Hot Corrosion Behavior of Ni-Cr-W-C Alloys in Impure He Gas*

By Taizo OHMURA,** Kensho SAHIRA,** Akihiko SAKONOOKA** and Noboru YONEZAWA**

Synopsis

Influence of the minor alloy constituents such as Al, Mn and Si on the hot corrosion behavior of Ni-20Cr-20W-0.07C alloy was studied in 99.995 %He gas at 1 000°C, in comparison with the behavior of commercial Ni-base superalloys (Hastelloy X and Inconel 617).

The low oxidizing potential in the impure He gas usually causes selective oxidation of the elements described above and the growth of oxide whiskers on the surface of specimen at elevated temperatures.

The intergranular attack was caused by selective oxidation of Al, Si and Mn. The spalling of oxide film was restrained by additions of Mn and Si, providing tough spinel type oxide film on the surface and 'keys' on the oxide-matrix interface respectively.

The amount and morphology of the oxide whiskers depended on Si and Mn contents. Si of more than 0.29% without Mn always caused the growth of rather thinner whiskers with smooth surface, and the whiskers analyzed by electron diffraction patterns and EPMA to be Cr_2O_3 containing Si. Mn addition changes the whiskers to thicker ones of spinel type oxide (MnCr_2O_4) with rough surface.

On the basis of these results, the optimum contents of Al, Mn and Si to minimize the growth of whiskers, the intergranular attack, and the spalling of oxide film were discussed.

I. Introduction

For the tube materials of the intermediate heat exchanger for the very high temperature gas-cooled reactor (VHTGR), Ni-Cr-W-C alloys have been reported to have superior high temperature properties, *e.g.*, high temperature strength,¹⁾ hot workability,²⁾ and structural stability under long time exposure at elevated temperatures.³⁾

However, the hot corrosion behavior of these alloys in He gas has not been studied.

Oxidizing potential of He gas for VHTGR will not be so low as that of pure He gas because of the contaminations of O_2 , H_2O , H_2 , CO , CO_2 and CH_4 in it, which may cause the selective oxidation of the constituents in some Ni base alloys.^{4,5)} In some cases, oxide films produced on the alloys in low oxidizing potential atmosphere are not so tight as ones produced in air, therefore they have inferior adherence, and deeper intergranular attack and the internal oxidation are observed beneath the surface.⁶⁾ The temperature dependence of the oxidizing potential of the elements in the developmental Ni-Cr-W-C alloy is thermodynamically calculated as shown in Fig. 1. Environment of VHTGR is simulated to be in the range of 750° to 1 000°C and 25 to 250 of the oxidizing potential ($P_{\text{H}_2}/P_{\text{H}_2\text{O}}$).⁷⁾ This diagram indicates that Ni and W will not be oxidized but Cr, Mn, Si and Al will be oxidized. As Mn, Si, Al and/or Ti are important degassing elements for the Ni base alloys, it is necessary

to reveal the behavior of these elements in the impure He gas at elevated temperature.

In this study, the behavior of Ni-20Cr-20W-0.07C alloys having variable contents of Mn, Si and Al as additives was investigated in comparison with Hastelloy X and Inconel 617 which are known to have the superior heat resistance. Much attention was paid to the role of Mn which had been reported to form a tight spinel type oxide scale with Cr on the surface in that atmosphere.

II. Experimental Procedure

1. Specimen

The chemical compositions of specimens and the conditions of solution heat treatment area are listed in Table 1. The brief bars in the table indicate no addition of the constituents. In case of no addition, the contents of Mn, Si, Al and Ti, which were important elements for this study, were 0.001%, 0.1%, 0.02% and 0.03%, respectively. Ni-20Cr-20W alloy (F-11) and Ni-20Cr-20W-0.11Al alloy (E-11) melted in vacuum induction furnace were used as the standard masterheat. They were remelted with additives of pure Mn and Si metals and graphite in an

Fig. 1. Temperature dependence of oxidizing potential of elements contained in Ni-Cr-W-C alloys, showing a gas condition of HTGR planned at JAERI and the test condition in this paper

* Originally published in *Tetsu-to-Hagane*, **62** (1976), 1550, in Japanese. English version received January 7, 1977.

