

INTERGRANULAR SULFUR ATTACK IN NICKEL AND NICKEL-BASE ALLOYS

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Abstract

The phenomenology of intergranular sulfur attack in nickel and nickel-base alloys and the resulting embrittlement on post-exposure tensile testing was investigated. Using Ni 270 as a model material, specimens were exposed at temperatures between 450°C and 800°C to gaseous sulfur environments with sulfur partial pressures ranging from 10^{-8} atm. to 10^{-4} atm. Increasing exposure temperature and increasing sulfur partial pressure increased the severity of the sulfur attack as measured by post-exposure tensile testing in air. Measurements of the maximum depth of intergranular fracture on room temperature tensile specimens were used to calculate the activation energy for the sulfur penetration as 74 KJ/mol. Auger analyses indicate that the level of sulfur on the grain boundaries increases with increasing temperature and increasing sulfur partial pressure. The implications of these data for nickel-base alloys are discussed.

Introduction

Many high temperature alloys will be operating in increasingly corrosive environments in the future. Mechanical property degradation resulting from oxygen attack as well as attack by more aggressive gaseous species such as sulfur and chlorine has become a critical issue. There is now a growing realization that assessment of the full extent of environmental damage to these alloys requires looking beyond the surface scale formation. The diffusion of oxygen from the environment down grain boundaries, resulting in embrittlement and enhanced crack propagation, has been well-documented in nickel and nickel-base alloys (1). Limited preliminary work on the effects of grain boundary penetration of other aggressive environmental gaseous species on nickel and nickel-base superalloys implies that tensile ductility, stress rupture life, and crack propagation resistance are all more seriously impaired by sulfur than by oxygen (2). For example, Figure 1 compares the elongations obtained in Ni 270 after 50 hours exposure at 800°C in air, sulfur, and chlorine atmospheres and readily demonstrates the profound effect of gaseous sulfur on the ductility of nickel. Figure 2 shows that the stress rupture life of IN738, a cast nickel-base alloy, is drastically reduced by two orders of magnitude after exposure in a sulfur environment at 800°C. Clearly then, the intergranular embrittlement of nickel and nickel-base alloys by sulfur vapor warrants serious consideration.

The embrittlement of nickel and nickel-base alloys due to the intergranular segregation of sulfur from the nickel-base matrix is widely reported in the literature (3-7). The presence of sulfur reduces grain boundary cohesion and results in decreased tensile ductility, enhanced crack propagation, and lower impact resistance. The current investigation was undertaken to verify as well as characterize the embrittlement caused by sulfur which is present in the operating environment, diffusing down grain boundaries and causing a degradation of mechanical properties. This study is based on the premise that the intergranular penetration of sulfur from the environment leads to the same reduction in grain boundary cohesion as that caused by intergranular sulfur segregation from the matrix. Therefore, pre-exposures of sufficient time and temperature in sulfur-containing environments may embrittle the grain boundaries

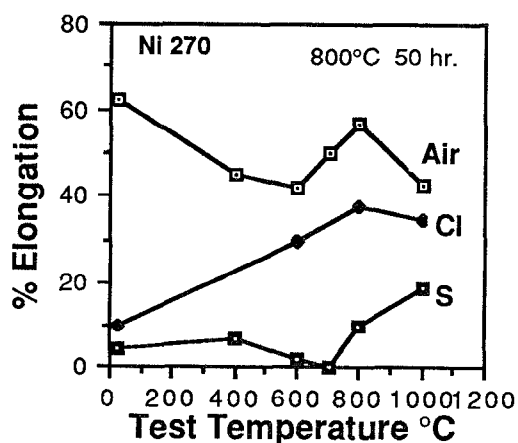


Fig.1 Tensile elongation of Ni270 after 50 hr. exposure in air, Cl, and S at 800°C.(2)

