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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	14
page range	347-362
year	1962
URL	http://hdl.handle.net/10097/27105

Effect of Molybdenum upon the High-Temperature Oxidation and the V_2O_5 Attack on Ni-Cr-Base Alloys*

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(Received November 8, 1962)

Synopsis

The high-temperature oxidation and the rate of corrosion by the V_2O_5 attack were examined with Ni-Cr-Mo, Ni-Cr-Co-Mo alloys containing about 19 per cent chromium and with some commercial heat-resisting alloys. In addition, the oxides composing thin oxide films or scales in these alloys were identified from observations of electron and X-ray diffractions. Following results were obtained.

(1) Addition of molybdenum to Ni-Cr alloys increased the weight loss due to scaling above 1000°C, four sorts of oxides, Cr_2O_3, spinel phase $NiOCr_2O_3$, NiO and $NiOMoO_3$, being formed in the scales. Above 1200°C $NiOMoO_3$ decomposed soon after the formation, with the volatilization of MoO_3, and thus the oxidation losses remarkably increased in Ni-Cr-Mo alloys. In these alloys, a rapid formation of oxides was observed at 1350°C, owing to the formation of molten phase of $NiOMoO_3$ in the scales. (2) A rapid oxidation occurred in Ni-Cr-10 Co–5 Mo alloy at 1300°C, owing to the formation of melt of (Ni, Co)$OMoO_3$ in the scale. The similar rapid oxidation was observed in molybdenum-containing Ni-base, Co-base and Fe-Ni-Co-Cr base heat-resisting alloys, which is considered to be associated with the formation and the fusion of (Ni, Co)$OMoO_3$, corresponding to nickel and cobalt content. (3) Addition of molybdenum increased the corrosion rate by V_2O_5 attack on Ni-Cr and Ni-Cr-Co alloys. Also the V_2O_5 attack was increased by molybdenum content in commercial heat-resisting alloys. Of the molybdenum-containing Fe-base, Co-base and Ni-base heat-resisting alloys, Ni-base alloys were the most resistant to the attack, Fe-base alloys being the least.

I. Introduction

In the development of high temperature materials it was conceived that the addition of molybdenum would increase the hot strength of heat-resisting alloys. However, molybdenum was found to have a very deleterious effect on the oxidation resistance of such alloys. Catastrophic oxidation occurs in a certain concentration region of iron-nickel-chromium-molybdenum alloys, such as Timken 16–25–6, above 900°C(1)(2). MoO_3 evaporates from surfaces of nickel-molybdenum alloys above about 1100°C(3). In cobalt-molybdenum alloys, a very rapid conversion of the metal into oxide occurs and the scale becomes porous by volatilization of MoO_3

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* The 1072nd report of the Research Institute for Iron, Steel and Other Metals.

(1) W.C. Leslie and M.G. Fontana, Trans. ASM, **41** (1949), 1213.

(2) S.S. Brenner, J. Electrochem. Soc., **102** (1955), 16.

(3) S.S. Brenner, J. Electrochem. Soc., **102** (1955), 7.

at 1200°C(4). As to the accelerating oxidation by melt of V_2O_5, that is, "vanadium attack", iron-base alloys containing molybdenum are less resistant to the attack than those containing no molybdenum(5)(6), and nickel-base alloys are more resistant than iron-base alloys(6). The attack is increased by adding Na_2SO_4 to V_2O_5(5)(6)(7)(8). In respect of Ni-Cr-base heat-resisting alloys, effects of addition of molybdenum on the oxidation and the V_2O_5 attack have not yet been reported.

On the other hand, it has been reported(9)(10)(11)(12)(13)(14)(15) that Cr_2O_3, spinel phase $NiOCr_2O_3$ and NiO formed in thin oxide films and scales of nickel-chromium alloys. In the scales of nickel-molybdenum alloys, formations of NiO, $NiOMoO_3$ (3)(4) and MoO_2(3) have been reported.

With thin oxide films and scales formed in nickel-chromium-molybdenum alloys, no report has been received so far.

Such being the case, the high-temperature oxidation and the V_2O_5 attack were examined with Ni-Cr-Mo, Ni-Cr-Co-Mo and commercial molybdenum-containing heat-resisting alloys, together with the study on the thin oxide films and scales formed in Ni-Cr-Mo and Ni-Cr-Co-Mo alloys.

II. Experimental

1. Preparation of specimens

The alloys were prepared by using a vacuum high-frequency furnace. Their compositions are shown in Table 1. Each alloy contained about 19 per cent

Table 1. Chemical compositions of specimens (%).

Alloy	Cr	Co	Mo
NC	19.18	—	
NCM 5	19.06	—	6.41
NCM10	18.85	—	11.05
NCM15	18.70	—	17.51
NCM20	18.78	—	22.02
NCC10	18.82	10.25	—
NCCM	19.63	10.41	4.98

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(4) A. Preece and G. Lucas, J. Inst. Metals, **81** (1952/53), 21.
(5) F.C. Monkman and N.J. Grant, Corrosion, **9** (1953), 460t.
(6) S.H. Frederick and T.F. Eden, Corrosion, **11** (1955), 19t.
(7) C.T. Evans, ASTM, STP, **108** (1950), 59.
(8) G.W. Cunningham and A. des Brasunas, Corrosion, **12** (1956), 389t.
(9) C.J. Smithells, S.V. Williams and J.W. Avery, J. Inst. Metals, **40** (1928), 269.
(12) B. Lustman, Trans. AIME, **188** (1950), 995.
(11) E.A. Gulbransen and McMillan, J. Ind. Eng. Chem., **45** (1953), 1734.
(12) J. Morean and J. Bénard, Compt. rend., **237** (1953), 1417.
(13) G.E. Zima, Trans. ASM, **49** (1957), 924.
(14) E.A. Gulbransen and K.F. Andrew, J. Electrochem. Soc., **106** (1959), 941.
(15) K. Fueki, Denkikagaku, **26** (1958), 357.

chromium. Several commercial heat-resisting alloys were also prepared, the compositions being given in Table 2. Specimens, 15 mm in diameter and 5 mm in thickness in most cases, and 5 mm in diameter and 2 mm in thickness for electron diffraction, were cut from bars forged and then hot rolled. Prior to each experiment, specimens were solution-treated or homogenized in a vacuum furnace (10^{-3} mmHg), polished by 5/0 emery paper, and then degreased by benzol and alcohol.

Table 2. Chemical compositions of tested heat-resisting alloys (%).

