

## A STUDY ON THE ELECTRICAL CHARACTERISTICS AND OXIDATION RESISTANCE OF THE STS434L-HIGH CHROME POWDER GREEN COMPACT AT THE HIGH-TEMPERATURE

Metallic oxide layer of heat resistant element contributes to the high-temperature oxidation resistance by delaying the oxidation, and also has positive effect on the electrical resistivity increase. In this study, the green compacts of Fe-Cr-Al powder mixed with STS434L were oxidized at 950°C up to 210 hrs in order to consider the effect of metal oxide on the oxidation and electrical resistance. It exhibited the low oxidation resistance in case of 434L only, however it increased as the amount of Fe-Cr-Al powder in the 434L compact. The higher electrical resistivity was observed at the Fe-Cr-Al compact with and 434L powder. The metal oxides of  $(\text{Fe}_{0.6}\text{C}_{0.4})_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  contributed to the electrical resistivity, whereas  $\text{Al}_2\text{O}_3$  took a role of oxidation resistance.

*Keywords:* Stainless steel, FeCrAlloy, Oxidation resistance, Metallic oxide

### 1. Introduction

Because the general traditional manufacturing method can not satisfy the demand of integrated and minimized heating element, powder metallurgy method has been raised as the most useful method. In case of applying to the manufacturing of a high temperature heating element by P/M, it has issues to be considered but has not been many studied yet. Fe-Cr-Al alloys have been researched when it was realized that additions of Al led to improvements in the scaling resistance of iron and steels [1]. Haultman [2] reported that the heat resistance of steels at 1000°C improved remarkably when the Al content was raised to between 4 and 9%. Also, Ziegler [3] noted an improvement in performance with increasing Al content in studies on Fe-Cr-Al alloys and claimed that alloys with 8% Al were comparable in oxidation resistance to Fe-Cr-Ni alloys. Other workers also noted that the addition of Al improved scaling properties in the range 900 ~ 1200°C, and it was observed that oxidation took place in accordance with a parabolic rate law [4-6]. Fe-Cr-Al alloys form a protective  $\text{Al}_2\text{O}_3$  film layer only at low content about 5% Al due to retaining internal oxidation effectively by Cr playing the role of absorbing agent for oxygen [2,7]. According to A. Bautista and F. Velasco [8], the addition of other oxidative metallic elements that have larger affinity for oxygen for forming oxide layer can improve the adhesion of oxide layer to the base alloy or increase high-temperature oxidation resistance. The formed metal oxide on the surface by adding strong oxidative metal element such as Al and Si play a role of the

oxide layer of base alloy which can protect inner alloy at high temperature and be expected to increased electrical resistance by formation various composite oxides [9-12]. As the oxides such as  $\text{SiO}_2$  were added to STS434L, the electrical resistance was increased by generating various composite oxides in previous study [13]. It is considered that composite oxides affect the oxidation resistance as well as electrical resistivity. In order to use the heat resistant material at high temperature, the protective oxide should be formed well on the surface and also oxide layer should be stable, [14,15] because the stability of electrical resistivity at high temperature is also much influenced by the type of oxide scale. Therefore the type and role of the formed oxides that affect high temperature oxidation resistance and electrical resistivity need to be studied.

In this paper, high temperature electrical resistivity and the oxidation stability was studied at the STS434L of ferritic stainless steel that has low coefficient of expansion and excellent high temperature oxidation resistance [13,16] mixed with the Fe-Cr-Al (FeCrAlloy) powder. And also the role of oxides that affect the oxidation and electrical resistance were analyzed.

### 2. Experimental procedure

In this study STS434L powder that has average particle size of 40  $\mu\text{m}$  and irregular shape of Daido Corporation (Japan), and FeCrAlloy powder that has average particle size of 30  $\mu\text{m}$  and spherical shape made by Sandvik Osprey Ltd (United

