

Research Article

Statistical Study of the Effects of the Composition on the Oxidation Resistance of Ni-Based Superalloys

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The effects of alloying elements (Co, Cr, Mo, W, Al, Ti, and Ta) on the oxidation resistance of Ni-based superalloys are studied using the Response Surface Methodology (RSM). The statistical analysis showed that Al and Ta generally improve the oxidation resistance of the alloy, whereas Ti and Mo degrade the oxidation resistance. Co, Cr, and W did not alter oxidation rate significantly when examined by the mass gain averaged for all model alloys. However, it is remarkable that the degree of the effects of alloying elements varied with the concentration of other elements. Further, the effect of each element was sometimes found to be reversed for alloy groups specified by the concentration of another element.

1. Introduction

Ni-based superalloys have excellent high resistance to oxidation and corrosion as well as remarkable mechanical properties at high temperatures. These alloys are used essentially for gas turbine blades of power plants, aerospace systems, heat exchangers, and chemical reactors. The durability of materials largely depends on the oxidation resistance in these systems. Ceramic coatings are widely used to protect the alloy surface from the high temperature gas, but extremely high resistance of alloy itself is still required to prevent sudden failure due to defect or degradation of coatings [1, 2].

Therefore researchers have studied the oxidation behavior and tried to find ways to improve the oxidation resistance as well as the mechanical properties of superalloys. Ni-based superalloys contain Co, Cr, Mo, and W for solid solution strengthening and Al, Ti, and Ta for precipitation strengthening, generally. Cr and Al are well known to improve the oxidation resistance because they form Cr_2O_3 or Al_2O_3 , respectively, acting as protective barriers [3–5]. The beneficial effect of Cr_2O_3 is limited up to 871°C (1600°F) due to volatility

and Al_2O_3 is responsible for the oxidation resistance at higher temperatures [6–9]. However, excessive alloying of Cr and Al in superalloys causes degradation of mechanical properties [8]. Mo and W can increase high temperature strength of the superalloys but they have been known to lower the oxidation resistance [10–14]. Nevertheless, some recent researches suggested that Mo facilitates growth of continuous Cr_2O_3 layer by lowering oxygen activity on the surface of Ni-Mo-Cr alloys [15] and W suppresses volatilization of Cr oxide from Ni-Cr-W alloys at a high temperature over 1100°C [16]. Ta was reported to increase oxidation resistance when its concentration is less than 1 at.% by promoting rapid growth of Al_2O_3 layer but was found to reduce the oxidation resistance when the concentration is higher as 3 at.% [17]. Park et al. [18] suggested that Ta exerts different effects on the oxidation resistance depending on the Al concentration in Ni-based superalloys.

The previous reports imply that the effects of alloying elements disagree with each other, due possibly to the alloy composition. The effects of other elements on the role of an element in oxidation should be considered as well. However

it is impossible practically to examine the effects of each element under full combination of other elements concentration, because it requires huge number of experiments. Therefore, more systematic approach is necessary to elucidate the complicated effects of many alloying elements of superalloys. The DOE (Design of Experiments) can be a solution for this problem in that it provides an efficiently designed set of experiments. It is a statistical technique to design experimental parameters to analyze efficiently the relation between the independent variables, concentrations of alloying elements for an example, and the responses, oxidation rate for an example. The DOE is successfully used in screening and optimization of a process or a material [2, 19–23]. The averaged effect of an alloying element over whole test range and also the interactions with other elements can be analyzed from a minimum number of experiments. We can predict the response value of untested point or seek a point which will give a specific response by statistical analysis. Another advantage of using DOE is that all the information is given quantitatively with corresponding probability. Thus we can compare the effects of alloying elements in quantity.

In this work, the effects of alloying elements (Co, Cr, Mo, W, Al, Ti, and Ta) on the oxidation resistance of Ni-based superalloys are studied by a DOE. The cyclic oxidation behavior of Ni-(0~15)Co-(8~15)Cr-(0~5)Mo-(0~10)W-(3~8)Al-(0~5)Ti-(0~10)Ta-0.1C-0.01B alloys was examined and the results were discussed by statistical analysis on the weight changes as well as by the structure and the composition of oxide scales.

2. Experimental Procedures

The alloy composition was designed by Box-Behnken scheme of RSM (Response Surface Methodology). The Box-Behnken method is employed when high efficiency is required due to the large number of the factors, that is, independent variables, and the optimum response is not supposed to be found at the limit values of all factors. The range of alloy composition was (0~15)Co-(8~15)Cr-(0~5)Mo-(0~10)W-(3~8)Al-(0~5)Ti-(0~10)Ta-0.1C-0.01B and the list of alloys designed for the test in this study is shown in Table 1. The alloys were made in a vacuum arc melting furnace and cut into a coupon of 10 mm diameter and 3 mm height and finished by #600 SiC paper.

Alumina crucibles of 20 mm \times 20 mm \times 15 mm ($W \times D \times H$) were used to contain the specimens during oxidation tests, in order to measure the weight of the specimens including the scales fallen with cycling. The crucibles were preoxidized at 1000°C for 100 h to ensure no weight change during experiments.

The specimens were put in the furnace at 400°C and the temperature was increased up to 850°C at the rate of 3.75°C. After 15 h, the furnace was cooled down slowly by waiting for 2 h with the power off and then with the door open for about 2 h. The specimens were pulled out of the furnace when the temperature was 400°C. The weight of each specimen was measured with its crucible at the room temperature of 20~25°C. The phase, morphology, and composition of oxide

TABLE 1: List of alloy compositions used in this study.