Alloy	C	Si	Mn	Cr	Ni	Fe	Co	Mo	W	Al	Ti	Nb	N_2
Nimonic 75	0.06	0.32	0.66	19.93	Bal.	—	—	—	—	—	0.41	—	—
Nimonic 80 A	0.03	0.18	0.33	19.59	〃	—	—	—	—	1.22	2.42	—	—
Inconel X	0.08	0.43	0.51	15.72	〃	8.53	—	—	—	0.60	2.70	0.82	—
M 252	0.11	0.42	0.35	19.27	〃	—	10.81	9.37	—	0.81	2.98	—	—
Udimet 500	0.04	0.61	0.51	17.08	〃	4.46	15.25	4.30	—	2.36	2.79	—	—
Hastelloy R 235	0.16	0.51	0.50	15.44	〃	11.10	—	5.51	—	1.95	2.46	—	—
Timken 16-25-6	0.05	0.72	1.05	16.66	24.74	Bal.	—	5.70	—	—	—	—	0.165
LCN 155	0.08	0.78	1.30	22.28	20.24	〃	20.80	3.46	2.40	—	—	1.12	0.163
S 816	0.38	0.82	1.26	19.92	19.30	—	42.29	3.51	3.51	—	—	4.06	—

2. Procedure

In the study of high temperature oxidation in air, specimens were weighed, heated in air in a tube furnace, descaled by using an electrolytic method in a fused salt bath of Na_2CO_3–NaOH mixture⁽⁸⁾ and weighed again. Thus, oxidation losses were obtained.

In the study of V_2O_5 attack, specimens were weighed, dipped in V_2O_5 or V_2O_5-Na_2SO_4 mixture melted in silica crucibles, heated in air in a muffle furnace, descaled by the above method and weighed again. Thus, corrosion losses were obtained.

In these cases, the values of three specimens were averaged.

In the study of thin oxide films, specimens were heated in air at 850°C for 5 min and 30 min, and at 1000°C for 2 min. Oxides in thin oxide films were identified by using electron diffraction in reflection under the camera length of 309 mm and the voltage of about 50KVP. The wave length was measured by using gold film.

In the study of scales, specimens were heated in air at 850, 1000, 1100, 1200, 1300, 1350 and 1400°C for a long duration. Oxides composing the scales were identified by using X-ray diffractometer. Cu K_α radiation was used for Ni-Cr and Ni-Cr-Mo alloys and Cu K_α and Co K_α radiation for Ni-Cr-Co-Mo alloys. Oxides were identified by means of diffraction data from ASTM X-ray Diffraction Data Cards. The diffraction data of $NiOMoO_3$ and $CoOMoO_3$ were obtained from those produced synthetically in the present experiment.

III. Results

1. High-temperature oxidation in air

Fig. 1 shows the oxidation losses in such alloys as NC, NCM5, NCM10, NCM15

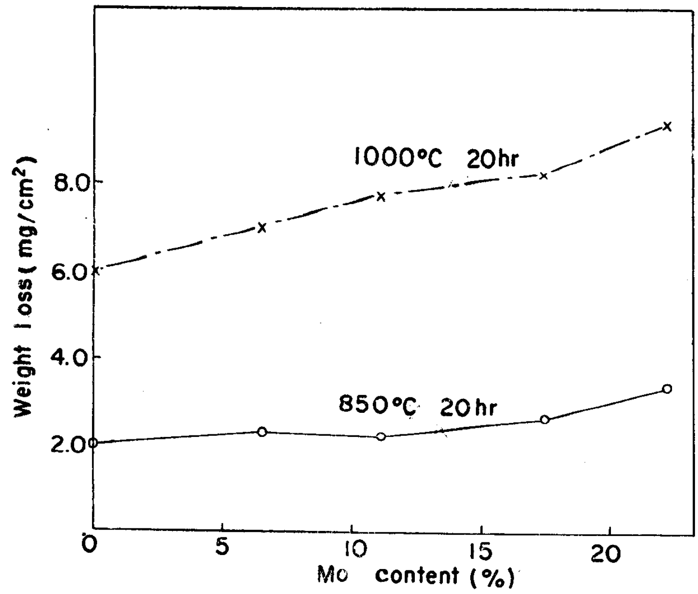

Fig. 1. Effect of molybdenum on the oxidation of Ni-19Cr alloy in still air.

and NCM20 heated at 850 and 1000°C for 20 hrs. Chromium content in each alloy was considered constant, so Fig. 1 shows the relation between the molybdenum content and the oxidation loss. At 850°C, an appreciable effect of the addition of molybdenum was not observed up to about 11 per cent, and oxidation losses increased slightly by the addition of molybdenum above about 17.5 per cent. At 1000°C, molybdenum addition appreciably increased the loss due to scaling of Ni-Cr alloys.

Specimens of NC, NCM5, NCM10, NCM15 and NCM20 were heated at temperatures 850∼1350°C for 1 hr, and the relationship between the heating temperature and the oxidation loss is shown in Fig. 2. A marked increase in oxidation loss in alloys containing molybdenum was observed above 1200°C, and then MoO_3 volatilizing from the surfaces of specimens was noticed at the tube wall of the furnace. As the heating temperature was raised, the volatilization of molybdenum became more remarkable. In nickel-chromium-molybdenum alloys, the scales became glazy and a very rapid oxidation occurred at 1350°C. These behaviors at this temperature were considered similar to those in armco iron, iron-aluminium alloys and iron-silicon alloys observed by Mishima and Sugiyama(16) at "temperatures of oxidation-resistance limit". It is considered that a molten phase forms in the scales at this temperature. The results on NCCM and NCC10 are shown in Fig. 3. No appreciable difference was observed between these alloys up to 1200°C. No volatilization of MoO_3 was observed in NCCM at these temperatures. In NCCM, the scale became glazy and MoO_3 volatilized, so a rapid oxidation occurred at 1300°C. This behavior was similar to those observed above in nickel-chromium-molybdenum

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(16) T. Mishima and M. Sugiyama, Tetsu to Hagane, 36 (1950), 184.

