Compatibility of Stainless Steels with Oxygen-Contaminated Helium

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Appendix A

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1. Introduction

Pressurized helium possesses several advantages as a CTR and blanket cooling medium: it is chemically inert, it is not activated by neutron irradiation, and it does not interact with magnetic fields. However, reactive gaseous impurities present in a helium coolant stream, such as 0_2, N_2, CO, CO_2 and CH_4 maintain their chemical activity in the inert helium gas. The problems associated with the resulting gas-metal reactions must be recognized before nominally pure helium, or helium with intentional impurities added, is approved for use in an actual CTR system. As purposeful additions of 0_2 to the primary helium coolant are being considered as a means of reducing T_2 activity, special consideration must be given to the long-term effect of a continuously replenished 0_2 contaminant on the stainless steel structure.

2. Objectives

The primary objective of the present work is to estimate the extent of stainless steel corrosion and mechanical property degradation which will result from the use of oxygen-contaminated helium as the primary coolant in the UWMAK-II design. Secondary objectives, related to the concept of tritium control by 0_2 additions to the helium coolant, involve estimation of the 0_2 necessary to maintain the system's "normal" oxidation rate, and estimation of the potential release rate of nascent tritium by T_20 oxidation of the helium-steam heat exchanger tubing.

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3. Conclusion and Comments

- The metal loss rate due to oxidation of an austenitic stainless steel in helium contaminated with O_2 at 10^{-2} Torr at 650°C is estimated to be $\sim 3 \times 10^{-5}$ cm/yr. Reduction of net metal cross-section by corrosion does not appear to be a matter of concern, though the foregoing value does not take into account possible enhancement of corrosion rates by radiation.
- The presence of 10^{-2} Torr O_2 in the helium coolant should cause no significant deterioration in the long-term tensile, creep, and creep-rupture properties of an austenitic stainless steel at 650°C. Resistance to creep deformation is likely to be higher than in the case of a completely inert system. The O_2 is likely to have a deleterious effect on fatigue life, however, especially if the fatigue is fixed-strain, rather than fixed-load, as in the former case no benefit is gained from oxidation strengthening.
- Low concentrations of N_2 present in the helium will most likely result in an increase in creep strength over values obtained _in vacuo_.
- Presence of reducing gases, such as H_2 and CO, can cause a decrease in creep strength, if the oxidizing power of the gas is such that selective oxidation of steel constituents occurs, e.g., oxidation of Cr, Ti, or Nb.
- Hydrocarbon impurities tend to carburize stainless steels, with an initial increase in creep strength but ultimate embrittlement.
- Presence of CO and CO_2 will generally carburize austenitic steels, causing an increase in creep strength and eventual embrittlement. Low partial pressures (i.e., a few micro-atmospheres) of CO and CO_2 should

be tolerable, however, as high-temperature gas reactor materials are generally performing well in such environments.

- At a pressure of 10^{-2} Torr, the impingement rate of O_2 molecules on the stainless steel surface at 650°C is a factor of $\sim 10^5$ greater than the oxygen supply required to maintain the steel's oxidation rate. This suggests that maintaining an O_2 pressure of 10^{-2} Torr is both adequate, to maintain the anticipated oxidation kinetics, and practical, from an operational standpoint.
- If the T_2O present in the primary system participates substantially and continuously in the "normal" stainless steel oxidation in the helium-steam heat exchanger there is a good possibility of finding unacceptable permeation of the heat exchanger tubing by the nascent T formed during the oxidation reaction. Conversely, protium from the steam side will tend to pass into the primary coolant by the same mechanism, contaminating the T_2O residing in the molecular sieve.
- Sulfur-bearing or carbonaceous materials (such as oil) must be rigorously excluded from the primary helium system.
- There are experimental data indicating that the mechanical properties of Nb-stabilized steels, such as Type 347, are superior to Ti-stabilized steels, such as Type 321, in contaminated helium environments of low oxidizing potential.