** Mitsubishi Metal Research Institute, Kitabukuro, Omiya 330.

Table 1. Chemical compositions and solution heat treating condition of specimens (wt%)

Alloys	C	Mn	Si	Al	Ti	Cr	W	Mo	Fe	Co	Ni	Solution heat treatment
E-11	0.04	—	—	0.11	—	21.00	18.62	—	—	—	bal.	1 275°C×1 hr
E-31	0.08	0.39	—	0.11	—	21.00	18.62	—	—	—	"	"
E-32	0.06	0.89	—	0.11	—	21.00	18.62	—	—	—	"	"
E-33	0.07	1.31	—	0.11	—	21.00	18.62	—	—	—	"	"
E-40	0.03	—	0.29	0.11	—	21.00	18.62	—	—	—	"	"
E-41	0.07	—	0.35	0.11	—	21.00	18.62	—	—	—	"	"
E-42	0.01	—	0.76	0.11	—	21.00	18.62	—	—	—	"	"
E-43	0.08	—	0.97	0.11	—	21.00	18.62	—	—	—	"	"
E-51	0.07	0.81	0.73	0.11	—	21.00	18.62	—	—	—	"	1 250°C×1 hr
F-11	0.11	—	—	<0.02	—	20.0*	20.0*	—	—	—	"	1 275°C×1 hr
F-32	0.08*	0.81	—	<0.02	—	20.0*	20.0*	—	—	—	"	"
F-42	0.06	—	0.72	<0.02	—	20.0*	20.0*	—	—	—	"	"
F-51	0.07	0.76	0.48	<0.02	—	20.0*	20.0*	—	—	—	"	1 250°C×1 hr
Hastelloy X	0.07	0.54	0.39	0.3	—	21.28	0.57	8.99	17.86	0.79	"	1 150°C×15 min
Inconel 617	0.07	0.04	0.43	1.20	0.35	20.5	—	8.5	—	12.0	"	1 177°C×15 min

* aim point

Ar induction furnace and cast to small ingots.

These ingots were hot-forged and hot-rolled at 1 200°C to the sheets of 4 mm in thickness. After solution heat treatment these sheets were cut to specimens whose dimension was 3×10×10 mm. These specimens were polished finally with No. 1500 emery paper and washed in acetone and dried thoroughly.

2. Hot Corrosion Test

The arrangement of the hot corrosion testing apparatus used here is shown in Fig. 2. This apparatus had six independent test zones made of quartz tubes of 12 mm in diameter, and six specimens could be simultaneously tested. At each corrosion test, a specimen of E-11 which had standard chemical composition (0.11%Al; Si and Mn not added) was always contained among six specimens as the standard specimen. The specimens were set in the test room vertically and a plane of 3×10 mm of each specimen confronted the gas flow. Moisture content of He gas, whose nominal purity was 99.995%, was measured at the inlet and the outlet of the testing zone, but other impurities were not measured in this experiment.

Cylinder to cylinder difference of the moisture content in He gas at this test was sufficiently small and the amount of it was kept around 1 ppm during corrosion test run of 100 hr. The testing temperature was 1 000°C and flow rate of He gas was 50 to 100 cc/min for a unit surface area of the specimen (cm²).

After the corrosion test, the measurement of weight gain, the surface observation with an optical microscope and a scanning electron microscope, the measurement of depth of internal oxidized layer, and the electron probe microanalysis of the layer on the section were done. In some cases the oxide film was analyzed with X-ray diffraction and EPMA, and the oxide whisker grown on the specimen surface was analyzed in a transmission electron microscope. As a change in the appearance of oxidized surface along He gas flow was observed, all the specimens were examined

Fig. 2. Flow chart of the apparatus for the hot corrosion test in He gas

at upper position of them.

For the evaluation of corrosion resistance of super-alloys in high temperature He gas, the following items were considered to be of specific importance:

- 1) weight gain which corresponds to the rate of oxidation
- 2) adherence of the surface oxide film to the matrix
- 3) depth of the internal oxidation.

A reliable value of weight gain to estimate the oxidizing rate could hardly be obtained because of the spalling of oxide scale and decarburization, so corrosion resistance was mainly evaluated by the adherence of the oxide film and the depth of the internal oxidation in this work.