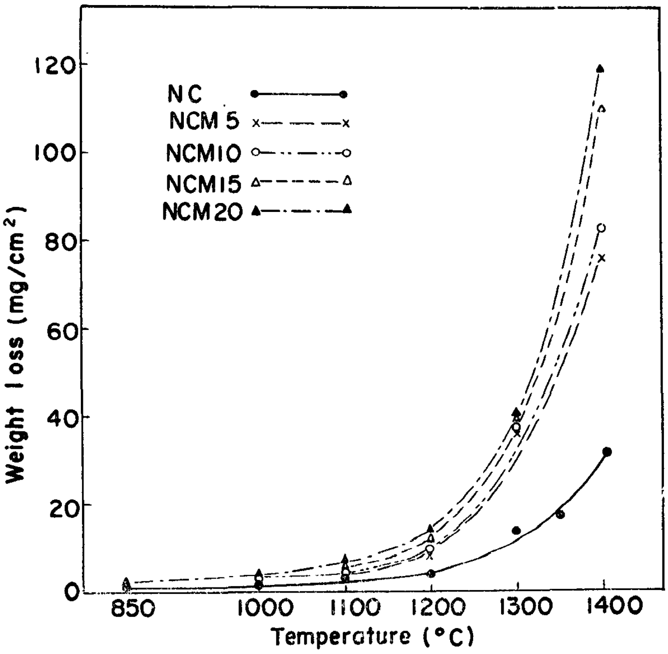

Fig. 2. Relation between temperature and oxidation loss of Ni-Cr and Ni-Cr-Mo alloys.

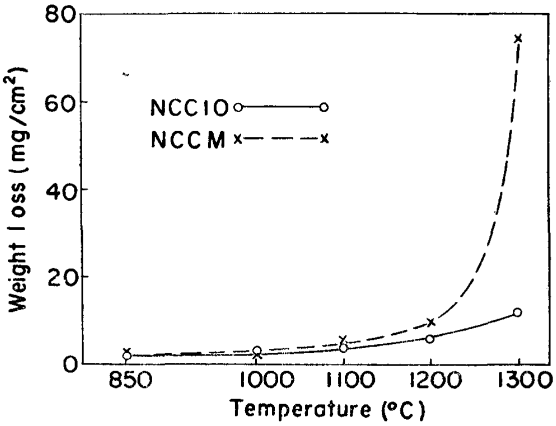

Fig. 3. Relation between temperature and oxidation loss of Ni-Cr-Co and Ni-Cr-Co-Mo alloys.

alloys at 1350°C. In nickel-chromium-base alloys containing molybdenum and about 10 per cent cobalt, the temperature at which molten phase formed in the scale, the so-called "the temperature of oxidation resistance limit", was considered to be lowered to 1300°C, compared with those temperatures of nickel-chromium-molybdenum alloys.

2. Temperatures of oxidation-resistance limit of alloys containing Mo

Figs. 4 and 5 show the relationship between the heating temperature and the oxidation loss in commercial heat-resisting alloys shown in Table 2, except

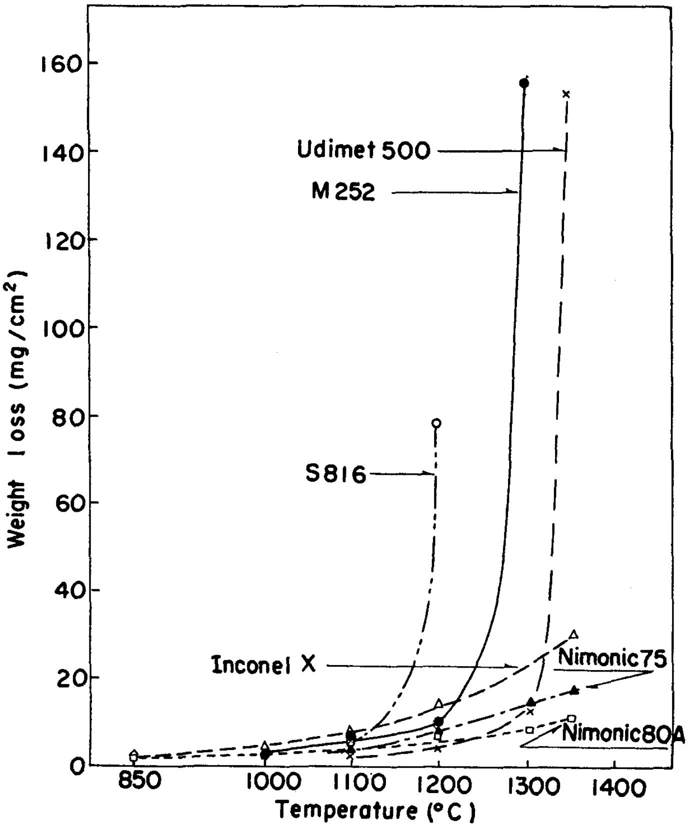

Fig. 4. Relation between temperature and oxidation loss of Ni-base and Co-base alloys.

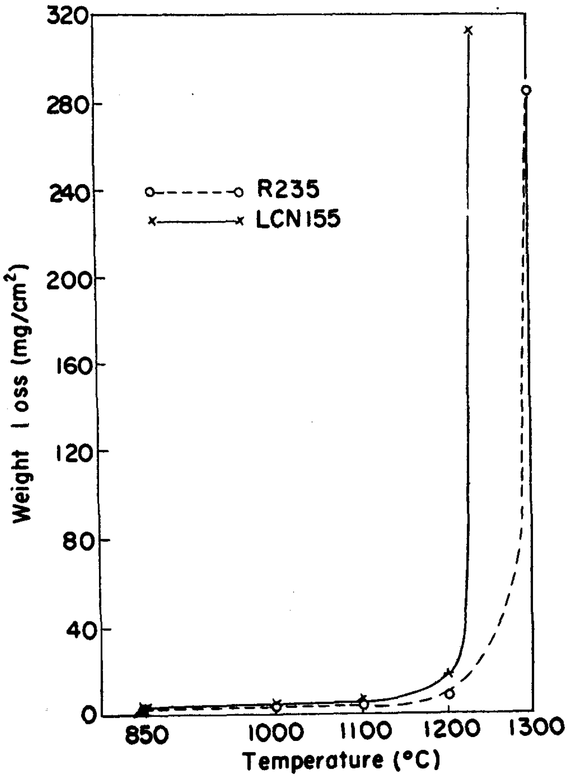

Fig. 5. Relation between temperature and oxidation loss of LCN 155 and Hastelloy R 235.