4. Corrosion Rates in Oxygen-Contaminated Helium

The oxidation rates of stainless steels under projected UWMAK-II primary coolant operating conditions (650°C, 10^{-2} Torr O_2) have not been determined experimentally and so must be estimated from available data. In order to estimate the oxidation rates, the small amount of quantitative experimental data available will be evaluated for applicability, and the results extrapolated into the temperature and pressure range of interest. Though the hazards associated with extrapolation of corrosion data are well known, it appears to be a useful procedure in the present case, as extreme changes in the corrosion rate control mechanisms are not expected under the new (extrapolated) conditions.

The potentially important enhancement of oxidation rates by radiation has not been considered in this review.

4.1 Mechanisms

The mechanisms of oxidation of stainless steel in high-temperature gaseous environments are extremely complex and not at all well understood. Some qualitative generalizations are possible, though they are derived from the results of high-temperature work (> 700°C) and so may not accurately describe conditions existing at 650°C and below.

Caplan and Cohen(1) exposed specimens of Types 302, 330, and 309 stainless steels to dry air and wet air at temperatures in the range 871° - 1093°C. They continuously monitored the weight changes during oxidation, and analyzed the crystal structure of the scales formed by X-ray diffraction. The longest test reported was of ~1000 hr duration.

Moisture in the air greatly accelerated the oxidation rate of Type 302ss; the effect on Type 309 was much less marked. The weight gain vs time curves were not smooth in either gaseous environment but exhibited sharp "breaks", caused by a temporary loss of protection by the oxide scale. The two major scale constituents were found to be spinels, of the general form M_3O_4, capable of wide composition variability:

$(Fe, Ni, Mn)\,0 \cdot (Fe, Cr, Mn)_2\,0_3$

and rhombohedral oxides, M_20_3:

$(Fe, Cr, Mn)_2\,0_3$.

The scale composition was found to vary not only with depth, but from one area to another on the specimens. A further complicating factor was the profound effect of prior surface treatment on oxidation rates. An electropolished sample of Type 309ss showed a lower oxidation rate than an abraded sample, and specimens abraded and preheated in high purity helium showed still greater oxidation rates. The authors concluded that a realistic interpretation of the scaling observed would be impossible, because of the many unknown factors contributing to the oxidation process and the inherent complexity of commercial alloys.

Yearian, Randell and Longo(2) studied the films formed on commercial steels varying in Cr content from 5 to 26 percent after exposure in air and oxygen in the temperature range 700° -1160°C for times up to 100 hr. They concluded that for exposures resulting in metal loss rates < 10 mg/cm^2-day, the essential scale component is Cr_20_3. (This finding is relevant to the UWMAK-II blanket-heat exchanger system.) This is accompanied by α Fe_20_3 in an amount increasing with the iron content of the alloy and the rate of attack. When the alloy contains a few tenths percent Mn, the scale may include relatively large quantities of $MnCr_20_4$, especially in the case of high Cr alloys and for low temperature oxidations in air.

Very high temperature data on the oxidation of Type 304Lss in steam and air have been reported by Bittel, Sjodahl, and White.(3) Temperatures were in the range 1000° to 1375°C; test durations were a matter of hours. The oxidation rates in steam were much greater than those in air at equivalent temperatures. The rate control in steam is ascribed to diffusion through a Fe-Ni-Cr spinel layer. The protective oxide film for the air oxidation case was found to be essentially Cr_2O_3. They further found that the oxidation kinetics data for pure Cr reported by Hagel(4) agreed very well with their air oxidation results.

If a metal forms a protective film as it oxidizes, with diffusion through the oxide film exerting the rate control, parabolic oxidation kinetics are expected:

$$W^2 = Kt \qquad (1)$$

where: W = oxygen weight gain, mg/cm^2
K = parabolic rate constant, $\left(\frac{mg}{cm^2}\right)^2 sec^{-1}$
t = time in seconds.

