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**OXIDATION CHARACTERISTICS OF OXIDE DISPERSION  
STRENGTHENED (ODS) ALLOY**

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Oxidation Characteristics of Oxide Dispersion Strengthened (ODS) Alloy

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(Received December 4, 1995)

For the feasibility study of an oxide dispersion strengthened (ODS) alloy to apply to a high temperature structural material in advanced High Temperature Gas-cooled Reactors (HTGR<sub>s</sub>) and heat utilization systems of HTGR, the oxidation tests of Fe-Cr-Al-Y<sub>2</sub>O<sub>3</sub>-based ODS alloy in the simulated HTGR helium environment and the air were carried out together with two kinds of high temperature alloys, i.e., Hastelloy XR and Ni-Cr-W alloys. It was clarified that the ODS alloy had excellent oxidation characteristics in both the environments due to the formation of protective Al-based oxide scale with dispersed Y<sub>2</sub>O<sub>3</sub> on the alloy surface.

Furthermore, the comparison between Hastelloy XR and Ni-Cr-W alloys on the oxidation behavior was also discussed.

Keywords: ODS Alloy, HTGR, Oxidation, Carburization, High Temperature Alloy, Structural Material, Hastelloy XR Alloy, Ni-Cr-W Alloy

## 酸化物分散強化型 (ODS) 合金の酸化特性

日本原子力研究所東海研究所材料研究部  
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(1995年12月4日受理)

酸化物分散強化型 (ODS) 合金の高性能高温ガス炉及び熱利用系の高温部構造物用材料への適応性を検討するため、高温ガス炉近似ヘリウム雰囲気及び大気中で Fe-Cr-Al-Y<sub>2</sub>O<sub>3</sub> 系 ODS 合金の酸化試験をハステロイ XR 及び Ni-Cr-W 系耐熱合金とともに実施した。その結果、ODS 合金は、Y<sub>2</sub>O<sub>3</sub> が分散した Al 主体の酸化膜の形成により、高温ガス炉近似ヘリウム雰囲気及び大気中で優れた酸化特性を示すことを明らかにした。

さらに、ハステロイ XR と Ni-Cr-W 系耐熱合金の酸化挙動についても比較検討した。

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## 1. Introduction

An oxide dispersion strengthened (ODS) alloy with the favorable high temperature properties is considered to be one of the promising structural materials for future energy systems with arduous service conditions. At the Research Center Juelich (KFA) in Germany, the studies of ODS alloys for high temperature heat exchangers in advanced power stations have been performed [1].

According to the agreement on the exchange of information in the filed of R & D of HTR between the Japan Atomic Energy Research Institute (JAERI) and the KFA, the ODS alloy was supplied by the KFA. At the JAERI, for the feasibility study of ODS alloys to apply to a high temperature structural material in advanced High Temperature Gas-cooled Reactors (HTGRs) and heat utilization systems of HTGRs, the oxidation characteristics of the ODS alloy supplied by the KFA in the simulated HTGR helium environment and the air were investigated.

The oxidation behavior of the ODS alloy was evaluated by comparison with two kinds of high temperature alloys, i.e., Hastelloy XR and Ni-Cr-W alloys, because that both alloys are developed ones for HTGRs [2,3]. Hastelloy XR alloy has been adopted as the high temperature structural material in the High Temperature Engineering Test Reactor (HTTR) with 30MW in thermal output and outlet coolant temperature of 850°C for rated operation and 950°C for high temperature test operation which is currently under construction at Oarai Research Establishment [4], and Ni-Cr-W alloy is being developed as a high temperature structural material in advanced HTGRs with outlet coolant temperature of around 1000°C [3].

## 2. Experimental procedure

### 2.1 Materials

The ODS alloy supplied by the KFA is the commercial batch Fe-Cr-Al-Y<sub>2</sub>O<sub>3</sub> based one from the type MA956 (Inco Alloys International, Hereford, UK) [5]. The detailed chemical composition of the ODS alloy [5] is given in table 1

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together with other tested alloys, i.e., Hastelloy XR and Ni-Cr-W alloys. The test specimens were machined in a type of coupon of around 5 mm × 10 mm × 2 mm. Prior to the oxidation test, the surface of specimens was finished by wet abrasion paper (20 μm).

Table 1 Chemical compositions of tested materials (mass %).

|              | C     | Si    | Mn    | P     | S     | Cr                                | Co   | Mo   |
|--------------|-------|-------|-------|-------|-------|-----------------------------------|------|------|
| ODS          | 0.028 | 0.09  | 0.11  | 0.005 | 0.008 | 19.10                             | -    | -    |
| Hastelloy XR | 0.06  | 0.34  | 0.88  | 0.001 | 0.001 | 21.82                             | 0.03 | 9.04 |
| Ni-Cr-W      | 0.03  | 0.06  | 0.02  | 0.003 | 0.001 | 18.76                             | 0.02 | -    |
|              | W     | Fe    | B     | Al    | Ti    | Y <sub>2</sub> O <sub>3</sub> (Y) | Zr   | Ni   |
| ODS          | -     | 75.60 | 0.010 | 4.25  | 0.31  | 0.50                              | -    | -    |
| Hastelloy XR | 0.49  | 18.05 | 0.002 | <0.01 | <0.01 | -                                 | -    | Rem. |
| Ni-Cr-W      | 21.43 | 0.07  | 0.006 | 0.04  | 0.06  | (0.009)                           | 0.02 | Rem. |

## 2.2 Test conditions

The oxidation test in the simulated HTGR helium environment (helium) was carried out at 1000°C for 1000 h. Impurities levels in the helium are shown in table 2. The helium was supplied by using a recirculating loop system with a cryogenic purification unit and a quantified multi-impurities injection device.

