Journal of Nuclear Materials 295 (2001) 42–48

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Oxidation and its effects on the mechanical properties of Nb–1Zr [☆]

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Received 10 November 2000; accepted 2 February 2001

Abstract

The alloy Nb–1Zr is a high temperature material that is often considered for applications where strength and resistance to alkali metals are required. However, these favorable properties can be compromised because it lacks oxidation resistance in many environments. After reviewing the oxidation behavior of Nb–1Zr, additional studies were conducted in high temperature, low pressure gaseous oxygen environments to determine the effects of oxidation on the tensile properties and hardness of Nb–1Zr for a specific space system application. Strengthening and loss of ductility were found to occur from room temperature to 900°C following low pressure oxidation in vacuum or argon at 750°C and 900°C, respectively. In general, oxygen that is associated with zirconium as extremely fine zirconium–oxygen zones is responsible for the strengthening/embrittlement that is observed. Heat treatments that result in non-coherent ZrO_2 precipitates can neutralize the effects of oxygen on mechanical properties provided the total oxygen content is below that required to convert all of the Zr to oxide. © 2001 Published by Elsevier Science B.V.

1. Introduction

Although the oxidation behavior of refractory metals has long been studied [1–10], conclusions regarding effects on mechanical properties have not always considered how the experimental parameters affected the morphology of oxygen in the microstructure of the alloy. Refractory metals/alloys that exhibit significant oxygen solubility (V, Nb, Ta) can harden and/or embrittle at low oxygen pressures without formation of a significant oxide layer [11,12]. However, past studies have shown that the addition of alloying elements, especially those that have a strong affinity for oxygen (e.g., Ti, Zr, and Hf), significantly alter the oxygen morphology and, thus, the mechanical properties at a given oxygen concentration.

One of the general requirements for missions in space is a reliable source of electrical power. Radioisotopic Power Systems based on thermoelectric, Stirling engine, thermophotovoltaic and alkali metal thermal-to-electrical conversion (AMTEC) systems have all been studied. The AMTEC system is based on conduction of sodium vapor ions through a β''-alumina solid electrolyte tube [13]. Each AMTEC system cell is contained within an alloy cylinder which must exhibit good high temperature strength and corrosion resistance to sodium. One excellent candidate material for the AMTEC cell container is Nb–1Zr, a refractory metal alloy; however, the alloy lacks satisfactory high temperature oxidation resistance in many environments. Although the deep space environment does not contain significant oxygen, fabrication, testing and storage environments generally must be carefully controlled to guard against degradation in mechanical and corrosion properties of Nb–1Zr.

[☆] Research sponsored by the Office of Space and Defense Power Systems at the Oak Ridge National Laboratory, managed by UTBattelle, LLC for the US Department of Energy under contract number DE-AC05-00OR22725. The submitted paper has been authored by a contractor of the US Government under contract number DE-AC05-00OR22725. Accordingly, the US Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

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PII: S0022-3115(01)00495-0

Oxidation of Nb–1Zr is known to vary with oxygen pressure, temperature, and fabrication history/microstructure. Depending upon exposure conditions, dissolution of oxygen, formation of ZrO_2 internally, and formation of niobium oxides both internally and externally can occur. Above ~300°C external oxide scales on Nb–1Zr are generally not protective; they do not act as a diffusion barrier to oxygen and they can spall under either isothermal or thermal cycling conditions. Dissolved oxygen usually becomes preferentially associated with zirconium, (i.e., as an interstitial solution or as a very fine coherent precipitate) [14], and can both strengthen and embrittle the material. Even under vacuum or inert gas conditions, at >400°C this is a major concern since even low partial pressures of oxygen (10^3–10^4 Pa) can result in significant rates of embrittlement of the alloy. When low pressure oxidation results in oxygen being associated with zirconium, heat treatment at 1000–1600°C will precipitate non-coherent ZrO_2 which does not have an embrittling effect [14]. In addition to effects on mechanical properties, oxygen in Nb–1Zr is particularly important because even small quantities of oxygen (300–500 wppm) can lead to rapid attack by some alkali metals (e.g., lithium, sodium and potassium) if oxygen in Nb–1Zr is not precipitated as ZrO_2 [14].