These parabolic oxidation kinetics are found, incidentally, in the case of oxidation of pure chromium.

If the corrosion of a metal is not impeded by the thickening oxide scale, e.g., in the case of a cracked, porous, or non-adherent corrosion product, linear oxidation kinetics are frequently found, i.e.,

$$W = Kt. \qquad (2)$$

In this case "K" is a linear rate constant, of dimensions mg/cm^2-sec.

It is known that stainless steels generally exhibit oxidation rate behaviors lying somewhere between these two extremes,(5,6) with the behavior in any one instance dependent on the environment, the temperature, the particular alloy, its surface pretreatment, and the test duration. This variable behavior makes exact oxidation rates impossible to predict without recourse to experiment, as has been previously noted. However, the variable, unpredictable behavior becomes easier to understand with an appreciation of the complex reactions going on at the alloy surface.

4.2 Oxidation Rates Under UWMAK-II Conditions

The oxidation data most relevant to expected UWMAK-II conditions appear to be that of Eberle, Ely, and Dillon,(6) who have reported on the corrosion and mechanical property behavior of a number of candidate superheater materials. As part of their study they exposed specimens of a variety of stainless steels to laboratory air at 760°C for 1270 hr, then calculated the corrosion rates from weight change data. Their data are reproduced in Table I.

TABLE I

Corrosion Rates of Stainless Steels
in Air(6)
760°C, 1270 hr test duration

Steel	Corrosion Rate, mils per year (mpy)
A1S1 304	0.22
A1S1 321	0.14
A1S1 347	0.32
A1S1 316	0.13
A1S1 318	0.14

Average = 0.2 mpy = 5 x 10^{-4}cm/yr

The data of Table 1 are expressed in terms of a linear rate (mils per year). No attempt was made on the part of the authors to determine the strict time-dependence of the weight gain (metal loss)* observed. Even if the time dependence were known, the short test duration (53 days) would not permit accurate long-term extrapolation of the observed data to anything approaching the projected life time of the UWMAK-II primary system. For this reason, a conservative approach will be taken to the foregoing data: The average value

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*For 300 series stainless steels, 0.1 mil of metal ≈ 1.0 mg O_2/cm^2

of all the steels tested will be used, even though the corrosion rate for Type 316 is lower than the average; the corrosion rate law will be considered linear; and the corrosion rate exhibited for the first 53 days of the steel's exposure (the data of Table 1) will be considered representative of its long-term behavior, even though the rate is apt to slow down with increasing time. The last two assumptions are obviously closely related.

The corrosion rate of a steel will be substantially less at 650°C than at 760°C, if the mechanism of corrosion rate control does not change. If we make this reasonable assumption, we may estimate the corrosion rate at the lower temperature if the activation energy for the corrosion rate control process is known. Such an activation energy has not been reported for stainless steels for the temperature range and environments of interest. However, the 760°C corrosion rates reported for pure chromium(4) in 76 Torr O_2 lie within a factor of two, in terms of oxygen consumption, of the stainless steel data of Table 1. Because the mechanism of oxidation in both cases is thought to be diffusion of cations outward to the gas-metal interface through a metal-deficit lattice, the activation energy obtained for Cr oxidation should be approximately applicable to the stainless steel situation.

Consider the parabolic rate law for Cr:

$$W^2 = Kt, \quad \text{or} \quad W = K^{1/2}t^{1/2} \tag{3}$$

where $$K = 0.111 \exp\,(-59{,}000 \pm 1800/RT)\,(\text{gm-cm}^{-2})^2\ \text{sec}^{-1} \tag{4}$$

