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Key Words: supercritical water oxidation, high temperature steam, corrosion resistance, weight change, composition elements, surface treatment

Abstract

The test results from the literature, in English language, about corrosion resistance of the alloys under various steam conditions are summarized in this paper. The effect of the composition elements, the surface pre-treatment and the chemical environments on the corrosion behaviours of alloys are evaluated. The evaluation methods for the corrosion behaviours are: the weight change, the observation of the corrosion morphologies, the composition element analysis of the alloys, and the chemical analysis of the tested medium.

Die Korrosion von Werkstoffen unter überkritischen und Hochtemperatur-Bedingungen (eine kurze Literaturübersicht)

Zusammenfassung

Die experimentellen Ergebnisse der englischsprachigen Literatur über das Thema Korrosionsbeständigkeit von Metallegierungen unter verschiedenen Dampfbedingungen werden in diesem Bericht zusammengefaßt. Die Effekte der elementaren Zusammensetzung, der Konditionierung der Oberfläche und der chemischen Umgebung auf das Korrosionsverhalten der Legierungen wird diskutiert. Die Untersuchungsmethoden für die Beurteilung des Korrosionsverhaltens sind: Gewichtsänderung, die Beobachtung der Korrosionsmorphologie, die Analyse der Bestandteile der Legierungen und die chemische Analyse des getesteten Mediums.

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1. Introduction

Environment constraints continue to force the chemical industry to search for the new technologies to process the hazardous wastes. The supercritical water oxidation (SCWO) is just one of these technologies. Due to the advantages of the SCWO technology comparing with biological treatment method and incineration method for the treatment of the organic wastes, the interest in this technology has increased considerably in the recent years (1-3). However, almost all of the organic matters in the model wastes were oxidized in the temperature range 400-500 °C, i.e., above the critical conditions for water, only a small portion of the organic matter was oxidized at subcritical conditions (4). Therefore, the chemical environment of SCWO is rather severe for the materials used for the reactor and heat exchanger. In order to operate the SCWO equipments safely, the materials which are resistant to such a corrosive environment have to be found. The alloys tested concentrated on the iron- and nickel- base alloys for early work. Recently, the research put emphasis on the high-Ni, high-Cr alloys and Ni-base alloys, such as Inconel 625, Alloy 556, Hastelloy C22, C276, and other alloys (1). The practical difficulty for evaluation of the corrosion resistant materials is that the results obtained from a certain material during SCWO for a special waste can not be used to estimate the applicability of this material for another waste. Because of the dependence of the corrosion behaviour of materials on the chemical composition of the SCWO medium, a number of simulation tests to the practical systems and supplementary tests have to be performed for the materials research. The work on this field was started as early as 60's in KfK. In this paper, only some literature data in English are included.

2. The corrosion behaviour of materials under various steam conditions

2.1. Corrosion rate

The corrosion rate of materials is frequently evaluated by the weight change of specimens in the certain medium and at a given time. The corrosion rate of the materials in various steams are summarised as following:

2.1.1. The low-alloys ferritic steels

The special low-alloys ferritic steels were generally used as the tube material of the steam generator in the power stations (5). Their corrosion resistance to the high temperature water/steam have been reported since many years. These alloys presented here contain 1.1 to 8.7 % Cr, and were tested in TVA's Bull Run Steam Plant in supercritical steam at 3500 psi (24.5 MPa) and 1000 °F (538 °C) for time up to 15000 h (6). Fig.1 shows that the weight of all materials tested in supercritical steam has increased. The maximum and the minimum weight change at a given time varies only by a factor of 2. The maximum weight gain in 10000 h for these low-alloys is 10 mg/cm2 . It is obvious, that these alloys formed tenacious and nonspalling oxides when tested in supercritical steam.

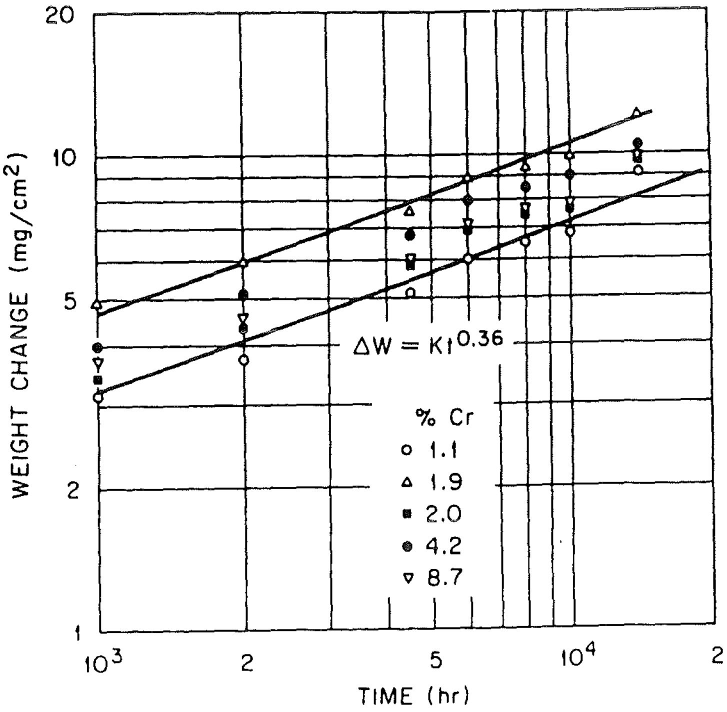

Fig.1: Weight changes of low-alloy ferritic steels in supercritical steam at 538 °C and 24.5 MPa (6)

2.1.2. Stainless steel and high-Cr, high-Ni alloys

The development of the supercritical boiler and high pressure power plants require heat resistant materials with high strength properties at high temperature. Many kinds of stainless steels and high-Cr, high-Ni alloys were developed and tested in supercritical and high temperature steam for this purpose (5-9). Spalling of the oxide scale on the materials may cause blockage inside superheater/reheater tube and severe erosion damage. From the corrosion point of view, the information on scaling behaviour of materials in high temperature steam becomes interesting and this information will also be useful for SCWO apparatus. The chemical composition of the tested stainless steels and high-Cr, high-Ni alloys are listed in Table 1 (5-7).