Oxidation rates for Nb–1Zr at 650–900°C, over a wide range of oxygen pressure (PO_2) and taken from several literature data sources [12,15–17], are shown in Fig. 1. At low PO_2 ($\lesssim 10^{-4}$–10^{-5} Torr/10^{-2}–10^{-3} Pa), oxidation occurs principally by internal oxidation and the rate appears to be a linear function of pressure. At 10 Pa and above, external oxide formation occurs more rapidly, and the data suggest a more complex relationship with pressure. Between 10^{-2} and 10 Pa, lower rates at constant temperature have been reported [15] with increases in PO_2 (i.e., rate reversals). At 871°C one reversal was reported [15] between 5×10^{-3} and 10^{-1} Pa and at 760°C two such reversals were reported in that pressure range. Accordingly, it is clear that extrapolations of data from low to high PO_2 or from high to low PO_2 are unlikely to produce an accurate prediction of actual rates. Furthermore, it should be emphasized that at low partial pressures and high temperatures, the overall oxidation rate (weight gain) is the same as the internal oxidation rate, but at higher pressures oxide scale formation is the principal contributor to measured weight gains.

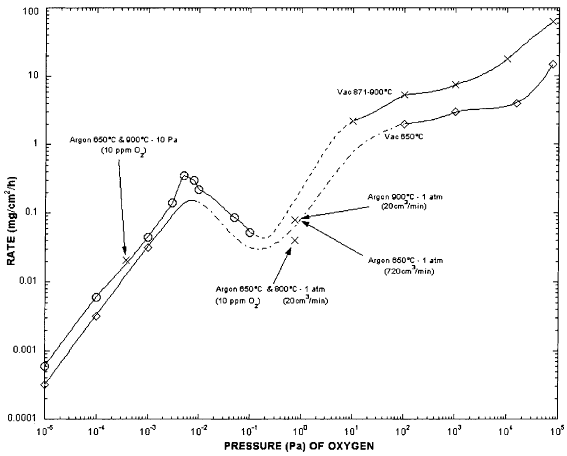

Fig. 1. Oxidation rate of Nb–1Zr as a function of PO_2. Data from [12,15–17].

The effect of oxygen on the room temperature mechanical properties of internally oxidized Nb–1Zr has also been previously reported [18]. Table 1 (taken from [18]) shows data obtained from sheet specimens that were annealed at 1600°C followed by oxidation at 1000°C. Room temperature tensile tests of these relatively large grained (80–100 μm), as-oxidized samples showed a large increase in room temperature strength and a corresponding decrease in ductility as oxygen concentration increased. Further heat treatment at 1600°C following oxidation (to form ZrO_2) neutralized the effect of oxygen on strength and ductility up to 1300–1400 wppm. Similar effects are manifested in the hardness of Nb–1Zr [19]. Fig. 2 (from [19]) shows the hardness of both Nb (Cb) and Nb–1Zr (Cb-1Zr) as a function of internal oxygen content. In this case the Nb–1Zr was oxidized at a temperature well above that required to form ZrO_2 during oxidation. Because oxygen was primarily present as ZrO_2, (rather than as an interstitial solid solution), there was little effect on the hardness of Nb–1Zr until the concentration of oxygen exceeded that required to react with all of the zirconium in Nb–1Zr. When this value was exceeded, the hardness of Nb–1Zr then corresponded with that exhibited by unalloyed niobium, an indication of matrix hardening. This effect has also been confirmed by hardness measurements across samples of Nb–1Zr oxidized at a series of increasing temperatures [20]. As shown in Fig. 3, profiles across a 1 mm thick samples show an increase in hardness with oxygen until the oxidation temperature reached 1077°C (1350 K). When oxidized at 1077°C, the sample showed no increase in hardness, even though it contained 1788 wppm, a much higher concentration than in the other samples. At this temperature, formation of ZrO_2 was as rapid as the oxidation rate; however, at $\leqslant$900°C formation of ZrO_2 was slower compared to the oxidation rate. Thus, during low pressure oxidation, effects of oxygen on the mechanical properties of Nb–1Zr are a strong function of the temperature.