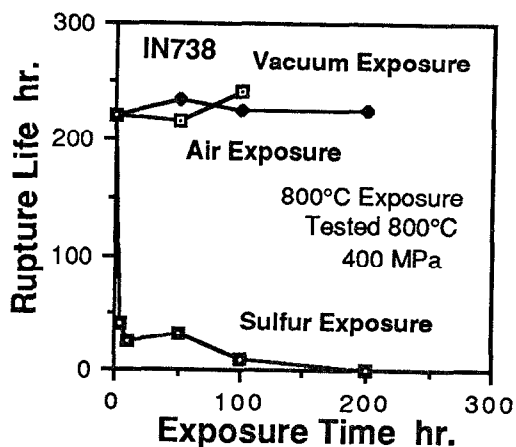


Fig. 2 Effect of prior 800°C exposure in air, vacuum and sulfur on the 800°C stress rupture properties of IN738.(2)

throughout the cross-section and result in a general reduction of ductility on subsequent tensile testing in air. The depth of intergranular mode on the tensile fracture surface could be used to delineate the extent of this embrittlement. On the other hand, fracturing specimens in a sulfur-containing environment would result in sulfur penetration localized at the crack tip. Such localized penetration is likely to be diffusion-controlled and stress-accelerated and may be the mechanism for reported instances of enhanced crack propagation in sulfur-containing environments (8,9).

The objectives of the current investigation are:

- 1) To confirm that elemental sulfur from a gaseous environment may enter nickel and nickel-base alloys via the grain boundaries and degrade their fracture resistance.
- 2) To establish the basic parameters of such a sulfur attack, describing the phenomenology of embrittlement, including its dependence on the sulfur activity, the time and temperature of exposure, as well as the alloy composition sensitivity.

Experimental Procedure

Metal/Metal Sulfide Mixtures

The initial experimental approach was similar to that used successfully to study oxygen embrittlement (1), including the use of nickel as a model material. Pre-exposures at elevated temperatures in sulfur-containing environments were followed by post-exposure mechanical testing in air. Powder mixtures of metal/metal sulfides were used to establish thermodynamically predetermined sulfur partial pressures at elevated temperatures. The tensile specimens of 2.5 mm gauge diameter and 9.5 mm gauge length, together with a quartz boat of the metal/metal sulfide mixture, were sealed in evacuated quartz tubes and heated in a furnace for 24 hours at temperatures between 400°C and 800°C. Elevated temperature tensile testing over the range of 250°C to 700°C was done at a crosshead speed of 2.5 mm per minute, particularly looking for an effect on mid-range ductility minima.

Controlled Sulfur Partial Pressure

A limitation of the initial experimental approach was that for a given metal/metal sulfide mixture, the exposure temperature of the specimens could not be varied independently of the established sulfur partial pressure. Also, the sulfides are notoriously non-stoichiometric, making it difficult to define precisely the sulfur partial pressure by thermodynamic calculations. Therefore, a second experimental procedure for exposure was designed. Elemental sulfur, for which there is well-established vapor pressure data (10), was used as the source of the sulfur partial pressure. The sulfur and the specimens were placed in a two-zone furnace which allowed for independent temperature control: a lower temperature for the sulfur powder to establish the desired sulfur partial pressure and a higher temperature for the specimens. The two zones are controlled in such a manner to develop a monotonic thermal gradient to insure that the specimens will see the partial pressure established by the temperature in the locality of the sulfur. A schematic of the actual equipment is shown in Figure 3. The specimens, along with a magnetically-movable quartz container for the sulfur, are sealed under