Table 1: Chemical composition of the tested materials

Alloy	C	Si	Mn	Cr	Ni	Mo	Ti	Nb	Fe	others
17-14CuMo	0.11	0.61	0.74	15.80	13.70	1.83	0.33	0.44	bal.	Cu: 3.07
AN31	0.09	0.49	1.47	16.06	13.52	1.53		1.07	bal.	V: 0.65, N: 0.07
Esshete 1250	0.11	0.41	6.00	16.09	12.19	1.19		0.87	bal.	V: 0.22
12R72V	0.10	0.41	1.98	15.38	14.61	1.16	0.3		bal.	
15-15N	0.12	0.66	1.50	15.99	15.58	1.58		1.07	bal.	W: 1.49, N: 0.13
321H	0.08	0.53	1.70	17.30	10.65		0.40		bal.	
347H	0.09	0.50	1.53	18.34	12.46			0.90	bal.	
Alloy 807	0.06	0.43	0.97	20.41	38.82		0.30	0.95	bal.	W: 4.55, Co: 7.66, Al: 0.38
Alloy 800H	0.08	0.50	1.21	21.15	32.31		0.50		bal.	Al: 0.48
HR3C	0.06	0.39	1.26	24.60	21.10			0.47	bal.	N: 0.25

These stainless steels with different contents of Cr and high-Cr, high-Ni steels were tested in high temperature steam at 973 K (523 °C) for 1000 h (7). Fig. 2 shows the thicknesses of the inner scale formed on these materials. Obviously, internal scaling is related to the Cr content of the steels. The steels containing more than 20 wt.% Cr and the fine-grained 347H have a better scaling resistance than the conventional coarse-grained stainless steels and the lean austenitic stainless steels. High-Cr, high-Ni alloys 807, 800H and HR3 have better scaling resistance than the stainless steels. Nearly no scale was formed on HR3 alloy containing 24% Cr. It became clear that the scaling resistance of the alloys in high temperature steam increased with Cr content of the alloys. If the oxide layer on the materials is very thin, it is very difficult to observe it by microscopy, and the weight change may be used to evaluate the thickness of the oxide layer. In supercritical steam of 538 °C and 24.5 MPa for 5000 h, the weight gain for 347S.S., Incoloy 800, Inconel 600, Inconel 718 and Hastelloy X are 1.5, 0.9, 0.5, 0.015 and 0.08 mg/cm^2, respectively (6).

2.1.3. Ni-base alloys

Ni-base alloys are frequently selected for the high temperature section of the SCWO equipments because of their superior corrosion resistance to the supercritical and high temperature steam, as well as the superheated steam containing hydrogen chloride (5-12). The corrosion rate and scaling of the alloys tested under the above medium conditions are summarised in Table 2. Their chemical compositions are listed in Table 3. Fig. 2 to Fig. 6 show the weight changes of tested alloys under various steam conditions.

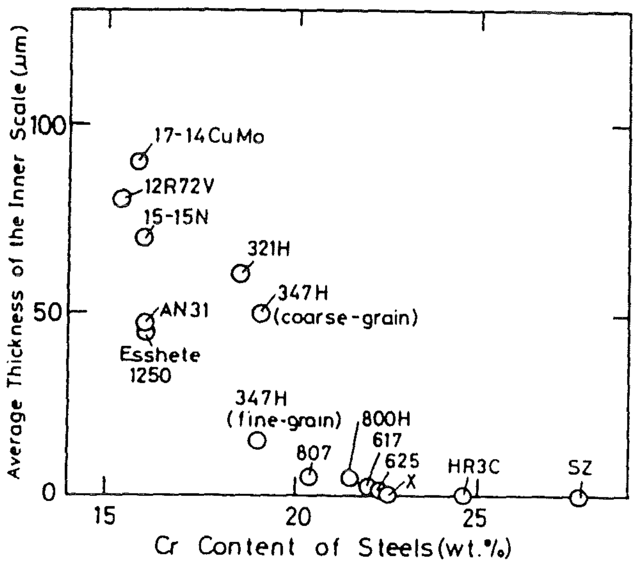

Fig. 2 The effect of the Cr content on the average thickness of the inner scale formed on austenitic stainless steels and Ni-alloy reacted with steam at 973 K for 1000 h (7)

Fig. 6 (5, 14) compare the corrosion rates of the 13% Cr, austenitic 18-8 Cr-Ni steels, high-Cr, high-Ni alloys and Ni-alloys in flowing superheated steam at 838 K (448 °C). It can be seen that the corrosion rates of Inconel 625 and Inconel 600 are relatively lower comparing with those of other steels. The chemical compositions of the alloys are listed in Table 4. The results of the early work by W.L. Pearl (15) indicated also that the corrosion rates of Inconel alloys in superheated steam are lower than that of the Incoloy, Hastelloy X and 304 S.S.. The results from the above tests have indicated that : 1) The alloys containing high Cr had an excellent scaling resistance to high temperature and supercritical steam containing oxygen. The higher the chromium content, the better the scaling resistance. This may due to the formation of the protective Cr_2O_3 on the surface of the alloys. 2) Alloys in high temperature steam containing oxygen appeared to form the oxide scale, while in superheated steam containing hydrogen chloride and oxygen, weight loss ocurred, and some composition elements are dissolved in the liquid effluent. 3) Ni-alloys exhibited always weight loss in $HCl+H_2O+O_2$ environment at 600 °C and 700 °C

(10, 12). The reason is that at the same time as the formation of the scale, the formation and volatilisation of Fe, Cl, O, Mo compounds also occur. The observed weight change is therefore the result of two opposite effects: a mass increase by oxygen incorporation into the scale and a mass decrease by evaporation of volatile compounds. Since the evaporation processes prevail, a weight loss is always observed (10). The oxides scale is slightly porous at the first 100 h, after 500 h, it becomes compact, and weight loss rate showed linear increases with time, then decreased slowly (13). Since many Mo-rich Ni-alloys normally include a few percent of iron, the iron will react with $HCl+H_2O+O_2$ to form the volatile Fe compounds. Therefore, their use in $HCl+H_2O+O_2$ atmospheres at high temperatures should be carefuly planned.