In order to determine effects of oxidation on the mechanical properties of Nb–1Zr at temperatures and partial pressures of oxygen expected during fabrication and operation of an AMTEC system, additional oxidation experiments were conducted as described below.

Table 1
Effect of oxygen in annealed (1600°C) niobium–1% zirconium alloy on its room-temperature tensile properties before and after heat treatment[a]

Oxygen concentration (ppm)	Treatment[b]	Tensile strength (MPa)	0.2% Offset yield strength (MPa)	Elongation in 2 in. (%)
150	b	370	321	11.0
310	b	444	399	11.0
650	b	671	671	2.0
1200	b	863	863	0.0
2100	b	949	949	0.0
3260	b	827	827	0.0
100	c	267	245	14.0
290	c	257	229	10.0
560	c	268	228	11.0
860	c	246	228	11.0
1360	c	247	197	14.0
100	d	245	221	11.0
440	d	231	205	9.5
480	d	223	196	10.5
1140	d	247	202	12.0
1390	d	225	188	12.0

[a] *Source*: Ref. [18].
[b] Oxidation at 1000°C.
[c] Oxidation followed by heat treating in vacuum for 1 h at 1600°C.
[d] Oxidation followed by heat treating in vacuum for 1 h at 1600°C and then heat treating in argon for 100 h at 816°C.

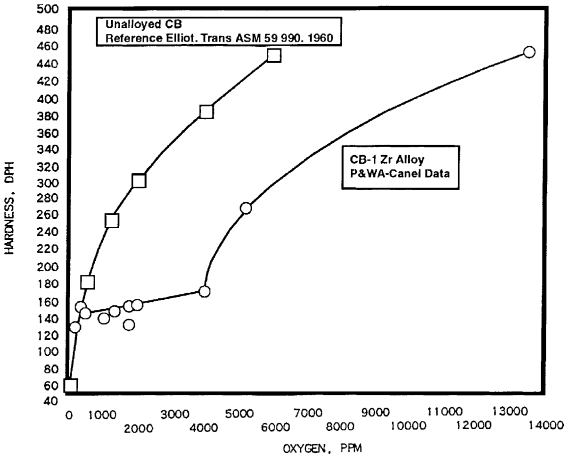

Fig. 2. Hardness of Nb and Nb–1Zr versus oxygen content [19].

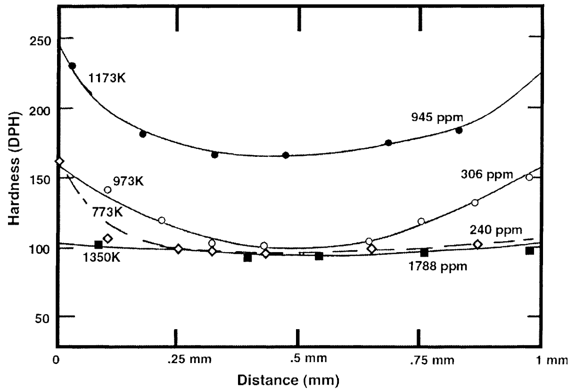

Fig. 3. Hardness profiles across plates of Nb–1Zr oxidized to varying degrees at different temperatures [20].

2. Experimental

The compositions of the Nb–1Zr alloys used in this study are shown in Table 2. Most of the samples tested were in the form of small tensile specimens, nominally 0.5 mm thick with 1.5 × 7.6 mm^2 long gage sections, that were stamped from cold-reduced sheet stock. Following fabrication the specimens were acid-cleaned and then vacuum annealed at 1300°C for 1 h (40–50 μm average grain size) prior to oxidation or mechanical testing. A few samples were also tested in the form of tubular

Table 2
Chemical analysis of Nb–1Zr

Element	Concentration (wt%)	
	Plate	Tubing
Zirconium	1.12	1.1
Tantalum	0.015	0.005
Tungsten	0.012	–
Molybdenum	0.001	–
Iron	<0.009	<0.005
Oxygen	0.023	0.003
Nitrogen	0.007	0.002
Carbon	0.004	<0.003
Hydrogen	<0.0001	<0.005

tensile specimens with gage sections 0.25 mm in wall thickness. The ends of the tubes were sealed with welded plugs and, following machining and welding, the specimens were cleaned and annealed as described above.

