Creep Rupture Properties of Nickel-base Heat Resisting Alloys in Two Impure Helium Environments of HTGR*

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Synopsis

The creep rupture properties of nickel base heat resisting alloys are investigated in two types of impure helium of He-2 and PNP-He at 1 000 °C, simulating a high temperature gas-cooled reactor (HTGR) environment. The alloys examined are four new alloys developed for heat exchangers of nuclear steelmaking system using HTGR. All the alloys are decarburized in some extent in PNP-He, while some of them are carburized in He-2 during the creep rupture testing, indicating that carbon activity of the gases is lower in PNP-He than in He-2 at 1 000 °C. Decarburization is found to be the most important of the environmental effects deteriorating the creep rupture properties of the alloys. The environmental effects of the formation of internal oxides and the depletion of gamma prime and α -W precipitates beneath the alloy surface are also examined.

I. Introduction

A nuclear steelmaking system has been developed as a national project in Japan. In the system, nuclear energy of a high temperature gas-cooled reactor (HTGR) is used as a process heat for direct steelmaking of iron ore. The primary helium, which comes out of HTGR at 1 000 °C and 40 atm, is heat transferred to the secondary helium through the medium of an intermediate heat exchangers. The secondary helium at 925 °C and 45 atm is utilized to heat a reducing gas for the direct steelmaking. The development of heat resisting alloys for the intermediate heat exchangers is one of the important subject for the system.

Helium coming out of HTGR contains small amounts of impurities, such as H₂O, H₂, CH₄, CO and CO₂, in concentration ranges between a few ppm and a few hundred ppm, in which heat resisting alloys are not only oxidized but also carburized or decarburized.¹⁾ Because the helium of HTGR makes an unique environment with a low oxygen potential,

corrosion rates in the helium are larger than in air. In Japan, a requirement of the creep rupture strength of more than 1 kg/mm² at 1 000 °C and 1×10⁵ h in the helium has been imposed to materials for the intermediate heat exchangers.

The nuclear systems utilizing HTGR have also been developed in F. R. Germany for coal gasification and in U.S.A. for electric power plants. The impurity levels in the helium of the systems are different each other. Since the corrosion behavior of heat resisting alloys depends on the impurity levels in the helium, creep rupture properties of heat resisting alloys are also considered to depend on the impurity levels.

In our institute, a creep rupture test has been carried out on many heat resisting alloys in two helium environments of HTGR, He-2 proposed in Japan and PNP-He (PNP; Prototypanlage Nukleare Prozeßwärme) proposed in F. R. Germany. The materials used are five candidate alloys, R4286,²⁾ SZ,³⁾ KSN,⁴⁾ 113MA⁵⁾ and NSC-1,⁶⁾ which have been developed in Japan for the intermediate heat exchangers, Hastelloy XR⁷⁾ (a modified alloy of Hastelloy X) and a commercial Inconel 617. The aim of the present paper is to compare the environmental effects of impure helium on the creep rupture properties, especially the creep rupture life, of four candidate alloys, R4286, SZ, KSN and 113MA, in He-2 and PNP-He at 1 000 °C.

II. Experimental Method

The chemical compositions of the alloys examined are given in Table 1.²⁻⁵⁾ These are nickel base superalloys, containing high concentrations of molybdenum and/or tungsten for solid-solution strengthening of the γ matrix. The second phases precipitated are

Table 1. Chemical compositions of the alloys tested. (wt%)

Alloy	C	Ni	Cr	W	Mo	Co	Al	Ti	Fe	B	Zr	S	Si	Mn	P	Nb
R4286	0.046	55.66	18.89	5.8	3.98	10.65	2.13	2.41	0.31	0.0036	0.054	0.004	0.06	—	0.002	—
SZ	0.04	61.877	27.65	5.04	5.02	—	—	—	—	0.0056	0.017	0.009	0.02	0.32	0.001	—
KSN	0.028	57.79	15.88	25.83	—	—	—	—	—	—	0.033	0.004	0.005	0.007	0.003	0.42
113MA	0.035	59.085	22.64	17.69	—	—	—	0.47	—	—	0.032	0.003	0.04	—	0.005	—

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(Cr, W, Mo)₂₃C₆ carbide and γ' (Ni₃(Al, Ti)) in R4286, (Cr, W, Mo)₂₃C₆ in SZ, (Cr, W)₆C and α -W (tungsten rich bcc phase) in KSN, and (Cr, W)₂₃C₆ and α -W in 113MA. The dimensions of the specimen are 6 mm in gauge diameter and 30 mm in gauge length.