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Kingdom) were used. Because the shape of the powders differs, the raw material powder was analyzed in order to clearly identify what kind of oxides generated as shown in Fig. 1. The STS434L powder having composition in table 1 was mixed with FeCrAlloy powder up to 100%. The only 100% FeCrAlloy powder was mixed with 2w/o acro wax and the others were mixed with 1w/o wax because of the FeCrAlloy powder to increase compactibility. The green compacts of FeCrAlloy powder mixed with STS434L were heated for 30°C/min to 300°C and pre-heated for 30 mins, then was heated again to 450°C for 1 hr to remove the acro wax. After second pre-heated at 450°C for 20 mins, the temperature was maintained at 950°C for 210 hrs in air by heating for 16°C/min to study the high temperature oxidation behavior of respective time. The weight change of each compact was also measured at different oxidation time. The formed each oxide layer was analyzed and phase change of the generated oxides were also observed through the X-ray diffraction meter after high-temperature oxidation test. The component analysis of generated oxides was measured through the EDS (Energy Dispersive Spectroscopy). In addition, it was compared with electrical resistivity to investigate the high temperature stability. The electrical resistance was measured by using the electrical resistivity device ‘Hioki 3540’ model after surface polishing and covering the silver paste to minimize the resistance of the surface.

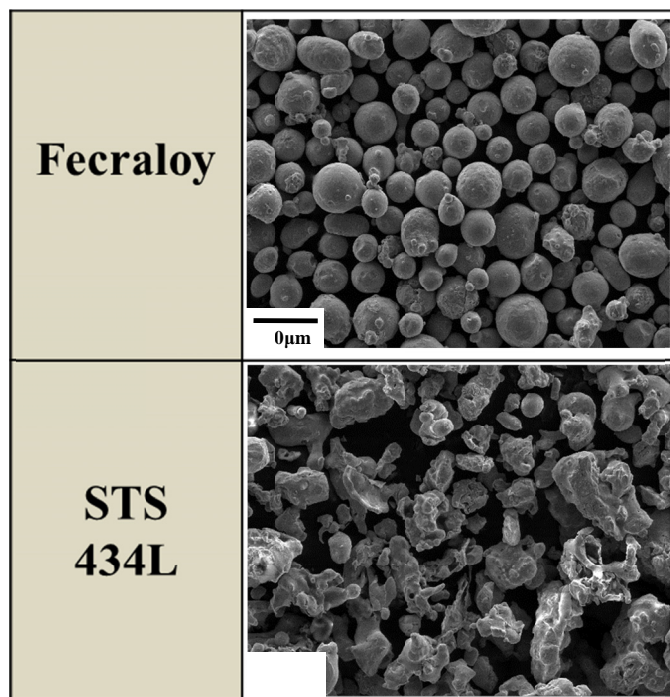


Fig. 1. SEM images of the used powder

TABLE 1

Composition of the used powder.(wt.%)

	C	Cr	Al	Mo	Si	Mn	Y	Fe
STS434L	0.01	16.73	—	1.09	0.8	0.17	—	Bal
FeCrAlloy	0.1	22.3	6.6	—	—	1	0.2	Bal

### 3. Results and discussion

Fig. 2 shows the amount of oxidation in accordance with the STS434L green compacts by changing the addition of FeCrAlloy powder up to 210 hrs at 950°C. The weight change ratios increased rapidly until 10 hrs oxidation time and then gradually increases until 210 hrs. The weight change ratio of 434L was highest up to 10% at 210 hrs oxidation time, and the weight change slope at FeCrAlloy added compacts were lower than that of 434L. Fig. 3 shows the density changes of 434L, FeCrAlloy and mixed compacts according to oxidation time. The relative density were low by adding FeCrAlloy that has spherical shape and poor compactibility. The weight gain by oxidation is greatly affected in accordance with density of green compact. Despite the low relative density, the FeCrAlloy showed lower weight increase than that of 434L as shown Fig. 2. It is considered that the Cr ion plays a role of absorbent that effectively inhibits internal oxidation about oxygen in matrix and the diffused Al to

