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High Temperature Corrosion of Nickel Based Heat Resistant Alloys and their Diffusion Brazed Parts

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Abstract

High temperature corrosion, hot corrsion, of nickel based alloys and their brazed parts was investigated using mixed ash composed of 90 %Na_2SO_4 + 10 %NaCl at 800-950 °C. The corrosion resistance of nickel alloys were determined by the value of effective chromium. The highest resistance was obtained in the alloy 738 LC with maximum effective chromium. The corrosion resistant 738 LC alloy formed Cr_2O_3 on surface layer as a main products after corrosion, the others formed mainly nickel oxides. High temperature oxidation is controlled by the aluminum to titanium ratio, the oxidation resistance became higher with the ratio. The brazed parts showed almost equal hot corrosion resistance to base metal exhibiting homogeneous distribution of each element in base metal after brazing heat cycle adopted in the present work. The activation energies obtained by hot corrosion test were ranging from 234 to 264 KJ/mol.

KEY WORDS : (Nickel Alloys) (High Temperature Corrosion) (Salts) (Oxidation) (Brazing) (Diffusion Brazing) (Filler Metals)

1. Intoroduction

The heat resistant nickel based super alloys has been widely used for jet engines, various turbines and boilers requiring excellent mechanical properties and chemical stabilities at high temperature. Liquid phase diffusion brazing[1),2)] is suitable to join nickel alloys bacause the method gave joint parts similar microstructure to base metal. Many studies have been conducted on high temperature characteristics of the joints, however, the creep properties are still inferior to base metal[1)-5)].

On the other hand, in recent years, the operation temperatures of many internal conbustion engines and other facilities has been shifting toward higher temperature to obtain high efficiency and to save fuels. And the attack in Na_2SO_4-NaCl atmosphere, that environment are produced by the reaction of sulpher in fuels and particles of salts from sea water and other environments, becomes an important problem to maintain the reliability of nickel based alloys at high temperature.

High temperature corrosion often called as hot corrosion is a complicated phenomena related to sulfidation, oxidation, chrolination in air atmosphere, composition of nickel alloy and temperature of atmosphere. The high temperature corrosion of nickel based alloys at joint parts joined by diffusion brazing have not been studied fully yet. The aim of the present work is to determine the hot corrosion resistance of nickel based alloys and their liquid phase diffusion brazed parts using mixed salts.

2. Materials and Experimental Procedures

2.1 Materials

The nickel based alloys used in this study are shown in **Table 1**. The all alloys are γ' precipitation type alloys with different content of chromium, aluminum and titanium that influences the corrosion characteristics at high temperature. The values of effective chromium defined by Lewis and Smith[6)], Cr_{ef} (mass %), are also listed in Table 1. The effective chromium is calculated by the following equation.

$$Cr_{ef} = [Cr] + 0.7\,[Al] + 1.1\,[Ti]$$

Here the elements in parenthes express the content of each element in mass%. **Table 2** shows .the chemical compositions of filler metals used for diffusion brazing. The filler metals were amorphus sheet with 35 μm in thickeness.

2.2 Diffusion brazing and high temperature corrosion test

Figure 1 shows the speciments for evaluation of corrosion resistance at brazed parts. Corrosion resistance were evaluated on base metal, Fig. 1 (a), brazing filler metal pretinned on base metal, Fig. 1 (b), the specimen is called coated specimen. Figure 1 (c) shows the lap specimen to investigate the cross section of diffusion brazed part after corrosion test.

Prior to brazing, base metals are polished by 600 grade emery paper. Brazing are conducted in a vacuum level of 6.3×10^{-3} Pa at 1200 °C for 20 min and subsequently

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Table 1 Chemical compositions of base metals, mass%

Base metals	Elements							Effective chromium Cr_{ef}
	Cr	Al	Ti	Mo	Co	Others*	Ni	
OM	7.8	6.3	0.7	6.0	11.5	4Ta, 1.5Hf, 0.3Si	bal.	12.9
713C	12.5	6.1	0.8	4.2	-	2Nb, 2.5Fe	bal.	17.7
738LC	15.9	3.5	3.4	1.7	8.5	2.5W, 0.7Nb, 0.2Fe	bal.	22.1

* B: 0.012~0.02, Zr: 0.03~0.07

Table 2 Nominal chemical compositions of filler metals, mass%

Filler metals	Elements				
	Cr	B	Si	Fe	Ni
15Cr	15	4.0	-	-	bal.
7Cr	7.0	3.2	4.5	3.0	bal.
0Cr	0.0	4.0	3.0	-	bal.