III. Results and Discussion

1. Adherence of Oxide Film and Internal Oxidization

Adherence of the oxide film was evaluated by the quantity of spalling of the film observed with an optical microscope. The appearance of spalling of the oxide film is shown in Photo. 1. He gas flowed from

Photo. 1. Surfaces of specimens corroded in 99.995%He gas at 1 000°C for 100 hr. Gas flowed from left to right. White spots show the spalling of oxide scale.

the left hand to right on the specimens. The appearance of the surface was not uniform and spalling of the oxide film, which is observed as white spots in Photo. 1, happened more often at the upper stream side.

The oxide scale spalling of all specimens studied here was schematically shown in the upper side of Fig. 3, and the followings were made clear from this result.

The adherence of the oxide film was improved by the addition of Mn. A small amount of addition of Si (up to 0.35%) improved the adherence, but an excess amount of addition of Si increased the spalling on the contrary. The simultaneous addition of Mn and Si improved the adherence markedly. The effect of the addition of Al was not clear. The adherence of Hastelloy X and Inconel 617 were very good.

The constitutions of the surface area were shown in Photo. 2. The maximum depth of the intergranular attack was measured on the photographs and the values were shown in Fig. 3. The addition of Mn or Si decreased the maximum depth of the intergranular attack, but an excess amount of Si did not bring a good result. The addition of Mn and Si decreased markedly the depth and this result corresponded to the effect of these elements on the spalling of the oxide film. The addition of Al increased, contrary to the case of spalling, the depth of the intergranular attack. Hastelloy X and Inconel 617 also showed the intergranular attack.

From these results, it is considered that one can get, by setting the optimum contents of Mn, Si and Al, Ni-20Cr-20W-0.07C alloy whose intergranular attack in He gas at elevated temperatures is less severe than that of Hastelloy X and Inconel 617.

The oxide scale was observed at the surface area in an EPMA. The results were shown schematically in Fig. 4. The film on the surface of specimens of E-11 and F-11 which did not contain Mn and Si was

Fig. 3. Influence of Al, Mn, and Si on the spalling of scales and intergranular attack in 99.995%He gas at 1 000°C for 100 hr.

composed of Cr_2O_3 and the selectively oxidized Al_2O_3 was observed at the grain boundary irrespective of the addition of Al. The intergranular attack in the alloy with Al addition (Al: 0.11%) was deeper than that in the alloy without the addition of Al (Al<0.02%).

The oxide film on specimen of E-33 which contained Mn and Si was constituted with two kinds of layers, *i.e.*, the external layer was composed of spinel type oxide (MnCr_2O_4 or Mn_3O_4), and the internal layer was made of Cr_2O_3 .

Al was condensed in the grain boundaries beneath the surface of the specimen containing Al and Mn, and seemed to make up Al_2O_3 , and Mn was condensed at further internal grain boundaries forming MnO .

When a small amount of Si was added to the alloy containing 0.11%Al, SiO₂ was substituted partially by Al₂O₃, and no Al₂O₃ was observed when Si was added more than 0.76%. In this case the oxide scale was made of Cr₂O₃, and spherical SiO₂ was formed at the oxide film-matrix interface encroaching into the matrix. This agrees with the result of Incoloy 800

Photo. 2. Intergranular attack in 99.995% He gas at 1000°C for 100 hr

Fig. 4. Schematic interpretation of oxidized surface structures of Ni-Cr-W-C alloys

by Shinoda, *et al.*⁸⁾

On E-51 specimen in which Mn and Si were added together, the oxide film of double layers was observed. The external layer contained Mn and Cr and the internal one was substantially made of Cr and quite little amount of Mn. The spherical oxide containing Si was also observed at the oxide film-matrix interface

as in the case of Si addition. No intergranular attack was observed in this specimen.

Both the intergranular and the transgranular attacks were observed in Hastelloy X and Inconel 617 and this tendency of oxidation was more evident in Inconel 617 containing a larger amount of Al than Hastelloy X.

From these results, it is to be concluded that there was a reciprocal relation between the tendency of the spalling of the oxide film and that of the selective oxidation, and this was remarkably influenced by the contents of Mn, Si and Al. This relation can be summarized as follows.

Al was an element to activate the intergranular oxidation, but it was suppressed more or less when the tight and tough spinel type oxide film was present.