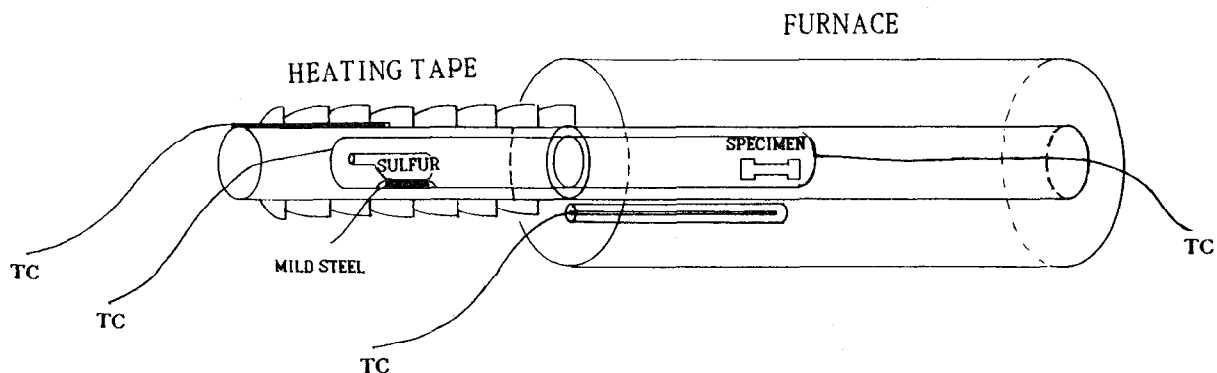


Fig. 3 Schematic of two-zone furnace for controlled sulfur partial pressure using elemental sulfur.

vacuum in a 50 cm long evacuated quartz tube. During evacuation, the vacuum is achieved by a Hg diffusion pump and is routinely better than 10^{-5} torr (10^{-8} atm). Prior to placement in the furnace, the sealed reaction tube is carefully positioned horizontally and the sulfur container is magnetically moved to the opposite end from the specimens. The detail of the schematic shows the unique design of the sulfur container. A small piece of mild steel, encased in quartz and attached to the bottom of the sulfur well, allows the container to be moved magnetically. The narrow neck is lightly stuffed with quartz wool prior to encapsulation to keep the sulfur powder contained during evacuation and handling. This simple gadget has worked well and has eliminated the need for a more elaborate system.

In order to establish the kinetics of the sulfur penetration, it became necessary to use specimens large enough to result in only partially intergranular fracture at higher temperatures and longer exposure times. Larger size specimens with 6.35 mm gauge diameter and 25 mm gauge length were exposed to the gaseous sulfur. Early in the investigation it was found that when sulfur attack occurred to the extent that it could be identified by a decrease in tensile ductility, it occurred with nearly equal severity across the range of test temperatures from 250°C to 700°C. Since the embrittlement could be measured at room temperature just as well as at elevated test temperatures, the subsequent tensile testing was done conveniently at room temperature.

Auger Studies

Pins for Auger analysis were machined to 2.5 mm diameter and were exposed to the various sulfur environments created by either the sulfide mixtures or by elemental sulfur in the two-zone rig, as described earlier. For sulfur analysis of the grain boundaries, the pins were fractured in situ in the high vacuum (10^{-8} torr) of the Auger and immediately analyzed. Additional pins were cut perpendicular to the growth direction of a directionally solidified ingot of Ni 270. These had a bamboo-type grain structure which could be fractured to expose only a single grain boundary in order to eliminate grain to grain differences in S/Ni peak ratios and possibly reveal a surface to center gradient in the amount of sulfur present on the grain boundary. The particular DS ingots we had were extremely gassy and only a few pins could be used. Nevertheless, Auger

results were obtained in both polycrystalline and DS pins for one of the exposure conditions.

Results and Discussion

In the experiments involving exposures to the sulfide mixtures, it was found that at a constant temperature, increasing sulfur partial pressures led to decreased tensile ductility in Ni 270 as shown in Figure 4. At 800°C the partial pressure of sulfur in equilibrium with the Ni/NiS mixture is approximately 4×10^{-4} atm. (11), and in equilibrium with the Cr/Cr₂S₃ mixture is approximately 1×10^{-8} atm. (12). Also, as shown in Figure 5, for a given sulfide mixture, increasing exposure temperature, and concomitant increased sulfur partial pressure, results in decreased ductility. The sulfur partial pressures in equilibrium with the Ni/NiS mixture are : 4×10^{-4} atm. at 800°C, 9×10^{-6} atm. at 600°C, and 2×10^{-8} atm. at 400°C (11). Because of the imprecision of final elongation measurements when there is prevalent surface cracking, the nonelastic elongation to maximum load is reported here. As mentioned previously, these figures indicate that when sulfur embrittlement did occur in Ni 270, it appeared to be equally severe over the full test temperature range, revealing no obvious mid-range ductility minimum.