Alloys	Co	Cr	Mo	W	Al	Ti	Ta	C	B	Ni
RSM-1	7.5	11.5	2.5	0	3	0	5	0.1	0.01	Bal.
RSM-2	7.5	11.5	2.5	10	8	0	5	0.1	0.01	Bal.
RSM-3	7.5	11.5	2.5	10	3	5	5	0.1	0.01	Bal.
RSM-4	7.5	11.5	2.5	0	8	5	5	0.1	0.01	Bal.
RSM-5	0	11.5	2.5	5	5.5	0	0	0.1	0.01	Bal.
RSM-6	15	11.5	2.5	5	5.5	5	0	0.1	0.01	Bal.
RSM-7	15	11.5	2.5	5	5.5	0	10	0.1	0.01	Bal.
RSM-8	0	11.5	2.5	5	5.5	5	10	0.1	0.01	Bal.
RSM-9	7.5	8	2.5	5	3	2.5	0	0.1	0.01	Bal.
RSM-10	7.5	15	2.5	5	8	2.5	0	0.1	0.01	Bal.
RSM-11	7.5	15	2.5	5	3	2.5	10	0.1	0.01	Bal.
RSM-12	7.5	8	2.5	5	8	2.5	10	0.1	0.01	Bal.
RSM-13	0	8	2.5	0	5.5	2.5	5	0.1	0.01	Bal.
RSM-14	15	15	2.5	0	5.5	2.5	5	0.1	0.01	Bal.
RSM-15	15	8	2.5	10	5.5	2.5	5	0.1	0.01	Bal.
RSM-16	0	15	2.5	10	5.5	2.5	5	0.1	0.01	Bal.
RSM-17	7.5	11.5	0	0	5.5	2.5	0	0.1	0.01	Bal.
RSM-18	7.5	11.5	5	10	5.5	2.5	0	0.1	0.01	Bal.
RSM-19	7.5	11.5	5	0	5.5	2.5	10	0.1	0.01	Bal.
RSM-20	7.5	11.5	0	10	5.5	2.5	10	0.1	0.01	Bal.
RSM-21	0	11.5	0	5	3	2.5	5	0.1	0.01	Bal.
RSM-22	15	11.5	5	5	3	2.5	5	0.1	0.01	Bal.
RSM-23	15	11.5	0	5	8	2.5	5	0.1	0.01	Bal.
RSM-24	0	11.5	5	5	8	2.5	5	0.1	0.01	Bal.
RSM-25	7.5	8	0	5	5.5	0	5	0.1	0.01	Bal.
RSM-26	7.5	15	5	5	5.5	0	5	0.1	0.01	Bal.
RSM-27	7.5	15	0	5	5.5	5	5	0.1	0.01	Bal.
RSM-28	7.5	8	5	5	5.5	5	5	0.1	0.01	Bal.
RSM-29	7.5	11.5	2.5	5	5.5	2.5	5	0.1	0.01	Bal.
RSM-30	7.5	11.5	2.5	5	5.5	2.5	5	0.1	0.01	Bal.
RSM-31	7.5	11.5	2.5	5	5.5	2.5	5	0.1	0.01	Bal.
RSM-32	7.5	11.5	2.5	10	3	0	5	0.1	0.01	Bal.
RSM-33	7.5	11.5	2.5	0	8	0	5	0.1	0.01	Bal.
RSM-34	7.5	11.5	2.5	0	3	5	5	0.1	0.01	Bal.
RSM-35	7.5	11.5	2.5	10	8	5	5	0.1	0.01	Bal.
RSM-36	15	11.5	2.5	5	5.5	0	0	0.1	0.01	Bal.
RSM-37	0	11.5	2.5	5	5.5	5	0	0.1	0.01	Bal.
RSM-38	0	11.5	2.5	5	5.5	0	10	0.1	0.01	Bal.
RSM-39	15	11.5	2.5	5	5.5	5	10	0.1	0.01	Bal.
RSM-40	7.5	15	2.5	5	3	2.5	0	0.1	0.01	Bal.
RSM-41	7.5	8	2.5	5	8	2.5	0	0.1	0.01	Bal.
RSM-42	7.5	8	2.5	5	3	2.5	10	0.1	0.01	Bal.
RSM-43	7.5	15	2.5	5	8	2.5	10	0.1	0.01	Bal.
RSM-44	15	8	2.5	0	5.5	2.5	5	0.1	0.01	Bal.
RSM-45	0	15	2.5	0	5.5	2.5	5	0.1	0.01	Bal.
RSM-46	0	8	2.5	10	5.5	2.5	5	0.1	0.01	Bal.
RSM-47	15	15	2.5	10	5.5	2.5	5	0.1	0.01	Bal.
RSM-48	7.5	11.5	5	0	5.5	2.5	0	0.1	0.01	Bal.
RSM-49	7.5	11.5	0	10	5.5	2.5	0	0.1	0.01	Bal.
RSM-50	7.5	11.5	0	0	5.5	2.5	10	0.1	0.01	Bal.
RSM-51	7.5	11.5	5	10	5.5	2.5	10	0.1	0.01	Bal.

TABLE 1: Continued.

Alloys	Co	Cr	Mo	W	Al	Ti	Ta	C	B	Ni
RSM-52	15	11.5	0	5	3	2.5	5	0.1	0.01	Bal.
RSM-53	0	11.5	5	5	3	2.5	5	0.1	0.01	Bal.
RSM-54	0	11.5	0	5	8	2.5	5	0.1	0.01	Bal.
RSM-55	15	11.5	5	5	8	2.5	5	0.1	0.01	Bal.
RSM-56	7.5	15	0	5	5.5	0	5	0.1	0.01	Bal.
RSM-57	7.5	8	5	5	5.5	0	5	0.1	0.01	Bal.
RSM-58	7.5	8	0	5	5.5	5	5	0.1	0.01	Bal.
RSM-59	7.5	15	5	5	5.5	5	5	0.1	0.01	Bal.
RSM-60	7.5	11.5	2.5	5	5.5	2.5	5	0.1	0.01	Bal.
RSM-61	7.5	11.5	2.5	5	5.5	2.5	5	0.1	0.01	Bal.
RSM-62	7.5	11.5	2.5	5	5.5	2.5	5	0.1	0.01	Bal.

scales of selected samples were analyzed by XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) equipped with EDS (Energy Dispersive Spectroscopy) after 20 cycles of oxidation tests.

