°C and at room temperature for 44 alloy specimens after oxidation for 250–275 h in environments with  $p_{\text{O}_2}$  in a range of  $1 \times 10^{-6}$  to 760 Torr. The maximum engineering stress, uniform elongation, and total elongation for specimens with various treatments are listed in Table 2. The exposure environments included  $p_{\text{O}_2}$  values of 760, 160, 0.15, 0.1,  $7.6 \times 10^{-4}$ , and  $1 \times 10^{-6}$  Torr. Among these, 160 and 0.15 Torr correspond to air and 99.999% He environments, respectively.

The stress/strain curves indicate that for a given exposure time and test temperature (500°C or room temperature), the  $p_{\text{O}_2}$  value in the preexposure environment

Table 1  
Effects of oxidation in air on tensile properties of 44 alloy

Exposure time (h)	Maximum eng. stress (MPa)		Uniform elongation		Total elongation		Measured crack length ( $\mu\text{m}$ )	
	RT <sup>a</sup>	500°C	RT <sup>a</sup>	500°C	RT <sup>a</sup>	500°C	RT <sup>a</sup>	500°C
	0	424	379	0.186	0.107	0.322	0.179	0
24	–	361	–	0.103	–	0.186	–	17
260	–	367	–	0.099	–	0.135	–	85
600	–	362	–	0.082	–	0.108	–	93
1050	–	341	–	0.059	–	0.075	–	137
2060	–	329	–	0.016	–	0.036	–	210

<sup>a</sup> RT = room temperature.

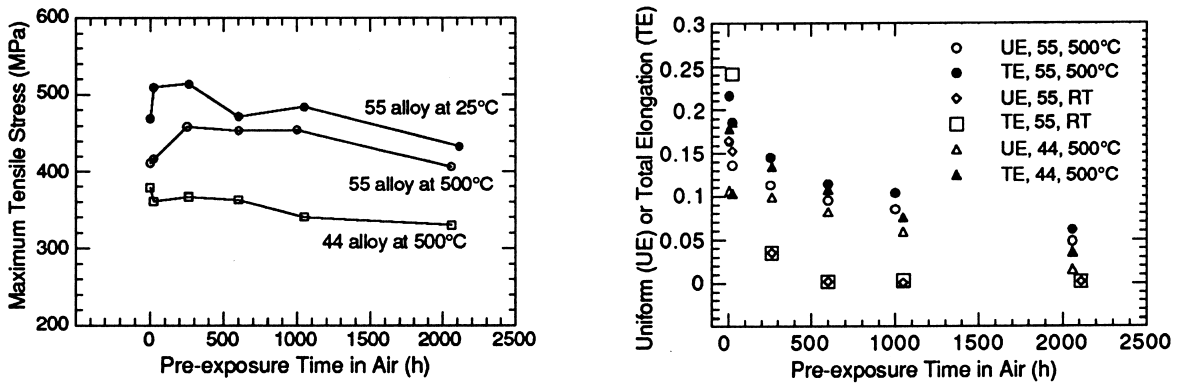


Fig. 3. Effect of preoxidation at 500°C on maximum tensile stress (left) and uniform and total elongation (right) for 44 and 55 alloys tested at 500°C and/or room temperature in air at a strain rate of  $1.8 \times 10^{-4} \text{ s}^{-1}$ .

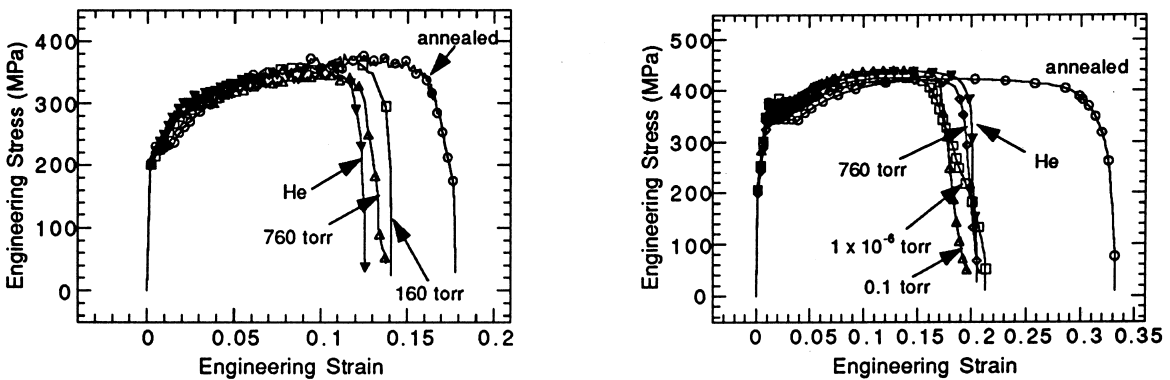


Fig. 4. Effect of oxygen partial pressure in the preexposure environment on stress–strain behavior of 44 alloy oxidized at 500°C for 250–275 h and tested at 500°C (left) and room temperature (right) in air at a strain rate of  $1.8 \times 10^{-4} \text{ s}^{-1}$ .

has very little effect on maximum engineering stress and uniform and total elongation. The results also indicate that the alloy with identical pretreatment exhibits lower values of maximum engineering stress and uniform and total elongation at 500°C than those at room temperature. For example, the maximum engineering stress values for He-exposed specimens were 438 and 359 MPa at room temperature and 500°C, respectively. The cor-

responding uniform elongation values were 0.140 and 0.089 while the total elongation values were 0.191 and 0.119. A similar trend was observed for specimens exposed to pure oxygen (Table 2).