Table 2: The corrosion rate of the nickel-alloys tested under various steam conditions

Alloys	Ref.	High temp. steam 973K 1000h	supercritical steam 811K, 10000h	steam+HCl+O_2 873-973K, 100h	SCWO with phenol 573-693K, 4-111s
Inconel 617	7	a little scale			
Inconel 625	7	a little scale			
Inconel X	7	nearly no scale			
SZ alloy	7	no scale			
Inconel 718	6		weight gain 0.01mg/cm^2		
Inconel 600	6		weight gain 0.45mg/cm^2		
Hastelloy N (rolled)	6		weight gain 0.40mg/cm^2		
Ni-29Mo-4Fe	13			weight loss at 973K: 22 mg/cm^2 at 873K: 4mg/cm^2	
Ni-29Mo	13			weight loss at 973K: 10mg/cm^2 at 873K: 6mg/cm^2	
Hastelloy B	10			weight loss at 973K :7mg/cm^2 at 873K :4mg/cm^2	
Hastelloy C-276	12				elements detected in liquid medium Fe:4μg/g medium Cr:0.1μg/g medium Co:0.03μg/g medium

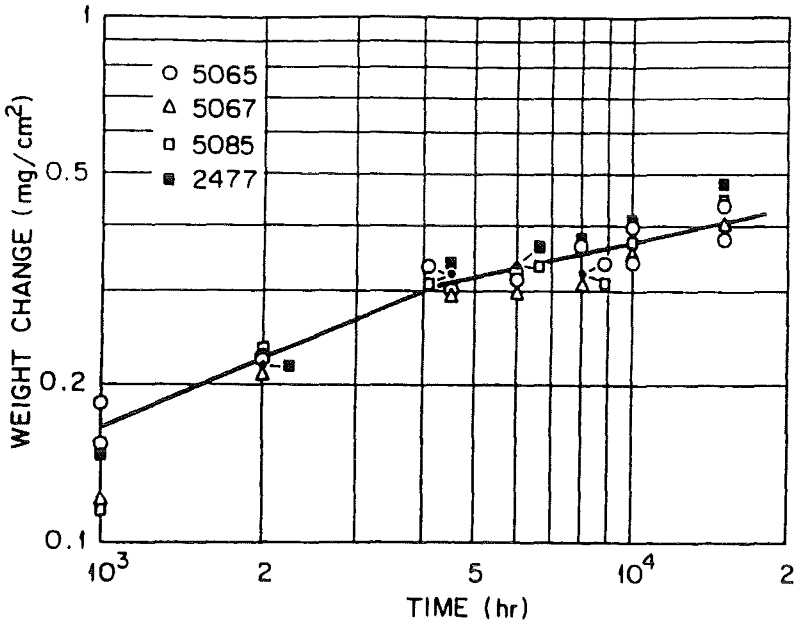

Fig. 3: Weight changes of Hastelloy N exposed to supercritical steam at 1000 °F and 3500 psi. (6)

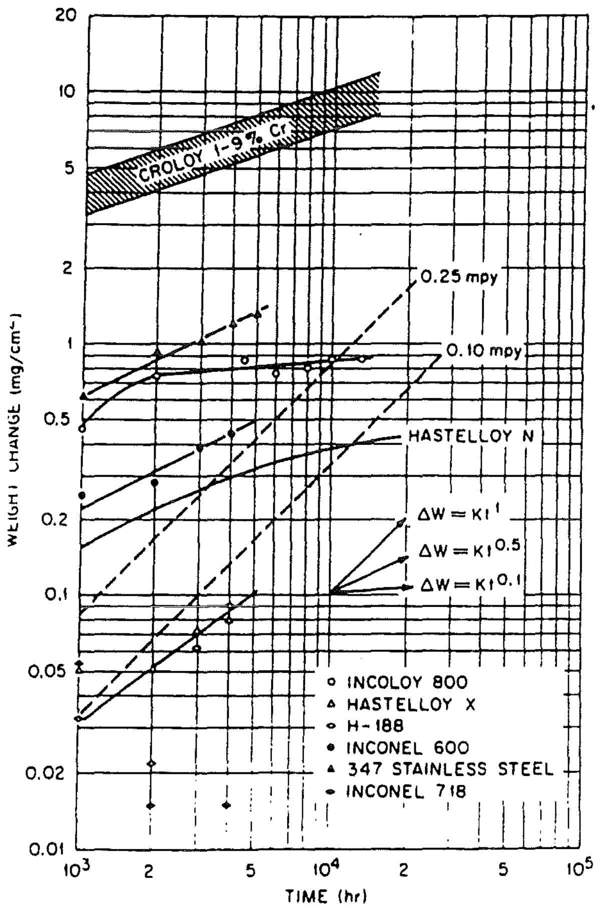

Fig. 4: Corrosion rates of several alloys in steam at 1000 °F and 3500 psi. (6)

Table 3: Chemical compositions of the Ni-alloys shown in Table 2

Alloys	C	Si	Mn	Cr	Ni	Mo	Ti	Fe	Nb	Al	others
Inconel 617	0.06	0.41	0.37	22.0	bal.	8.53	0.38	3.53		1.15	Co:12.53
Inconel 625	0.07	0.36	0.43	22.3	bal.	9.16	0.30	4.07	3.2	0.22	
Inconel X	0.06	0.38	0.70	22.5	bal.	8.71		16.5			Co:1.19, W:1.10
SZ alloy	0.04	0.02	0.32	27.9	bal.	5.35		1.24			W:4.72
Inconel 718	0.05			18.0	53.0	3.0	1.0		5.0	0.5	
Inconel-600	0.03			15.43	77.61			bal.			
Hastelloy N 185	0.05	0.10	0.46	5.9	bal.	11.0	0.91	3.8		<0.05	Co:0.03, Hf:<0.1, W:<0.1, Zr:0.98
Hastelloy N 231	0.05	0.12	0.03	7.0	bal.	12.0	<0.02	4.2	<0.05	<0.05	Co:<0.03, Hf:1.3, Zr:0.05, Y:1.2
Hastelloy N 2477	0.057	0.047	0.055	7.0	bal.	16.2	0.03	4.2	0.0005	0.02	P:0.008, S:0.004, V:0.01, Cu:0.01, Co:0.05 W:0.03, B:0.0002, Zr:<0.001, Hf<0.001
Ni-29Mo-4Fe					bal.	29		4			
Ni-29Mo					bal.	29					
Hastelloy B	0.05	0.3	0.96	0.2	bal.	27.2	<0.01	5.2			Cu:0.01, Co:0.48, V:0.2, Zr:<0.05
Hastelloy C-276		0.48	0.75	16.0	bal.	16.0	<0.01	5.8		0.2	Cu:0.01, Co:0.2, V:0.1, W:5.0, Zr:0.05