Timken 16–25–6 in which a catastrophic oxidation occurs.⑴ As shown in Fig. 4, a rapid oxidation by molten phase in the scales was not observed in alloys containing no molybdenum such as Nimonic 75, Nimonic 80A and Inconel X. With alloys containing molybdenum, the temperatures of oxidation-resistance limit were observed in Ni-Cr-Mo and Ni-Cr-Co-Mo alloys as shown above. These temperatures were about 1350°C with Udimet 500, about 1300°C with M252 and about 1200°C with S816 in Fig. 4, and about 1250°C with LCN 155, about 1300°C with Hastelloy R235 in Fig. 5. Oxidation losses at these temperatures in alloys containing high iron such as LCN 155 and Hastelloy R 235 were much higher than those in alloys shown in Fig. 4.

Molybdenum oxidizes easily and forms MoO_3 in the outer and suboxide in the inner layer. The oxidation becomes rapid and the vaporization of MoO_3 increases, owing to the formation of MoO_3 or MoO_3–suboxide melt at the melting point of MoO_3 (795°C) and above(17). In Fe-Ni-Cr-Mo alloys, molten phase of MoO_3 formed in the inner layer of the scale accerelates the catastrophic oxidation⑵. The temperatures of oxidation-resistance limit obtained above in Ni-base and Co-base alloys were much higher than the melting point of MoO_3. The oxidation behavior at these temperatures was different from that in catastrophic oxidation. Thus, the formation of molten phase at these temperatures might not be attributed to the melting of MoO_3.

NiO and MoO_3, CoO and MoO_3 were mixed both in the ratio of 1 mol: 1 mol. Each mixture was filled in a silica crucible, covered and heated. NiO-MoO_3 and CoO-MoO_3 mixture were fused at about 1350 and 1200°C, respectively. These melts were heated at the respective temperatures for 15 min and then cooled. After solidifying, spalling and violent disintegration occurred in them, and these were then powdered completely. The former colored light-green and the latter dark-purple. The "d" values and relative intensities of major diffraction lines obtained by X-ray diffractometer for these powders are listed in Table 3, compared with those of $NiOMoO_3$ in ASTM X-ray Diffraction Data Cards. It is observed that powders produced by fusing respectively the mixture NiO-MoO_3 and the mixture CoO-MoO_3 have the same crystallographic structure with each other. The results shown in Table 3 show that melts of NiO-MoO_3 and CoO-MoO_3 are $NiOMO_3$ and $CoOMoO_3$, respectively, and melting points of $NiOMoO_3$ and $CoOMoO_3$ are considered to be about 1350 and 1200°C, respectively.

The relationship between the temperature of oxidation-resistance limit obtained above and the cobalt and the nickel content respectively in Ni-base and Co-base alloys containing molybdenum is shown in Fig. 6. A dotted line was drawn between the melting points of $NiOMoO_3$ and $CoOMoO_3$. Preece and Lucas reported that rapid oxidation occurred and that porous scales were formed by the volatilization of MoO_3 in cobalt-molybdenum alloys at 1200°C⑷. It was considered that

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(17) E.S. Jones, J.F. Mosher, R. Speiser and J.W. Spretnak, Corrosion, **14** (1958), 2t.

Table 3. Lattice spacings obtained from fused NiO–MoO_3 and CoO–MoO_3 mixtures.

NiO-MoO_3 fused at 1350°C for 15 min		NiOMoO_3				CoO-MoO_3 fused at 1200°C for 15 min	
		ASTM 8-357		ASTM 9-175(3)			
Cu Kα						Fe Kα	
d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1
6.22	80			6.12	60	6.26	70
3.73	9			3.80	9	3.75	6
3.51	20			3.48	30	3.52	10
3.10	100	3.11	100	3.07	100	3.13	100
2.75	15	2.75	30			2.77	10
2.73	20			2.73	60	2.74	11
2.32	7					2.34	5
2.31	7			2.31	20	2.31	5
2.19	10	2.20	10	2.19	20	2.22	9
2.06	45	2.07	30	2.06	50	2.09	40
1.92	6			1.91	15	1.92	4
1.72	9	1.72	10	1.71	15	1.74	8
1.63	4			1.63	11	1.63	2
1.60	6			1.60	20	1.62	5
1.59	7					1.61	3
1.50	10			1.50	25	1.52	5
1.46	4			1.46	10	1.48	2

Voltage 30 kV	Voltage 30 kV
Current 10 mA	Current 10 mA
Time Const. 2 sec	Time Const. 2 sec
Scanning. Speed 1°/min	Scanning Speed 1°/min

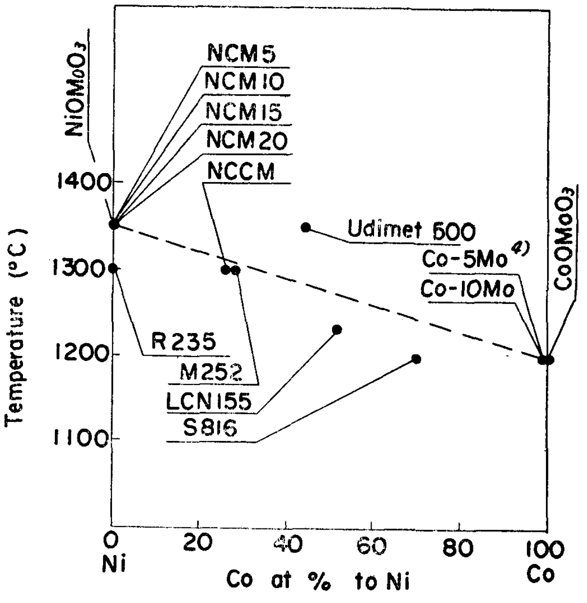

Fig. 6. Relation between the temperature of oxidation resistance limit and cobalt contents to nickel in Ni-base and Co-base alloys containing molybdenum.

this temperature was the temperature of oxidation-resistance limit of the alloys, and plotted in this figure, too. As cobalt and nickel content in the respective alloys increase, the temperatures of oxidation-resistance limit are lowered in accordance with the dotted line. Accordingly, it is considered that the oxidation behavior at the temperatures of oxidation-resistance limit is due to the formation and the melting of (Ni, Co)OMoO$_3$ in the scales. In commercial alloys, those temperatures of Hastelloy R235, S816 and LCN 155 are rather lowered and that of Udimet 500 is rather raised from the dotted line. These facts are considered to be affected by other alloying additions but nickel, cobalt and molybdenum.