The creep rupture test was carried out in He-2 and PNP-He at 1000 °C using lever type testing machines. The impurity contents in the helium are given in Table 2. A retort made of MO-RE II in the machine was coated by nickel in order to prevent the consumption of the impurities in the helium due to the reactions with metallic elements, such as chromium, in the retort. As will be described later, nickel was inert in the helium used in this experiment. To avoid off-gassing, the frange joined with the bellows at the upper side of the retort was fitted to the pullrod by an O-ring. Therefore, as the specimen was elongated by creep, the pullrod was displaced together with the bellows. The pressure of the helium was 0.4 kg/cm² in gauge pressure. The flow rate of the helium was 300 cc/min, which corresponded to 53 cc/min·cm² on the gauge portion of the specimen. This rate was sufficient for the present purpose. The applied stress was 3.7 and 3.0 kg/mm² for R4286, 2.3 and 1.9 kg/mm² for SZ, 3.0 and 2.3 kg/mm² for KSN, and 4.0 and 3.0 kg/mm² for 113MA. The temperature of the specimen was measured by two pairs of Pt/Pt-13%Rh thermocouples attached to the upper and lower sides of the gauge portion by nichrome wires of 0.1 mm in diameter. The creep curves were obtained by measuring the displacement of the pullrod by a dial gauge.

At the start of the test, the retort was evacuated to 10⁻⁶ Torr and the helium was supplied. After this procedure was repeated several times, the flow rate of the helium gas was kept at 300 cc/min and then the specimen was heated. The helium was supplied to the testing machines from a circulating helium loop. After the helium from the testing machines was purified to high purity helium, given amounts of impurity gases were added and then the helium was supplied to the testing machines. The details of the operation of the helium loop are described elsewhere.⁸⁾ The impurity concentrations in the helium were measured by a gas chromatograph and a hygrometer.

After the creep rupture testing, the fractured surface and the longitudinal cross section of the specimen were metallographically observed by scanning electron and optical microscopes. Concentration profiles were measured by an electron probe microanalyzer and carbon concentration by a LECO IR-12 carbon analyzer. The pieces for carbon analysis were taken from the surface layer of about 1 mm in depth by

using a water-cooled precision cutter, as shown schematically in Fig. 1.

III. Experimental Results

1. Comparison of Carbon and Oxygen Potentials between He-2 and PNP-He

Figure 1 shows carbon concentration of the surface layer, about 1 mm in thickness, of the alloys as a function of the test duration. The carbon concentration in each alloy is lower in PNP-He than in He-2. This indicates that carbon activity of PNP-He is lower than in He-2 at 1000 °C. All the alloys are decarburized in PNP-He. From the results in Fig. 1 and the alloy compositions in Table 1, it becomes evident that the alloys with high chromium concentration, such as SZ and 113MA, are scarcely decarburized in comparison with those with low chromium concentration, such as R4286 and KSN. The similar tendency has been reported by Yukitoshi *et al.*³⁾ for nickel-chromium-tungsten-molybdenum systems.

Oxygen potential in the two helium gases is compared by measuring the growth rate of internal oxides which is sensitive to the partial pressure of oxygen in the environment. A large number of internal oxides have formed in the alloy R4286 during the creep rupture testing; this is shown in Photo. 1. The internal oxides are identified as aluminum oxide by electron probe microanalysis. The kinetics of the internal oxidation are described by a parabolic rate law⁹⁾ as shown in Fig. 2. It should

Fig. 1. Carbon concentration of the surface layer, about 1 mm in thickness, of the alloys in He-2 and PNP-He at 1000 °C, as a function of duration of creep rupture testing. For carbon analysis, the hatched parts shown in the figure were cut from the gauge portion of the specimen by using a water-cooled fine cutter.

Table 2. Impurity contents in He-2 and PNP-He. (ppm)

	H ₂ O	H ₂	CH ₄	CO	CO ₂	N ₂
He-2	3	300	4	100	1	<5
PNP-He	1.5	500	20	20	1	<5

(a) 3.0 kg/mm² in He-2, $t_r=2\,221$ h
(b) 3.0 kg/mm² in PNP-He, $t_r=820$ h

Photo. 1. Internal oxides formed in R4286 after creep rupture testing in He-2 and PNP-He at 1 000 °C.