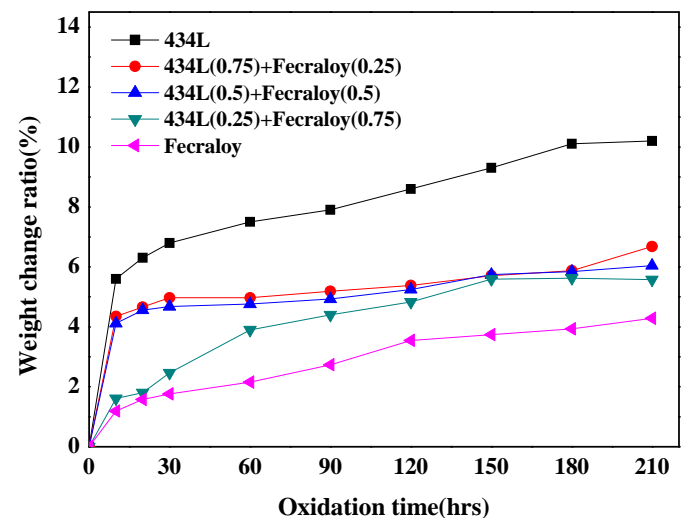


Fig. 2. Weight change ratio of respective specimens after oxidation tests at 950°C for 210 hrs in air

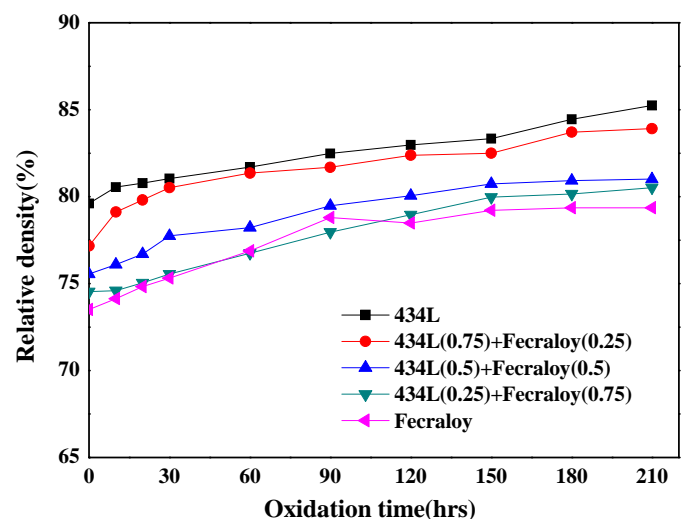


Fig. 3. Relative density of respective specimens after oxidation tests at 900°C for 210 hrs in air

surface forms the protective oxide layer such as  $\text{Al}_2\text{O}_3$  reacted with oxygen [7]. Fig. 4 shows the X-ray diffraction patterns in accordance with the oxidation time for each green parts after 210 hrs at  $950^\circ\text{C}$  in air. In XRD graph (a), even after oxidizing 434L for 210 hrs, only  $\alpha$  peak was observed and other oxides were not formed. However the increase in the amount ratio of FeCrloy to 434L, peak  $\alpha$  decreased while the other oxides such as  $\text{Cr}_2\text{O}_3$ ,  $(\text{Fe}_{0.6}\text{Cr}_{0.4})_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  appeared as shown in other graphs (b) and (c). Although graph (d) shows the similar peak of (a), except of single oxide peak at  $32^\circ$ , it exhibited the lowest oxidation weight change ratio as shown Fig. 2. It is considered that the formation of  $\text{Al}_2\text{O}_3$  even small amounts on grain boundary restrained the external intrusion of oxygen. Although the various oxides were generated, the Fe oxides such as  $\text{Fe}_2\text{O}_3$  did not significantly contribute to increase the oxidation resistance, but  $\text{Al}_2\text{O}_3$  among the  $\text{Cr}_2\text{O}_3$ ,  $(\text{Fe}_{0.6}\text{Cr}_{0.4})_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  had the

greatest contribution to oxidation resistance. From this result, it is thought that the Al ion forms metallic oxide that acts as a nucleation site of Cr at the base surface and promotes the growth of Cr oxides [7]. According to formed  $\text{Al}_2\text{O}_3$  by the diffused Al to grain boundary, it inhibited the external diffusion of Cr and the Cr critical concentration that forms Cr oxides was reduced. Fig. 5 shows EDS mapping results of 434L, FeCrloy and 434L mixed with FeCrloy after 210 hrs exposure at  $950^\circ\text{C}$ . In case of FeCrloy only, the most of Al were diffused into grain boundary and the oxidation hardly proceeded inside result from the excellent high-temperature oxidation resistance. When the 434L was mixed with FeCrloy, the 434L was selectively oxidized by higher oxidation tendency than FeCrloy. It was observed that the uniform layer of  $\text{Al}_2\text{O}_3$  on the particle surface and Fe-Cr oxide on the 434L particle boundary were formed. Fig. 6 shows the electrical resistivity of the specimens for each oxidation time.