3. Vanadium pentoxide attack

(i) Vanadium pentoxide attacks on Ni-Cr-Mo and Ni-Cr-Co-Mo alloys

Fig. 7 shows corrosion losses by V_2O_5, V_2O_5–10% Na_2SO_4 and V_2O_5–20% Na_2SO_4 melts on NC, NCM5, NCM10, NCM15 and NCM20 when heated at 850°C for 10 hr. As the molybdenum content was raised, the corrosion loss by V_2O_5 attack increased. In general, the corrosion loss increased, as Na_2SO_4 content in V_2O_5–Na_2SO_4 mixture was raised up to 20 per cent. In V_2O_5–20% Na_2SO_4 mixture, the corrosion loss in each alloy was remarkably high, but the effect of molybdenum upon them was not appreciable.

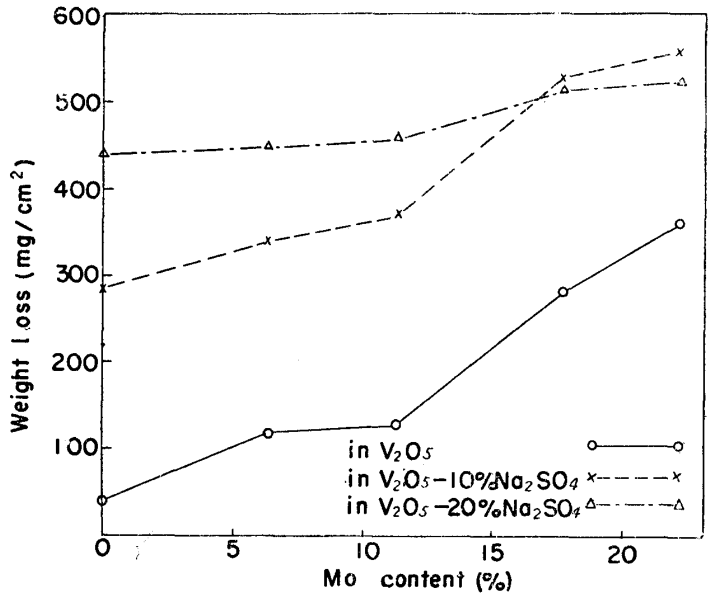

Fig. 7. Effect of molybdenum on the vanadium attack of Ni–19 Cr alloy at 850°C for 10 hr.

Corrosion losses by V_2O_5 and V_2O_5–10% Na_2SO_4 melts in NCC10 and NCCM when heated at 850°C for 10 hr are shown in Fig. 8. Also, the addition of molybdenum increased the corrosion loss by V_2O_5 in nickel-chrome-cobalt alloy.

(ii) Vanadium pentoxide attack on commercial heat-resisting alloys

Figs. 9 and 10 show corrosion losses by V_2O_5–10% Na_2SO_4 in commercial alloys

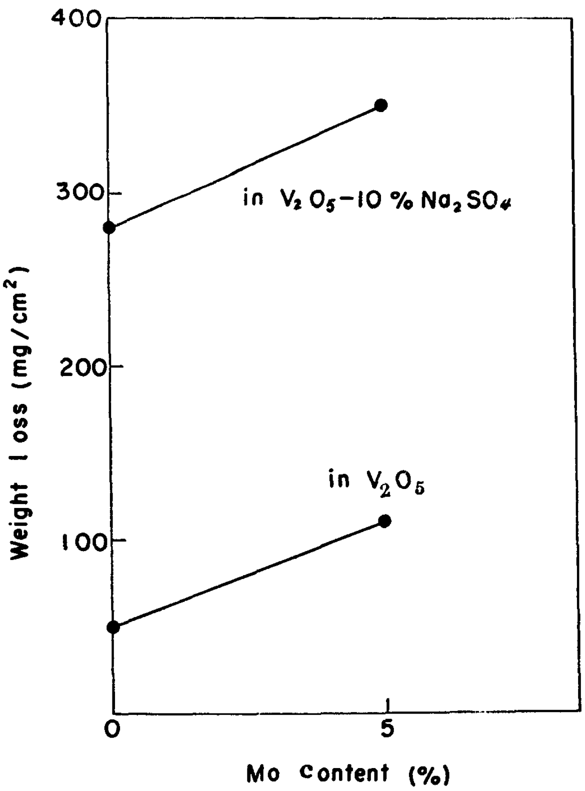

Fig. 8. Effect of molybdenum on the vanadium attack of Ni-Cr-10Co alloy at 850°C for 10 hr.

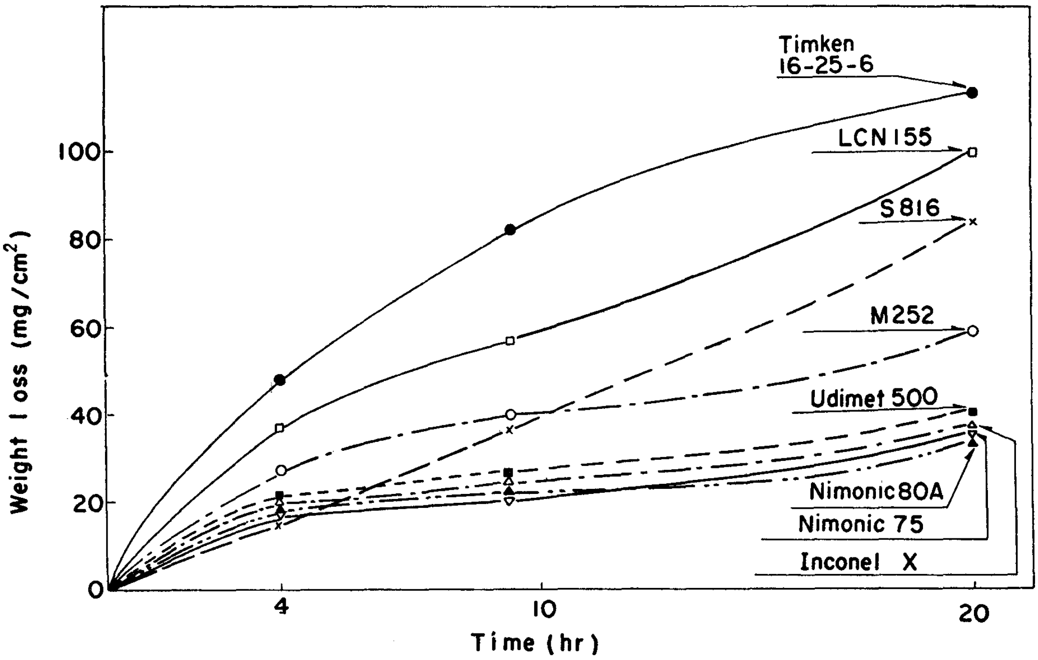

Fig. 9. Time-vanadium attack curves of heat-resisting alloys in V_2O_5-10 % Na_2SO_4 mixture at 700°C.