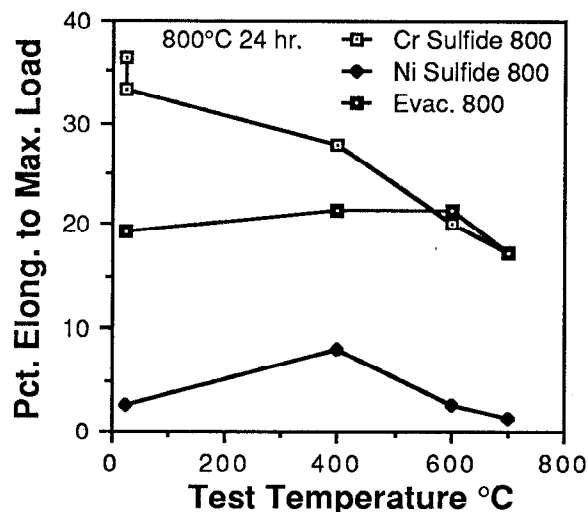


Fig. 4. Effect of various exposures at 800°C on tensile elongation of Ni 270

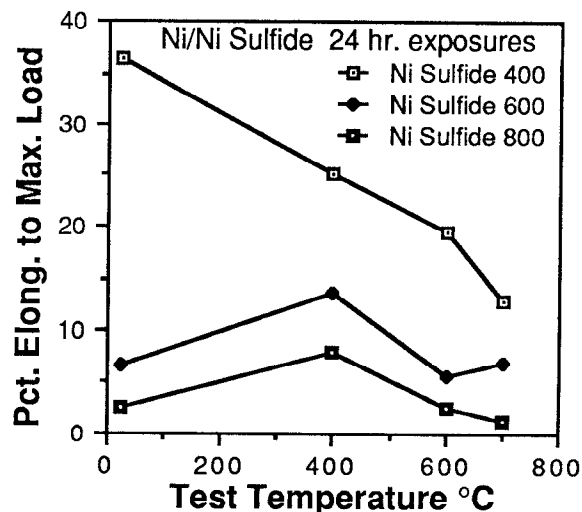


Fig. 5. Effect of Ni/Ni Sulfide exposures on post-exposure tensile elongation of Ni 270

Room temperature test results from exposures of Ni 270 to sulfur vapor in the two-zone rig are shown in Figures 6 and 7. As can be seen in Figure 6, at a constant sulfur partial pressure of 1.45×10^{-6} atm., equivalent to sulfur at 80 °C (10), increasing specimen temperature results in a systematic decrease in subsequent room temperature tensile ductility. At this sulfur partial pressure, little sulfur attack was noted at 450°C, but at 500°C the dramatic effect of the sulfur became evident, and increased in severity with increasing exposure temperature. Figure 7 shows that at a constant specimen temperature of 600°C, increasing sulfur partial pressure tends to decrease the room temperature tensile ductility. Sulfur partial pressures of 2×10^{-8} atm., equivalent to sulfur at 40°C (10), had no effect on the tensile properties. However at 6×10^{-8} atm., equivalent to sulfur at 50°C (10), there is a dramatic effect.

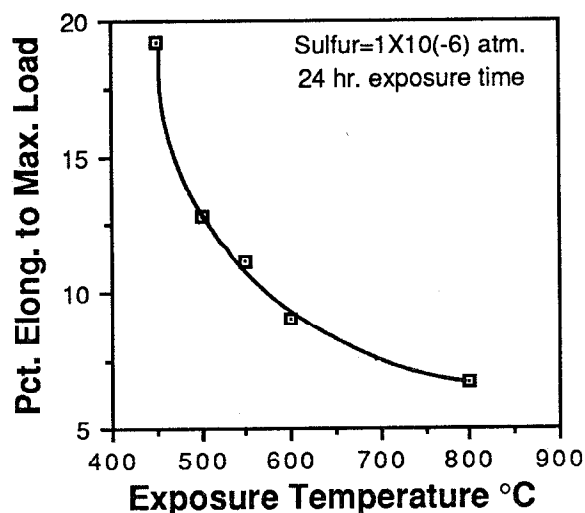


Fig. 6 Effect of exposure temperature at a constant sulfur partial pressure on room temperature tensile ductility of Ni 270