The mass gain after oxidation was statistically analyzed as a response surface model. The mass gain, that is, response, is expressed as a function of content of the seven alloying elements as the following equation [20]:

$$y = \beta_0 + \sum_{i=1}^{i=7} \beta_i x_i + \sum_{i=1}^{i=7} \beta_{ii} x_i^2 + \sum_{i=1}^{i=7} \sum_{j=1}^{j=7} \beta_{ij} x_i x_j, \quad (1)$$

where β_0 is the response at the center of the experiment, β_i is the coefficient of main effects, β_{ii} is the coefficient of quadratic effects, and β_{ij} is the coefficient of linear by linear interaction effect. The coefficients are calculated by a regression analysis with the least squares method. x_i is the level of a factor, that is, content of an alloying elements in this study.

3. Results

The mass gain of specimens is shown in Figure 1 as a function of oxidation cycles. The weight of the alloy specimens gradually increased and the increasing rate was slowly lowered with cycles, meaning that the oxidation rate of specimens is higher at the initial stage and then gradually decreased. The average mass gain after 20 cycles was 0.32367 mg/cm², the lowest was 0.14349 mg/cm² of RSM-2, and the largest was 0.73685 mg/cm² of RSM-40.

The pictures (Figure 2) of the specimens after tests show that oxide scale spalled off in the crucibles and the extent of spallation is depending on each alloy. It is seen that the alloy with high mass gain has much spalled oxide.

The mass gain value after oxidation test was analyzed statistically. Figure 3(a) is the main effect plots for the alloying elements on the mass gain, depicting the averaged effects of a specific element. Co, Cr, W, and Mo appeared to affect the mass gain rarely or very weakly. Al and Ta are shown to decrease the mass gain effectively, while Ti increases the mass gain.

The effects of elements are examined in more detail with the interaction plots in Figure 3(b). The interaction plots show the mass gain as a function of the content of a specific

element, separately under a given concentration of another element. The slope of the plots varies if an element has interaction with another element. In the Co-Cr interaction plot (the first column at second row in Figure 3(b)), the slope of plots is very small and practically not changed by the content of Cr. Co-Mo, Co-Al, and Co-Ti plots did not propose a meaningful interaction as well. However Co-Ta interaction plot (the first column at the last row in Figure 3(b)) showed that the slope is remarkably decreased by addition of Ta more than 5 wt.% in the alloy. It means that Co has an effect to increase mass gain by oxidation in an alloy without Ta but this effect is suppressed by Ta.

The mass gain versus Cr plot showed some disturbance with respect to the content of Co but it is not clear whether it is related to a meaningful effect of Co or merely to an experimental error. Cr and W appeared to have interaction in a way that Cr decreases oxidation rate in alloys without W but increases oxidation rate with W more than 5 wt.%. Ti is also suspected to have a weak effect to promote the mass gain increase by high Cr content. On the contrary, it seems that high concentration of Al or Ta slightly reduces the mass gain by increasing Cr content.

The slope of the mass gain versus Mo content plots suggests a possibility of weak interaction of Mo with Al, Ti, and Ta. It seems that Al or Ti promoted an increase of mass gain with increasing Mo content, while Ta suppresses the effect of Mo.

W appears to have clear interaction with Cr and may have weak interactions with Co and Ti. W reduces mass gain in low Cr (8 wt.%) alloys but increases mass gain in high Cr (15 wt.%) alloys. Co may have a similar effect with Cr while Ti may have the opposite effect.

Al significantly reduces the mass gain of superalloys and showed strong interaction with Ti and with Ta and a weak interaction with Mo. The effect of Al was stronger with high content of Ti while it was reduced by addition of Mo or Ta.

Ti did not have a significant interaction with other elements but it showed weak interactions with various elements. Ti generally increased mass gain with increasing its content in the alloy, and this effect seems to be a little stronger with high content of Cr, Mo, Al, and Ta.

The mass gain decreased by increasing Ta content. This influence appeared stronger when the content of Co, Cr, Mo, and W is higher while weaker with higher Al content.

The degree of influences of alloying elements and its significance were determined by regression analysis. Regression gives a coefficient and a significance probability for every term. The coefficients for a factor represent how strong its effect is. It is considered in RSM that the factor with the significance probability, commonly expressed as P value, lower than the significance level is effective really on the results. The significance level is set as 0.05, usually [21].

Table 2 shows the regression results. The terms for the content of Mo, Al, Ti, Ta, Al*Al, Co*Ta, Cr*W, and Al*Ta have P less than 0.05. It means that we can believe the effects of Mo, Al, Ti, and Ta and the interactions between Al-Al, Co-Ta, Cr-W, and Al-Ta couples as suggested by Figure 3 or by coefficients in Table 2 with high reliability. Nevertheless, we cannot ignore other terms entirely, because the terms with