Table 2 Impurities levels of helium environment (vol. ppm).

| H <sub>2</sub> | H <sub>2</sub> O | CO      | CO <sub>2</sub> | CH <sub>4</sub> |
|----------------|------------------|---------|-----------------|-----------------|
| 200~210        | 0.8~1.2          | 100~110 | 2~3             | 5~6             |

The test apparatus is made of fused quartz in the hot parts and of Pyrex glass in low - temperature regions. Three kinds of specimens were placed in one test



apparatus and exposed in equivalent condition at a time. The oxidation test in the air was also conducted at 1000°C for 1000 h.

Following exposure, the specimens were metallurgically and gravimetrically analyzed. These analyses included energy dispersive X-ray analysis and bulk carbon analysis.

### 3. Experimental results

#### 3.1 Oxidation resistance

##### 3.1.1 Change in mass

The surfaces of specimens oxidized in both the helium and air at 1000°C for 1000 h are shown in fig. 1. The scale spallation was not detected on the surfaces of the ODS alloy after exposure in the both environments, although for Hastelloy XR and Ni-Cr-W alloys the spallation of oxide scales was observed after oxidation in the air. In this connection, the amount of spalled scales was not measured.


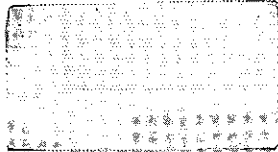
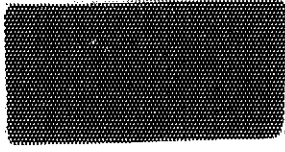
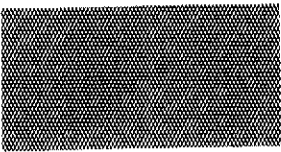
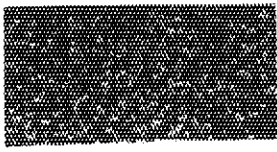
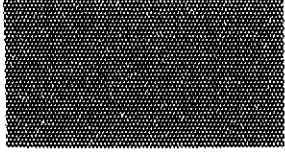
|     | ODS   | Hastelloy XR   | Ni-Cr-W  |
|-----|---|--|--|
| He  | <br>(brilliant gray) | <br>(light yellow green) | <br>(black)       |
| Air | <br>(brilliant gray) | <br>(black)              | <br>(black) 0.5cm |

Fig. 1 Surfaces of tested alloys after oxidation at 1000°C for 1000 h. ( ) are the colors of oxide scales and light yellow green is the color of Mn/Cr spinel type whisker on stable oxide scale.

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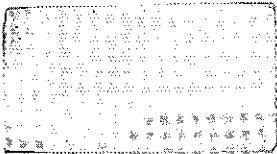
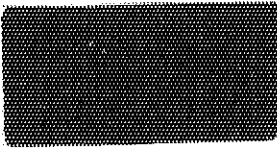
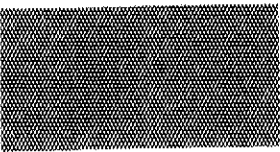
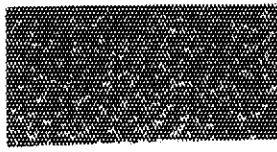
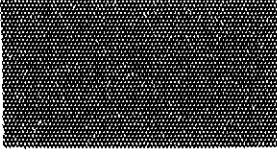
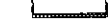
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| Air | <br>(brilliant gray) | <br>(black)              | <br>(black)  0.5cm |

Fig. 1 Surfaces of tested alloys after oxidation at 1000°C for 1000 h. ( ) are the colors of oxide scales and light yellow green is the color of Mn/Cr spinel type whisker on stable oxide scale.

The mass gains for each alloy after oxidation in both environments at 1000°C for 1000 h are summarized in table 3 and illustrated in fig.2.

Table 3 Mass gain of oxidized specimens (mg/cm<sup>2</sup>).

|        | ODS  | Hastelloy XR     | Ni-Cr-W         |
|--------|------|------------------|-----------------|
| Helium | 0.21 | 0.96             | 0.43            |
| Air    | 0.58 | 1.53+ $\alpha$ * | 3.15+ $\beta$ * |

\*  $\alpha$  and  $\beta$  are the amounts of oxygen in spalled scales but not measured.