Fig. 2. Parabolic plots of the internal oxidation depth of R4286 in He-2 and PNP-He at 1 000 °C.

be noted that the parabolic rate constant is about three times greater in PNP-He than in He-2. This difference is considered to be caused by the difference of the partial pressure of oxygen between the two helium gases, because the diffusion coefficient of oxygen in the alloy is not affected by the environments. The results in Fig. 2 suggest that the partial pressure of oxygen of the gases is larger in PNP-He than in He-2. Then, PNP-He is a more decarburizing and oxidizing environment in comparison with He-2 at 1 000 °C.

2. Comparison of Creep Rupture Properties

Figure 3 shows the stress-time to rupture curves

Fig. 3. Creep rupture strength of the alloys in He-2 and PNP-He at 1 000 °C.

Fig. 4. Creep curves of R4286 and SZ in He-2 and PNP-He at 1 000 °C.

of the alloys in He-2 and PNP-He at 1 000 °C. The creep rupture life is lower in PNP-He than in He-2 for R4286 and 113MA. For KSN it is nearly the same in the two gases. The creep rupture life of SZ is nearly the same in the two gases at 2.3 kg/mm², while that is slightly lower in PNP-He than in He-2 at 1.9 kg/mm². In the followings, the creep rupture properties of the four alloys are described individually.

1. R4286

The difference of the creep rupture life in two gases was most remarkable for R4286 of the four alloys used in this experiment. The creep strain rate of R4286 is larger in PNP-He than in He-2 from the initial stage of creep, as in Fig. 4. This indicates that the environment of impure helium deteriorates the creep rupture life of R4286 from the initial stage of creep in PNP-He.

Photograph 2 shows the microstructures of the longitudinal cross section of R4286 after the creep rupture testing. The precipitates along grain boundaries are identified as (Cr, W, Mo)₂₃C₆ carbide and the intragranular fine precipitates as γ' of Ni₃(Al, Ti) by electron probe microanalysis. Because of decar-

- (a) 3.0 kg/mm² in He-2, $t_r=2\ 221\ \text{h}$
 (b) 3.7 kg/mm² in PNP-He, $t_r=488\ \text{h}$

Photo. 2. Microstructures of R4286 after creep rupture testing in He-2 and PNP-He at 1 000 °C.

burization in PNP-He, grain boundary carbides are depleted in a wide range beneath the alloy surface during the creep rupture testing, as shown in Photo. 2(b). Grain boundary carbides are also depleted in He-2, Photo. 2(a), in which R4286 was carburized as shown in Fig. 1. The depth of the depleted zone is, however, very slight in comparison with that in PNP-He.

Figure 5 shows a line analysis of characteristic X-ray intensities of chromium, oxygen, aluminum and titanium across the longitudinal cross section of R4286. The surface oxide scale is rich in chromium and titanium. The major component is chromium oxide, probably Cr₂O₃. Beneath the alloy surface, internal oxides of aluminum form and γ' precipitates are depleted. The depletion of γ' is considered to be caused by the oxidation of aluminum and titanium which form γ' .

Figure 6 shows the depths of the grain boundary carbide depletion, the aluminum internal oxidation and the γ' depletion zones in the two gases, as a function of test duration. The depth of the grain boundary carbide depletion zone is about ten times greater in PNP-He than in He-2, owing to the decarburization of R4286 in PNP-He. The depths of the aluminum internal oxidation and the γ' depletion zones are also greater in PNP-He than in He-2, but the difference in the two gases is considerably smaller than in the case of the grain boundary carbide depletion. Therefore, the deterioration of the creep rupture life in PNP-He is considered to be caused mainly by a wide range depletion of grain boundary carbides. The deterioration of the creep rupture

Fig. 5. Characteristic X-ray intensity profiles of oxygen, chromium, aluminum and titanium on the cross section of R4286 after creep rupture testing of 488 h and 3.7 kg/mm² in PNP-He at 1 000 °C.

life due to decarburization in impure helium environments has also been reported for Inconel 617.^{8,10,11)}

2. KSN

In spite of the remarkable decarburization of KSN in PNP-He, the creep rupture life was almost the same in the two gases. The carbon concentration of KSN decreased from 280 to 30 ppm in both the surface

layer and the center part of the specimen during the creep rupture testing, indicating decarburization throughout the specimen. These suggest that the creep rupture strength of KSN is not mainly due to carbides.