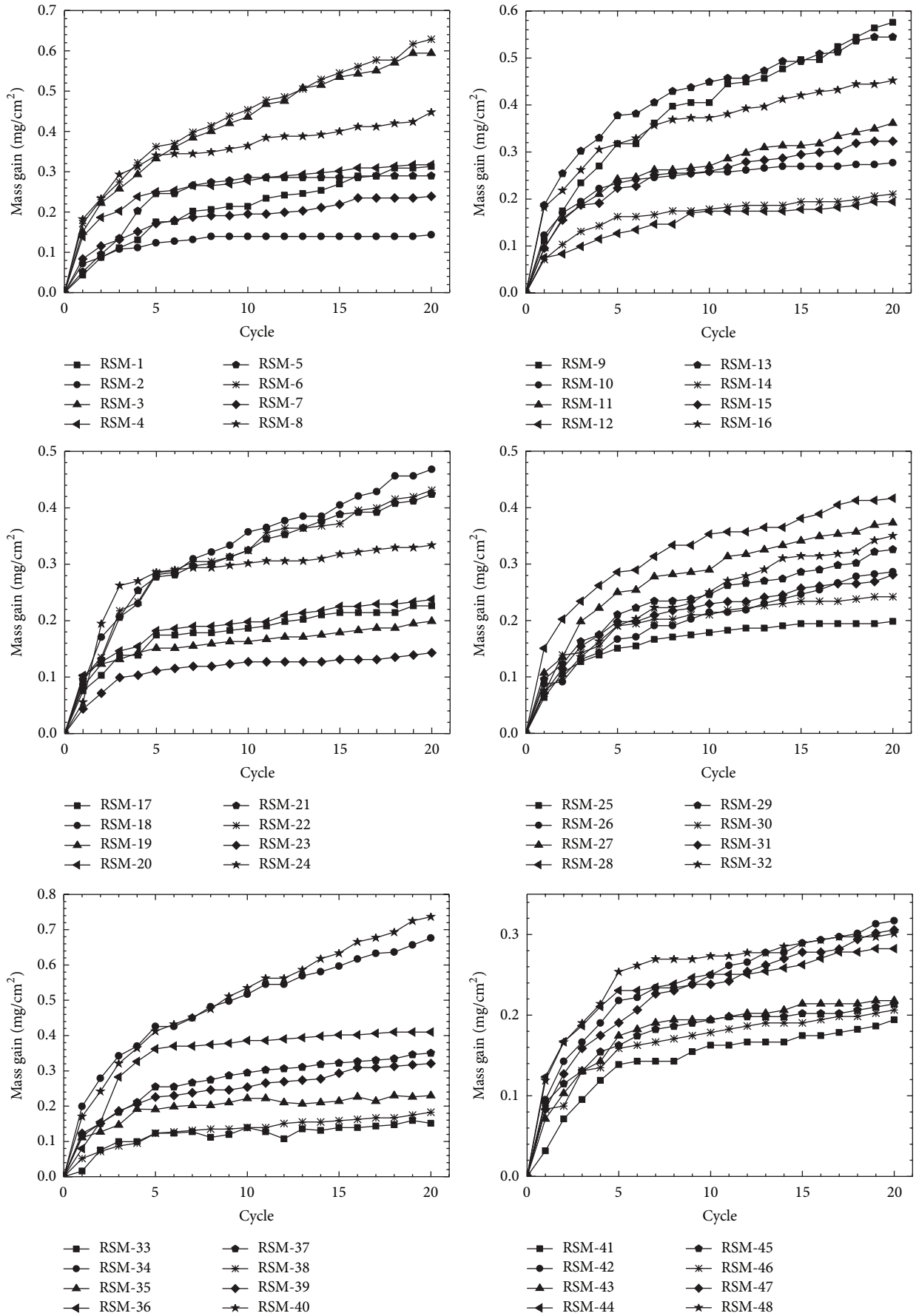


FIGURE 1: Continued.

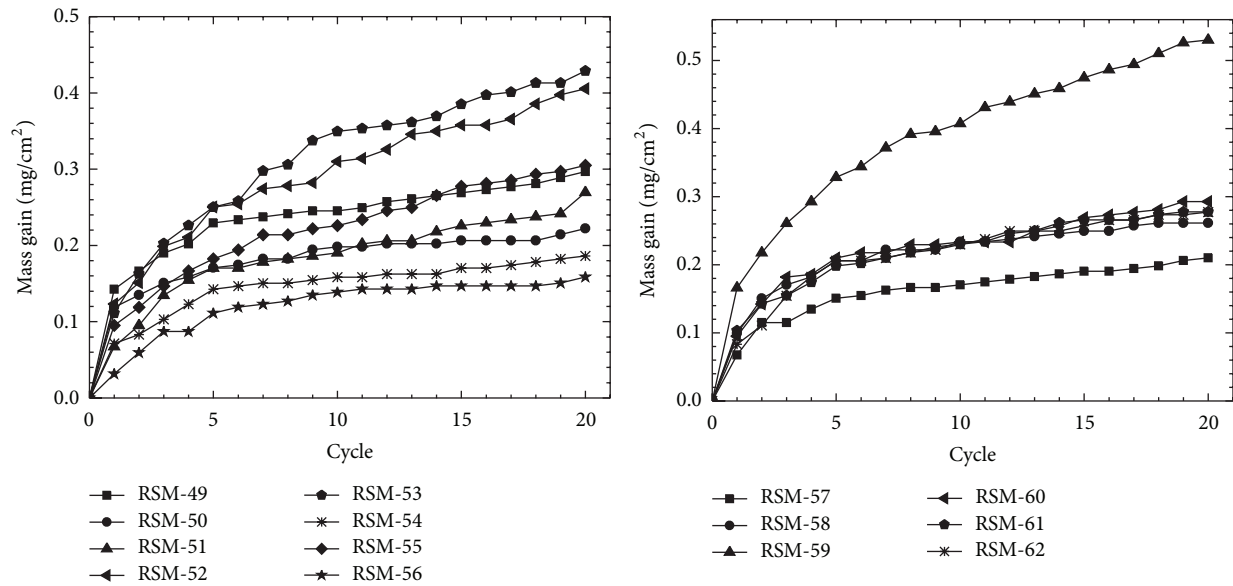


FIGURE 1: Mass gain of Ni-(0~15)Co-(8~15)Cr-(0~5)Mo-(0~10)W-(3~8)Al(0~5)Ti-(0~10)Ta-0.1C-0.01B alloys during cyclic oxidation at 850°C.

high P value also have probability, although it is relatively low, of acting as an important factor in the oxidation process.

Among the terms of $P < 0.05$, Al and Ta have negative coefficients. The value of their coefficients indicates that Al is much more effective than Ta to reduce mass gain involved by oxidation. Co also has negative coefficient but it is hardly accepted that Co inhibits oxidation since its coefficient is very small and the P is too large. Mo and Ti are highly probable to increase oxidation rate and the effectiveness of Ti is stronger than that of Mo. Cr and W might promote oxidation slightly but they are relatively less significant, based on the large P values.

Most of the P for quadratic or interaction terms were determined to be larger than 0.05 except for Al*Al, Co*Ta, Cr*W, and Al*Ta. The coefficient of Al*Al term is positive and indicates that reducing effect of Al on the mass gain would be weakened by high Al content. Such a tendency can be confirmed by Figure 3(a) which shows lower negative slope at higher Al content. The interaction term of Co and Ta has negative coefficient, meaning that these two elements reinforce the effect of each other to decrease the mass gain. On the contrary, Cr and W showed an interaction in a way that one of them increases the mass gain more significantly with an increase of the other element. In the case of Al and Ta, the interaction suppresses a decrease of mass gain by these elements, as shown by the positive coefficient. Interaction plots for Co-Ta, Cr-W, and Al-Ta couples shown in Figure 3(b) confirm these interactions.