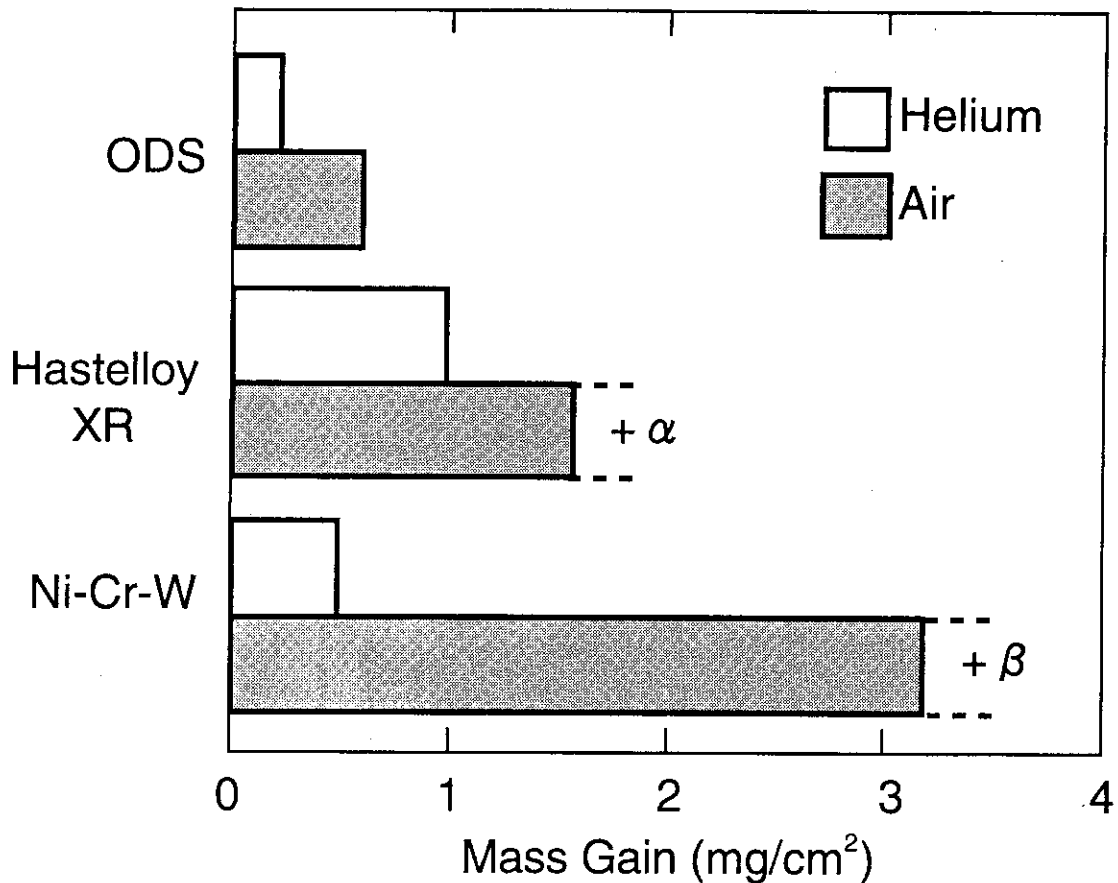


Fig. 2 Mass gain of oxidized alloys at 1000°C for 1000 h in helium and air.

### 3.1.2 Scale thickness

The cross-sectional views of surface oxide scales without spalled parts formed on the specimens are shown in fig. 3. The scale thickness measured in fig. 3 is given in table 4 and illustrated in fig. 4.

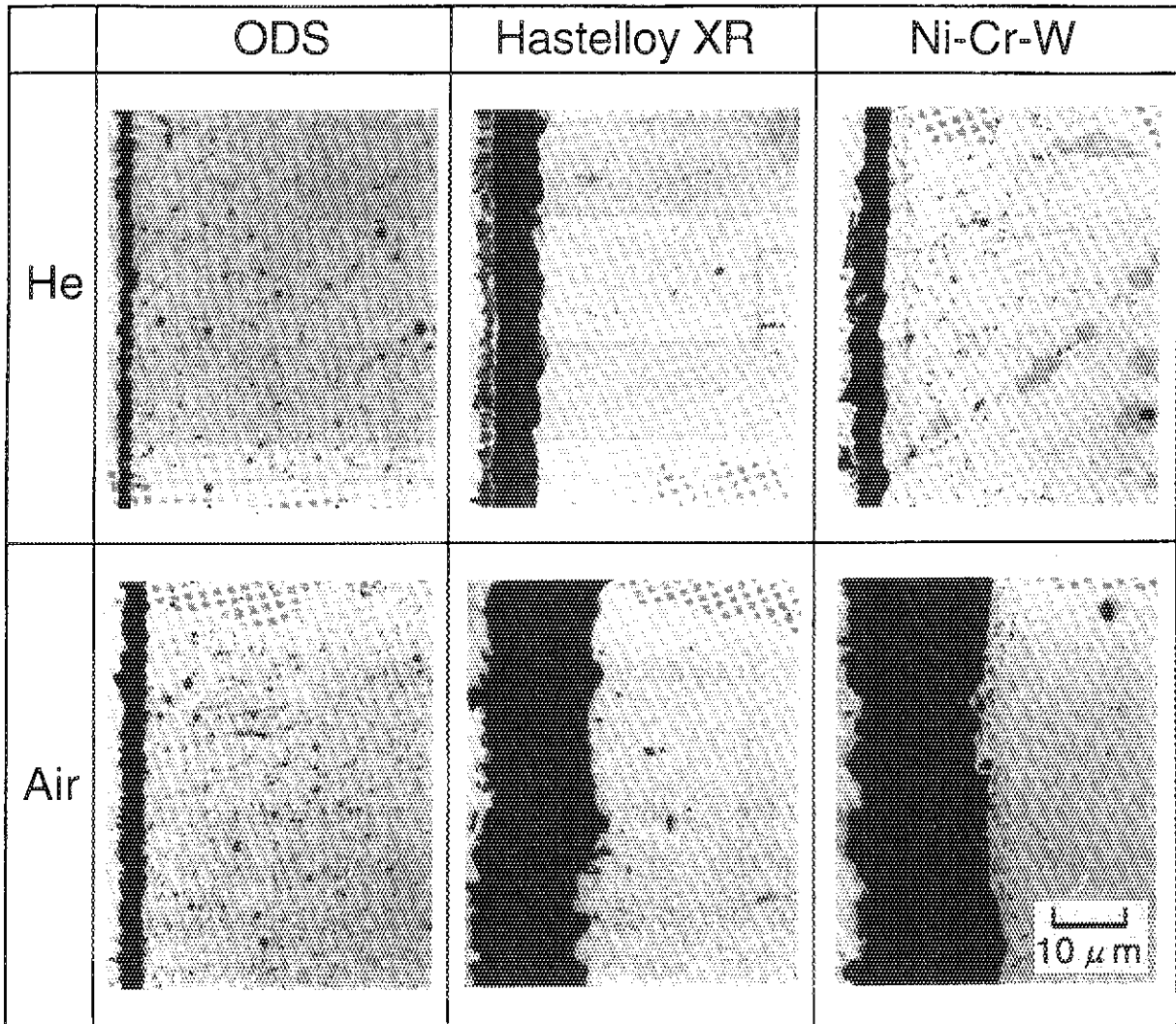


Fig. 3 Cross-sectional views of oxide scales formed in helium and air at 1000°C for 1000 h.