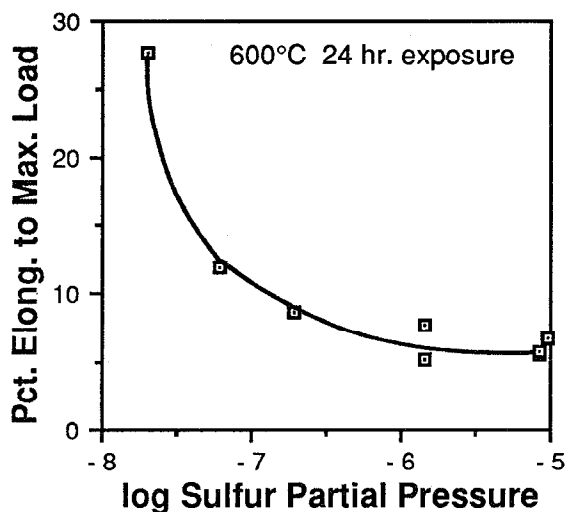


Fig. 7 Effect of sulfur partial pressure at 600°C on room temperature tensile ductility of Ni 270

It is the grain boundary diffusion of sulfur from the environment which causes the intergranular embrittlement. The possible formation of liquid films at the grain boundaries was not responsible for the attack, because significant embrittlement was achieved at temperatures below 635°C, the melting point of the lowest melting Ni/NiS eutectic. There was never any obvious surface scale formation on the Ni 270 specimens when they were removed from the reaction chamber. The machining marks were still clearly visible and yet the resultant embrittlement was dramatic. Because there was no detectable surface sulfide scale formed at the exposure temperatures and sulfur partial pressures, the sulfur on the grain boundaries is probably present as elemental sulfur segregation, rather than as a discrete sulfide phase. No grain boundary sulfides were apparent on the intergranular fracture surfaces when examined by SEM, or in the polished cross section when examined by optical microscopy. EDAX analysis (on the SEM) was not able to detect sulfur on either the fracture surface or the specimen surface. It is only from the Auger analysis of the intergranular fracture surface (broken in situ) that one can deduce that the embrittling species is the sulfur which has penetrated from the exposure environment. Brief ion milling readily depletes the sulfur on the grain boundary surface indicating that it is present in only the first few atom layers.

Some results of AES analyses on pre-exposed Ni 270 pins fractured in situ in the Auger, are shown as S/Ni peak height ratios in Table I. The analyses were made using a 10 KV beam with 2.5 nA beam current.

TABLE I

Auger Results for Various Exposures

<u>Exposure</u>	<u>Sulfur Partial Pressure</u>	<u>Structure</u>	<u>Ave.S/Ni $\pm 2\sigma$</u>
600°C/Ni/NiS: 24 hr.	9×10^{-6} atm.	Poly.	.512 \pm .30
600°C/S at 80°C: 24 hr.	1.45×10^{-6} atm.	Poly.	.440 \pm .23
600°C/S at 80°C: 24 hr.	1.45×10^{-6} atm.	D.S.	.566 \pm .08
800°C/S at 80°C: 24 hr.	1.45×10^{-6} atm.	Poly.	.624 \pm .13

Ten spots were analyzed moving across the diameter on each fracture surface. No obvious sulfur gradient from surface to center was found on either the polycrystalline or DS fracture surfaces. Due to the variability in the measurements from grain to grain, it was assumed that the data were normally distributed and the mean $\pm 2\sigma$ is indicated for each. As can be seen from the data, the average sulfur level detected on the intergranular fracture surface increased with increasing sulfur partial pressure and temperature of exposure. However, the level of sulfur was greater for the DS than for the polycrystalline pin of the same condition, and as was expected, variation among individual measurements was less for the DS pin than for the polycrystalline pin.