The phase of oxide scales was analyzed by XRD. The diffraction patterns for selected samples are presented in Figure 4. The alloys with the 1st~3rd, 30th~32nd, and 60th~62nd highest mass gain were selected to represent the high, moderate, and low oxidation rate, respectively. The XRD pattern showed that the scales were composed mainly of Cr₂O₃,

Al₂O₃, NiCr₂O₄, and TiO₂. A few peaks for NiO and CrTaO₄ were also measured.

The typical cross-sectional views of the oxidized specimens are shown in Figure 5. The composition of the oxide layers was analyzed by EDS. The oxide scale of RSM-40 (Figure 5(a)) is composed mainly of Cr₂O₃ layer. TiO₂ was observed at the outermost part. Strips (Figure 5(a)) or lumps (Figures 5(b) and 5(c)) of Al₂O₃ were developed under the Cr₂O₃ layer. Meanwhile, the scales for the group with middle-level oxidation rate did not have TiO₂ and the Al₂O₃ layer formed a continuous layer (Figures 5(d)~5(f)). The structure of the scale for the alloys with low oxidation rate was simply composed of a continuous Al₂O₃ layer (Figures 5(g)~5(i)).

Some regions showed unsound morphology which is a little deviating from those shown in Figure 5, especially of the alloys with middle or high oxidation rate. Cracks were developed between TiO₂ and Cr₂O₃ (Figure 6(a)) or between Cr₂O₃ and Al₂O₃ (Figure 6(b)) for the alloys with high oxidation rate, presumably due to the different thermal expansion coefficients and thermal residual stress. NiO particle was observed at the outer part of the scale and the Al₂O₃ was found at the middle of the scale for a region of RSM-48 (Figure 6(c)). The Al₂O₃ was discontinuous for some regions of RSM-60 (Figure 6(d)).

4. Discussion

The statistical analysis of the mass gain suggested that Al and Ta remarkably reduce the oxidation rate, while Ti promotes oxidation (Figure 3(a) and Table 2). The role of Cr is not noticed in the main effect plot in Figure 3(a). Co, Mo, and W also did not appear to have significant influences on oxidation. However, Figure 3(b) implies that Co, Cr, Mo, and W affect the mass gain for some cases according to the alloy



FIGURE 2: Pictures of Ni-(0~15)Co-(8~15)Cr-(0~5)Mo-(0~10)W-(3~8)Al-(0~5)Ti-(0~10)Ta-0.1C-0.01B alloys after oxidation tests at 850°C.

composition. It seems that the slope of mass gain versus content of an element of these four is very low after summing up the diverse cases.

Co has strong interaction with Ta, as shown in Figure 3(b), and low P value (0.030) of $\text{Co} * \text{Ta}$ term in

Table 2. Co increased mass gain remarkably for alloys without Ta but changed the mass gain of Ta-containing alloys hardly (Figure 3(b)). CoO in Ni-Co alloy is known to have high concentration of cation vacancy and low activation energy for cation migration [24]. Therefore Co-enriched oxide scale