Photograph 3 shows the scanning electron micrograph and Fig. 7 shows the concentration profiles of chromium and tungsten across the longitudinal cross section of KSN. The parts containing high concentration of tungsten in Fig. 7 correspond to the whitish fine precipitates in Photo. 3 and are identified as α -W. The α -W precipitates are depleted beneath the alloy surface. As can be seen from Fig. 7, the concentration of chromium is decreased and that of tungsten is increased in the α -W depleted zone in comparison with those in the bulk. The decrease of

chromium concentration is caused by the consumption of chromium due to the formation of the surface oxide scale consisting mainly of chromium. On the other hand, the increase of tungsten concentration is caused by the decrease of chromium concentration in the zone, which results in the increase of the relative tungsten concentration, and not by the diffusion of tungsten atoms from the bulk into the zone.

The depletion of α -W precipitates is considered to occur as follows. Figure 8 shows the phase diagram of nickel–chromium–tungsten system at 1 000 °C, by Kikuchi *et al.*¹²⁾ The alloy KSN is regarded as a nickel–chromium–tungsten ternary alloy, because it consists mainly of the three elements as in Table 1. The alloy composition of KSN is shown by an open circle in the phase diagram. When only α -W precipitates without any oxidations, phases present in KSN at 1 000 °C should be γ and α -W phases, having compositions at both sides of the conjugate line passing through the open circle. However, as the concentration of chromium beneath the alloy surface decreases by the formation of the chromium oxide scale on the alloy surface, the composition of the γ phase changes in the direction of $S_1 \rightarrow S_2 \rightarrow S_3$ along the phase boundary. When the concentration of chromium decreases beyond the point S_2 , the change in the alloy composition from the two phase region of ($\gamma + \alpha$ -W) to the γ single phase will occur. This results in the re-resolution of the α -W precipitates. Thus, even under the condition where the oxidation of tungsten does not occur, the re-resolution of α -W

Fig. 6. Depths of grain boundary carbide depletion, aluminum internal oxidation and γ' depletion of R4286 in He-2 and PNP-He at 1 000 °C, as a function of duration of creep rupture testing. Volume fraction of these affected zones is also shown in the right-hand side of ordinate, where the specimen diameter is assumed to be 6 mm.

Fig. 7. Characteristic X-ray intensity profiles of chromium and tungsten on the cross section of KSN after creep rupture testing of 2 127 h and 2.3 kg/mm² in PNP-He at 1 000 °C.

Photo. 3. Scanning electron micrograph of the cross section of KSN after creep rupture testing of 2 127 h and 2.3 kg/mm² in PNP-He at 1 000 °C. Whitish fine precipitates in the alloy are α -W, which are depleted near the alloy surface.

precipitates proceeds through the decrease in the concentration of chromium beneath the alloy surface due to the formation of the chromium oxide scale.

Figure 9 shows the depth of the α -W depleted zone of KSN as a function of the test duration. It is almost the same in the two gases. Therefore, it is considered that the creep rupture life of KSN in PNP-He is not deteriorated, because the creep rupture strength of KSN is determined by precipitation strengthening by the α -W precipitates and solid-solution strengthening of the γ matrix.

3. 113MA

The creep rupture life of 113MA was somewhat lower in PNP-He than in He-2, although the difference is not larger than that of R4286. Photograph 4 shows microstructures of the longitudinal cross section of 113MA. Precipitates along grain boundaries are

identified as $(\text{Cr}, \text{W})_{23}\text{C}_6$ carbide and fine intragranular precipitates as α -W. The depth of the grain boundary carbide depleted zone is larger in PNP-He than in He-2, because of decarburization in PNP-He. Despite of carburization in He-2, grain boundary carbides are also depleted beneath the alloy surface in He-2. This is similar to the case in R4286 shown in Photo. 2(a). As can be seen from Photo. 4(a), carbides formed by carburization are located mainly at a distance more than $100\ \mu\text{m}$ away from the alloy surface, where carbides are distributed not only along grain boundaries but also on the twin in the matrix. α -W precipitates are also depleted beneath the alloy surface as shown in Photo. 5.