Measurements of the maximum radius of intergranular fracture were made on SEM fractographs of the larger size 6.35 mm gauge diameter tensile specimens as well as on those smaller 2.5 mm gauge diameter specimens where only partial intergranular fracture occurred. These measurements relate to the depth of sulfur penetration and were used to calculate an activation energy for the process. The typical diffusion relationship of $x \propto t^{1/2}$ gives a good description of the data, where x is the penetration distance in centimeters and t is the exposure time in seconds; for data at one temperature, x^2/t plots are not ordered with t . Therefore, one can assume an equation of the form:

$$x = K\sqrt{D_{gb} t} \text{ where } D_{gb} = D_0 \exp (-Q/RT)$$

Although K and D_0 cannot be obtained directly, the activation energy, Q , for the process can be determined by plotting $\ln x^2/t$ vs. $1/T$, and the slope of the best fit line through the data will be $-Q/R$. In this case the activation energy for intergranular sulfur penetration in Ni 270 was found to be 74 KJ/mol.

It is interesting to compare the kinetics of this sulfur penetration with those of oxygen penetration as shown in Figure 8. The present data for sulfur in Ni 270 are plotted alongside results for oxygen penetration made by measuring the depth of gas bubble formation (CO_2) in Ni 270 (13). Also shown on the graph are some results for a nickel-base superalloy, Rene 80, where the depth of oxygen penetration was determined by sequentially machining away embrittled material until ductility was restored (14). The kinetics of the sulfur penetration are much faster (the line lies higher on the graph) and the activation energy is much lower (the slope is less steep) at 74 KJ/mol for sulfur than for oxygen in Ni 270 at 274 KJ/mol or oxygen in Rene 80 at 280 KJ/mol.

The activation energy for S^{35} volume diffusion in pure nickel has been reported as 376 KJ/mol in polycrystalline specimens at temperatures above 1000°C (15) and as 218.6 KJ/mol for single crystals at temperatures between 800°C and 1225°C (16). For polycrystalline specimens at temperatures between 800°C and 1000°C, it has been measured as 192 KJ/mol (17). Investigators have noted that sulfur prefers to diffuse along grain boundaries at lower temperatures and that the diffusivity becomes non-linear with inverse temperature (18). For example, data for the diffusion of S^{35} into fine grained TD nickel (18) indicates an activation energy of 159 KJ/mol at

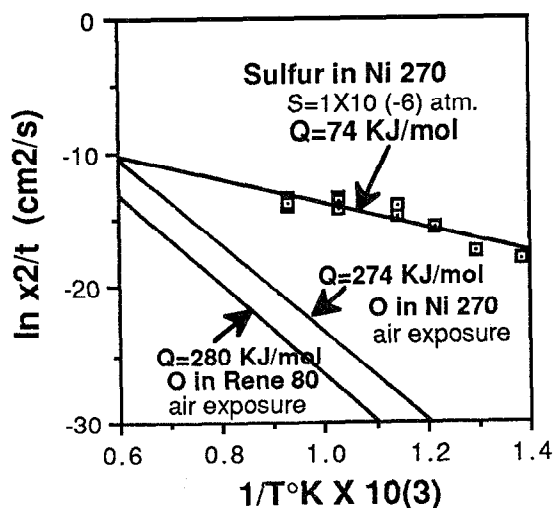


Fig. 8 Plot of $\ln x^2/t$ vs. $1/T$ comparing sulfur penetration in Ni 270 to oxygen penetration in Ni 270 (11) and Rene 80 (12).