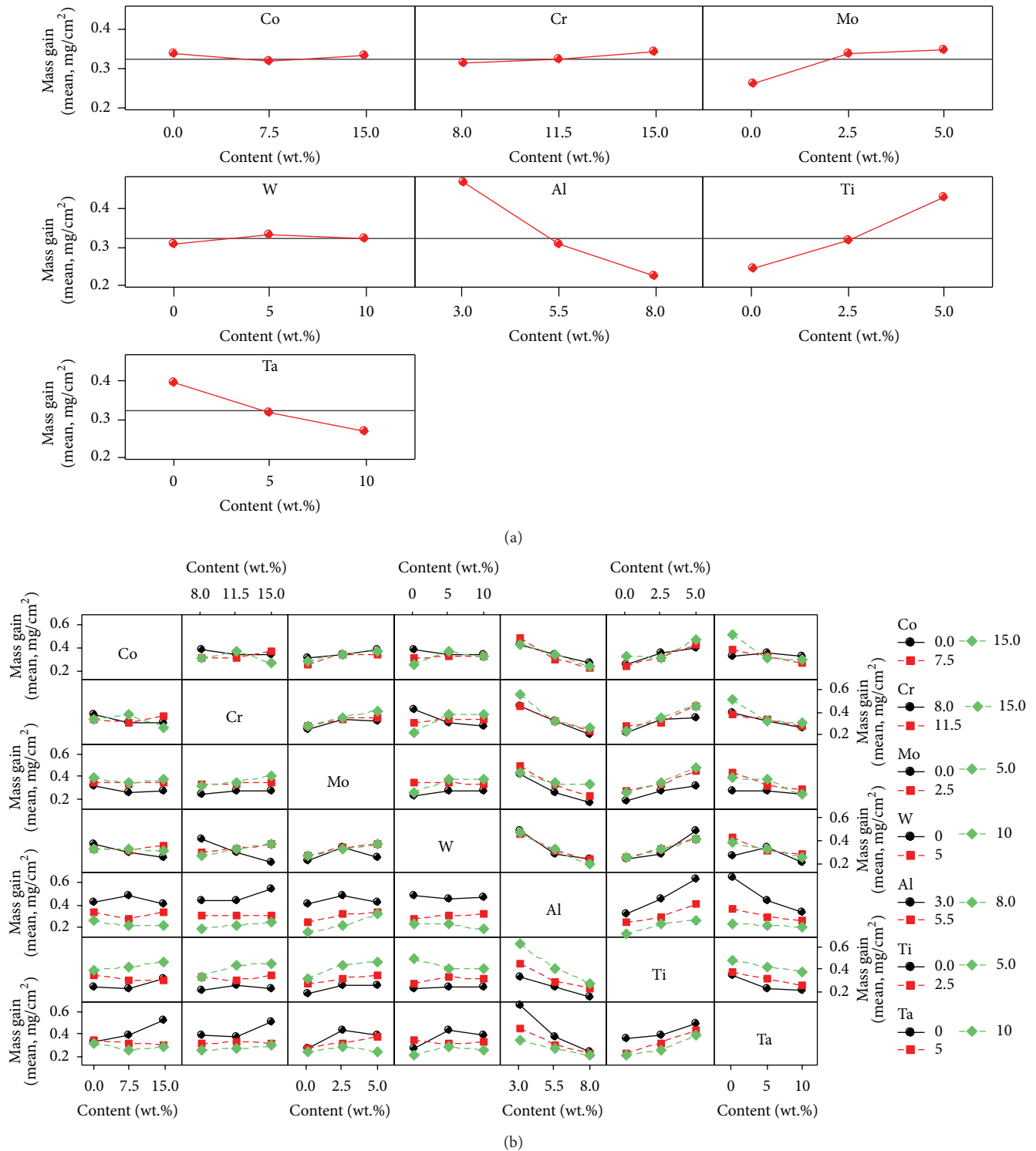


FIGURE 3: (a) Main effects and (b) interactions of alloying elements on the mass gain by oxidation at 850°C.

is anticipated to have low protectiveness. However, when Ta is incorporated in the oxide, the concentration of cation vacancy would be reduced due to the high valence of Ta ion. It seems that 5 wt.% of Ta is enough to cancel out the effect of Co in the alloys used in this study.

Cr forms a protective Cr₂O₃ scale, especially at a temperature lower than about 900°C. Thus it is expected that high content of Cr results in low mass gain. Figure 3(b) shows that the beneficial effect of Cr strongly stands out only in the alloys without W. The Cr₂O₃ might be weak because

TABLE 2: Results of regression analysis for mass gain after oxidation tests ($S = 0.07235$, R -square = 87.5%, and R -square (adjusted) = 70.7%).

Term	Coefficient	SE coefficient	T	P
Constant	1.09641	0.398121	2.754	0.011
Co	-0.00155	0.016121	-0.096	0.924
Cr	-0.03997	0.043708	-0.914	0.369
Mo	-0.02271	0.048362	-0.47	0.643
W	-0.04579	0.024181	-1.894	0.069
Al	-0.12666	0.053758	-2.356	0.026
Ti	0.02162	0.048362	0.447	0.659
Ta	-0.01862	0.024181	-0.77	0.448
Co*Co	0.00048	0.00035	1.373	0.181
Cr*Cr	0.0011	0.001608	0.687	0.498
Mo*Mo	-0.00319	0.003151	-1.011	0.321
W*W	-0.00024	0.000788	-0.307	0.761
Al*Al	0.00677	0.003151	2.15	0.041
Ti*Ti	0.00448	0.003151	1.422	0.167
Ta*Ta	0.00083	0.000788	1.055	0.301
Co*Cr	-0.00002	0.000974	-0.021	0.983
Co*Mo	0.00024	0.001364	0.174	0.864
Co*W	0.00079	0.000682	1.153	0.26
Co*Al	-0.00037	0.001364	-0.271	0.789
Co*Ti	-0.00016	0.001364	-0.12	0.905
Co*Ta	-0.00156	0.000682	-2.293	0.03
Cr*Mo	0.00168	0.002923	0.574	0.571
Cr*W	0.00451	0.001462	3.086	0.005
Cr*Al	-0.00141	0.002923	-0.482	0.634
Cr*Ti	0.0027	0.002923	0.924	0.364
Cr*Ta	-0.00125	0.001462	-0.858	0.399
Mo*W	0.00152	0.002046	0.741	0.465
Mo*Al	0.00558	0.004093	1.363	0.185
Mo*Ti	0.00346	0.004093	0.845	0.406
Mo*Ta	-0.00237	0.002046	-1.16	0.257
W*Al	-0.0005	0.002046	-0.244	0.809
W*Ti	-0.00199	0.002046	-0.971	0.341
W*Ta	-0.00076	0.001023	-0.742	0.465
Al*Ti	-0.0071	0.004093	-1.734	0.095
Al*Ta	0.00575	0.002046	2.808	0.009
Ti*Ta	0.00068	0.002046	0.331	0.743

the temperature in this study is close to the temperature by which Cr oxide becomes volatile. In addition, it is known that W inhibits formation of Cr_2O_3 layer [10, 11].

Figure 3 shows that Mo slightly increased oxidation rate. However, the slope of mass gain versus Mo content plot becomes nearly zero or negative with low content of W, Al, or Ti. On the contrary, the slope was larger with low Ta content. The interaction coefficients for these terms are larger than 0.05 (Table 2) but it cannot be ignored completely. Many researchers [25–30] reported that Mo is detrimental to oxidation resistance. Mo forms volatile oxide in air. Further, it retards formation of Cr_2O_3 and increases possibility of oxide spallation [10, 11]. It is noted that the above research results

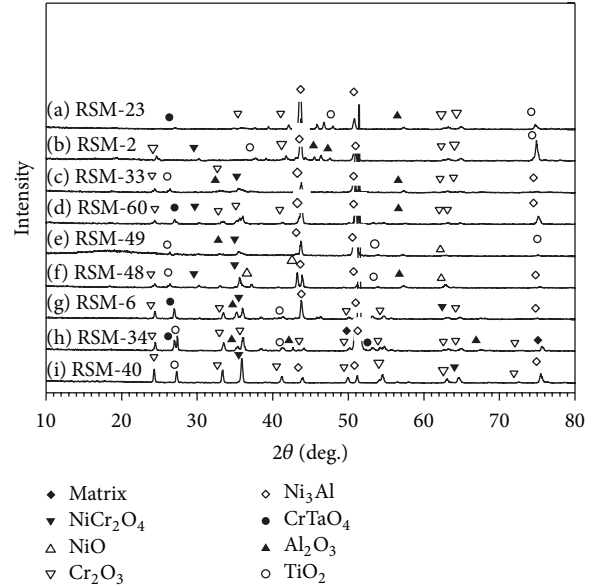


FIGURE 4: X-Ray Diffraction pattern for selected alloys with (a)~(c) high, (d)~(f) moderate, and (g)~(i) low oxidation rate after cyclic oxidation at 850°C.

are for alloys without Ta. Nevertheless, it is also suggested that formation of MoO_2 and MoO_3 reduces oxygen activity facilitating selective oxidation of Cr to form continuous Cr_2O_3 layer on Ni-Mo-Cr alloys at 900°C [15]. The interaction of Mo with other elements, as shown in Figure 3, may imply that W, Al, and Ti increase instability of Mo oxide whereas Ta stabilizes Mo oxide to some extent.