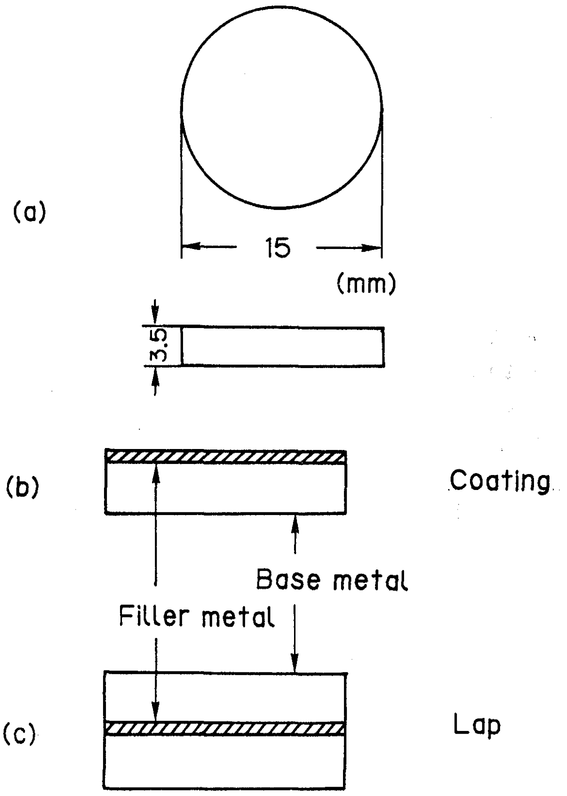

Fig. 1 Shape and size of specimens for hot corrosion tests, base metal (a), coated specimen with filler metal (b), lap specimen, filler metal was inserted between two base base metals (c)

diffusion treated at 1180 °C for 2 h. The successive treatment is called as diffusion brazing. After diffusion brazing, brazed specimens were aged at 1120 °C for 2 h followed by at 845 °C for 24 h in argon gas atmosphere for the precipitation of γ'.

Mixed corrosive ash composed of 90 % Na_2SO_4 + 10 % NaCl (mass%), the composition was reported to be highly aggressive to nickel base metal at high temperature[7),8)], was mainly used for high temperature corrosion test. A predetermined certain amount of ash was coated on specimen surface[9)] and set in an air furnace maintained at a the test temperature. After heating for a decided time corrosion resistance was evaluated by the change of weight of the specimen before and after corrosion test. Corroded speciments were put in a boiled aqueous solution of 18 %NaOH + 3 %$KMnO_4$ for 30 min followed by 10 %$(NH_4)_2HC_6H_5O_7$ aqueous boiling solution for 30 min to remove the corrosion products formed on the surface of specimen[9),10)] and then weighed, the treatment is called descaling. Cross sectional obsevation test was also adopted in lap specimen. The high temperature corrosion test using 90 %Na_2SO_4 + 10 % NaCl maxed ash is called SO_4 test in the present paper.

Mixed ash with 70 %V_2O_5-30 %(9 Na_2SO_4-1 NaCl) was also used for alloy 713 C, the test is called as V_2O_5 test in this paper. Air oxidation test without coating of mixed ash was also conducted at 1000 °C, the test is called oxidation test.

3. Results and Discussions

3.1 Corrosion resistance of base metal

The weight loss of base metal after high temperature corrosion test increased almost linearly with the amount of coated ash between 10 ~ 40 mg/cm^2. The corrosion of three alloys proceeded almost homogeneously from the surface showing no evidence of grain boundary corrosion, therefore, the measurement of weight loss is proved to be effective for the evaluation of the hot corrosion resistance of nickel alloys.

Figure 2 shows the effect of temperature and holding time on weight loss by hot corrosion. The plots are mean values of 2 ~ 4 specimens. Even some scatterings were observed in alloy OM, the weight loss increased almost linearly with the composition of alloys, the alloy 738 LC showed the best corrosion resistance and the alloy OM the worst, the alloy 713 C had the medium corrosion resistance under the test condition. It is reported that the rise of temperature did not always introduce the increment of wight loss in Ni-10, 20 Cr-2, 5 Al alloys with Na_2SO_4-NaCl mixed ash[11], however, in the present study, the weight loss increased with the rise of test temperature.