The instantaneous rate of oxidation may be found by taking the derivative of Eq. (3) with respect to time:

$$\frac{dw}{dt} = \frac{K^{1/2}}{2t^{1/2}} \frac{mg}{cm^2\text{-sec}} \tag{5}$$

At any given time, the instantaneous oxidation rate is proportional to $K^{1/2}$. A temperature correction to $K^{1/2}$ may be determined which is applicable to the linear kinetics we have assumed:

$$\frac{\text{Oxidation Rate at 760°C}}{\text{Oxidation Rate at 650°C}} = \frac{K_{760}^{1/2}}{K_{650}^{1/2}} = \left(\frac{e^{-\frac{59,000}{(1033)(1.99)}}}{e^{-\frac{59,000}{(923)(1.99)}}} \right)^{1/2} = 5 \tag{6}$$

From Eq. (6) we find that a 5-fold reduction in oxidation rate could be expected in lowering the temperature from 760°C to 650°C. This reduces the assumed oxidation rate from 0.2 mpy (Table 1) to 0.04 mpy, or $\sim 10^{-4}$cm/yr.

Determining the effect of reduced pressure on the oaidation rate involves a somewhat less certain extrapolation. Hagel notes that pressure effects predicted by theory are not at all well borne out in the case of Cr oxidation.(4) (Theory predicts a very small effect of pressure, but an even smaller effect is found.) Charlot and Westerman(7) studied the effect of oxygen pressure on the oxidation rate of Hastelloy X-280 over the pressure range 0.039 to 25 Torr at 1120°C. It was found that the parabolic oxidation rate constant is proportional to the one-fifth power of the oxygen pressure:

$$K \left(\frac{mg}{cm^2}\right)^2 sec^{-1} \propto P_{O_2}^{1/5} \text{ Torr} \tag{7}$$

Because this alloy is believed to oxidize at a rate determined by the diffusion of cations through a Cr_2O_3 - rich layer(8) we can tentatively justify application of Eq. 7 to the oxidation of stainless steel.

It should also be noted that an oxygen pressure of 10^{-2} Torr at 650°C is sufficient to oxidize all of the principal metallic constituents of a 300 series stainless steel, thereby minimizing the possibility of selective attack, which can occur in the presence of reducing species, such as CO or H_2.

If we utilize the same procedure as in Equations (5) and (6) we find that

$$\frac{\text{Oxidation rate in air (150 Torr } O_2)}{\text{Oxidation rate in } 10^{-2}\text{Torr } O_2} \propto \left(\frac{150 \text{ Torr}}{10^{-2}\text{Torr}} \right)^{1/10} = 3 \qquad (8)$$

By applying this factor of 3 to the one-atmosphere air data of 0.04 mpy we obtain a value of <u>0.01 mpy</u> ($3\text{x}10^{-5}$cm/yr) for the metal loss rate of stainless steel at 650°C and 10^{-2} Torr pressure. This value is reasonable, but the approximations used and the assumptions made in obtaining the value must be recognized. It appears that there need be no concern that gross corrosion effects will significantly reduce the net metal section of any UWMAK-II structural component operating under the temperature-pressure conditions described, though it must be reiterated that radiation-enhancement of the oxidation rates has not been considered in this treatment.

4.3 Oxygen Demands

It is next necessary to determine the oxygen demands imposed on the contaminated helium to satisfy the oxidation rates described in the foregoing section. A stainless steel penetration rate of 0.01 mpy is approximately equivalent to 0.1 mg O_2/cm^2-yr, or 3×10^{-12}gm $O_2/\text{sec-cm}^2$. The impingement rate of O_2 molecules on the steel surface at 650°C and 10^{-2} Torr pressure is 2×10^{-7} gm O_2/cm^2-sec. There is a factor of 10^5 times more oxygen incident on the surface at 10^{-2}Torr than is required to maintain the expected oxidation rate, so that there appears to be no unusual oxygen transmission or makeup demands under the expected operating conditions.

If the area of the blanket tubing is assumed to be $4\text{x}10^8$ cm^2, ~ 40 kg of oxygen/yr will be required to satisfy the oxygen consumption demands of the corroding stainless steel. This is a modest quantity, approximately equivalent to the contents of 5 common (size H) cylinders.