Pre-test oxidation at low oxygen pressures was carried out in the ultra-high vacuum Sievert's apparatus shown in Fig. 4. It consists of a gas supply, an alumina reaction tube coupled to a vacuum system, and a high temperature furnace around the reaction tube. After initially pumping the system to a low pressure ($\leqslant 10^{-6}$ Pa), oxygen gas was introduced through a micrometering valve while the system was being evacuated. Ionization gages located before and after the specimen were used to monitor the oxygen pressure. For tests in argon at 1 atm, the pumping system valve was closed, and the argon was vented through an oil bubbler system.

Nb–1Zr sheet samples were oxidized at 750°C for 3–16 h in an oxygen gas environment of 10^{-3} Pa. These conditions produced oxygen levels of ~500–3500 wppm in the Nb–1Zr. After the oxygen gas micrometering valve was closed, an ultra-high vacuum was reestablished, and the samples were heated for 2 h at 750°C for additional homogenization of the oxygen across the sample thickness. Nb–1Zr sheet samples were also exposed to an argon–oxygen mixture at 650–900°C at either a total pressure of 10 Pa maintained by a mechanical vacuum pump or 1 atm (20–720 ml/min). Both weight change and selected chemical analysis were used to monitor oxygen uptake.

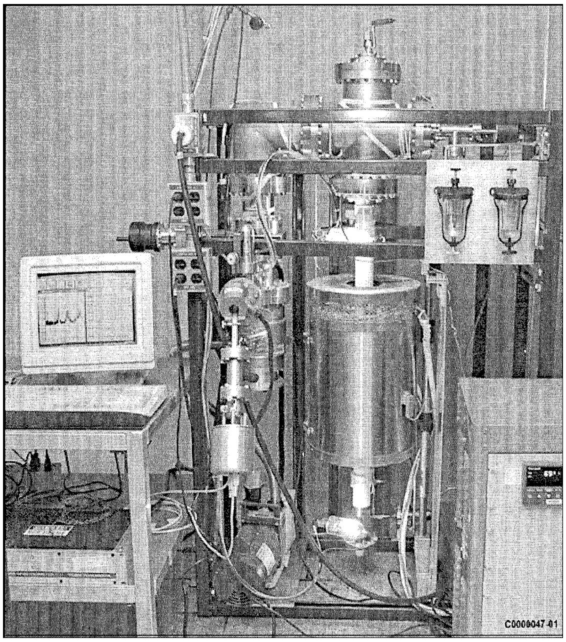

Fig. 4. Ultra-high vacuum Sievert's apparatus.

3. Results

3.1. Oxidation in argon

Oxidation rates in argon–oxygen obtained in the present study are plotted in Fig. 1 along with previous literature data obtained in various vacuum environments. At 10 Pa argon pressure and $PO_2 = 3 \times 10^{-4}$ Pa, oxidation rates closely correlated with results at the same oxygen partial pressure under vacuum conditions. At the higher partial pressures, there is little comparative data, but weight increases in argon appeared to be somewhat lower than at similar partial pressures of oxygen in vacuum. Oxidation rates were fairly insensitive to temperature in the range studied (650–900°C) and were $2–8 \times 10^2$ mg cm^{-2} h^{-1}.

Room temperature tensile tests were performed on two specimens that were exposed to Ar-10 vppm oxygen for 24 h at 900°C and 10 Pa. Both samples gained ~3400 wppm oxygen and showed significant increases in strength with low tensile ductilities (1.25–2.0%).