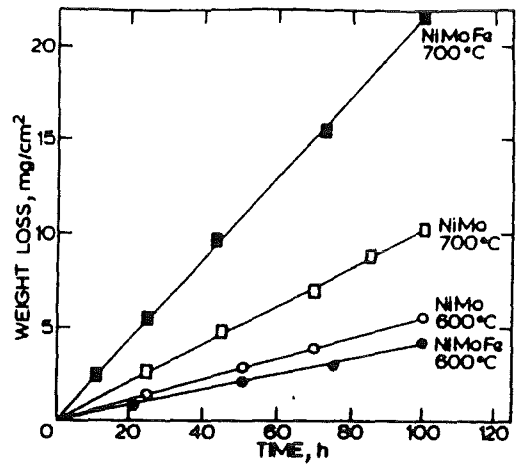

Fig.5: Weight loss as a function of exposure time observed for the ternary alloy corroded at 600 °C and 700 °C in 21% HCl (13)

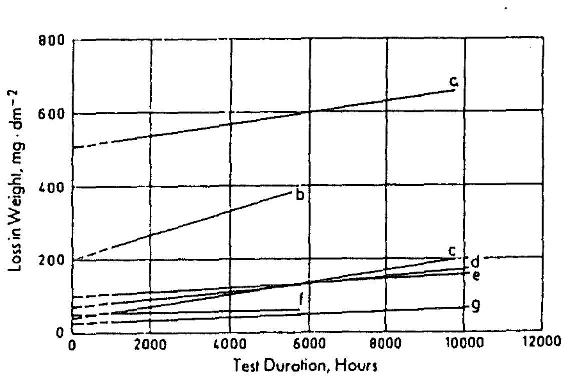

Fig.6: Weight loss of Cr-Ni steels and nickel-alloys in flowing superheated steam at 838 K (14).

a. 406 S.S. b. 304 S.S.
c. Incoloy 825 d. Hastelloy X
e. Incoloy 800 f. Inconel 625
g. Inconel 600

Table 4: The chemical composition of the alloys shown in Fig. 6

Alloys	C	Cr	Al	Ni	Mo	Ti	Fe	Nb/Ta
AISI 406s.s.	0.07	13.09	3.88				bal.	
AISI 304s.s.	0.03	18.70		9.29			bal.	
Incoloy 825	0.047	17.0	0.32	46.8	2.7	0.25	bal.	
Hastelloy X	0.10	21.68		46.6	9.17		bal.	
Incoloy 800	0.05	20.61	0.30	32.03	0.41		bal.	
Inconel 625	0.03	21.98		62.31			bal.	4.24
Inconel 600	0.03	15.43		77.61			bal.	

2.2. Corrosion morphologies and corrosion products

Many kinds of techniques were employed to study the corrosion morphologies and corrosion products for tested alloys under various steam conditions, such as optical microscopy, scanning and transmission electron microscopy, electron and X-ray microanalysis, Auger spectroscopy, pH-potential diagram measurement, chemical analysis and neutron activation analysis of the tested medium, and so on. The corrosion morphologies and corrosion products of various materials under the steam conditions are summarised in Table 5. Obviously, the Ni-alloys containing higher Cr have better oxidation resistance to the high temperature steam than stainless steels, especially than the lower-Cr stainless steels. For the medium of superheated steam with HCl and O_2, the Ni-Mo alloys containing low Cr and Fe are not the best selection, Fe and Mo are attacked by steam at 973 K. The Ni-alloys containing higher Cr and less Fe, such as Hastelloy C-276, Inconel 625 and SZ alloy, may be better for this medium. HR 3C alloy, containing high Cr, high Ni and no Fe, may also be a good material for the medium of superheated steam with HCl and O_2.

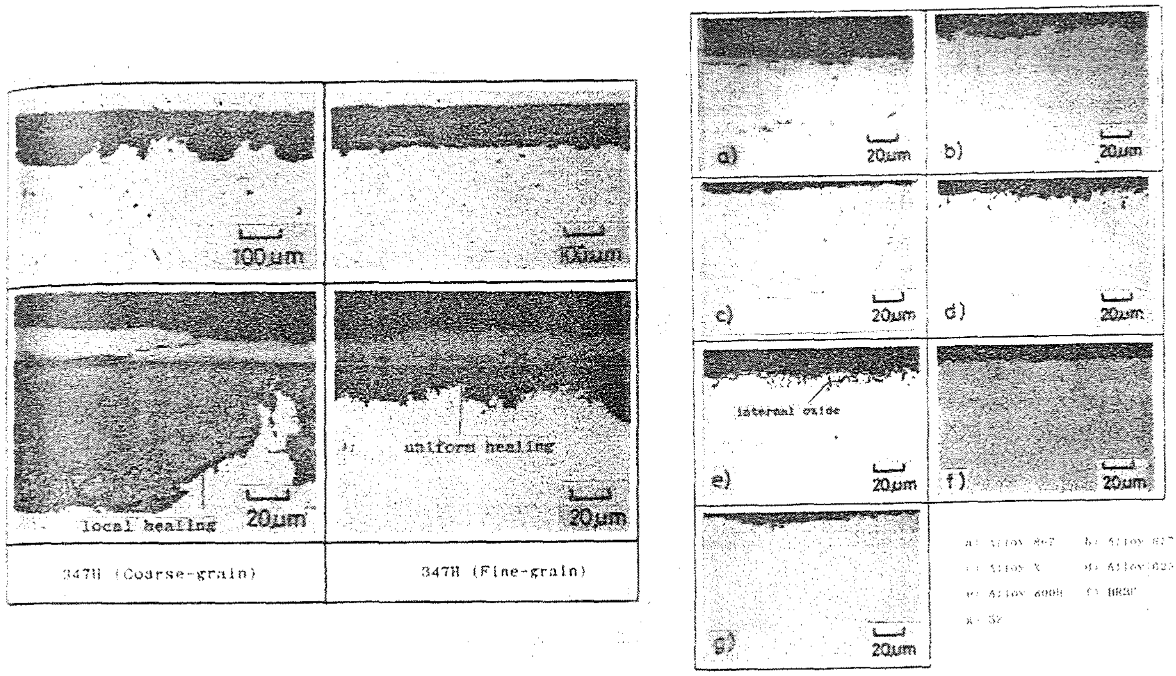

Fig. 7: Optical micrographs of the cross section of the stainless steel and Ni-base alloys reacted with steam at 973 K for 1000 h (not etched) (7)