4.4 T_2O as Oxidant

A legitimate concern in T control is the possibility that T_2O will enter into the stainless steel oxidation reactions, liberating nascent T which would be able to diffuse through the walls of the primary system.

It is expected that T_2O will be present in the system at a pressure of ~ 1×10^{-3} Torr. If the O_2 pressure is maintained at 10^{-2} Torr, a level greatly in excess of that required to maintain the "normal" oxidation rate (see Section 4.3), it will be at a pressure only ~ 10 times greater than that of the T_2O. (By the reasoning of section 4.3 it must be noted that the pressure of T_2O is also maintained at a level greatly in excess of that required to maintain "normal" oxidation of the stainless steel.)

Let us conservatively* assume that only T_2O enters into the corrosion of the primary helium coolant/steam heat exchanger and that all nascent T liberated from the reaction will permeate the heat exchanger walls. Assume that the heat exchanger material corrodes at the same rate as the primary system material, i.e., assume it is equivalent to a 300 series stainless steel. As the average temperature of the heat exchanger is only 460°C, we must compute the oxidation rates expected at this lower temperature by means of the same approximation technique used before [Eq. (6)]:

$$\frac{\text{Oxidation Rate at } 650°\text{C}}{\text{Oxidation Rate at } 460°\text{C}} \propto \left(\frac{e^{-\frac{59{,}000}{1.99 \times 923}}}{e^{-\frac{59{,}000}{1.99 \times 733}}} \right)^{1/2} = 64 \qquad (9)$$

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*"Conservative" is always used herein in the sense of anticipating the most extreme, or worst, case.

The oxygen consumption rate at 460°C would then be expected to be approximately

$$3 \times 10^{-12} \frac{\text{gm } O_2}{\text{sec-cm}^2} \times \frac{1}{64} = 4.7 \times 10^{-14} \frac{\text{gm } O_2}{\text{sec-cm}^2} \qquad (10)$$

For each gram oxygen consumed in the corrosion reaction, 2/16 gm T will be liberated, or

$$\text{T liberation rate} = \frac{2}{16} \times 4.7 \times 10^{-14} = 5.8 \times 10^{-15} \frac{\text{gm T}}{\text{sec-cm}^2} \qquad (11)$$

If we multiply the value of Eq. 11 by the heat exchanger area, we obtain

$$5.8\text{x}10^{-15} \frac{\text{gm T}}{\text{sec-cm}^2} \times 8.3\text{x}10^8 \text{cm}^2 \times 8.6\text{x}10^4 \frac{\text{sec}}{\text{day}} = 0.42 \frac{\text{gm T}}{\text{day}} \qquad (12)$$

or

$$0.42 \frac{\text{gm T}}{\text{day}} \times 9600 \frac{\text{Ci}}{\text{gm T}} = \underline{4000 \text{ Ci/day}} \qquad (13)$$

While the result of Eq. 13 is based on rather conservative assumptions, the result is far higher than the 1.8 Ci/day estimated by Wittenberg on the basis of T permeation of heat exchanger tubing. It should be noted also that the assumption of preferential metal oxidation by the T_2O molecule in the presence of a preponderance of O_2 is not overly extreme, as this phenomenon is found in the oxidation of zirconium alloys in this temperature range.

It would appear that generation of T by steel oxidation remains an open question, and one that may eventually require a laboratory study for resolution. If T generation is found to be a problem under the test parameters described, a logical solution would be to increase the O_2 pressure and decrease the T_2O pressure. The latter could be accomplished by increasing the size and/or reducing the temperature of the molecular sieve bed.