In V_2O_5 test on alloy 738 LC, the weight loss also increased with the square root of holding time. The addition of V_2O_5 to mixed ash of 90 %Na_2SO_4 + 10 %NaCl increased the weight loss up to 70 %V_2O_5, where the maximum weight loss was obtained, further addition of V_2O_5 gradually decreased the weight loss (**Fig. 3**). Kusaka *et al.* had investigated the effect of composition of mixed ash on the corrosion resistance of various heat resistant steels, reporting that the most sensitive ash composition was different in each steels, however, in V_2O_5-(90 %Na_2SO_4-10 %NaCl) system, all heat resistant steels showed the maximum weight loss in 70-80 %V_2O_5 at 700 °C[12]. The results are similar to the present study. The alloy 738 LC is highly corrosion resistant even in V_2O_5 test when compared to the alloy OM.

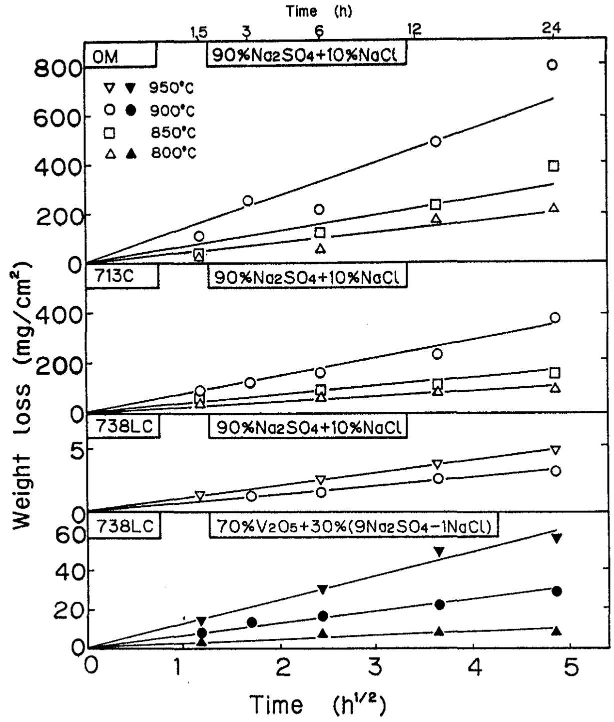

Fig. 2 Effect of temperature and time on weight loss for three nickel alloys

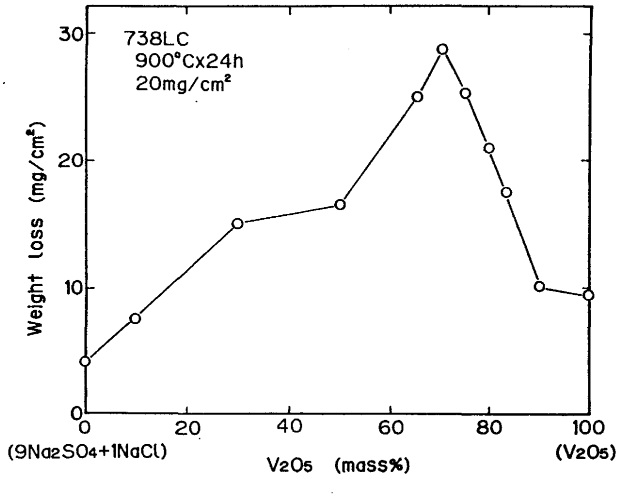

Fig. 3 Effect of addition of V_2O_5 to mixed ash on weight loss of 738 LC alloy tested at 900°C for 24 h

Figure 4 represents the SEM and distribution of each elements at the cross section after hot corrosion test. The difference in the height of line in bulk alloy corresponded to the difference in analytical current. The most thick residual corrosion layer was observed in alloy 713 C, whereas the thickness was less than 10 μm in both OM and 738 LC alloys. In alloy OM with maximum weight loss, major portion of corroded layer must be removed by descaling treatment after hot corrosion test. Considerably much amount of chromium remained at the surface layer of alloy 738 LC with high corrosion resistance, however, chromium was almost completely depletted in other two alloys with less corrosion resistance. The other elements showed no significant change in corroded layer except aluminum and molybudenum, the intensity of these elements becomes slightly weak in corroded layer. in alloy 713 C the corroded layer was consisted of two layers, chromium was depleted in outer layer, in inner layer phase with applicably high concentration in chromium and molybudenum was found in chromium depleted layer. From these observations chromium was depleted in corroded layer of less corrosion resistant alloys, on the other hand, highly corrosion resistant alloy did not form chromium depleted layer, this must be important to maintain the hot corrosion resistance in SO_4 atmosphere.