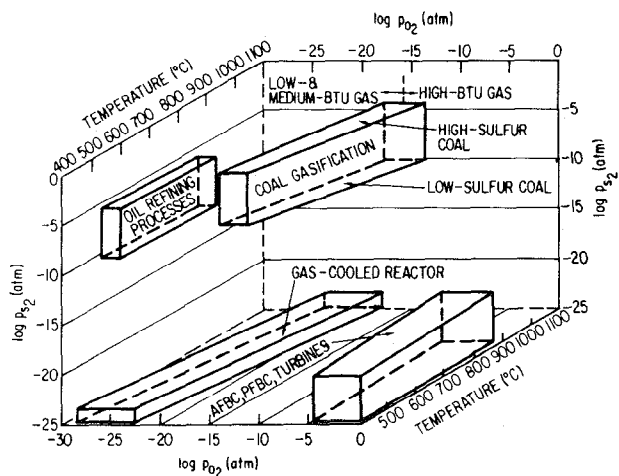


Fig. 9 Sulfur-Oxygen-Temperature diagram indicating operating conditions in various commercial processes. (17)

temperatures above 900°C. However, data were reported for 850°C and 775°C, although these lower temperature data were purposefully disregarded in the calculation of the activation energy because of the non-linearity with the higher temperature data. If a separate calculation is done for only these lower temperature data, an activation energy of 51 KJ/mol is found. Therefore, our value of 74 KJ/mol for the activation energy of sulfur penetration in Ni 270 measured at temperatures between 450°C and 800°C, although much lower than any found in the literature, seems reasonable in light of the TD nickel data. Typically the activation energies for grain boundary diffusion are significantly lower than for volume diffusion, which corresponds to our findings here.

Commentary

To predict the implications of these data relative to the performance of nickel-base alloys in sulfur-containing environments is not a simple task. Certainly, the kinds of sulfur partial pressures used in this study are typically found in many industrial environments as shown in Figure 9 (19). For instance, in both coal gasification and oil refining processes, the sulfur partial pressures are in the range 10^{-5} atm. to 10^{-10} atm. at temperatures from 500°C to 1000°C. Even in environments where sulfur partial pressures are much lower, localized concentrations are always a possibility. For example, gas turbines often encounter severe sulfidation even though the overall conditions would indicate such reactions should not occur. Although elemental sulfur penetration and embrittlement in Ni 270 has been demonstrated in the absence of visible corrosion products, the effects of external scale formation and internal alloying elements on such sulfur penetration in specific nickel-base alloys must be addressed on an individual basis. For certain alloys such as IN738 the embrittlement by sulfur penetration has been clearly shown (2). In general, nickel-base alloys do show an acceleration of fatigue crack propagation in sulfur environments indicating their general susceptibility to the detrimental effects of sulfur (8,9). Having demonstrated the drastic intergranular embrittlement which can occur in

Ni 270, it is hoped that by identification of such a phenomenon, a broad awareness of the possibility of intergranular sulfur embrittlement in nickel-base alloys will be developed.

Conclusions

1. Sulfur penetrates from the environment down grain boundaries in Ni 270 during pre-exposures at temperatures above 450°C and sulfur partial pressures above 6×10^{-8} atm., resulting in a degradation of tensile ductility on subsequent room temperature tensile testing in air, by inducing intergranular fracture.
2. Increasing exposure temperature in the range 450°C to 800°C while maintaining a constant sulfur partial pressure 1.45×10^{-6} atm., equivalent to the partial pressure of elemental sulfur at 80°C (10), greatly increases the severity of the embrittlement.
3. Increasing sulfur partial pressures above 6×10^{-8} atm. at a constant exposure temperature of 600°C increases the severity of the embrittlement.
4. Measurements of the depth of intergranular fracture indicative of the extent of the sulfur penetration were used to calculate an activation energy of 74 KJ/mol for sulfur penetration in Ni 270 in the range 450°C to 800°C. This is lower than the activation energy typically given for volume diffusion of sulfur in nickel, which is consistent with the fact that the sulfur penetration is a grain boundary phenomenon. Intergranular sulfur penetration is faster than intergranular oxygen penetration in Ni 270.
5. Auger analyses indicate that both increasing sulfur partial pressure and increasing temperature increases the level of sulfur found on the grain boundaries. After the same exposure, the level of sulfur detected on a single grain fracture was greater than on a corresponding polycrystalline fracture surface. No gradient in sulfur level from surface to center was detected by Auger.
6. Results similar to these found for sulfur attack in Ni 270 are indicated for some nickel-base alloys. However, extension of this phenomenon to individual nickel-base superalloys will require more specific experiments.

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