Table 4 Scale thickness of tested alloys ( $\mu\text{m}$ ).

|        | ODS | Hastelloy XR | Ni-Cr-W |
|--------|-----|--------------|---------|
| Helium | 1.0 | 5.1          | 3.4     |
| Air    | 3.0 | 14.0         | 19.0    |

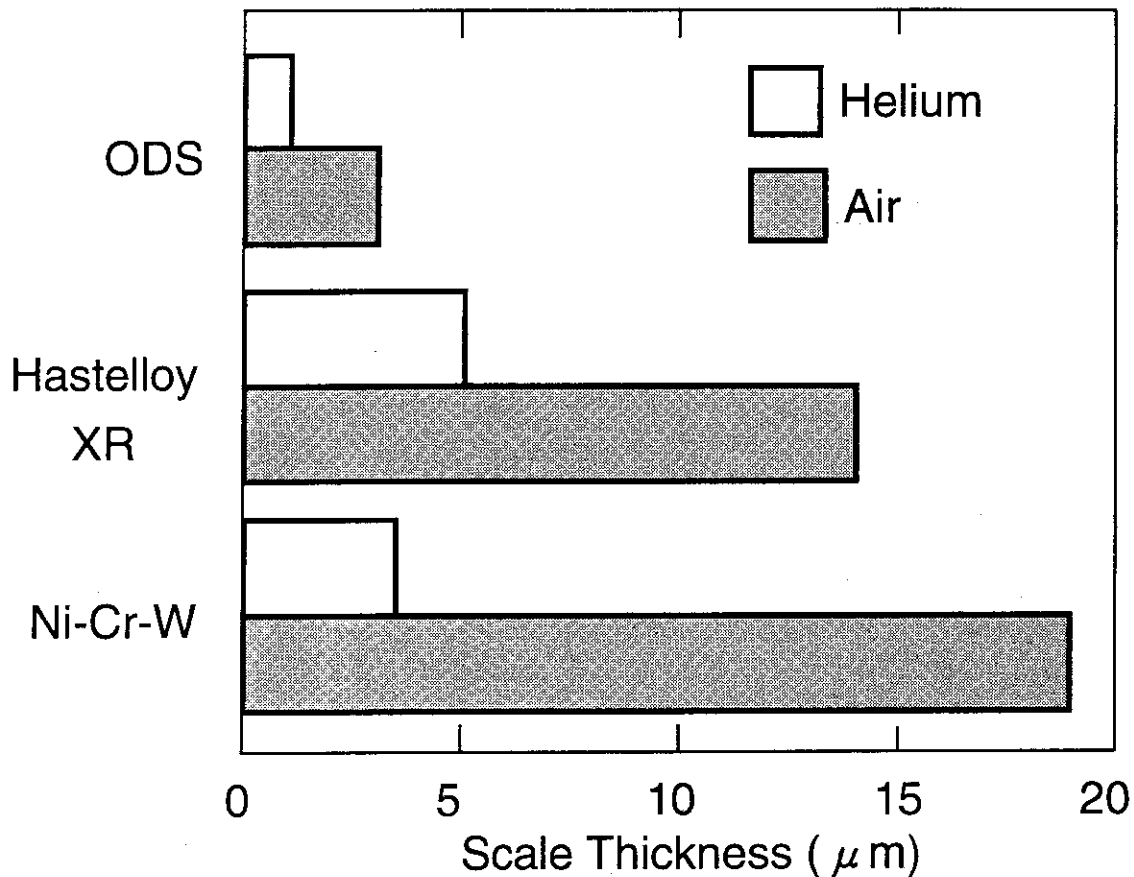


Fig. 4 Scale thickness of tested alloys.

As can be seen from fig.s 2 and 4, in the helium the oxidation resistance of the ODS alloy was superior to Hastelloy XR and Ni-Cr-W alloys. It indicates that the ODS alloy has so excellent oxidation resistance in the helium, because that Hastelloy XR [6] and Ni-Cr-W [7] alloys have fine oxidation properties in the helium compared with other high temperature alloys. In addition, the ODS alloy also showed the best oxidation characteristics without scale spallation in the air.

### 3.2 Carburization and/or decarburization behavior

In the helium, an alloy is carburized or decarburized. For an alloy, whether carburization or decarburization is dependent on the chemical composition of

alloy and the test temperature. For evaluating carburization and/or decarburization behavior, carbon analyses were carried out for bulk specimens oxidized in the helium. For the comparison of carburization and/or decarburization resistance of different size of specimens, the change in carbon content must be expressed as change in carbon mass per unit surface area, which is given by the following formula ;

$$\Delta M = \Delta C(W/A)/100,$$

where  $\Delta M$  is the mass of carbon increase or decrease ( $\text{mg}/\text{cm}^2$ ),  $\Delta C$  is the increase or decrease in carbon content (mass %),  $W$  is the mass of untested specimen (mg) and  $A$  is the surface area of specimen ( $\text{cm}^2$ ).

The results of carbon analysis are given in table 5. It was clarified from table 5, that the ODS and Hastelloy XR alloys were slightly carburized and Ni-Cr-W alloy was decarburized. The mass of carbon increase for the ODS alloy was less than that of Hastelloy XR alloy. It means that the carburization resistance of the ODS alloy is superior to Hastelloy XR alloy.

*Table 5 Change in carbon content of alloys oxidized in helium.*

|              | Carbon Content (mass %) |        | Change in carbon content (%) | Change in carbon mass ( $\text{mg}/\text{cm}^2$ ) |
|--------------|-------------------------|--------|------------------------------|---|
|              | 0 h                     | 1000 h |                              |   |
| ODS          | 0.0180                  | 0.0202 | +0.0022                      | +0.01   |
| Hastelloy XR | 0.0588                  | 0.0704 | +0.0116                      | +0.08   |
| Ni-Cr-W      | 0.0285                  | 0.0063 | -0.0222                      | -0.17   |

### 3.3 Analysis of surface scales

Energy dispersive X-ray analysis was carried out to identify the oxide scales formed on the surfaces of the ODS alloy in both environments. The results of line analyses of Al and Cr through cross section of the surface oxide scale formed in the helium at  $1000^\circ\text{C}$  for 1000 h are shown in fig. 5 as an example.