3.2. Oxidation in low PO_2 vacuum

Tensile test results as a function of oxygen content of the Nb–1Zr were obtained at room temperature, 750°C, 850°C and 900°C, and these are summarized in Table 3 and Fig. 5. For the specimen geometry and under these oxidation/mechanical testing conditions, there was an increase in strength accompanied by a loss in ductility at all temperatures. The samples generally exhibited significant ductility (>5% uniform elongation) up to ~1500 wppm oxygen, but low ductility (<5% uniform elongation) at ~3500 wppm oxygen. It is interesting that there was apparently little effect of oxygen on ductility between ~500 and 1500 wppm. The tensile ductility of a tubular tensile specimen (oxidized on the external surface only) was determined at 850°C and was expectedly low based on its oxygen content of 4200 wppm (Table 4 and Fig. 5).

Hardness measurements were made across the thickness of selected tensile samples after oxidation in vacuum or argon, and the results are plotted versus oxygen concentration in Fig 6. The increase in hardness mirrored the increase in strength shown in Fig. 5. Note that there was an approximately linear increase in hardness with oxygen content up to ~3500 wppm oxygen. Also, when the sample containing ~3500 wppm oxygen (amount that reacts stochiometrically with ~1% Zr in the alloy to form ZrO_2) was heat treated at 1300°C following oxidation at 750°C, hardness decreased and was approximately the same as before oxidation. However, when the sample containing ~9600 wppm oxygen was similarly heat treated, the decrease in hardness was relatively small. The hardness of Nb–1Zr containing ~9600 ppm oxygen that was heat treated at 1300°C corresponds to that shown in Fig. 2 for Nb–1Zr

Table 3
Tensile test results for Nb–1Zr sheet specimens

Specimen number	Oxygen increase (ppm)	Tensile test temperature (°C)	YS (MPa)	UTS (MPa)	Uniform elongation (%)	Total elongation (%)
N13	0	RT	150	248	17.5	31.7
N12	577	RT	241	338	6.7	14.6
N7	1530	RT	386	552	7.7	12.2
N18	3500[a]	RT	593	593	3.4	3.4
N1	0	750	138	234	16.2	
MN3	0	750	103	228	23	23
N10	690	750	172	255	9.0	14.5
N5	1490	750	317	379	8.2	12.6
N4	3551	750	–	352	2.1	2.1
N2	0	850	117	221	23.7	24.5
MN4	0	850	221	255	11.3	12.9
N9	630	850	172	241	6.4	13.0
N8	1467	850	269	434	10.4	14.7
MN1	3551	850	228	228	1.5	1.5
N20	0	900	110	214	19.6	21.3
MN5	0	900	110	234	20.3	21.0
N11	637	900	–	145	1.5	3.2
N6	1549	900	296	331	5.6	9.8
N17	3500[a]	900	386	386	3.7	3.7

[a] Approximate.

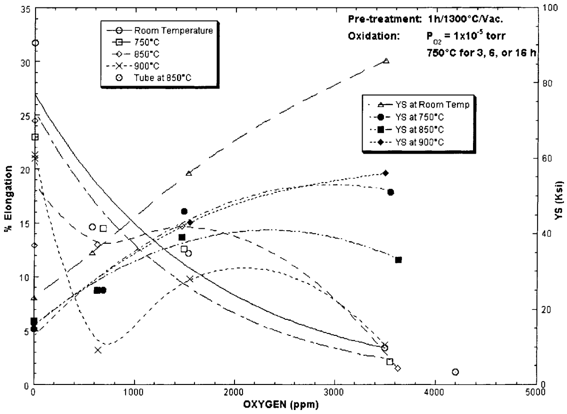

Fig. 5. Effects of oxygen on tensile properties of Nb–1Zr.

containing a similar oxygen concentration but which was oxidized at ~1600°C. It also corresponds to the hardness of unalloyed niobium containing ~5000–6000 wppm [19]. High temperature oxidation or heat treatment at 1300°C following oxidation at a lower temperature leads to formation of ZrO_2 which, as shown in Table 1 and Fig. 6, does not contribute to hardening/strengthening or loss in ductility of Nb–1Zr. However, once the Zr in Nb–1Zr is consumed, subsequent hardening of the niobium matrix will occur. A similar type of interaction has been reported [21] for the tantalum base alloy T111 (Ta-8 W-2 Hf).