Figure 5 is the plots of the corrosion rate, the slope of straight lines in Fig. 2, against effective chromium, Cr_{ef}. The corrosion rate became small with Cr_{ef}, especially the rate was drastically suppressed when Cr_{ef} exceeded 20 %. It has been known that the hot corrosion resistance of nickel and nickel based alloys was improved by increasing the chromium content[8),13)-15)] therefore, hot corrosion resistance of nickel base metal is determined by Cr_{ef}.

Molybudenum is known to be an detrimental element to hot corrosion resistance[10], that corresponded to the present results, the corrosion resistance was deteriorated by increasing the molybudenum content. The addition of more than 10 %Co cobalt seems to be useless in alloy with 7 %Cr, alloy OM, but very effective in more than 15 %Cr.

The hot corrosion resistance of the three alloys were found to be immune to diffusion brazing heat cyles. The V_2O_5 test results on alloy 738 LC are shown in **Fig. 6** as an example. Heat cycles were given in a vacuum and argon gas atmospheres. All heat cycles of diffusion brazing (a), subsequent aging treatment (b), aging

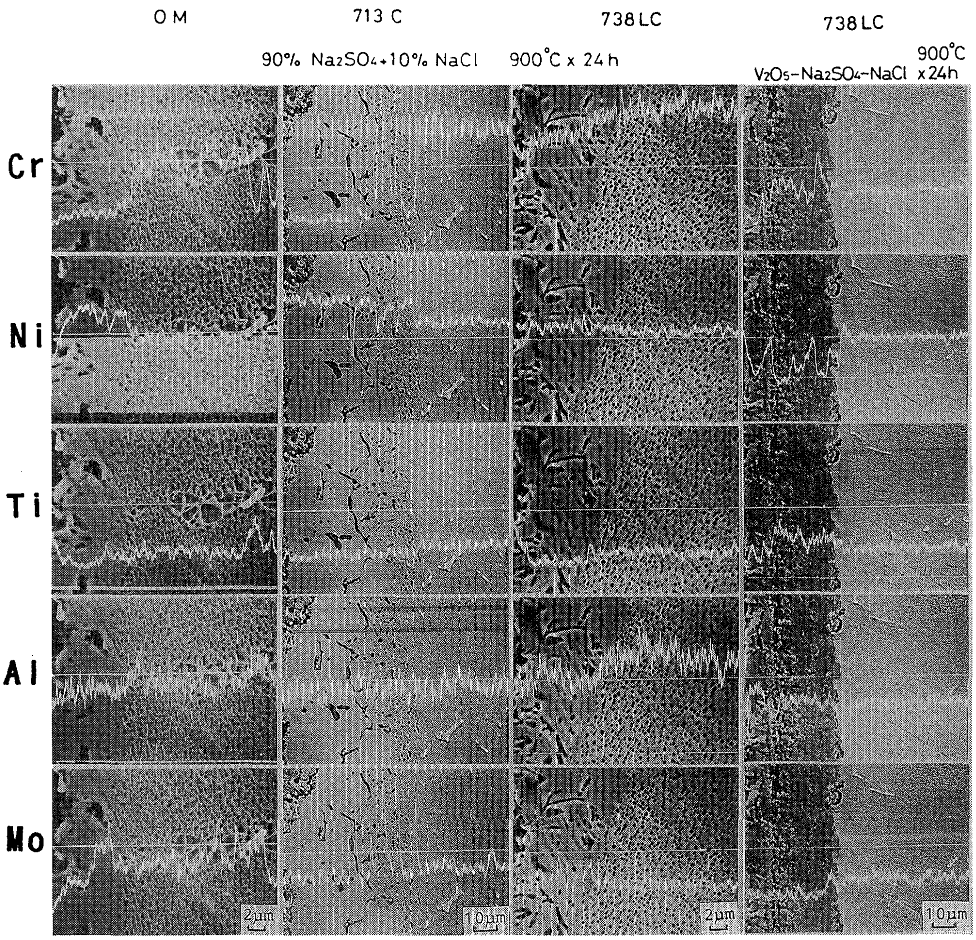

Fig. 4 SEM and EDX line analysis on alloys after hot corrosion tests at 900°C for 24 h