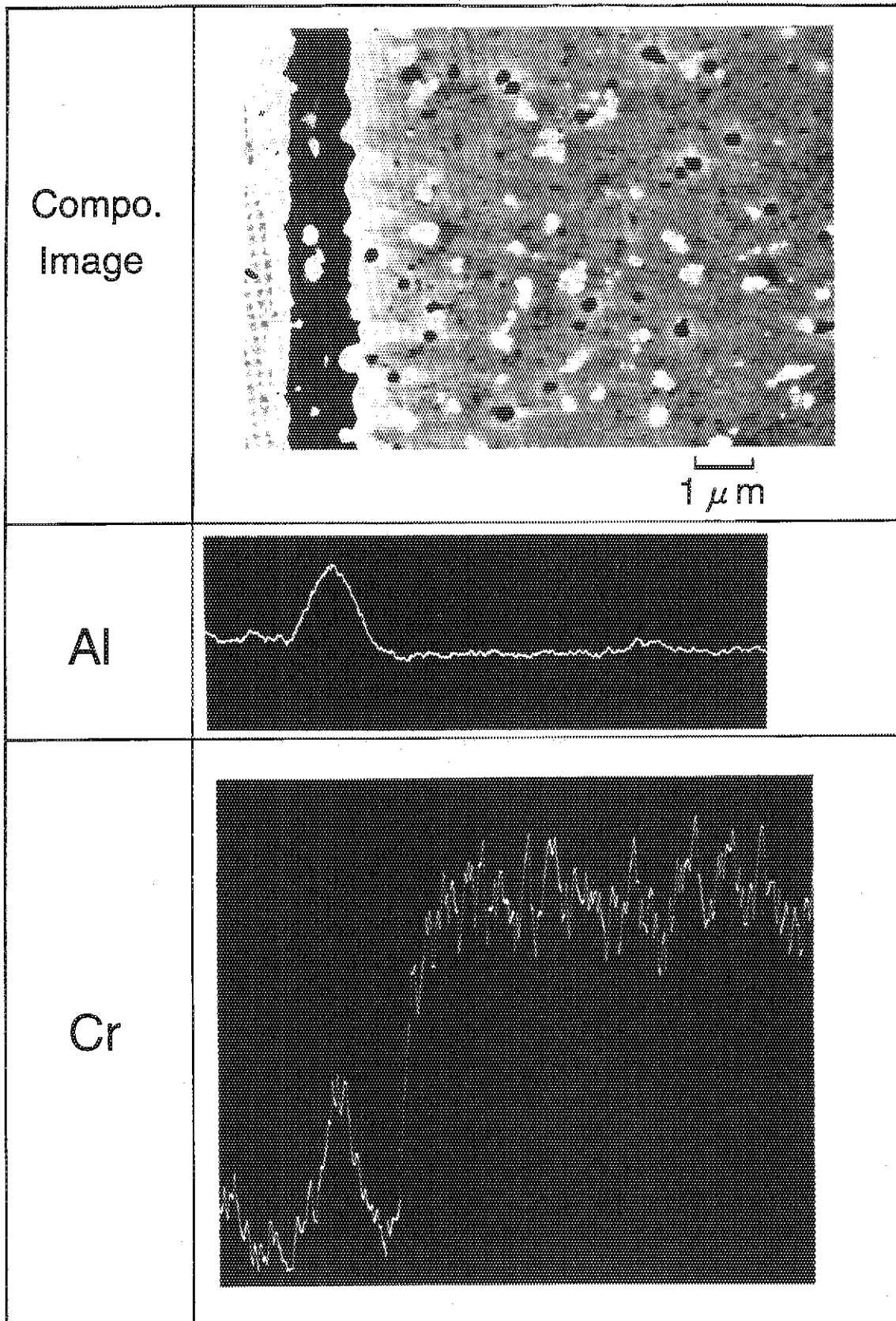


Fig. 5 Line analyses of Al and Cr through cross section of surface oxide formed on ODS alloy in helium.

From the results of analyses for the surface scales, it was confirmed that the oxide scales of the ODS alloy formed in both environments were Al-based including a small amount of Cr ones with dispersed  $Y_2O_3$ . Furthermore, it was judged that the white particles in the composition image of surface oxide scale in fig. 5 was  $Y_2O_3$ .

Regarding other tested alloys, it has been already known that the oxide scales formed on Hastelloy XR in the air and Ni-Cr-W alloys in both the helium and their are Cr-based ones, and in the helium Hastelloy XR is covered by Cr/Mn-based oxide scale.

## 4. Discussion

### 4.1 Change in mass due to oxidation

To evaluate the change in mass due to oxidation only in the helium, the change in carbon mass caused by carburization or decarburization might be considered. The mass gains due to oxidation, i.e., oxygen mass gains, are given in table 6. The oxygen mass gains of three alloys tested in the helium are illustrated in fig. 6 together with comparative data for scale thickness, which indicated that the comparative tendency of oxidation resistance for three tested alloys well corresponded to the results of scale thickness.