The coefficient for W is very small and its P value is large (Table 2), and the slope of mass gain versus W content in the main effect plot (Figure 3(a)) is very low. Therefore, W has a little effect on the oxidation resistance at 850°C, generally. However, it is noticed that the sign of the slope of mass gain versus W content plot is reversed by Cr concentration (Figure 3(b)) and that the P value of the interaction term is lower than the significance level (Table 2). W decreased mass gain of alloys without Cr, meaning that it forms a protective oxide or reduces diffusion of ions through the scale. When Cr is added to alloy in 15 wt.%, W increases mass gain. W^{6+} might increase cation vacancy concentration in the Cr-rich oxide which is mainly composed of Cr^{3+} , and hence the diffusion of ions through the oxide layer is facilitated.

Al is the most important alloying element governing the oxidation resistance. The cross-sectional images in Figure 5 correspond well to the fact that Al protects the alloy by forming Al_2O_3 acting as a barrier layer and it is more protective when the oxide forms a continuous layer than a discontinuous layer [31]. The SEM images shown in Figures 5(a)~5(c) indicate that discontinuous Al_2O_3 cannot have high resistance to oxidation. Continuous Al_2O_3 layer ensures high oxidation resistance and it provides better protection when the scale is composed solely of Al_2O_3 without outer Cr_2O_3 layer (Figures 5(d)~5(f)) or irregularities (Figures 6(c)~6(d)).

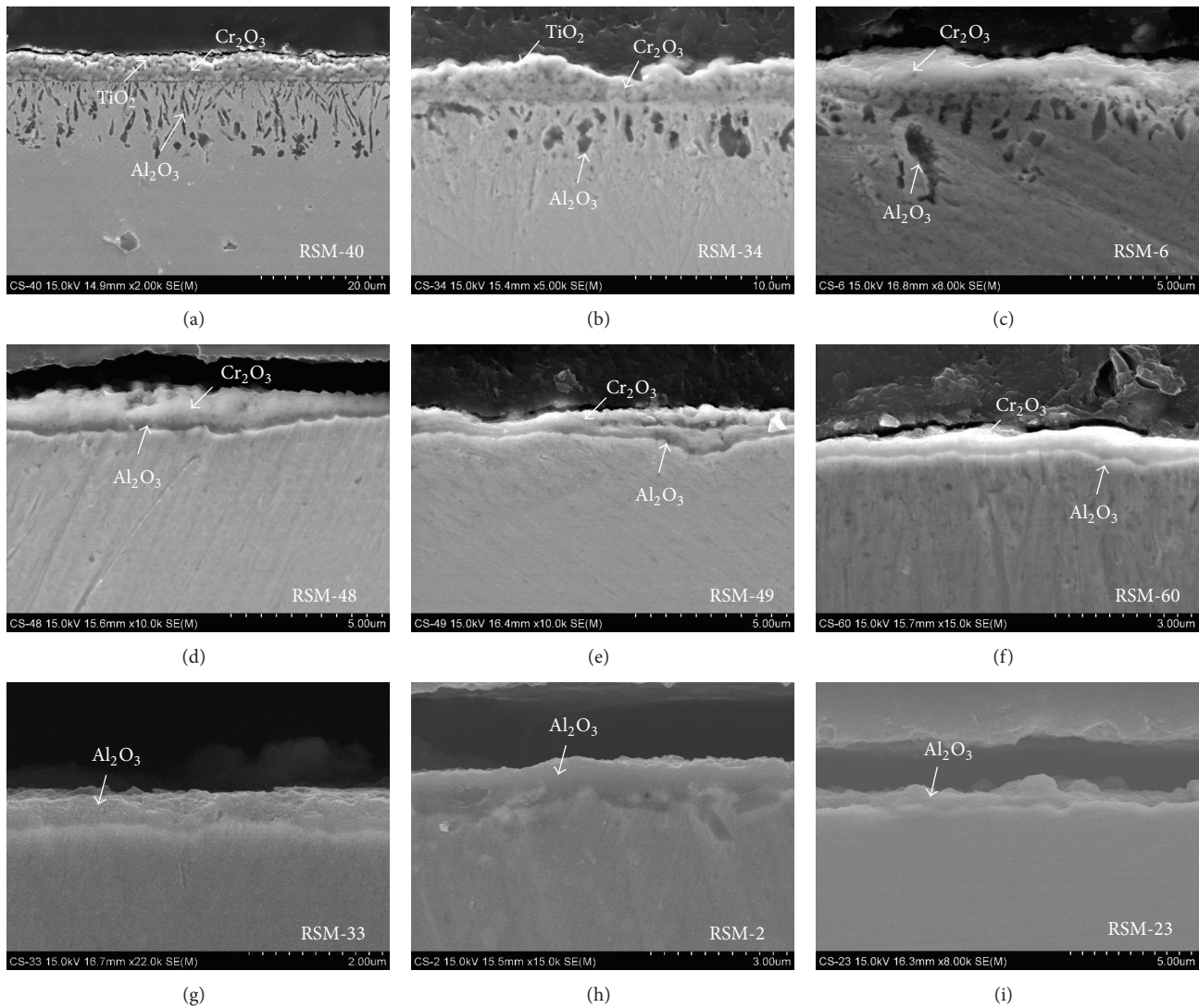


FIGURE 5: SEM images for the selected alloys with (a)~(c) high, (d)~(f) moderate, and (g)~(i) low oxidation rate after cyclic oxidation at 850°C.