Figure 10 shows the depths of the grain boundary carbide and the α -W depleted zones as a function of the test duration. The difference of the depth of the grain boundary carbide depleted zone in the two gases is larger than that of the α -W depleted zone. Therefore, the deterioration of the creep rupture life

Fig. 8. Phase diagram of the nickel-chromium-tungsten ternary system at $1\ 000\ ^\circ\text{C}$, by Kikuchi *et al.*¹²⁾ The open circle shows the composition of KSN. As the chromium concentration decreases due to the formation of chromium oxide scale, the composition of the γ phase changes in the direction of $S_1 \rightarrow S_2 \rightarrow S_3$. This changes the alloy phase from $(\gamma + \alpha\text{-W})$ to γ single phase.

Fig. 9. Depth of α -W depleted zone of KSN in He-2 and PNP-He at $1\ 000\ ^\circ\text{C}$, as a function of duration of creep rupture testing.

Grain boundary carbide depleted zone

- (a) $3.0\ \text{kg/mm}^2$ in He-2, $t_r = 1\ 643\ \text{h}$
 (b) $3.0\ \text{kg/mm}^2$ in PNP-He, $t_r = 979\ \text{h}$

Photo. 4.

Microstructures of 113MA after creep rupture testing in He-2 and PNP-He at $1\ 000\ ^\circ\text{C}$. Precipitates at the grain boundaries are chromium-tungsten carbides, and those in the matrix are α -W.

Photo. 5.
Scanning electron micrograph of the cross section of 113MA after creep rupture testing of 979 h and 3.0 kg/mm² in PNP-He at 1 000 °C. The α-W precipitates in 113MA are found to have a larger size than those in KSN.

Fig. 10. Depths of grain boundary carbide and α-W depleted zones of 113MA in He-2 and PNP-He at 1 000 °C, as a function of duration of creep rupture testing. Volume fraction of these affected zones is also shown in the right-hand side of ordinate, where the specimen diameter is assumed to be 6 mm.

of 113MA in PNP-He is considered to be due to a wide range depletion of grain boundary carbides.

4. SZ

The creep rupture life of SZ at 2.3 kg/mm² was nearly the same in the two gases, but at 1.9 kg/mm² it was lower in PNP-He than in He-2. As can be seen from Fig. 4, the creep curves of SZ are nearly the same up to the stage of steady state creep in the two gases. The difference in the creep rupture life is due to the difference in the time to the tertiarily creep in the two gases.

No evidence was found for the presence of cracks on the alloy surface of the longitudinal cross section of the fractured specimen. The fracture surface in Photo. 6 indicates an intergranular brittle fracture. It is considered that only a crack formed at the initial stage of the tertiarily creep propagates along grain boundaries without a formation of subcracks. Therefore, the difference in the creep rupture life of SZ at 1.9 kg/mm² is due to the difference in the time to the nucleation of the crack.

At 2.3 kg/mm², carbon concentration of SZ was higher in He-2 than in PNP-He and the creep rupture life was nearly the same in the two gases, while at 1.9 kg/mm² carbon concentration was nearly the same and the creep rupture life was longer in He-2 than in PNP-He. Thus, the difference in the creep rupture life at 1.9 kg/mm² is not due to the difference

Photo. 6. Fracture surface of SZ after creep rupture testing at 1.9 kg/mm² in PNP-He at 1 000 °C, showing an intergranular fracture.

in carbon concentration, but due to the difference in probability of the occurrence of the crack.

IV. Discussion

1. Carbon Activity of the Impure Helium Gases

All the alloys examined were decarburized in some extent in PNP-He, while some of them were carburized in He-2. This indicated that carbon activity of the gases was lower in PNP-He than in He-2 at 1 000 °C. Decarburization was found to be the main reason for the deterioration of the creep rupture life of R4286 and 113MA, of which creep rupture strength was partly due to precipitation strengthening by M₂₃C₆ type carbide, in PNP-He. In this section, carbon activity of He-2 and PNP-He is evaluated by using the equation for steady-state carbon activity proposed by Quadakkers and Schuster.¹³⁾