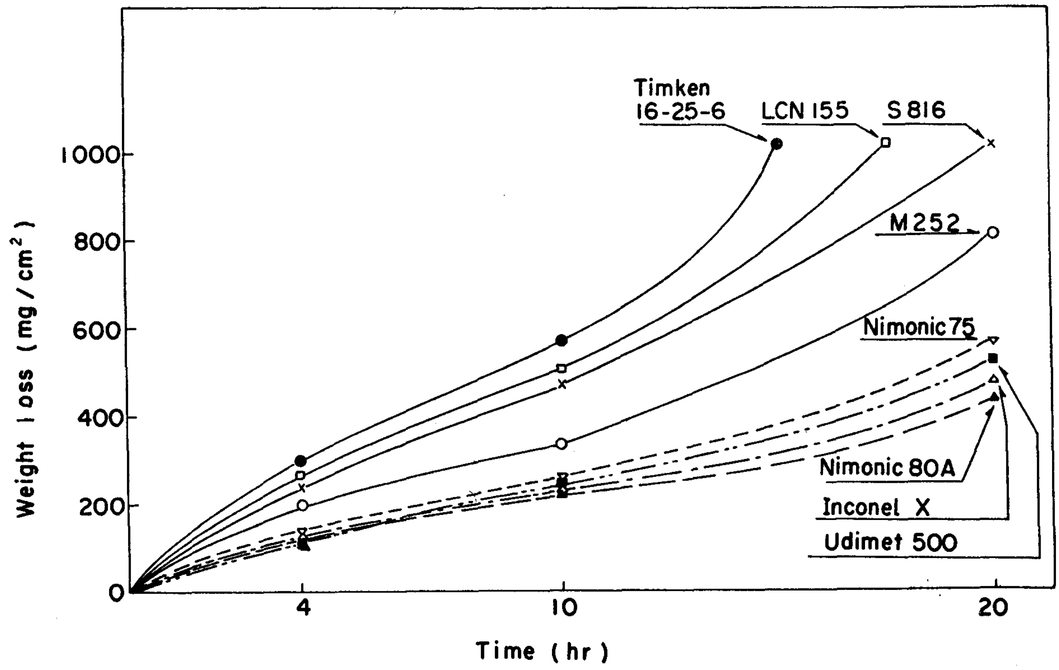

Fig. 10. Time-vanadium attack curves of heat-resisting alloys in V_2O_5-10 % Na_2SO_4 mixture at 850°C.

in Table 2 when heated at 700 and 850°C, respectively, for 4, 10 and 20 hrs. In each alloy, the corrosion loss markedly increased in cource of time at 700 and 850°C. The corrosion rate at 850°C was much higher than that at 700°C. In Ni-base alloys containing no molybdenum, such as Nimonic 75, Nimonic 80A and Inconel X, the corrosion rates were nearly equal to one another. Compared with these alloys, in alloys containing molybdenum the corrosion rate increased. Comparing molybdenum-containing alloys, with one another, Ni-base alloys were the most resistant to V_2O_5 attack, whereas Fe-base alloys was the least resistant. In spite of containing molybdenum, Udimet 500 was much resistant because of an appreciable effect of addition of aluminium. In S816, the corrosion rate was low for the first 4 hr and then rapidly increased at 700°C, but showed at 850°C a curve similar to those for other alloys.

From these results, it is considered that the addition of molybdenum increases the corrosion rate by V_2O_5 attack not only on Fe-base alloys(5)(6) but also on Ni-base and Co-base alloys.

4. Thin oxide films formed in Ni-Cr-Mo alloys

The oxides composing the thin oxide films formed on the surfaces of NC, NCM5, NCM10, NCM15 and NCM20 were identified from the observation of electron diffraction in reflection. The results are listed in Table 4. In this Table and the following, oxides in a column were arranged in order of the intensity of the diffraction patterns in the case of identifying two or more oxides. When heated at 850°C

Table 4. Oxides detected by electron diffraction (in reflection) in the thin oxide films formed on the surfaces of Ni–Cr and Ni–Cr–Mo alloys.

Temperature	Time	NC	NCM 5	NCM 10	NCM 15	NCM 20
1000°C	2 min	Cr_2O_3 $NiOCr_2O_3$	$NiOCr_2O_3$ s.a. Cr_2O_3	$NiOCr_2O_3$ tr. Cr_2O_3	$NiOCr_2O_3$	$NiOCr_2O_3$
850°C	30 min	Cr_2O_3 s.a. $NiOCr_2O_3$	$NiOCr_2O_3$	$NiOCr_2O_3$	$NiOCr_2O_3$	$NiOCr_2O_3$
	5 min	Cr_2O_3	Cr_2O_3 s.a. $NiOCr_2O_3$	$NiOCr_2O_3$ s.a. Cr_2O_3	$NiOCr_2O_3$ tr. Cr_2O_3	$NiOCr_2O_3$ tr. Cr_2O_3

s.a.: small amount; tr.; trace

for 5 min, Cr_2O_3 was the only oxide in the oxide film. In alloys containing molybdenum, the oxide films consisted of spinel phase $NiOCr_2O_3$ and Cr_2O_3 at that temperature for the same heating duration. In course of time at 850°C and as the temperature was raised to 1000°C, the formation of $NiOCr_2O_3$ in addition to Cr_2O_3 was observed in the oxide films of NC. It is considered that Cr_2O_3 forms in the inner layer and $NiOCr_2O_3$ in the outer layer. The formation of $NiOCr_2O_3$ was remarkably observed in the thin oxide films of nickel-chromium-molybdenum alloys. It is considered that the rate of formation of $NiOCr_2O_3$ rises as the molybdenum content increases. Early in the oxidation at 850 and 1000°C, oxides of molybdenum and molybdates were not observed in the oxide films of molybdenum-containing alloys.

5. Scales formed in Ni-Cr-Mo alloys

In Table 5 are shown the oxides which were detected by X-ray diffraction in the scales of NC, NCM5, NCM10, NCM15 and NCM 20. Cr_2O_3 was the only oxide in the scale of NC at 850°C. Putting this and the results in Table 4, very thin film of $NiOCr_2O_3$ was considered to be formed on the surface of Cr_2O_3 at that temperature. The formations of Cr_2O_3, $NiOCr_2O_3$ and NiO were observed in the scale of NC at 1000°C. Putting this and the results in Table 4, it is considered that Cr_2O_3, $NiOCr_2O_3$ and NiO are formed in order from inner to outer layer in the scale. The rate of formation of $NiOCr_2O_3$, especially of NiO, became high as the temperature was raised.