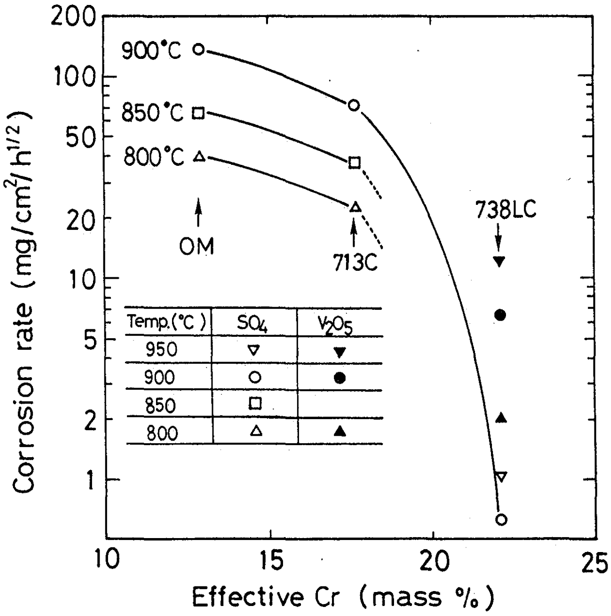

Fig. 5 Plots of corrosion rate vs. effective chromium

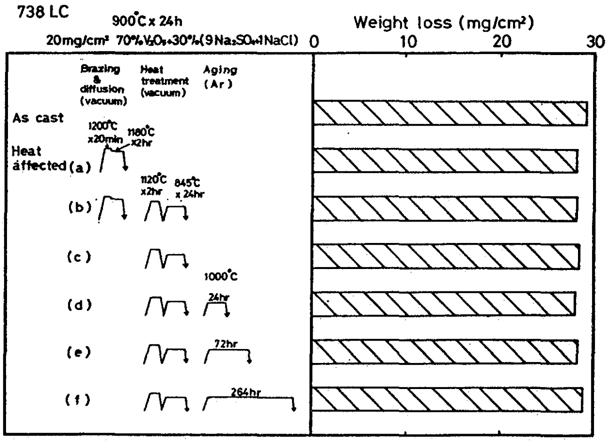

Fig. 6 Weight loss of 738 LC alloy after various heat treatments, tested at 900°C for 24 h using mixed ash with 70%V_2O_5

treatment only (c), high temperature holding (d)-(f) had no effects on corrosion resistance. The microstructure was almost the same after various heat treatment (**Fig. 7**). The size of γ' is nearly the same showing no drastic growth had occurred.

Figure 8 is the results of oxidation test of as cast materials in air. High weight loss means the more severe oxidation, because the weight loss was measured after descaling. Oxidation also proceeded linearly with the square root of holding time. The weight loss of SO_4 test at 950 °C for 24 h and oxidation test at 1000 °C for 24 h were about the same. The weight losses in alloys OM and 713 C were only 0.2 and 0.3 mg/cm^2 respectively, the alloys showed superior oxidation resistance to 738 LC in contrast to the SO_4 test.

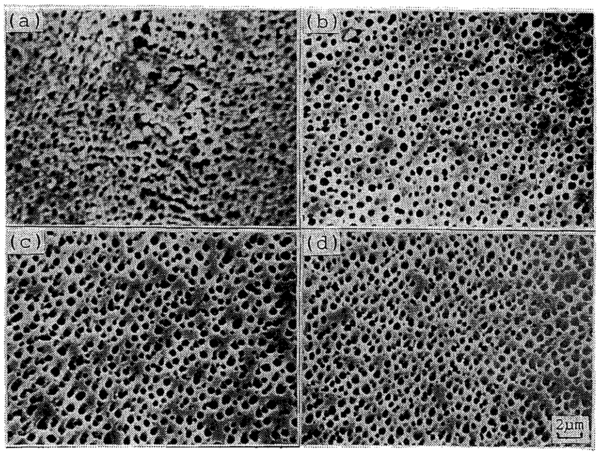

Fig. 7 SEM of 738 LC alloy after duffusion brazing heat cycle and heating at 1000°C for 0 h (a), 72 h (b), 144 h (c) and 264 h (d)