Recently, Quadakkers and Schuster provided some expressions describing carbon activity of a flowing helium gas with small amounts of impurities of H₂O, H₂, CH₄ and CO, by considering the kinetics of carbon transferring reactions between the metal surface and the environment. The expression for carbon activity, termed as steady-state carbon activity a_C^{ss} , was given by

$$a_C^{ss} = \frac{k_7 \cdot P_{CH_4} + k_8 \cdot P_{CO} \cdot P_{H_2}}{k_8' \cdot P_{H_2O}} \dots\dots\dots(1)$$

where P_{CH_4} , P_{CO} , P_{H_2} and P_{H_2O} are partial pressure of CH₄, CO, H₂ and H₂O, respectively, in the supplied helium and k_7 is the reaction constant for the carbon transferring reaction

and k_8 and k'_8 are the reaction constants for the another reaction

In Eqs. (2) and (3), $[\text{C}]$ is the carbon concentration at the metal surface, which equilibrates with the carbon in solution. They have also shown that $k'_8 \gg k_7$, and that as long as the $P_{\text{CH}_4}/P_{\text{H}_2\text{O}}$ ratio is not too high, the methane effect on a_{C}^{ss} is of no great importance and a_{C}^{ss} is mainly determined by the second term of the right hand of Eq. (1), namely,

$$a_{\text{C}}^{\text{ss}} = \frac{k_8 \cdot P_{\text{CO}} \cdot P_{\text{H}_2}}{k'_8 \cdot P_{\text{H}_2\text{O}}} \quad \text{.....(4)}$$

In our case, the $P_{\text{CH}_4}/P_{\text{H}_2\text{O}}$ ratio is evaluated from the values given in Table 2 to be 1.3 for He-2 and 13 for PNP-He, which are considered to be not too high. In the following, we compare the value of a_{C}^{ss} between He-2 and PNP-He, by using Eq. (4). The values of k_8 and k'_8 are the same for the two gases because of the reaction constants, although the numerical values are at present unknown. Then, we obtain

$$\frac{a_{\text{C}}^{\text{ss}}(\text{PNP-He})}{a_{\text{C}}^{\text{ss}}(\text{He-2})} = 0.67$$

This means that carbon activity of PNP-He is lower than that of He-2, which is mainly due to the large difference of P_{CO} between the two gases. The lower carbon activity of PNP-He than He-2 derived above agrees qualitatively with the present results. Thus we conclude that the lower carbon activity of PNP-He than He-2 results mainly from the much lower concentration of CO in PNP-He than in He-2.

The first term of the right hand of Eq. (1) cannot be neglected when the $P_{\text{CH}_4}/P_{\text{H}_2\text{O}}$ ratio is very high. Quadakkers and Schuster claimed that if the ratio is exceeded a critical value, the methane effect on a_{C}^{ss} will be of great importance and a_{C}^{ss} will increase sharply. However, at present the critical value is not evaluated, because the value of the reaction constants are unknown.

2. Environmental Effect on the Creep Rupture Life

1. R4286

The difference in the creep rupture life of R4286 in the two gases was the most remarkable of the four alloys in this experiment. The creep rupture life in PNP-He was about one-third of that in He-2.

Depletion of γ' and grain boundary carbide precipitates decreases precipitation strengthening beneath the alloy surface. In particular, a wide range depletion of grain boundary carbides in PNP-He causes mainly the deterioration of the creep rupture life. Internal oxides of aluminum, having a needle-like feature as in Photo. 1, are also formed in R4286. The internal oxides affect the propagation of cracks rather than the alloy strength. In fatigue, it has been reported¹⁴⁾ that needles of internal oxides accelerate the propagation of cracks. The internal oxides formed in PNP-He are longer and sharper than those in He-2 as shown in Photo. 7. This suggests that the acceleration of the crack propagation by internal oxides is greater in PNP-He than in He-2. A large number of cracks is found on the alloy surface of R4286. This is due to the formation of the aluminum internal oxides.

Volume fractions occupied by the grain boundary carbide and the γ' depleted zones and by the aluminum internal oxidation zone are shown in the right-hand side of Fig. 6. The diameter of the gauge portion of the specimen was assumed to be 6 mm, which was the value of the diameter before the test, although the diameter of the fractured specimen varied along the gauge portion. The volume fraction shown in Fig. 6 gives a measure of the time dependence of each factor in the case of a test at low stress, where the diameter is little changed after a long time. The volume fraction occupied by the grain boundary carbide depleted zone reaches 60 % even at 1 000 h in PNP-He. This factor affects remarkably the creep rupture life even at a short time, since the decarburization rate is large. On the other hand, the volume fraction occupied by the γ' depleted zone is estimated to be about 20 % at 3 000 h in He-2.

Photo. 7. Morphology of the surface cracks formed in R4286 after creep rupture testing at 3.7 kg/mm² in (a) He-2 and (b) PNP-He at 1 000 °C.