4. Discussion

This study sought to determine whether oxidation under prototypic pressure/temperature conditions expected during fabrication, testing and storage of an AMTEC system cell would embrittle Nb–1Zr. In previous studies, significant room temperature tensile embrittlement has been reported for oxygen levels as low as 650 ppm [18], but good ductility has also been reported at 6000 ppm [9].

Previously cited studies have demonstrated that oxidation of Nb–1Zr proceeds by the following steps:

$$O_2 \rightarrow O_{\text{chemisorbed}} \overset{\text{diffusion}}{\longrightarrow} O_{\text{dissolved}}$$
$$\rightarrow \text{Internal oxide/Oxide film.}$$

Adsorption, the first step in oxidation, depends upon the number of oxygen atoms that strike the surface and the sticking coefficient (fraction that adsorb). Therefore, parameters such as temperature, volume of gas to surface area of metal, surface condition of metal, surface wraps, etc. can all be important to the rate of oxidation for any test system being evaluated. The rate of oxidation is also pressure sensitive, and linear, logarithmic, parabolic, and other complex functions of pressure have all been reported [4,11,22]. Therefore, it is important that the oxygen partial pressure be well characterized for the process being evaluated. In addition there is evidence that oxidation may also depend upon PO_2/P_{system} in that

Table 4
Effect of oxygen on the mechanical properties of Nb–1Zr tubular specimen[a]

Specimen	Condition	Oxygen (ppm)	Tensile properties at 850°C			
			YS (MPa)	UTS (MPa)	Uniform elongation (%)	Total elongation (%)
A-2	As annealed (1 h/1300°C/vac)		76	152	19.3	19.3
A-1	Oxidized (6 h/850°C/1 × 10^{-5} Torr)	4200[b]	234	234	1.2	1.2

[a] Gage = 25.4 × 6.86 O.D. × 0.254 wall (mm). Shoulder = 12.7 × 7.62 O.D. × 0.635 wall (mm).

[b] Overall weight change during oxidation was 1130 ppm; concentration in 0.25 mm gage section was calculated based on ratio of gage surface area to total surface area and weight of gage section.

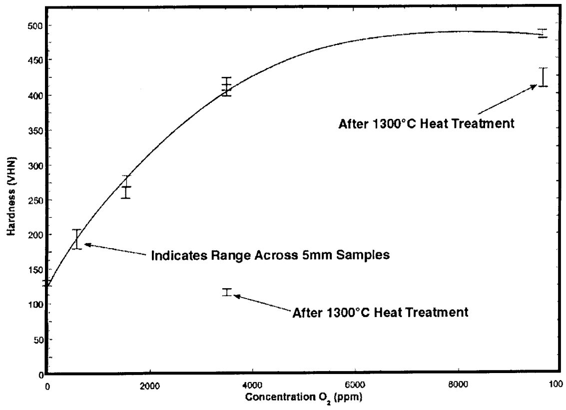

Fig. 6. Effect of low pressure oxidation at 750°C on the hardness of Nb–1Zr.

lower rates have sometimes been observed at equivalent oxygen pressures in 1 atm air or inert gas compared with a vacuum (low total system pressure) [20]. However, the limited results of this study that were conducted in argon did not confirm the large decreases in rate that have been implied.