Table 5: Corrosion morphologies and corrosion products of the alloys in supercritical and high temperature steam (7-15)

Alloys	corrosion morphologies	corrosion products
stainless steel containing <21% Cr in 973 K steam for 1000 h	duplex scale, uniform thickness for outer scale, irregular for inner spinel, local healing of the scale refers to the formation of the local protective Cr_2O_3, more uniform healing of the Cr_2O_3 for 347H S.S.	outer: Fe_3O_4, Fe_2O_3 inner:$(Fe,Cr)_3O_4$ spinel subsurface: Cr_2O_3 for the fine-grained 347 S.S (see Fig. 7)
high-Cr S.S., Ni- alloys in 973 K steam for 1000 h	duplex thin oxide scale and uniform healing of protective Cr_2O_3 layer, if alloys contain a little Al as an alloying element, internal oxide probably is Al_2O_3. The uniform protective Cr_2O_3 scale is very thin and it is difficult to see with 500 x microscopy	outer: Fe_3O_4 inner: Cr_2O_3, Al_2O_3
Hastelloy B Ni-29Mo-4Fe Ni-29-Mo in steam + HCl $+O_2$ at 873-973 K for 100-500 h	a slightly porous corrosion layer; it becomes compact near the external surface after 500 h, therefore, the weight loss was linear at first 100 h, then it becomes less than linear; the morphology of the interface between the corrosion layer and the alloy was quite regular	$NiFe_2O_4$ +NiO+Si, Mn, Co, Cr MoO_2 +NiO Mo, Fe, Cl, O compounds NiO, $FeMoO_3$, MoO_2, $NiFe_2O_4$ NiO MoO_2 + NiO MoO_2 (from external surface to the alloy scale interface)
Hastelloy C-276 in supercritical water with phenol	alloying elements Fe, Cr, Co dissolved in liquid medium with a relatively low corrosion rate which is at the levels very near the NAA detection limits; no Ni was detected and no metals were detected in the solid material accumulated in the reactor product filter	Fe: 4 μg/g medium Cr: 0.1μg/g medium Co: 0.03μg/g medium
304,316 S.S. in supercritical water	passivation film of Cr is lost in this medium conditions and an ionic species CrO_4^{-2} dissolves in the medium. Iron was oxidated into Fe_2O_3	Fe_2O_3, CrO_4^{-2} (see Fig. 8)

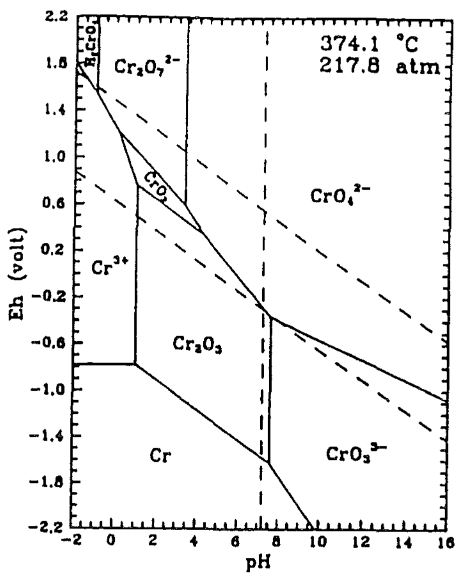

Fig. 8: pH-potential diagram for Cr-H2O system at critical conditions (11)

3. The parameters effecting the corrosion resistance of the alloys

3.1. Composition elements of the alloys

It is well known that the composition elements have influence on the corrosion resistance of the alloys. But only the influence of Cr and Fe are summarised in this paper.

3.1.1. Chromium

As described above, the Cr content has a considerable influence on the oxidation resistance of alloys in high temperature and supercritical steam. The higher Cr content is favourable to the oxide scaling resistant of the alloys (6, 7, 16-19). Fig. 2 and Fig. 4 show that the higher the chromium content, the better the scaling resistance. Whether iron-alloys, stainless steels or Ni-alloys, their scale thickness or weight gain is related considerably to the Cr content. Less chromium content leads to the more scale thickness. The scale of the alloys containing > 20% Cr is rather thin, and for the HR3C and SZ alloy containing > 24% Cr, the oxide scale nearly do not form.

The excellent scaling resistance to the high temperature steam for the alloys containing higher chromium has resulted from the formation of the protective oxide layer Cr_2O_3 on the surface of the alloys. Table 5 shows that for the stainless steels containing < 21% Cr, the duplex scale formed which consists of Fe_3O_4, Fe_2O_3 and $(Fe,Cr)_3O_4$ spinel is not protective. The protective Cr_2O_3 layer can be found at local positions only. But for the high-Cr alloys, the protective Cr_2O_3 scale is very thin and uniform.

3.1.2. Iron and other minor alloying elements

F. Gesmundo (13) and E. Ruedle et al. (10) have investigated the corrosion resistance of the Hastelloy B, Ni-29-Mo and Ni-29Mo-4Fe alloys in a hydrogen chloride-water vapour atmosphere with some oxygen at 600 °C and 700 °C. All three kinds of alloys showed weight loss in this environment. Fig. 9 indicates that Hastelloy B exhibits the smallest weight loss comparing with the other two alloys at 700 °C, and the weight loss of the Ni-29Mo alloy is the highest at 600 °C.
The great weight loss of Ni-29Mo-4Fe at 700 °C is presumably due to the highly porous scale formed on it, which allows penetration of the steam containing HCl and oxygen to enhance the reaction between alloys and $HCl+H_2O+O_2$, and to form volatile products including compounds of Fe. Because there are some additional minor alloying elements in Hastelloy B, they promote the formation of a more compact scale which limits the weight loss. Obviously, the influence of the Fe and the minor alloying elements on the weight loss is significant at 700 °C. While, this influence becomes not considerable at 600 °C.