Fig. 5 shows the variations in maximum engineering stress and uniform and total elongation as a function of  $p_{O_2}$  value in the preexposure environment for 44 alloy specimens tested at room temperature and at 500°C. The

Table 2  
Effects of oxygen partial pressure on tensile properties of 44 alloy

$p_{O_2}$ in exposure environment (Torr)	Maximum eng. stress (MPa)		Uniform elongation		Total elongation		Measured crack length ( $\mu\text{m}$ )	
	RT <sup>a</sup>	500°C	RT <sup>a</sup>	500°C	RT <sup>a</sup>	500°C	RT <sup>a</sup>	500°C
$1 \times 10^{-6}$	426	–	0.127	–	0.217	–	80	–
$7.6 \times 10^{-4}$	443	–	0.110	–	0.145	–	90	–
0.1	441	–	0.133	–	0.202	–	95	–
0.15 (He)	438	359	0.140	0.089	0.191	0.119	80	70
160	–	367	–	0.099	–	0.135	–	85
760	422	347	0.148	0.097	0.208	0.135	80	80

<sup>a</sup> RT = room temperature.

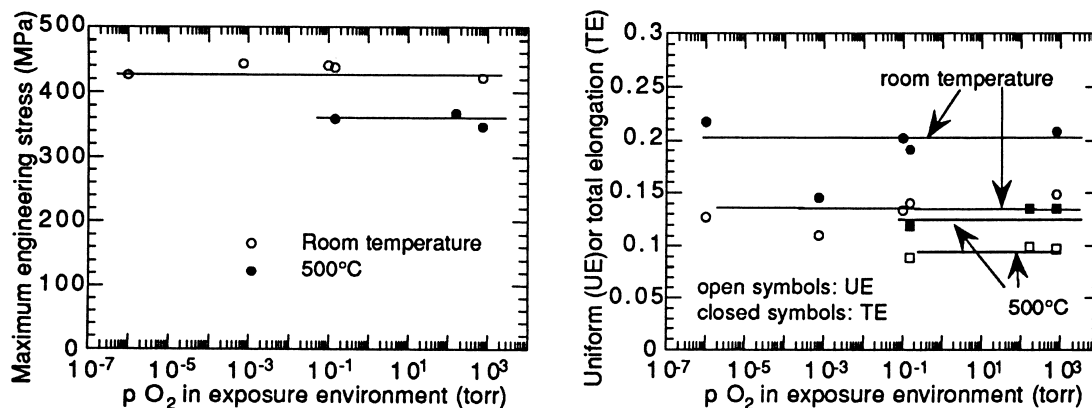


Fig. 5. Effect of oxygen partial pressure in the preexposure environment on maximum engineering stress (left) and uniform and total elongation (right) for 44 alloy oxidized at 500°C for 250–275 h and tested at room temperature and at 500°C at a strain rate of  $1.8 \times 10^{-4} \text{ s}^{-1}$ .

plots indicate that the  $p_{O_2}$  value in the preexposure environment has virtually no effect on any of the tensile properties reported in this paper.

#### 3.4. Microstructural observations

Axial cross sections of several of the tested specimens were examined by SEM. Fig. 6 shows 44 alloy specimen sections tested in as-annealed condition and after oxidation in air for 24, 260, 600, 1050, and 2060 h in air at 500°C. The photomicrographs show that as oxidation time increases, both cracks in the transverse direction and the crack spacing in the axial direction increase. Furthermore, as the oxidation time increases, the specimen undergoes little necking at the gage section during the tensile test. It is evident, especially from specimens

exposed for 1050 and 2060 h, that fracture occurred by propagation of one of the transverse cracks and that because the core of the alloy was somewhat ductile, the crack-propagation direction in the core region was at an angle of  $\approx 45^\circ$ . Similar observations were reported earlier for 55 alloy specimens exposed to air for different time periods [2]. 44 alloy specimen sections, tested after oxidation at 500°C in environments with  $p_{O_2}$  values of  $1 \times 10^{-6}$ ,  $7.6 \times 10^{-4}$ , 0.1, 760 Torr and 99.999% He at a  $p_{O_2}$  value of 0.15 Torr, also exhibited transverse cracking. The results indicate that the specimen surfaces equilibrate with oxygen in the environment and the increased oxygen concentration at the surface diffuses into the alloy with time. Even at a lowest  $p_{O_2}$  value of  $1 \times 10^{-6}$  Torr, the oxygen concentration at the surface must be high enough to initiate cracks on axial loading