Mn or Ti brought about, as was observed on Inconel 617, the spinel type oxide layer (MnCr_2O_4 , Mn_3O_4 , TiCr_2O_4 , etc.)⁶⁾ which was so tight and tough to prevent itself from spalling and sufficiently delay the diffusion of oxygen into the alloy matrix to reduce the intergranular attack of the alloy which contained even a harmful element as Al in it.

On the other hand, Si played a role to produce spherical oxide at the oxide film-matrix interface which keyed the oxide film to the matrix and prevent the spalling of the film.

An excess amount of Si made the SiO_2 to be the continuous layer which promoted the spalling of the oxide film on the contrary because of a large expansion due to the transformation of cristobalite ($\beta \rightarrow \alpha$).

The addition of Mn and Si together, because of the respective advantages of these elements, brought about tight and tough oxide film which was keyed in the matrix by the spherical SiO_2 .⁹⁾ The intergranular attack by oxide increased with increase of active elements as Al and Ti, and was suppressed by

the tight and tough oxide film adhering on the matrix.

2. Oxide Whisker

Whiskers of several $10\ \mu$ in diameter were observed on the surface of the specimens in this study as had been observed on many kinds of alloy exposed in impure He gas at elevated temperatures.⁵⁻⁸⁾

Scanning electron micrographs of the surface of E-42 specimen are shown in Photo. 3. The appearance varied with the position on the surface from upper side to lower side along the gas flow. At the upper stream side, the spalling of the scale and a continuous ditch, which seemed to correspond to the grain boundary,

were observed, and the surface of films which adhered to the matrix was rather smooth and no whisker was observed on it.

The surface became rougher at the lower side and whiskers grew on it. Thick whiskers grew at the tail end. These result indicates the mechanism of the growth of the whiskers that oxide sublimated first, then it deposited on the tips of whiskers.¹⁰⁾

The growth of the whiskers was influenced by the contents of Mn and Si in the alloys as it is shown in the scanning electron micrographs (Photo. 4). No whisker was observed on any specimen of Si free, except for E-33 specimen containing a large amount of

A: front edge B: 1.5 mm C: 3 mm D: 5 mm E: 7.5 mm F: tail end

Photo. 3. Scanning electron micrographs of E-42 specimen surface corroded in 99.995%He gas at 1000°C for 100 hr, showing the different appearances with positions along the gas flow

A: E-11 B: E-32 C: E-33 D: E-42 E: E-51 F: Hastelloy X

Photo. 4. Scanning electron micrographs of specimen surfaces corroded in 99.995%He gas at 1000°C for 100 hr

Mn (1.31%).

A small addition of Si brought the growth of whiskers on the surface, and their number and thickness increased with the increase of Si content.

The lumpish oxide product was observed on the specimen on which whisker did not grow as shown in Photos. 4 (A) and (B).

A small amount of whiskers grew on the surface of E-33 specimen with no Si and a large amount of Mn; however, the morphology of them was quite different from that of the whiskers grown on the specimens having Si, that is, the whiskers were shorter and rather blocky.

The content of Al did not influence the growth of the whiskers. Thick whiskers grew also on Hastelloy X and Inconel 617.

The elements contained in the whiskers which had grown at the tail end of E-42 specimen were examined with EPMA as shown in Photo. 5. Si and Cr seemed to be contained in whiskers in this case, and Mn was also found in the whiskers when the alloy contained Mn.

Bright-field images and diffraction patterns of Whiskers took with a transmission electron micro-

scope are shown in Photo. 6. The whiskers which grew on the specimen containing Si without Mn were rather straight with smooth surfaces and they were identified as hexagonal crystals whose lattice parameter was a little bit larger than that of pure Cr_2O_3 , that is, $a=4.99 \text{ \AA}$, $c=13.28 \text{ \AA}$ and $c/a=2.66$ in this case, and $a=4.954 \text{ \AA}$, $c=13.584 \text{ \AA}$ and $c/a=2.742$ for the pure Cr_2O_3 , respectively.¹¹⁾ This result indicated that the whiskers were composed of Cr_2O_3 which solved Si in it.

On E-51 specimen containing both Mn and Si, two kinds of whisker, thin one with smooth surface and thick one with rough surface, were observed. The latter was a cubic crystal whose lattice parameter was $8.52 \text{ \AA}$.