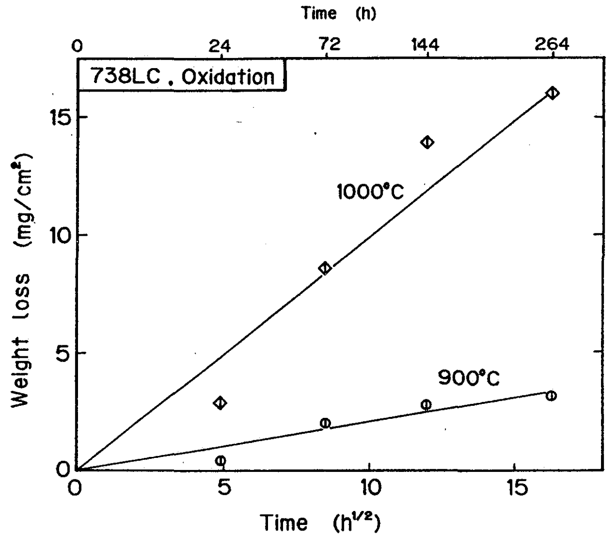

Fig. 8 Weight loss of 738 LC alloy after oxidation test

Table 3 shows the formed compounds, determined by X-ray diffraction analysis. All compounds are oxides, and the compounds showed only a few weak diffraction lines are presented in parenthes. The alloy 738 LC with the highest corrosion resistance to SO_4 test formed Cr_2O_3 as the most dominant products under both SO_4 and oxidation tests. The alloy OM with the least resistance to SO_4 test formed Ni_2O_3 were very weak. The alloy 713C with medium corrosion resistance formed mainly nickel oxides, Cr_2O_3 also existed to some extent. The excellent hot corrosion resistance might be brought by the Cr_2O_3 oxide formed at surface layer as shown in Fig. 3. Therefore, increment of Cr_{ef} might enhanced the stability of Cr_2O_3 in corrosion atmosphere and/or the formation of it.

On the contrary, alloys OM and 713 C had superior oxidation resistance to alloy 738 LC, the former alloys formed Al_2O_3 as a main product. The alloy 738 LC formed oxides of chromium and nickel as main products and the diffractions from Al_2O_3 were extremely weak. The results were coincided well with the alloy composition, alloys OM and 713 C with higher aluminum to titanium ratio had more excellent oxidation properties than ally 738 LC with less aluminum to titanium ratio. Similar results had been obtained in other Ni-Cr-Co-Mo alloys[13], **Table 4** summarized the results. The high temperature oxidation resistance becomes superior with increasing the ratio of Al/Ti. The resistance was inferior in the alloys with the value nearly 1 or less. The stable Al_2O_3 film protective to oxidation might be formed homogeneously in the alloy with higher ratio of Al/Ti. It was reported that the addition of titanium to Ni-20 Cr up to 3% enhanced the oxidation at 1000~12000 °C[16]. In the present study, Al_2O_3 film in an air atmosphere.

Figure 9 is the Arhenius plots of the corrosion and oxidation rates, the slope of straight lines in Fig. 2. In all conditions the plots showed straight relations. The calculated activation energies are listed in **Table 5**.

Table 3 Results of X-ray diffraction analysis of nickel base metals after corrosion tests at 900°C for 24 h

Base metals	Hot corrosion		Oxidation
	SO_4	V_2O_5	in air
OM	Ni_2O_3 $[Cr_2O_3][NiO][NiCr_2O_4]$ $[Cr_2(MoO_4)_3]$	--------	Al_2O_3 $[Cr_2O_3][NiO][NiCr_2O_4]$ $[Cr_2(MoO_4)_3]$
713C	NiO, Ni_2O_3, Cr_2O_3 $[Cr_2(MoO_4)_3][NiCr_2O_4]$ $[NiCrO_4][Al_2O_3]$	--------	Al_2O_3 $[Cr_2O_3][NiO][NiCr_2O_4]$ $[Cr_2(MoO_4)_3]$
738LC	Cr_2O_3, Ni_2O_3 $[NiO][NiCr_2O_4]$	Cr_2O_3, $NiCr_2O_4$, NiO $[Al_2O_3][CoCrO_4]$	Cr_2O_3, Ni_2O_3, $CoCrO_4$ $[NiO][NiCr_2O_4][Al_2O_3]$

[ ]: only a few week lines were found

Table 4 Oxidation resistance and ratio of aluminum to titanium

Materials	Elements (mass%) Cr	Al	Ti	Ratio of Aluminum to Titanium, Al/Ti	Oxidation resistance at 900℃	References
OM	7.8	6.3	0.7	9.0	Excellent	This work
713C	12.5	6.1	0.8	7.6	Excellent	
738LC	15.9	3.5	3.4	1.0	Not good	
B-1900	8.0	6.0	1.0	6.0	Excellent	Bornstein *et al.*, 14)
U-700	14.5	4.3	3.4	1.3	Not so good	
Waspaloy	19.5	1.25	3.0	0.4	Not good	