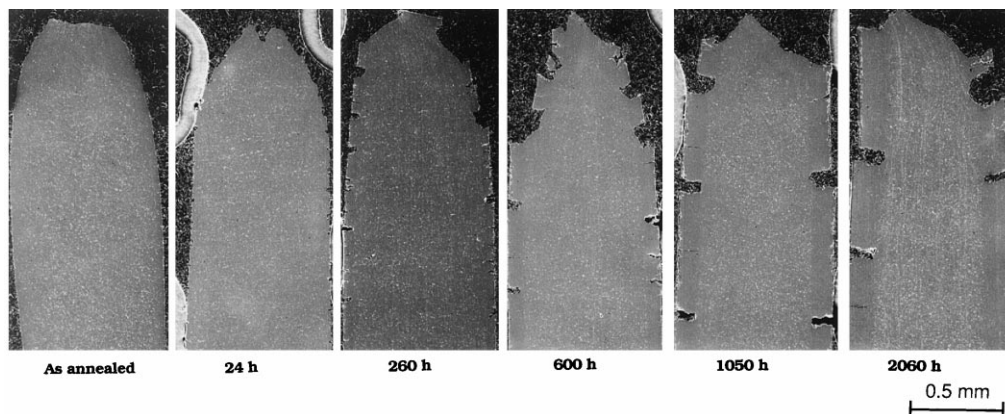


Fig. 6. Scanning electron photomicrographs of axial sections of 44 alloy specimens tensile-tested at 500°C in as-annealed condition and after oxidation in air at 500°C for several exposure times.

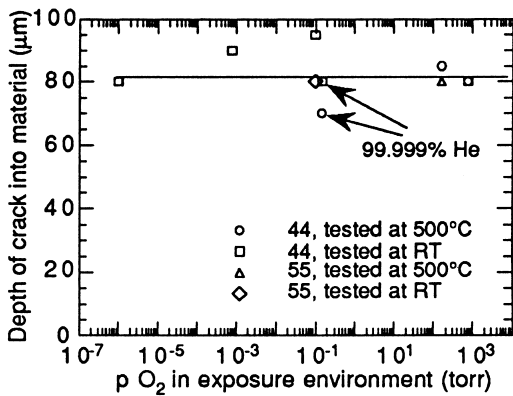


Fig. 7. Measured depths of cracks in 44 and 55 alloy specimens after exposure for 250–275 h in various oxygen-containing environments.

of the specimen. The depth of the crack is determined by diffusion of oxygen which in turn is dictated by the time and temperature of preexposure.

Fig. 7 shows a plot of measured crack depths for specimens exposed to environments with different  $p_{O_2}$  values. Over the entire range of  $p_{O_2}$  values used in the present study,  $\approx 250$  h exposure at 500°C resulted in crack depths in a range of 70–95  $\mu\text{m}$ . These results, even though obtained from a relatively short exposure time of  $\approx 250$  h, indicate similar cracking propensity for 44 and 55 alloys and at room temperature and at 500°C and this propensity is independent of oxygen pressure in the exposure environment. This observation coupled with embrittlement of the alloys after  $\approx 2000$  h exposure in air (discussed earlier) makes one infer that the alloy can embrittle even in environments with low  $p_{O_2}$  values, if exposed for times comparable to those of the air exposures conducted in this program. The ongoing experiments will examine this issue and develop models for life prediction of alloys as a function of time, temperature, and oxygen level.

#### 4. Summary

A systematic study was conducted to evaluate the oxidation kinetics of V–4Cr–4Ti alloy and to establish

the role of oxygen ingress on the tensile behavior of the alloys at room temperature and at 500°C. Several conclusions can be drawn from the investigation.

- No grain growth was observed at temperatures between 500°C and 800°C and for times up to 5000 h.
- Maximum engineering stresses for the alloy were substantially lower than those for 55 alloy for the same oxidation treatment.
- Uniform and total elongation values for the alloy were 1.6% and 3.6% at 500°C after 2060 h oxidation in air at 500°C.
- Maximum engineering stress for the alloy at room temperature was in the range 422–441 MPa after  $\approx 250$  h exposure at 500°C in environments with a  $p_{O_2}$  range of  $1 \times 10^{-6}$  to 760 Torr. The corresponding uniform and total elongation values were 11–14.4% and 14.5–21.7%, respectively.
- Measurements on crack depths in various specimens showed that the depth is independent of  $p_{O_2}$  in the preexposure environment and was in a range of 70–95  $\mu\text{m}$  after 250–275 h exposure at 500°C.

#### Acknowledgements

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