Within the steam generator pressure tubing, the reaction between steam and the pressure tube alloy will constitute a continuous source of nascent protium. The protium will tend to permeate the pressure tubing and enter the primary coolant, where it will become oxidized and eventually reside, along with the T_2O, in the molecular sieve. While this does not constitute a material compatibility problem, it is worth considering if an attempt is made to evaluate the purity of the tritium oxide residing in the molecular sieve. It should also be taken into account in sizing the molecular sieve beds, so that sufficient capacity is assured.

5. Mechanical Properties

The effects of corrosive environments on the long-term mechanical properties of a structural material are of obvious concern to the system designer, as any degradation process must be anticipated and suitable allowance made, if necessary, to ameliorate the effect. This may be accomplished by environment control, material selection, increase in sectional area, design modification, or a combination of two or more of these factors. In general, a high-temperature corrosive attack consists of one or more of the following:

1) Surface reaction, with uniform or selective loss of alloy constituents;
2) Subsurface reaction, such as internal oxidation;
3) Contaminant solution effects.

In addition to the foregoing, undesirable changes in the metal microstructure may take place due to the operating temperature alone, such as precipitate coarsening, sensitization, sigma phase precipitation, etc. In this section the effect of various high-temperature environments on the mechanical properties of stainless steels will be reviewed and the results analyzed for applicability to the UWMAK-II reactor design.

Most of the available data concerning the effect of environment on the high-temperature mechanical properties of stainless steels consist of creep and creep-rupture studies. The data are found to be highly variable and difficult to interpret, as the results depend in an intricate manner on temperature, stress level, reactive gas(es) present, steel composition, specimen geometry, and specimen pretreatment.

The creep, stress-rupture, tensile, impact, and fatigue properties of Type 316 ss in air, helium, and sodium at 650°C have been reported by Kirschler and Andrews.(11) The creep rates in helium and sodium were slightly higher than in air. The stresses required to produce 1 per cent creep in helium and sodium in 10,000 hr were within 15 percent of the corresponding stress in air. The stress-rupture tests, to 4000 hr maximum time, showed no significant difference in rupture strengths in any of the three environments. In the cyclic strain tests the specimens fatigued in air withstood the least cycles before failing and the specimens in helium the most. At 1 per cent cyclic strain, the specimens in air failed in ~ 1500 cycles, while the specimens in helium withstood ~40,000 cycles. The fatigue test yielded the only results which were environment-sensitive.

LeMay, Truss, and Sethi(12) determined the creep properties of Type 347ss over the temperature range 604°-791°C in air, nitrogen, argon, and vacuum ($5\text{x}10^{-6}$ Torr). They found the rupture life to be lower in air than in argon or vacuum over the entire temperature range. The elongation at fracture was higher in air than in the other environments in every test; the lowest elongation-at-fracture reported was 13 per cent and the lowest reduction-in-area 16 per cent. Both of these minimums came from tests in the argon environment. It is possible that selective oxidation and intergranular attack was taking place in the argon tests.

Eberle, Ely, and Dillon(6) performed tensile and impact tests on specimens of Types 304, 321, 347, 316, and 318 steels after exposure of 6950 hr to a 760°C superheater atmosphere, i.e., steam on one side and flue gas on the other. Both steam and flue gas are more corrosive towards these steels than air. The tube wall thicknesses ranged from 1 cm (Type 347) to 1.2 cm (all other steels). In both room-temperature and 732°C tensile tests, the alloys which had seen superheater service exhibited higher yield and ultimate strengths and lower ductilities than the control specimens. The lowest post-service room temperature ductility (elongation in 1.5 in.) was 22 percent, for Type 347ss; the lowest 732°C ductility was 57.3 percent, also for Type 347. The room temperature Charpy impact values (for half-width specimens) were found to be significantly reduced by the superheater exposure. Type 304 retained 44% of its pre-exposure impact strength, while Type 318 retained the least, only 20% (8.9 ft-lb). The authors concluded that "the remaining notch toughness appears to be adequate for superheater service if there is no further significant decrease."