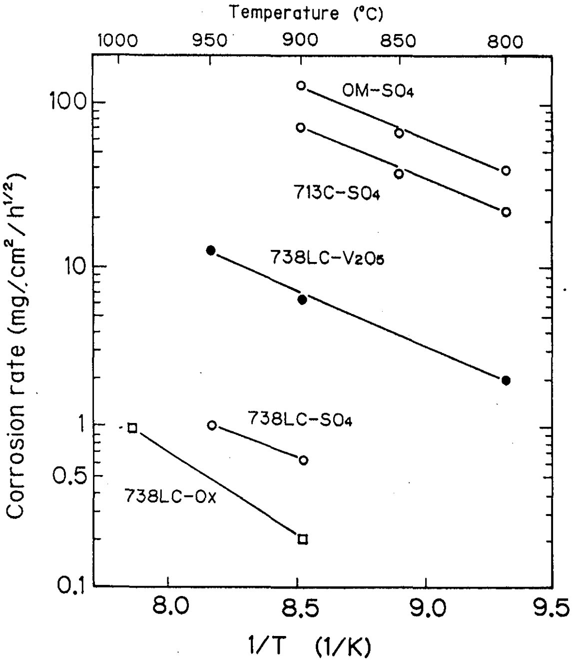

Fig. 9 Plots of corrosion rate vs. 1/T

Irrespective of alloy composition and test atmosphere, the energies are ranging from 234 to 264 kJ/mol, the values rather close to the activation energy of interdiffusion of chromium and nickel, 257 kJ/mol[17]. As the corrosion in SO_4 test is the chromium depletion process from nickel matrix, the correspondence in alloys OM and 713 C suppose that the diffusion of nickel and chromium conntrolled the corrosion rate of this system. The activation energy for sulfidation are ranging between 167 and 285 kJ/mol[18], the values of the present work existed within this range, therefore, it may be said that the formation process of sulfide may have some contribution to the controlling process of the corrosion. The activation energy of diffusion of sulpher in nickel is quite large, 377 kJ/mol.

The activation energy was relatively large in alloy 738 LC for V_2O_5 test. As the V_2O_5 test were conducted up to 1000 °C, the rate controlling process at 1000 °C may not similar to at 800-900 °C, this might cause the difference in activation energy. In air oxidation, the obtained activation energy of 395 kJ/mol was obtained, that is much larger than the activation energy of diffusion of oxygen, 301 kJ/mol, aluminum, 268 kJ/mol and titanium, 257 kJ/mol in nickel respectively[17].

Table 5 Activation energies calculated from the corrosion rate of base metals in test atmospheres

Base metals	Atmospheres	Activation energies (kJ/mol)
OM	SO_4	255
713C	SO_4	249
738LC	SO_4	234
738LC	V_2O_5	264
738LC	air	395

3.2 Corrosion resistance of brazed part

Figure 10 shows the weight loss of coated specimen after SO_4 test. In every condition coated specimens did not show larger weight loss than base metals. The same results were obtained in 15 Cr, 7 Cr and 0 Cr filler metals. Under the brazing and corrosion conditions adopted in the present work, the corrosion resistance of coated specimen maintained the same resistance as the base metal. The reason that the coated specimen tested at 900 °C for 24 h showed smaller weight loss than base metal is not unclear.

Figure 11 indicates the cross section of lap specimen after corrosion tests. No preferntial corrosion at brazed area was observed in both 738 LC and 713 C alloys, also in both 15 Cr and 7 Cr filler metals. Similar to the coated specimens, diffusion brazed parts had similar corrosion resistance to base metal. The reason might be attributable

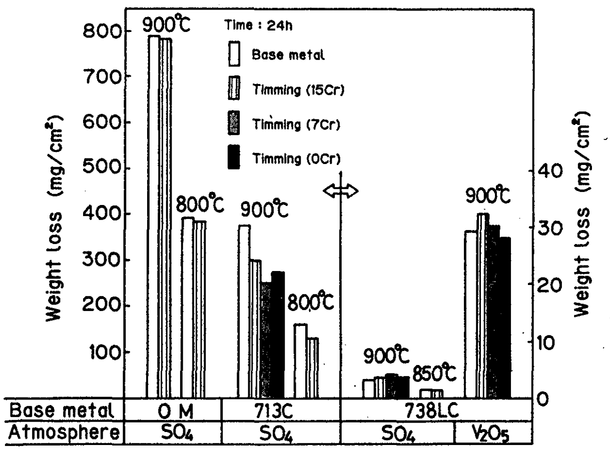

Fig. 10 Weight loss of coated specimens after hot corrosion tests for 24 h

to that the brazed prarts had similar concentrartion distribution of each element to the base metal owing to the long duffusion brazing cycle.