In the scales of nickel-chromium-molybdenum alloys, Cr_2O_3 with a small amount of $NiOCr_2O_3$ was observed at 850°C. At 1000°C, $NiOMoO_3$ formed in these scales, and the rate of formation of $NiOMoO_3$ became high as the molybdenum content increased. These scales form dark-green surface layer, light-green inner layer and green innermost layer. The dark-green surface layer was easy to break off by spalling on cooling. Putting these results and that shown in Table 2, it is considered that the scales formed in Ni-Cr-Mo alloys at 1000°C consist of three layers: The innermost layer of Cr_2O_3, the intermediate layer of $NiOCr_2O_3$ and the

Table 5. Oxides detected by X-ray diffraction in the scales formed on the surfaces of Ni-Cr and Ni-Cr-Mo alloys.

Temperature	Time	Layer	NC	NCM 5	NCM 10	NCM 15	NCM 20
1400°C	3 hr	outer		NiO $NiOCr_2O_3$ tr. $NiOMoO_3$	NiO $NiOCr_2O_3$ tr. $NiOMoO_3$	NiO $NiOCr_2O_3$ s.a. $NiOMoO_3$	NiO $NiOCr_2O_3$ s.a. $NiOMoO_3$
1350°C	3 hr	outer	l.a. NiO $NiOCr_2O_3$	NiO $NiOCr_2O_3$ s.a. $NiOMoO_3$	NiO $NiOCr_2O_3$ s.a. $NiOMoO_3$	NiO $NiOCr_2O_3$ s.a. $NiOMoO_3$	NiO $NiOCr_2O_3$ s.a. $NiOMoO_3$
		inner	Cr_2O_3	MoO_2 $NiOMoO_3$ Cr_2O_3 tr. $NiOCr_2O_3$	MoO_2 $NiOMoO_3$ Cr_2O_3 s.a. $NiOCr_2O_3$	MoO_2 $NiOMoO_3$ Cr_2O_3 s.a. $NiOCr_2O_3$	MoO_2 $NiOMoO_3$ Cr_2O_3 s.a. $NiOCr_2O_3$
1200°C	5 hr	outer	l.a. NiO Cr_2O_3 $NiOCr_2O_3$	l.a. NiO $NiOCr_2O_3$ Cr_2O_3	l.a. NiO $NiOCr_2O_3$ Cr_2O_3	NiO* $NiOMoO_3$ $NiOCr_2O_3$	NiO* $NiOMoO_3$ $NiOCr_2O_3$
		inner		NiO Cr_2O_3	NiO Cr_2O_3	Cr_2O_3	Cr_2O_3
1100°C	5 hr	outer	l.a. NiO Cr_2O_3 $NiOCr_2O_3$	l.a. NiO $NiOCr_2O_3$ $NiOMoO_3$	l.a. NiO $NiOCr_2O_3$ $NiOMoO_3$	l.a. NiO $NiOCr_2O_3$ $NiOMoO_3$	l.a. NiO $NiOCr_2O_3$ $NiOMoO_3$
		inner		Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3
1000°C	10 hr		NiO Cr_2O_3 $NiOCr_2O_3$	NiO Cr_2O_3 $NiOCr_2O_3$ $NiOMoO_3$	NiO Cr_2O_3 $NiOCr_2O_3$ $NiOMoO_3$	NiO $NiOMoO_3$ $NiOCr_2O_3$ Cr_2O_3	$NiOMoO_3$ NiO $NiOCr_2O_3$ Cr_2O_3
850°C	20 hr		Cr_2O_3	Cr_2O_3 tr. $NiOCr_2O_3$	Cr_2O_3 tr. $NiOCr_2O_3$	Cr_2O_3 tr. $NiOCr_2O_3$	Cr_2O_3 s.a. $NiOCr_2O_3$

* on unexposed surface.
l.a.: large amount; s.a.: small amount; tr.: trace.

surface layer which is a mixture of NiO and $NiOMoO_3$, enriching NiO in the outmost. The higher rates of oxidation at 1000°C in Ni-19 Cr alloys with molybdenum were considered to be associated with the presence of $NiOMoO_3$ in the oxide layers. In the scales formed in Ni-Cr-Mo alloys at 1100°C, the formation of NiO MoO_3 was observed similar to that discussed on the scales at 1000°C. The scales formed at 1200°C spalled off violently. NiO, Cr_2O_3 and $NiOCr_2O_3$ were noticed in these disintegrated powders, $NiOMoO_3$ being absent. In the scales of NCM15 and NCM20 which contained high molybdenum, $NiOMoO_3$ was clearly noticed at 1200°C in the more or less covered surfaces, such as contact with heating-boats, which is shown in Table 5. Brenner(3) reported that $NiOMoO_3$ decomposed above 1150°C, releasing MoO_3. It is considered that $NiOMoO_3$ decomposes soon after the formation, with the volatilization of MoO_3 and leaving NiO on the surfaces at 1200°C. The rapid increase of oxidation loss and the volatilization of MoO_3 are found to be due to the formation and the decomposition of $NiOMoO_3$.

The scales of nickel-chromium-molybdenum alloys at 1350°C consisted of NiO, NiO_2O_3 and $NiOMoO_3$ in the outer layer and MoO_2, $NiOMoO_3$ and Cr_2O_3 in the inner layer. Considering that the melting point of $NiOMoO_3$ was about 1350°C, the formation of the molten phase in the scales of the above-mentioned alloys was confirmed to be due to the formation and the fusion of $NiOMoO_3$. When $NiOMoO_3$ formed in the scales of Ni-Mo alloys, the formation of MoO_2 was observed in its inner layer⁽³⁾. The formation of MoO_2 in Ni-Cr-Mo alloys did not take place below 1350°C. Then, it is considered that the rate of formation of $NiOMoO_3$ in Ni-Cr-Mo alloys is lower than that in Ni-Mo alloys, and that MoO_2 becomes noticable at 1350°C, due to the formation of a large amount of $NiOMoO_3$. In spite of the decomposition of $NiOMoO_3$ above 1200°C, $NiOMoO_3$ was detected by X-ray diffraction in the

Table 6. Oxides detected in the thin oxide films and the scales formed on the surfaces of Alloy NCCM.