McCoy(13) studied the creep-rupture behavior of Type 304 ss in Ar, CO, CO_2, H_2, N_2, O_2 and air at temperatures of 816°C and 927°C. The environments listed in order of a decreasing strengthening effect at 816°C and 3,400 psi stress are CO (lowest strain rate), CO_2, N_2, air, Ar, H_2 and O_2 (highest strain rate). The results are similar at 927°C and 1200 psi stress, except that Ar and H_2 environments yielded higher strain rates than the O_2 environment. McCoy pursued the effect of O_2 pressure on creep rate by exposing specimens to Ar-O_2 mixtures at 1 atm total pressure at 816°C. He found a maximum creep rupture life and a minimum creep rate at ~10 ppm O_2 in Ar. These effects were considered "inexplicable". Exposure of the specimens to the CO-CO_2 environments resulted in carburization and hardening of the specimens, hence the increase in creep strength. Nitrogen is thought to strengthen the steel through a hardening mechanism near the sample surface.

The puzzling effect of 0_2 on creep strength was investigated in more detail by Rodriquez,(14) who again exposed Type 304ss specimens to Ar-0_2 mixtures at 815° and 927°C. At concentrations of 0_2 in the range 0 to 70 ppm, the creep rate decreases with increasing 0_2 content at 815°C and 3400 psi stress. For 0_2 concentrations between 70 and 250 ppm, the rate increases to a maximum value. The creep rate again decreases at 0_2 concentrations above ~250 ppm, with the creep rate in pure 0_2 approximating the low rate found at ~70 ppm. At 927°C and 2000 psi stress the data follow the same trend. Metallographic analysis showed no evidence of internal oxidation and no increase of oxygen in the bulk samples with increasing oxygen level in the environment. The surface crack densities were found to increase with oxygen concentration in the environment, as reported by McCoy. The average crack depth attained a maximum value at ~250 ppm oxygen, i.e., the level corresponding to maximum creep rate. Rodriquez explains the oxygen pressure dependence of creep rate on the basis of the properties of the oxide scale formed in the different environments, i.e., a hard, tenacious scale will produce a higher creep strength than a weak, easily spalled layer.

Smith, Shahinian, and Achter(15) determined fatigue crack growth rates in Type 316ss at 500° and 800°C as a function of 0_2 pressure. Crack growth rates showed a sharp increase with 0_2 pressure in an intermediate pressure range (10^{-3} to 1.0 Torr), but little change at pressures outside this range. At 500°C, 1 Torr 0_2 pressure reduced the fatigue life by a factor of ~100 compared with that in vacuum; at 800°C the effect was somewhat smaller. A model in which the rate of fresh metal surface production equals the rate of surface coverage by gas molecule adsorption explains the 500°C results, but at 800°C the model does not fit the experimental data. The authors note that oxidation strengthening, leading to increased fatigue resistance, can take place at the higher temperature. Smith and Shahinian(16) found that the rate of strain hardening of Type 316ss during cyclic straining prior to crack initiation is dependent on O_2 pressure, with a pressure as low as $5x10^{-4}$Torr causing hardening at 500°C. A pressure of 10^{-3}Torr initiated hardening at 800°C.

The high-temperature gas-cooled reactor concept has been resonsible for a great deal of research work on the effect of contaminated helium on mechanical properties of stainless steels and superalloys.(17-20) While most of the helium atmospheres used in the studies are contaminated with CO and H_2, rather than O_2, the temperatures are in the appropriate range, and the relatively low oxidizing power of the atmospheres used could represent a possible transient condition in a CTR system.

Weinberg and Scoffin(17) exposed tensile and impact-tensile specimens of Types 321H, 347, 304 and 403 stainless steels and Inconel to impure helium at 650°C and 760°C for times to 3000 hr. Two helium impurity levels were used: 200-300 ppm CO with 200-300 ppm H_2, and 2000-3000 ppm CO with 2000-3000 ppm H_2. Oxidation rather than carburization appeared to be the major corrosion process. Both carburization and decarburization were observed. None of the materials studied exhibited a large change in mechanical properties after the 650°C exposure. After the 760°C exposures only moderate changes in mechanical properties were observed for all materials except Type 321ss, which exhibited a large decrease in ductility after 1500 hr in the high-impurity environment.