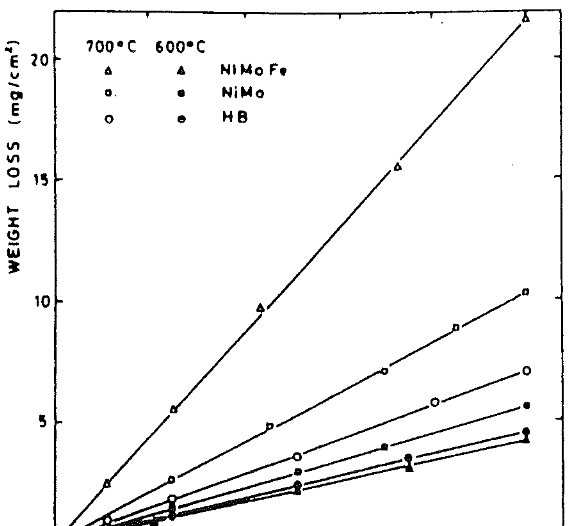

Fig. 9: Weight loss as a function of exposure time observed for the Hastelloy B corroded at 600 °C and 700 °C. For comparison, the data obtained for the alloy Ni-29Mo and Ni-29Mo-4Fe (10) are included

3.2. Grain size of the alloys

Kowaka and Nagata (16) have emphasised and demonstrated the importance of grain size of the base metal to the oxidation in high temperature steam. Their data indicated that the oxidation rates of fine-grained 304, 316, 321 and 347 S.S. are considerably smaller than coarse-grained steels in steam at 923 K. This effect can be attributed to the uniform formation of protective Cr_2O_3 scale along grain boundaries of the alloys at interfaces between the base metal and the oxide scale (7, 20). Fig. 10 showed the influence of the grain size and Cr content on the thickness of the inner scale of the alloys. It is clear that the oxide scale on fine-grained 347H steel was much thinner than that on the coarse-grained 347H steel. Therefore, fine-grained alloys may be favourable to the corrosion resistance of the alloys in high temperature steam.

3.3. The methods of the surface pre-treatment for the specimens

The methods for the surface pre-treatment of the alloys is rather important to evaluate their corrosion resistance. The surface pre-treatment causes structural changes of the alloys and may influence the corrosion characteristics (6, 19, 21). For example, cold working did not have a detectable influence on the corrosion of 2.25Cr-Mo steel in supercritical steam. However, cold working caused a large reduction in the corrosion rate of type 201 S.S. with either the formation of a bcc phase or the spinel $MnFe_2O_4$. Cold working has a lesser influence on the other high Cr steels, generally decreased the corrosion rates. For various Ni-alloys, their corrosion rates were sometimes decreased, but the changes were smaller than a factor of 2.

The influence of the surface pre-treatment methods on the corrosion rate of the alloys can be seen from Fig. 11 and Fig. 12 (6). The electropolish surface of Hastelloy N has a better oxidation resistance in supercritical steam than that of other surfaces. The corrosion rate of annealed stainless steels was much higher than that of cold worked stainless steels. The test results by Kinoshita et al. (22) indicated also that ground stainless steels and Ni-alloys have generally better scaling resistance in high temperature steam than the pickled one. The same results are also reported in Ref. (5). For austenitic Cr-Ni-steels in high temperature steam, the favourable influence of mechanical pre-treatment can be seen from Fig. 13 and Fig. 14. These results were confirmed by laboratory experiments and the field tests in power stations of almost 3 year's duration (24000 h) (5, 23). In these field tests, the pipes of the austenitic steel AISI 347 S.S. were ground integrally (steam side) and exposed for about 3 years to steam of 175 atm., at a temperature up to 953 K. The pipes were almost unchanged after this test period. Surface treatment by shot penning also proved effective in the case of austenitic steels and prevented scaling by steam at the high temperature.

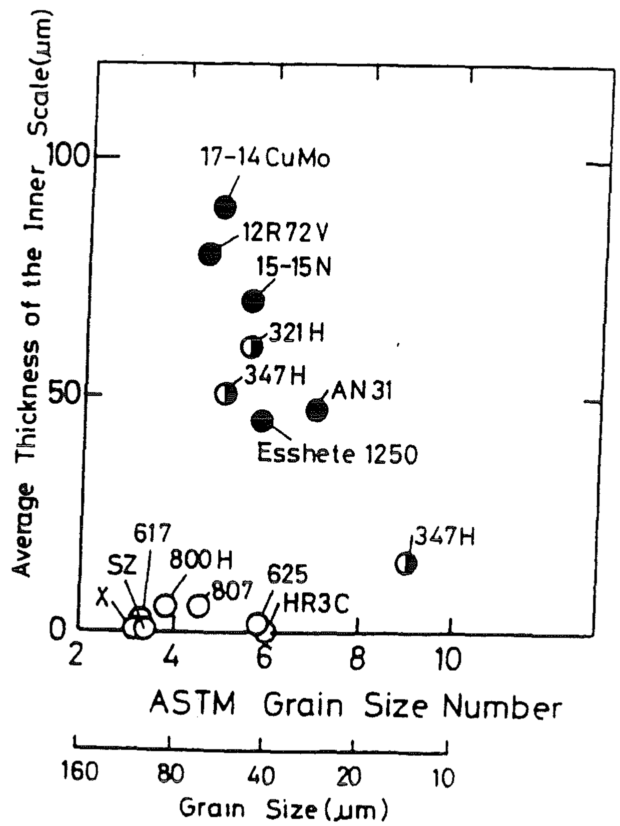

Fig. 10: Effect of the grain size and Cr content of the alloys on average thickness of the inner scale formed on them (7)