Temperature	Time	Layer	Diffract method	Oxides
1300°C	5 hr	outer	X-ray	(Ni, Co)O Sp. s.a. $(Ni,Co)OMoO_3$
		inner	X-ray	Sp. $(Ni,Co) OMoO_3$
1200°C	5 hr	outer	X-ray	l.a. (Ni,Co)O Sp. Cr_2O_3
		inner	X-ray	Cr_2O_3
1100°C	5 hr	outer	X-ray	l.a. (Ni,Co) O Sp. Cr_2O_3
		inner	X-ray	Cr_2O_3
1000°C	10 hr	outer	X-ray	(Ni,Co) O Sp.
		inner	X-ray	Cr_2O_3 tr. Sp.
	2 min		E.D.R.	Sp. s.a. Cr_2O_3
850°C	20 hr		X-ray	Cr_2O_3
	30 min		E.D.R.	Sp.
	5 min		E.D.R.	Cr_2O_3 s.a. Sp.

l.a.: large amount: s.a.: small amount. tr.: trace.
Sp.: Spinel phase (Ni, Co)OCr_2O_3.
E.D.R.: Electron diffraction in reflection.

scales formed at 1350°C. This is also considered to be due to the formation of a large amount. Relative intensities of X-ray diffraction patterns of $NiOCr_2O_3$ to NiO in these scales were higher than that in the scales of NC at 1350°C. Then, it was considered that the formation of $NiOCr_2O_3$ was accelerated by the molten phase of the scale. Above 1350°C $NiOMoO_3$ rapidly formed, fused and decomposed in the scales, releasing MoO_3 and leaving NiO. Regarding this, the results obtained from X-ray examination confirmed that the relative amount of $NiOMoO_3$ to NiO and to Cr_2O_3 in the scales formed at 1400°C was smaller than that at 1350°C.

6. Scales formed in Ni-Cr-Co-Mo alloy

In Table 6 are shown the oxides which were detected by electron and X-ray diffraction in the thin oxide films and the scales formed in NCCM. In the scales at 1300°C (Ni, Co)$OMoO_3$ was detected, while the molten phase formed in the scales at this temperature. Then, it was found that the rapid oxidation at 1300°C was due to the formation and the fusion of (Ni, Co)$OMoO_3$ similar to that discussed on $NiOMoO_3$ in the scales of Ni-Cr-Mo alloys at 1350°C. In the inner layer of the scale of Ni-Cr-Co-Mo alloy at the temperature of oxidation-resistance limit, 1300°C, the formation of MoO_2 was not noticed. This is considered to be due to a small amount of molybdate formed, compared with the scales of Ni-Cr-Mo alloys at 1350°C. In the inner layer of this scale, Cr_2O_3 was not detected, the formation of spinel phase (Ni, Co)OCr_2O_3 being observed remarkably. It is considered that the formation of spinel phase oxide is accelerated by the cobalt content, the formation of molybdate being suppressed thereby. Similar results were obtained for the scales of NCCM at 1000～1200°C. At higher temperatures than 1000°C, (Ni, Co)OCr_2O_3 and (Ni, Co)O were formed, while molybdates were absent. It is thus considered that the addition of cobalt suppresses the formation of molybdate in nickel-chromium-cobalt alloys.

Summary

The present study on molybdenum-containing Ni-Cr-base alloys containing about 19 per cent chromium and on some commercial heat-resisting alloys may be summarized as follows:

(1) Addition of molybdenum to Ni-Cr alloys increased the oxidation loss at higher temperature than 1000°C. It accelerated the oxidation loss at above 1200°C, owing to the volatilization of MoO_3. At about 1350°C, a rapid conversion of the metal into oxide took place owing to the formation of molten phase in the scale. The temperature of oxidation-resistance limit of Ni-Cr-Mo alloys is probably above 1350°C.

(2) Cr_2O_3 and spinel phase $NiOCr_2O_3$ formed in the thin oxide films of Ni-Cr-Mo alloys at 850 and 1000°C. The formation rate of $NiOCr_2O_3$ increased, owing to the molybdenum content.

Four sorts of oxides, Cr_2O_3, $NiOCr_2O_3$, NiO and $NiOMoO_3$, formed in the scales of Ni-Cr-Mo alloys above 1000°C. Above 1200°C, $NiOMoO_3$ decomposed soon after the formation, with the volatilization of MoO_3 and leaving NiO. It was found that the formation of molten phase in the scales of these alloys at 1350°C was due to the fusion of $NiOMoO_3$ formed.

(3) Addition of molybdenum had no appreciable effect on the weight loss due to scaling of Ni-Cr-10Co alloy below 1200°C. The rapid oxidation by molten phase in the scales occurred in Ni-Cr-10Co-5Mo alloy at 1300°C.

The temperatures of oxidation-resistance limit were similarly observed in molybdenum-containing Ni-base, Co-base and Fe-Ni-Co-Cr heat-resisting alloys. These temperatures were lowered, owing to cobalt or nickel content in alloys. This is considered to be associated with the formation and the fusion of (Ni, Co)$OMoO_3$, corresponding respectively to nickel and cobalt content.

(4) In the scales of Ni-Cr-10Co-5Mo alloy, the formation of spinel phase (Ni, Co)OCr_2O_3 was accelerated by the cobalt content, and the formation of (Ni, Co) $OMoO_3$ was suppressed thereby. At 1300°C, (Ni, Co)$OMoO_3$ was formed and fused. It is considered that the rate of formation of (Ni, Co)$OMoO_3$ at that temperature is lower than that of $NiOMoO_3$ in Ni-Cr-Mo alloys at 1350°C. Spinel phase (Ni, Co)OCr_2O_3 grew remarkably at 1300°C.

(5) Addition of molybdenum increased the corrosion rate by V_2O_5 attack on Ni-Cr alloys, and had a similar effect on Ni-Cr-10Co alloy. The corrosion rate by V_2O_5 attack was increased by molybdenum content in commercial heat-resisting alloys. Of the molybdenum-containing Fe-base, Co-base and Ni-base heat-resisting alloys, Ni-base alloys were the most resistant to the V_2O_5 attack, Fe-base alloys being the least.

Acknowledgements

The authors are grateful to Prof. S. Ogawa and Dr. D. Watanabe of the Institute for their valuable suggestions and supports in the electron diffraction observations.