Figure 12 shows microstructure and distribution of elements at cross section of brazed part. At brazed parts the morphology of γ' was different from the base metal, γ' was prolonged. It seems that γ' gradually became spherical shape during holding at 1000 °C, however, the morphology was not so homogeneous as base metal. All elements including titanium, aluminum, molybudenum and cobalt, that were not originally existed in filler metal diffused into brazed part homogeneously. As indicated in Fig. 4, the hot corrosion resistance of these alloys are governed by Cr_{ef}, the value of Cr_{ef} at brazed part would be almost the same as in base metal by homogeneous distribution of each element, thus the brazed parts exhibited the same hot corrosion resistance.

The microstructure at brazed part was slightly different from base metal, however, the concentration and corrosion resistance were almost the same as the base metal, therefore, the difference in γ' size and distribution did not bring the decrease in corrosion rsistance.

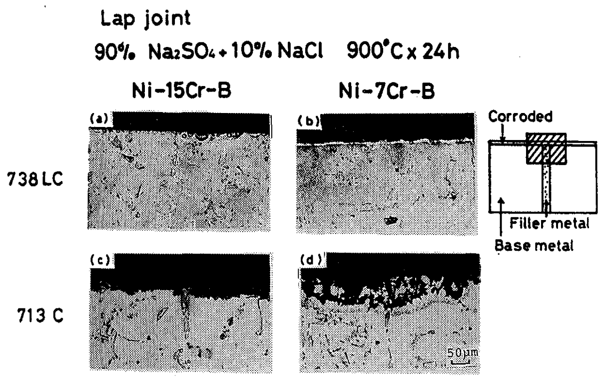

Fig. 11 Cross section of lap specimens after hot corrosion test at 900°C for 24 h

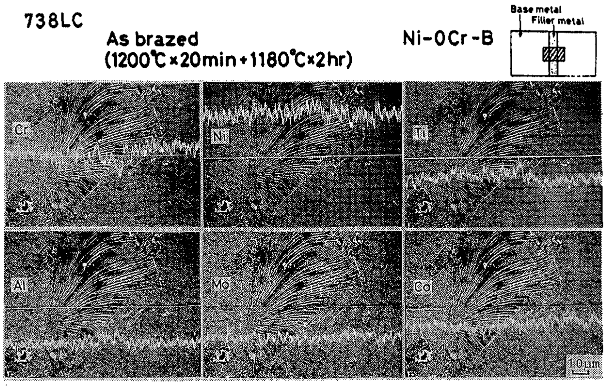

Fig. 12 SEM and EDX line analysis on diffusion brazed part of 738 LC alloy, brazed with 0 Cr filler metal

4. Conclusions

The hot corrosion resistance of three nickel based metal and its diffusion brazed part was investigated by weight loss using mixed ash. The obtained results are summarized as follows.

(1) The corrosion resistace of nickel alloys corresponded well with the effective chromium, Cr_{ef}. The weight loss decreased remarkably with the increase of Cr_{ef}, the alloy 738 LC with Cr_{ef} of 22.1 % scarcely attacked at 900 °C under coated mixed ash.

(2) The alloy 738 LC formed Cr_2O_3 as a main products on surface layer after hot corrosion test, on the other hand alloys OM and 713 C formed nickel oxides as NiO and Ni_2O_3. The excellent hot corrosion resistance of 738 LC alloy might be broght by Cr_2O_3.

(3) The addition of V_2O_5 to the mixed ash incresed the weight loss, the maximum value was obtained at 70 %V_2O_5 + 30 %(9 Na_2SO_4 + 1 NaCl).

(4) The alloys with 6 %Al, OM and 713 C, showed higher oxidation resistance than the alloy 738 LC in air atmosphere. The former two alloys formed Al_2O_3 and the latter formed Cr_2O_3 and Ni_2O_3 indicating the formation of Al_2O_3 is effective to reduce the oxidation in air.

(5) The weight loss in hot corrosion test increased with the square root of holding time. The activation energies calculated from the slope of the Arhenius plot of corrosion rate and holding temperarure were ranging from 234 to 264 kJ/mol, the values were almost nearly equal to the activation energy of interdiffusion of nickel and chromium, 257 kJ/mol.

(6) The hot corrosion resistance of diffusion brazed parts were almost the same at base metal. This is attributable to the homogeneous distribution of base metal elements in brazed parts after brazing heat cycle adopted in the present work.

(7) Within the range of the present work, the hot corrosion resistance of base metal had no dependence on heat treatment conditions.

Acknowledgements

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