Substantial parts of the whiskers grown on Hastelloy X were thicker ones with rough surface and they were identified to be cubic crystals of $8.42 \text{ \AA}$ in lattice parameter. These lattice parameters were very close to that of the spinel type oxide MnCr_2O_4 ($a=8.54 \text{ \AA}$) observed on Hastelloy X by Hickman.¹²⁾ Taking the result of EPMA into consideration, these thicker whisker were concluded to be spinel type oxides containing Mn and Cr. The difference of morphology between Cr_2O_3 type whisker and spinel type one seemed to be caused by the difference of the habit direction of crystal growth between them. The direction was almost limited to c axis of hexagonal crystal for the former,¹³⁾ on the other hand, it was not limited to one axis of cubic crystal for the latter.

Through this study, it has remained unknown why whiskers grew on the alloys containing Si and few whiskers grew on the Si-free alloy.

IV. Conclusions

The hot corrosion behavior of Ni-Cr-W-C alloys in 99.995% He gas at 1000°C , and the influence of the minor alloy constituents such as Mn, Si and Al on it were studied.

(1) The adherence of the oxide film and the depth of the intergranular attack were related each other. When the tight and tough spinel type oxide film was formed, the intergranular attack was suppressed.

(2) When the oxide film was not tight and easy to spall off, intergranular attack by oxides was more often observed at the surface area and Al promoted the attack.

(3) An optimum content of Si minimized the spalling of the oxide scale by producing the spherical SiO_2 oxide particles between the oxide film and the matrix which played a role of keys between them.

(4) The thinner whiskers with smooth surface grown on the oxide surface were Cr_2O_3 type oxide crystals, on the other hand, the thicker whiskers with rough surface were spinel type crystals composed of Cr and Mn. The former was observed on the alloys which contained more than 0.29% of Si and the latter was observed on the alloys containing Mn.

(5) Alloys like F-51 and E-51 the corrosion resistivity of which in impure He gas at elevated tempe-

A: secondary electron image
B: Cr $K\alpha$
C: Si $K\alpha$

Photo 5. Electron probe micrographs of the whiskers grown at tail end of E-42 specimen corroded in 99.995% He gas at 1000°C for 100 hr

A: E-42
B: E-51
C: Hastelloy X

Photo. 6. Bright-field image and diffraction patterns of the whiskers grown on the surface of specimens corroded in 99.995%He gas at 1 000°C for 100 hr

rature was superior to that of Hastelloy X or Inconel 617 were found.

Acknowledgements

The authors would like to greatly acknowledge many helpful suggestions by Prof. R. Tanaka and the late Dr. T. Shinoda, Tokyo Institute of Technology.

REFERENCES

- 1) T. Ohmura, K. Sahira, A. Sakonooka and N. Yonezawa: *Tetsu-to-Hagané*, **61** (1975), S322.
- 2) T. Ohmura, K. Sahira, A. Sakonooka and N. Yonezawa: *Tetsu-to-Hagané*, **61** (1975), S323.
- 3) T. Ohmura, K. Sahira, A. Sakonooka and N. Yonezawa: *Tetsu-to-Hagané*, **61** (1975), S764.
- 4) T. Kondo: *J. Atomic Energy Society of Japan*, **15** (1973), 295.
- 5) T. Kondo: *Bull. Japan Inst. Metals*, **13** (1974), 93.
- 6) The Japan Society for the Promotion of Science: Second Report on the Heat Resistant Materials for HTGR, (1974).
- 7) T. Kondo, M. Shinoda, H. Nakajima and N. Kikuyama: Preprint of the "Symposium on Environment and Strength", Japan Inst. Metals and the Japan Society for the Promotion of Science, Tokyo, Aug., (1975), 39.
- 8) T. Shinoda, T. Ohtani, and R. Tanaka: Report of the 123 Committee of the Japan Society for the Promotion of Science, **16** (1975), 245.
- 9) B. Lustman: *Trans. AIME*, **188** (1950), 995.
- 10) R. Takagi: *J. Phys. Soc. Japan*, **12** (1957), 1212.
- 11) ASTM: Powder Diffraction File, (1967), No. 6-504.
- 12) J. M. Kickman: *Iron Age*, **12** (1948), 90.
- 13) G. W. Sears and R. C. DeVries: *J. Chem. Phys.*, **39** (1963), 2837.