The morphology of Al_2O_3 is dependent on oxygen partial pressure in the gas [32] and concentration of other alloying elements, such as Ta, in the alloy [18]. Thereby the effects of various alloying elements on the oxidation rate can be discussed in a view of their influences on Al_2O_3 formation, in addition to their role as a diffusion barrier by themselves. Ti and Ta are revealed to have interaction with Al from Figure 3(b) and Table 2. High concentration of Ti appears to enhance the influence of Al on the mass gain, whereas Ta significantly suppresses the effect of Al. The three selected alloys with discontinuous Al_2O_3 layer (Figures 5(a)~5(c)) have high Ti content (≥ 2.5 wt.%, two of them have 5 wt.%) and low Ta content (≤ 5 wt.%, two of them have 0 wt.%). Contrastively, the three selected images with single layer of continuous Al_2O_3 (Figures 5(g)~5(i)) are of the alloys with 0~2.5 wt.% Ti (two of them have 0 wt.%) and 5 wt.% Ta. The midgroup alloys (Figures 5(d)~5(f)) have 2.5 wt.% Ti and 0~5 wt. Ta (two of them have 0 wt.%).

Ti increases oxidation rate regardless of alloy composition (Figure 3), although the P value for the Ti term is high as 0.659 (Table 2). In addition, TiO_2 was found only on the alloys with high oxidation rate (Figures 5(a) and 5(b)). Therefore, Ti can be regarded as harmful to the oxidation resistance with some suspicion. The increasing effect on the mass gain is alleviated by an increase in Al content (Figure 3(b)). Formation of TiO_2 appeared to be impeded in an alloy with high Al content; RSM-6, which has 2.5 wt.% and 5.5 wt.% Al, does not have TiO_2 layer (Figure 5(c)) on it while RSM-40 has 3 wt.% Al and the same concentration of Ti.

Ta is the element that is believed to have strongest interaction with Al, as proposed by the lowest P value (0.009) of $\text{Al} \cdot \text{Ta}$ term among the interaction terms concerning Al (Table 2). The positive value (0.00575) of the coefficient for $\text{Al} \cdot \text{Ta}$ term indicates that high Ta concentration weakens the effect of Al to reduce mass gain by an increasing effect which is proportional to Al content. This proposition is supported

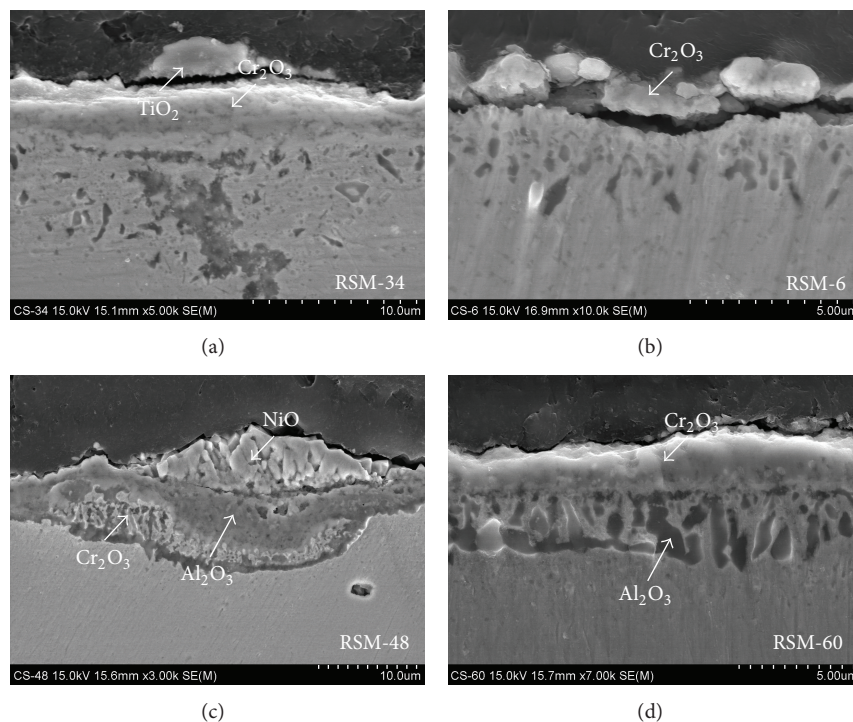


FIGURE 6: SEM images for (a) RSM-34, (b) RSM-6, (c) RSM-48, and (d) RSM-60 after oxidation at 850°C, showing local regions of irregularity.

well by previous works reporting that Ta retards formation of Al_2O_3 and hence continuous Al_2O_3 can be hardly formed with high Ta concentration [33–35].

5. Conclusions

The oxidation resistance of Ni-based alloys was evaluated as a function of alloy composition, based on Response Surface Methodology (RSM). The mass gain by cyclic oxidation test at 850°C reduced significantly by increasing Al and Ta content in the alloy but increased with Ti and Mo content, in average. The main effect of Co, Cr, and W on the oxidation rate was very small.

The oxide scale consisted of single continuous layer of Al_2O_3 for the alloys with low oxidation rate. Medium Ta content (5 wt.%) and low Ti content (≤ 2.5 wt.%) are considered to favor formation of protective Al_2O_3 scale.

The main effects and interactions of alloying elements on the oxidation rate are found as follows:

- (i) Al is the most effective element to improve oxidation resistance. The degree of effectiveness was enhanced by Ti and suppressed by Ta.
- (ii) Ta has strong interaction with Al, in which Ta weakens the effect of Al to reduce oxidation rate quantitatively. Ta itself reduces oxidation rate but this effect nearly disappeared when the Al content is high as 8 wt.%.
- (iii) Ti oxide is often found in the scale on the alloys with high oxidation rate and appeared to increase mass

gain by oxidation. But the detrimental effect can be reduced by addition of Al.

- (iv) Mo slightly increased the oxidation rate but its effect was mitigated by addition of Ta.
- (v) Co increased oxidation rate of alloys without Ta. However, it rarely affects the oxidation rate in the alloys with Ta.
- (vi) Cr remarkably decreased oxidation rate of alloys without W. In the alloys with W, Cr did not exert a significant influence.
- (vii) W reduced oxidation rate of alloys without Cr but increased oxidation rate of alloys with 15 wt.% Cr.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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