In general, however, control specimens encapsulated in vacuo and held at the test temperatures were affected as greatly as the specimens exposed to the impure helium environments.

Wood, Farrow, and Burke(18) studied the effect of air and impure helium on the creep and rupture behavior of Type 316ss at 800°C. The helium environments were maintained at two impurity levels: "nominally pure", with a maximum total impurity level of ~1000 ppm (largely H_2, CO, H_2O, and N_2), and "nominally impure", with a nominal composition of 1000 ppm H_2, 1000 ppm CO, and 100 ppm H_2O. The rupture times were found to be shorter and creep rates higher in both helium environments than in air. A rough averaging of the widely scattered data points yields a factor of four lower creep rate in air than in the helium environments, and a factor of three increase in rupture time in air over the helium environments. Metallographic examination of failed specimens revealed a pronounced difference in oxidation between the specimens tested in air and those tested in helium. Specimens tested in air showed thick, relatively uniform scales, while those tested in helium showed non-uniform oxide layers, grain boundary oxide penetration, and generally selective attack. The authors suggest that the lower creep strength in the contaminated helium is due to preferential oxidation of Cr, Al, and Ti at the grain boundaries in the low-oxidizing-potential helium, resulting in a lowering of the grain boundary surface energy and mechanical opening of the grain boundaries.

Cook, Barford, and Willoughby(19) cite some preliminary results for Type 316ss creep tested at 750°C in air, vacuum (10^{-5} Torr), and impure helium (He + 500 ppm CO, 500 ppm H_2, and 50 ppm H_2O at 10 psig). The creep rate in the impure helium was substantially higher (about a factor of two) than the creep rates in the air and vacuum environments. Again, the higher rate is ascribed to a selective oxidation of the alloy in the impure helium, with sub-surface penetration of the reactive environment and depletion of alloying elements near grain boundaries. These findings are consistent with those of Wood, et.al.(18)

Board(21), Huddle(22), and Darras(23) have all noted the apparent superiority of Nb-stabilized steels, such as Type 347, to Ti-stabilized steels, such as Type 321, in contaminated helium environments. These conclusions are consistent with the findings of Weinberg and Scoffin,(17) who reported an example of poor performance of Type 321 steel. Board(21) further concludes that "it would seem prudent at this stage to restrict the choice of materials for the steam cycle HTR [High Temperature Reactor] to alloys which do not depend on titanium and aluminum for strengthening." Such a restriction would, of course, rule out the use of gamma-prime hardened alloys, such as Incoloy 800 and Nimonic PE-16.

It must be recognized that stainless steels are being used extensively in high-temperature gas-cooled fission reactors. The alloys are generally performing well. Dragon Project and AVR (Arbeitsgemeinschaft Versuchsreaktor AVR GmbH., Dusseldorf) experience indicate essentially no compatibility problems with structural materials in normal (contaminated) helium service.(24,25)

Sulfur and carbonaceous materials must be rigorously excluded from the primary coolant. Board(20) points out that sulfur in ppm quantities can attack nickel-bearing alloys by forming the NiS/S eutectic, which melts at 508°C. The eutectic may then oxidize, freeing the sulfur. Carbonaceous materials, such as methane, lubricating oils or greases, diffusion pump oil, etc., can react rapidly with stainless steel surfaces at high temperature, causing gross carburization and embrittlement. While this type of attack may be considered beyond that expected from lightly contaminated helium, there is a possibility that it could occur, e.g., in the event of an oil leak or some other unexpected ingress of carbon-bearing material. Such fault conditions must be anticipated and appropriately guarded against.

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