At high temperatures (~500°C or greater) and low PO_2 ($\leqslant 10^{-3}$ Pa), oxygen first adsorbs on the specimen surface; it then moves into the specimen by diffusion as an interstitial solute. As it diffuses, oxygen is preferentially trapped by Zr as a finely coherent zirconium–oxygen zone. The oxygen–zirconium interaction front moves further into the sample with increasing oxidation time [12,14,20]. In general, these studies have confirmed that it is the coherent Zr–O zone that strengthens the Nb–1Zr while significantly reducing its ductility. However, when an internally oxidized sample of Nb–1Zr was heated at a sufficiently high temperature (process is temperature/time dependent), ductility was recovered (and strength reduced). If sufficient oxidation occurs such that all the Zr in Nb–1Zr has reacted to form ZrO_2, then further oxidation can result in dissolution of interstitial oxygen by the Nb matrix followed by formation of NbO_x phases as was indicated by the hardness results shown in Figs. 2 and 6. In general, at system temperatures operating up to ~900°C and low PO_2, internal oxidation occurs that embrittles Nb–1Zr. However, in contrast with results reported in a previous study, a concentration as low as 1500 wppm oxygen in medium grain-size (40–50 μm) Nb–1Zr resulted in significant loss in ductility from room temperature to 900°C. The combination of test conditions that resulted in internal formation of non-coherent Zr–O and the particular grain size of the material that was tested likely contributed to this threshold value. At 3500 ppm elongations were further reduced to <4%. Although these decreases occurred from oxygen exposures that were 16 h or less, the surface area to volume ratio of the samples was considerably higher than that proposed for the AMTEC cell system, thereby accelerating the wppm rate of increase. Nevertheless, much lower partial pressures of oxygen ($<10^{-3}$ Pa) would be required to prevent significant loss of ductility of an AMTEC cell after long time exposures.

The processes described above are temperature dependent and would occur at slower rates if the temperature is decreased. Even though oxidation begins to occur in air above 300°C, the diffusion rate of oxygen is sufficiently low such that oxidation effects are confined to surface oxide films [23]. Thus, at lower temperatures, oxidation effects on mechanical properties would be essentially determined by how much of the Nb–1Zr reacts to form a surface oxide. Whatever the temperature, if an oxide film grows or spalls and regrows, it consumes the base material and reduces its strength through loss of effective load-bearing cross-sectional area. Loss of strength would be determined by how much of the base material has reacted, but significant loss in ductility should only occur to the extent that dissolved oxygen is present in the matrix below the oxide film. Thus oxygen concentrations associated with internal oxidation need to be distinguished from those associated with oxide film formation.

The mechanical effect of a particular oxidation exposure depends upon the resulting internal concentration of oxygen and, therefore, the surface area affects the total oxygen increase (wppm) for a given volume. For a fixed surface area of Nb–1Zr, as the section thickness decreases, the ratio of the concentration of oxygen in the matrix and/or the relative thickness of a surface film to the total section thickness increases. Thus, oxidation effects on mechanical properties will increase with increasing surface area to volume ratio of the component or with decreasing section thickness for components with similar surface areas.

5. Summary

When Nb–1Zr is exposed to oxidizing environments at high temperatures, internal oxidation can occur even at relatively low oxygen partial pressures such as might be encountered in some vacuum or inert gas systems. However, oxidation behavior and accompanying effects on mechanical properties can be quite different depending upon exposure time, temperature, partial pressure of oxygen, grain size of the material and geometry of the component.

When Zr–O interaction zones or very fine coherent precipitates form during internal oxidation, an increase in tensile strength and decrease in tensile elongation can occur. In this study, after oxidation at 750°C at low pressure, significant changes in strength and ductility with the addition of 1500 wppm oxygen were measured from room temperature to 900°C. However, with further heat treatment, e.g., 1 h at 1300°C following oxidation, to form non-coherent ZrO_2 precipitates, hardness measurements show little effect of oxygen on mechanical strength/ductility unless oxygen concentrations exceed the amount that can be reacted to form ZrO_2.

At oxygen partial pressures of $\sim 10^{-4}$ Pa, rates of oxidation of Nb–1Zr at 650–900°C were similar whether in argon or vacuum. At higher pressures ($\sim 10^{-2}$–1 Pa), oxidation rates in argon appeared to be lower than in vacuum. However, the effects of a given oxygen concentration on mechanical properties were similar in both environments.

Although information on oxidation of Nb–1Zr has been previously reported, oftentimes results of mechanical testing have failed to recognize or include any discussion of how material and oxidation conditions may have affected its microstructure and mechanical properties. Thus, many different critical levels of oxygen that cause embrittlement have been cited, leading designers to be confused or misled as to what protective requirements are needed for Nb–1Zr. The data and its interpretation that was presented here are an attempt to clarify, or at least call attention to, the many complexities and nuances that are possible. Unfortunately, in the end, data for a specific application may still be required in spite of the significant literature database.

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