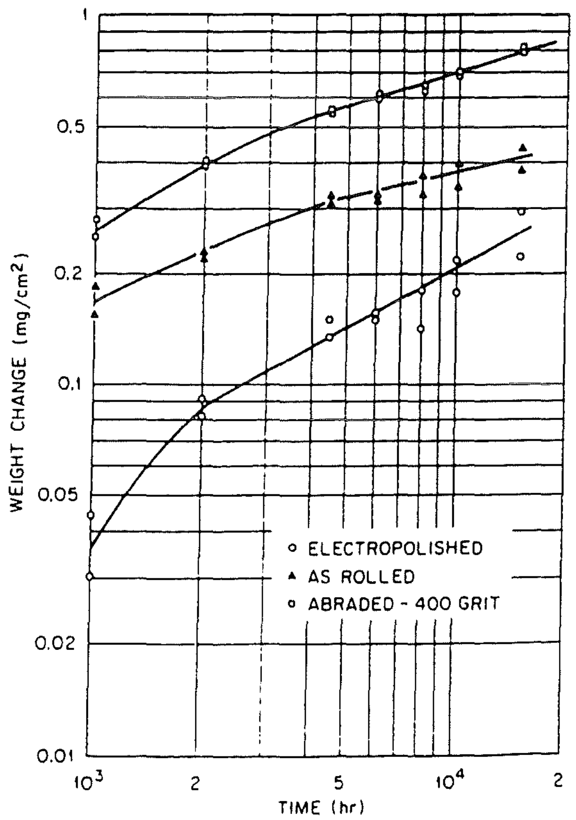

Fig. 11: Effect of surface polish on the corrosion of Hastelloy N in steam at 1000 °F and 3500 psi (6)

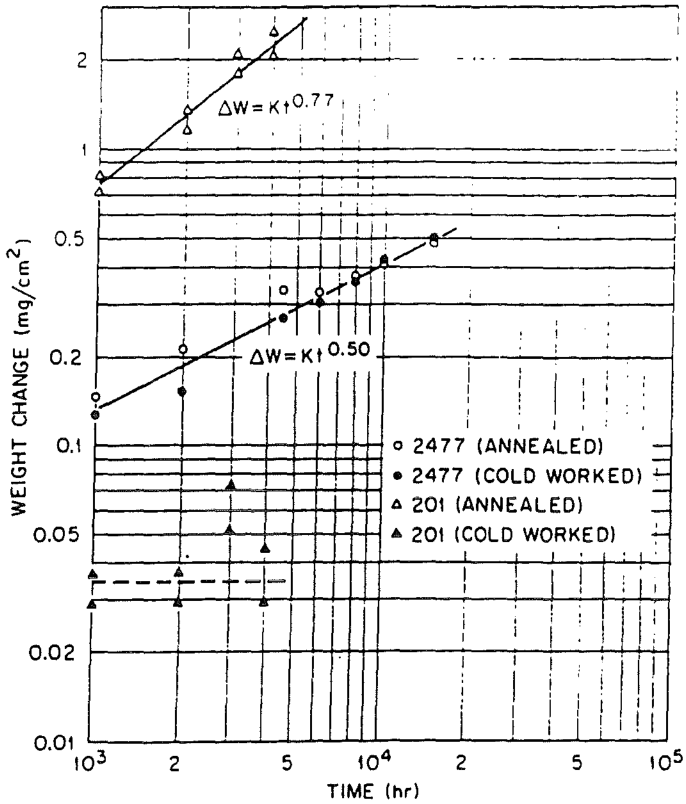

Fig.12: Effect of cold work on the corrosion of Hastelloy N 2477 and type 201 S.S. in steam at 1000 °F and 3500 psi (6)

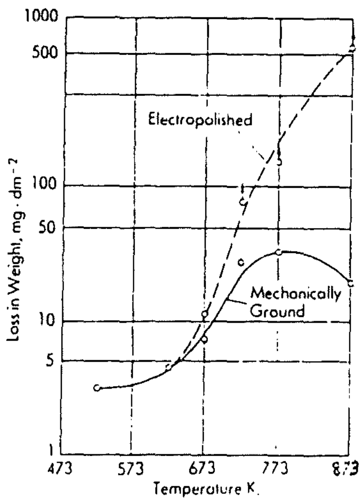

Fig.13: Effect of different pre-treatments on the weight loss of an Cr-Ni steel in steam at 673 K (5)

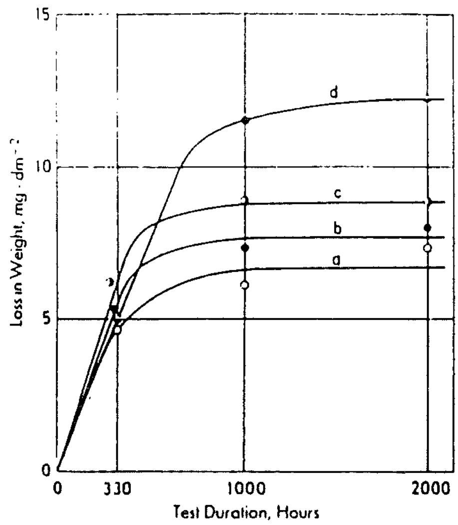

Fig.14: Effect of the surface pre-treatments on the corrosion of an CrNi steel in steam at 673 K (5)
(a) ground with carborundum (particle size 80)
(b) rolled
(c) polished with abrasive paper 600
(d) electropolished

3.4. The environment conditions

In general, the corrosion characteristics of the alloys during supercritical water oxidation are related considerably to the environment conditions, such as temperature, pressure, chemical composition and pH value of the medium, and so on. For instance, the corrosion behaviour of iron alloys and stainless steels are rather different in supercritical water and ambient conditions (11), Cr_2O_3, Fe_2O_3 and Fe_3O_4 are the oxidation products at ambient conditions, while, CrO_4^{-2} and Fe_2O_3 may be the corrosion products at supercritical conditions. It seems that chromium may join in the formation of the passivation film for iron alloys at ambient conditions, but at supercritical conditions, this passivation is lost due to the formation of a soluble oxidation product of chromium. This result is consistent with the phenomenon observed in the polarization analysis of pure iron and 304 S.S. at ambient and supercritical conditions (24), where although the corrosion current density of iron exceeded that of 304 S.S. by a factor of three at ambient conditions, the two were comparable at supercritical water conditions.