Table 6 Mass gains due to oxidation.

|              | Mass gain<br>(mg/cm <sup>2</sup> ) | Carbon mass<br>gain (mg/cm <sup>2</sup> ) | Oxygen mass<br>gain (mg/cm <sup>2</sup> ) |
|--------------|------------------------------------|---|---|
| ODS          | 0.21                               | +0.01                                     | 0.20                                      |
| Hastelloy XR | 0.96                               | +0.08                                     | 0.88                                      |
| Ni-Cr-W      | 0.43                               | -0.17                                     | 0.60                                      |



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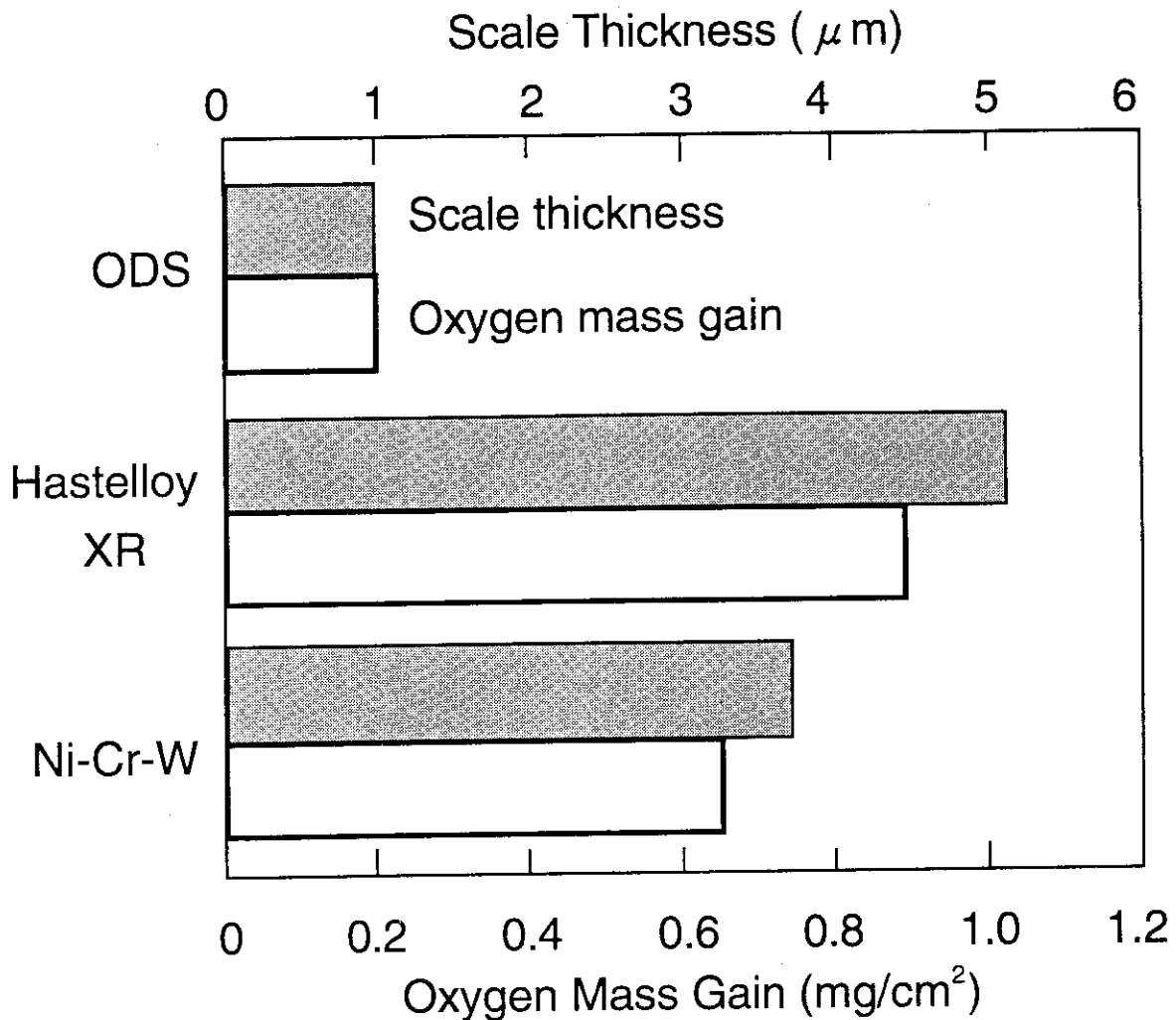


Fig. 6 Oxygen mass gains of alloys oxidized in helium together with comparative data for scale thickness.

#### 4.2 Oxidation resistance of the ODS alloy

The ODS alloy exhibited the best oxidation resistance in both environments, and the carburization resistance was also superior to Hastelloy XR alloy. The ODS alloy was covered by Al-based oxide in both environments. Other two alloys, Hastelloy XR and Ni-Cr-W alloys, were covered by Cr-based oxide. It has been well known that  $\text{Al}_2\text{O}_3$  is more stable than  $\text{Cr}_2\text{O}_3$ . Therefore, the best oxidation resistance of the ODS alloy within the tested alloys was attributed to the Al-based

oxide scale. Furthermore, the contribution of  $Y_2O_3$  uniformly dispersed in Al-based oxide scale and the matrix ought to have been much on the resistance to both oxidation and scale spallation [8], although the scale growth rate increased with an increase of  $Y_2O_3$  content in the range 0.17~0.7% [5].

The conclusion is that Al-based oxide scale with dispersed  $Y_2O_3$  effectively played the role of barrier against outward and/or innerward diffusion of anion and cation compared with Cr-based oxide.