For a long time testing, not only the grain boundary carbide depleted zone but also the γ' depleted zone may become the important factors affecting the creep rupture life.

2. KSN

The creep rupture life of KSN was nearly the same in the two gases, although this alloy was significantly decarburized in PNP-He. This is due to the fact that the creep rupture strength of KSN is determined mainly by precipitation strengthening by α -W and solid-solution strengthening of the γ matrix. According to Watanabe and Chiba¹⁵⁾, carbides in the composition of KSN are presumed to be M_6C type. It has been known that M_6C type carbide has no effect on the creep rupture strength of the alloys. Therefore, the creep rupture life of KSN is considered to be little affected by decarburization.

3. 113MA

The creep rupture life was lower in PNP-He than in He-2, although the difference was not larger compared to the case of R4286. The creep rupture strength of 113MA is due to precipitation strengthening by α -W and $M_{23}C_6$ type carbide, and to solid-solution strengthening of the γ matrix. $M_{23}C_6$ precipitates are known to increase the creep rupture strength substantially.¹⁵⁾ The deterioration of the creep rupture life in PNP-He is caused by decarburization which results in a wide range depletion of $M_{23}C_6$ carbide along grain boundaries. While the precipitation strengthening by α -W and solid-solution strengthening of the γ matrix determine the rupture strength of KSN, the presence of $M_{23}C_6$ carbide also increases the strength of 113MA. Therefore, it is considered that the creep rupture life of 113MA is deteriorated by decarburization in contrast to KSN.

The volume fractions occupied by the grain boundary carbide and the α -W depleted zones are shown in the right-hand side of Fig. 10, where the specimen diameter is assumed to be 6 mm as in the case of R4286. The volume fraction occupied by the α -W depleted zone is only 5 % at 2 000 h. However, the intermediate heat exchangers of HTGR will be operated over a long period of several years, and therefore the effect of the α -W depleted zone on the creep rupture life may become important after a long time operation. Because α -W precipitates are depleted through the decrease of chromium concentration beneath the alloy surface as a result of the formation of chromium oxide scale, the improvement of corrosion resistance becomes increasingly important.

In spite of the carburization of 113MA and R4286 in He-2, grain boundary carbides are depleted beneath the alloy surface as shown in Photos. 2(a) and 4(a), although the detailed mechanism is not known at present. The formation of carbides due to carburization occurs at some distance from the alloy surface. Similar observations have been reported on Alloy 800¹⁶⁾ when carburization and oxidation take place simultaneously.

4. SZ

SZ was hardly decarburized even in PNP-He, showing a good resistance to corrosion. Therefore,

a large difference in the environmental effects on the creep rupture life was not observed in the two gases.

V. Conclusions

The creep rupture properties of four nickel base superalloys, which have been newly developed in Japan for the intermediate heat exchangers of HTGR, are investigated in two impure helium gases, He-2 and PNP-He, at 1 000 °C. The main results are:

(1) The carbon concentration of the alloys after the creep rupture testing is lower in PNP-He than in He-2. All the alloys are decarburized in PNP-He. The growth rate of the aluminum internal oxides in R4286 is larger in PNP-He than in He-2. These results indicate that PNP-He is a more decarburizing and oxidizing environment in comparison with He-2 at 1 000 °C, which is considered to result mainly from the much lower concentration of CO in PNP-He than in He-2.

(2) The creep rupture life of R4286 in PNP-He is one-third of that in He-2. This is mainly by the depletion of the grain boundary carbides due to decarburization in PNP-He. Depletion of γ' precipitates and formation of aluminum internal oxides have occurred beneath the alloy surface.

(3) The creep rupture life of KSN, containing the highest tungsten concentration of 26 % of the alloys examined, is almost the same in the two environments, although this alloy is remarkably decarburized in PNP-He. Since the creep rupture strength of KSN is mainly due to precipitation strengthening by the α -W precipitates and solid-solution strengthening of the γ matrix, the creep rupture life is considered to be little affected by decarburization.

(4) The creep rupture life of 113MA is lower in PNP-He than in He-2, which is caused by decarburization in PNP-He. Because the creep rupture strength of 113MA is due to not only α -W but also $M_{23}C_6$ type carbide, the creep rupture life is lowered by decarburization.

(5) SZ is hardly decarburized even in PNP-He, showing a good resistance to corrosion. The creep rupture life of SZ is almost the same in the two environments.

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