The influence of temperature on the weight loss of Inconel 625 in flowing superheated steam was investigated in 1967 by Pearl et al. (25), the results is shown in Fig.15. It is clear that the weight loss of Inconel 625 in flowing superheated steam increased considerably with the temperature, and the exposure time. The weight loss of the Inconel 625 increasing with the exposure time becomes severe at high temperature. Table 6 shows the weight loss and the proportion carried away by the steam of the oxides formed by the action of steam. The weight loss of alloys due to the corrosion by superheated steam also was observed by Sakakibara and Otoguro et al. (17, 18), who investigated the influence of temperature and pressure on the corrosion rate of steels, such as SUS 347 HTB, 17-14CuMo, and newly developed 20Cr-25Ni, 22Cr-35Ni alloys. The results has shown that the weight loss of austenitic stainless steels and high-Cr, high-Ni alloys increases with the steam temperature and pressure. This behaviour about the dependence of weight loss on temperature is the same as that of Ni-alloys. The influence of temperature on the scaling resistance of the ferritic-steels in high temperature steam was also investigated by Eberle et al. (26). The results indicated that at 1100 °F, the differences in scaling resistance between the ferritic steels were found to be small and not significant for most steam applications. At 1200 °F, differences in the scaling rates of ferritic steels became marked. The increasing in scaling rate of the 9Cr-1Mo was not significant, but that of other ferritic steels was considerable.

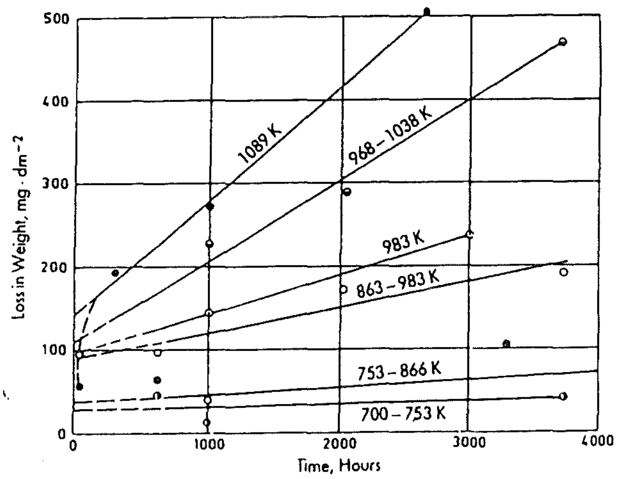

Fig.15: Influence of temperature on the weight loss of Inconel 625 in flowing superheated steam (25)

Table 6 Corrosion rate of Inconel 625 in the flowing superheated steam (5, 25)

Temperature K	weight loss (descaling) g.m-2.month-1	entrained by steam $g.m^{-2}.month^{-1}$	ratio of total weight loss to amount of the entrained oxide %
866 to 977	2.14	2.06	96
977	3.64	2.05	56
966 to 1039	7.16	5.24	73
1089	9.72	6.20	64

When the high temperature and pressure steam contains chloride, the chloride ion-induced stress corrosion of the materials will occur (5, 27, 28). The tests with various materials for superheated pipes in PWR showed that Inconel alloys are least susceptible to chloride-induced stress corrosion cracking. Except for the chloride, alkali and phosphates can also cause the stress corrosion cracking of high chromium steels, Cr-Ni steels and Ni-alloys (28, 29).

The study on the corrosion rate of 12Kh18N12T steel in steam superheaters of supercritical pressure boilers (30) indicated that addition of hydrazine decreases oxygen concentration in steam, and changes the scale on the internal side of the pipes with formation of the suboxide layer which increases stress corrosion resistance of the pipes.

To avoid stress corrosion cracking of reactor pipes exposed in superheated steam, Incoloy 800 and a new Ni-alloy NiCr22Mo9Nb4TiAl are recommended to be used for superheater (5). The chemical composition of this Ni-alloy is :

C	Si	Mn	Cr	Mo	Nb	Fe	Al	Ti	Ni
0.10	0.50	0.50	20/23	8/10	3.15	0.50	0.40	0.30	bal.

It is also recommended to perform heat treatment of stainless steels and in such way to prevent sensitisation to stress corrosion cracking.

On the other hand, according to the investigation of the metal corrosion in supercritical pressure boilers (31), the corrosion rate of the equipment decreased with increasing pH of the water. The presence of even a limited amount of the impurities of acid leads to a significant reduction in pH. Such impurities of acid in the working medium include organic compounds that penetrate the equipment in the form of colloidal solution and are gradually converted to ionic forms during thermolysis. With the reduction in pH, the corrosion processes on steels became intensified. Therefore, keeping of a suitable pH value in supercritical water may be favourable to corrosion resistance of the alloys in it.

The influence of the high temperature steam exposure on the mechanical properties of the alloys has been investigated in the past two decades (32-34). The results showed that all of the ferritic-Cr Mo-steels would be suitable for superheater service at 1100 °F from the view of the mechanical properties of materials. However, if the scaling resistance is also considered, the best candidate for service at 1200 °F appears to be the 9Cr-1Mo steel. Cr-Ni S.S. and other austenitic alloys would be more suitable for service at 1200 °F and 1350 °F.

Summary

1. The high Cr-alloys and Ni-alloys appear to form oxide scale on its surface in high temperature and supercritical steam. The higher the chromium content in the alloys, the better the scaling resistance.
2. The alloys exhibit weight loss in superheated steam containing HCl and O_2. The observed weight change is the result of two opposite effects: a mass increase by oxygen incorporation into the scale and a mass decrease by evaporation of volatile compounds. Since the evaporation processes prevail, a weight loss is observed.
3. The investigation results on the corrosion resistance to the supercritical and high temperature steam have indicated that the Ni-alloys, such as Hastelloy C-276, Inconel-625, SZ alloy and high Cr steel HR 3C, containing high Cr, high Ni and less Fe, have excellent scaling resistance to high temperature and supercritical steam as well as the steam containing HCl and O_2.
4. The composition elements, surface pre-treatment and grain size of the alloys have an influence on the corrosion resistance of the alloys. The suitable pre-treatment, improvement in alloying elements and the fine-grained structure which could be used to prevent alloys from corroding in the steam.
5. The corrosion characteristics of the alloys during SCWO are related closely to the environment conditions, therefore, the results obtained from a certain material during SCWO for a special waste can not be used to estimate the applicability of this material for another waste. A number of simulation tests to the practical system and supplementary tests have to be performed for the material research.

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