#### 4.3 Reliability of obtained data

The reliability of obtained data must be taken into account because of only one value for each alloy. To confirm the reliability, the relationship between the scale thickness calculated based on the mass gain and the measured scale thickness was investigated. Assuming that the surface oxide scales formed on the ODS, Hastelloy XR and Ni-Cr-W alloys are 100%  $Al_2O_3$ , 100%  $Cr_2O_3$  and 100%  $Cr_2O_3$ , respectively, the mass of oxide scale is calculated by following formula ;

$$M_{oxide} = M_{oxygen} \times (2A_m + 3A_o) / (3A_o),$$

where  $M_{oxide}$  and  $M_{oxygen}$  are the masses of oxide and oxygen in the oxide, and  $A_m$  and  $A_o$  are the atomic masses of metal and oxygen, respectively. The masses of oxide scales formed on three alloys in the helium are led as follows;

$$\begin{aligned} \textcircled{1} \text{ the mass of } Al_2O_3 \text{ on ODS} &= 0.20(\text{mg/cm}^2)(27 \times 2 + 16 \times 3) / (16 \times 3) \\ &= 0.43 \text{mg/cm}^2, \end{aligned}$$

$$\begin{aligned} \textcircled{2} \text{ the mass of } Cr_2O_3 \text{ on Hastelloy XR} &= 0.88(\text{mg/cm}^2)(52 \times 2 + 16 \times 3) / (16 \times 3) \\ &= 2.79 \text{mg/cm}^2 \end{aligned}$$

and

$$\begin{aligned} \textcircled{3} \text{ the mass of } Cr_2O_3 \text{ on Ni-Cr-W} &= 0.60(\text{mg/cm}^2)(52 \times 2 + 16 \times 3) / (16 \times 3) \\ &= 1.90 \text{mg/cm}^2. \end{aligned}$$

In addition, the densities of  $Al_2O_3$  and  $Cr_2O_3$  are 4.045 and 5.283  $g/cm^3$ , respectively. The scale thickness is given by the mass of oxide divided by the density of oxide and led as follows ;

$$\textcircled{1} \text{ the scale thickness on ODS} = 0.43(\text{mg/cm}^2) / 4.045(\text{g/cm}^3) = 1.1 \mu\text{m},$$

$$\textcircled{2} \text{ the scale thickness on Hastelloy XR} = 2.79(\text{mg/cm}^2) / 5.283(\text{g/cm}^3) = 5.3 \mu\text{m}$$

and

③ the scale thickness on Ni-Cr-W =  $1.90(\text{mg}/\text{cm}^2) / 5.283(\text{g}/\text{cm}^3) = 3.6 \mu\text{m}$ .

The calculated scale thickness and measured one are summarized in table 7, which indicated that the calculated data were about the same as the measured ones.

It can be concluded that the values obtained by mass measurement and carbon analysis are quite reasonable ones and the reliability of obtained values is secured.

Table 7 Comparison between calculated and measured scale thickness ( $\mu\text{m}$ ).

|                            | ODS | Hastelloy XR | Ni-Cr-W |
|----------------------------|-----|--------------|---------|
| Calculated scale thickness | 1.1 | 5.3          | 3.6     |
| Measured scale thickness   | 1.0 | 5.1          | 3.4     |

#### 4.4 Oxidation behavior of Hastelloy XR and Ni-Cr-W alloys

##### 4.4.1 Comparison between Hastelloy XR and Ni-Cr-W alloys

Concerning the oxidation behavior of Hastelloy XR and Ni-Cr-W alloys in the helium, the oxidation resistance of Ni-Cr-W alloy was superior to Hastelloy XR alloy because of lower Cr content and Y addition for Ni-Cr-W alloy, as well as the previous results [7]. In the helium an oxidation resistance of alloy increases with an increase in Cr content [9,10]. On the other hand, the result in the air was quite on the contrary. It might be due to lower Cr content of Ni-Cr-W alloy compared with Hastelloy XR alloy. In high oxidation potential environment such as the air, an oxidation resistance of alloy decreases with a decrease in Cr content, and a small amount of Y, e.g., around 90 ppm, may not be so effective to improve the oxidation resistance.

##### 4.4.2 Estimation of amount of spalled oxides

For estimation of the amount of oxides spalled from the surfaces of Hastelloy XR and Ni-Cr-W alloys after oxidation in the air, the total mass gains of both alloys after oxidation were calculated from the scale thickness. To calculate the

total mass gain, it was assumed that the surface oxide scales formed on Hastelloy XR and Ni-Cr-W alloys were 100% Cr<sub>2</sub>O<sub>3</sub>, the scales observed in fig. 3 had no layer spallation and change in carbon content was not occurred. The mass of oxide is given by the scale thickness multiplied by the density of oxide and led as follows ;

① the mass of Cr<sub>2</sub>O<sub>3</sub> on Hastelloy XR =  $14.0(\mu\text{m}) \times 5.283(\text{g}/\text{cm}^3) = 7.40\text{mg}/\text{cm}^2$   
and

② the mass of Cr<sub>2</sub>O<sub>3</sub> on Ni-Cr-W =  $19.0(\mu\text{m}) \times 5.283(\text{g}/\text{cm}^3) = 10.04\text{mg}/\text{cm}^2$ .

In addition, the mass gain due to oxidation is calculated by following formula ;

$$M_{\text{oxygen}} = M_{\text{oxide}} \times (3A_{\text{o}}) / (2A_{\text{m}} + 3A_{\text{o}}).$$

The total mass gain due to oxidation of Hastelloy XR and Ni-Cr-W alloys are led as follows;

① the total mass gain of Hastelloy XR =  $7.40(\text{mg}/\text{cm}^2)(16 \times 3) / (52 \times 2 + 16 \times 3)$   
=  $2.34 \text{ mg}/\text{cm}^2$

and

② the total mass gain of Ni-Cr-W =  $10.04(\text{mg}/\text{cm}^2)(16 \times 3) / (52 \times 2 + 16 \times 3)$   
=  $3.17 \text{ mg}/\text{cm}^2$ .

In this connection, for the ODS alloy the mass of oxide and the total mass gain are given as follows ;

① the mass of oxide =  $3.0(\mu\text{m}) \times 4.045(\text{g}/\text{cm}^3) = 1.21\text{mg}/\text{cm}^2$   
and

② the total mass gain =  $1.21(\text{mg}/\text{cm}^2)(16 \times 3) / (27 \times 2 + 16 \times 3) = 0.57\text{mg}/\text{cm}^2$ .

Table 8 shows the comparison between calculated and measured mass gains and is illustrated in fig. 7 as a relationship between calculated and measured mass gains. In the case of ODS alloy without scale spallation, the calculated and measured mass gains were almost the same. This means that the estimation method was quite reasonable. The results indicated that the amount of oxide spalled from Hastelloy XR,  $\alpha$ , was much more than that of Ni-Cr-W alloy,  $\beta$ , and  $\beta$  was nearly zero.

It can be concluded that the oxide scale formed on Ni-Cr-W alloy at 1000°C in the air is more stable than that on Hastelloy XR alloy. This conclusion corresponded to the previous result [11] at 950°C in the air, although this

tendency reversed above 1100°C.

Table 8 Comparison between calculated and measured mass gains ( $\text{mg}/\text{cm}^2$ ).

|                              | Hastelloy XR           | Ni-Cr-W               | ODS  |
|------------------------------|------------------------|-----------------------|------|
| Calculated mass gain         | 2.34                   | 3.17                  | 0.57 |
| Measured mass gain           | $1.53 + \alpha$        | $3.15 + \beta$        | 0.58 |
| Oxygen mass in spalled oxide | 0.81<br>( $= \alpha$ ) | 0.02<br>( $= \beta$ ) | -    |

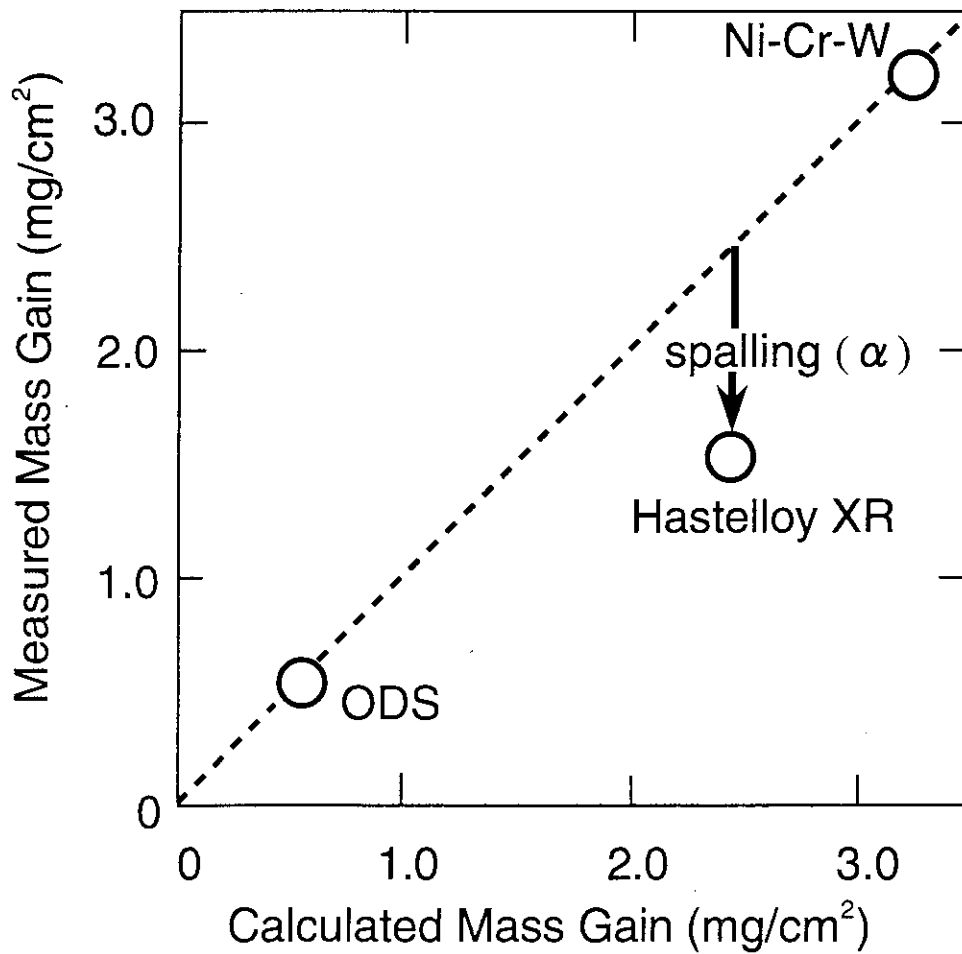


Fig. 7 Relationship between calculated and measured mass gains.

## 5. Conclusions

To study the oxidation characteristics of Fe-Cr-Al-Y<sub>2</sub>O<sub>3</sub> -based ODS alloy, the oxidation tests were carried out in the simulated HTGR helium environment and the air at 1000°C for 1000 h together with Hastelloy XR and Ni-Cr-W alloys. The conclusions obtained showed that :

- (1) The ODS alloy exhibited the best oxidation resistance in both the environments within the tested alloys.
- (2) The carburization resistance of the ODS alloy was superior to Hastelloy XR alloy.
- (3) The excellent oxidation characteristics of the ODS alloy might be caused by the formation of protective Al-based oxide with dispersed Y<sub>2</sub>O<sub>3</sub> on the alloy surface.

Moreover, concerning the oxidation behavior of Hastelloy XR and Ni-Cr-W alloys, it was known that in the simulated HTGR helium environment the oxidation mass gain of Ni-Cr-W alloy was less than that of Hastelloy XR alloy, on the other hand, the result in the air was quite on the contrary, although Ni-Cr-W alloy possessed better resistance to scale spallation compared with Hastelloy XR alloy.

## Acknowledgements

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Moreover, concerning the oxidation behavior of Hastelloy XR and Ni-Cr-W alloys, it was known that in the simulated HTGR helium environment the oxidation mass gain of Ni-Cr-W alloy was less than that of Hastelloy XR alloy, on the other hand, the result in the air was quite on the contrary, although Ni-Cr-W alloy possessed better resistance to scale spallation compared with Hastelloy XR alloy.

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