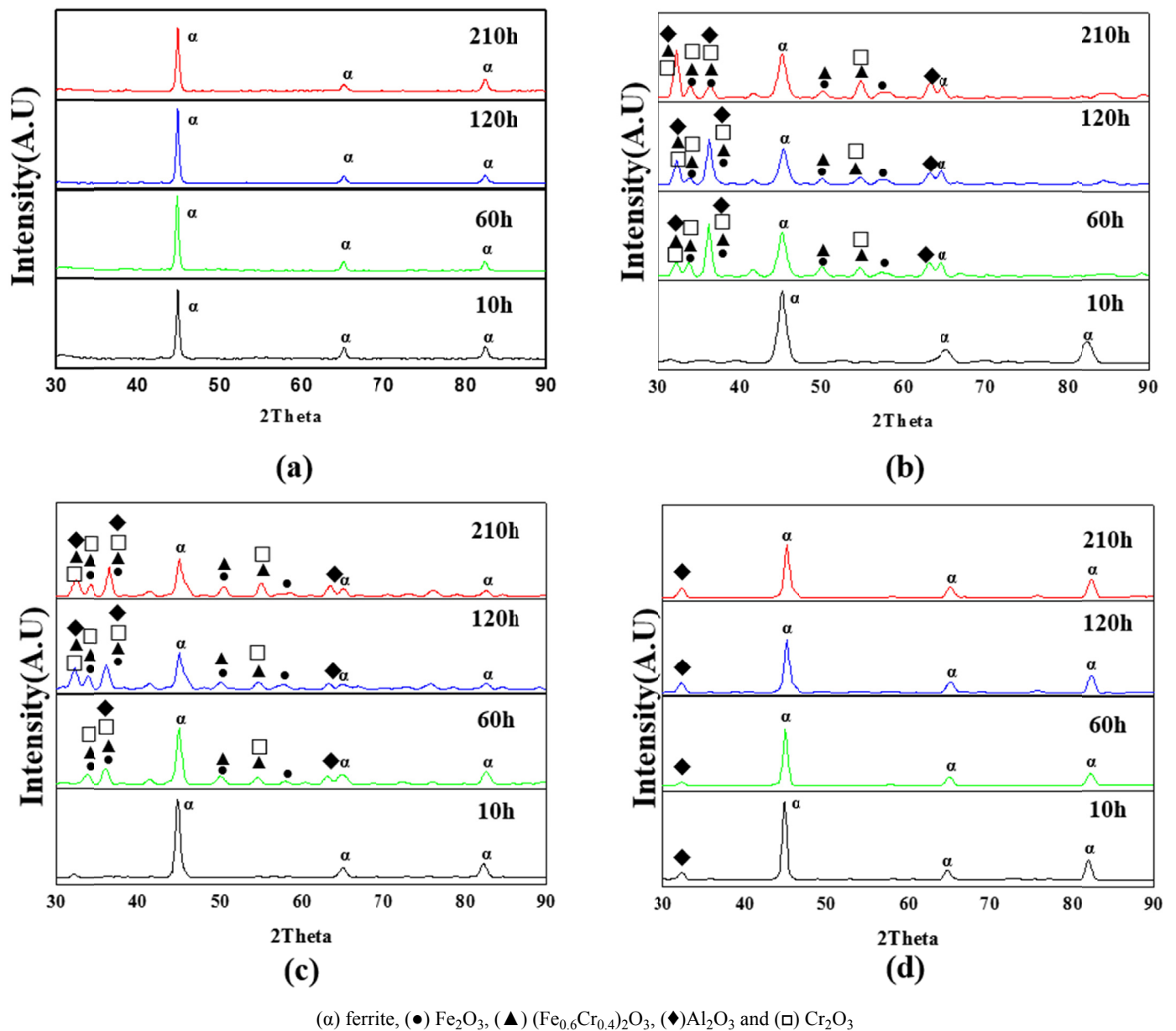


Fig. 4. X-ray diffractograms corresponding to respective specimens after different periods of exposure at  $950^\circ\text{C}$  in air: (a) 434L, (b) 434L (0.75) + FeCrloy (0.25), (c) 434L (0.25) + FeCrloy (0.75) and (d) FeCrloy

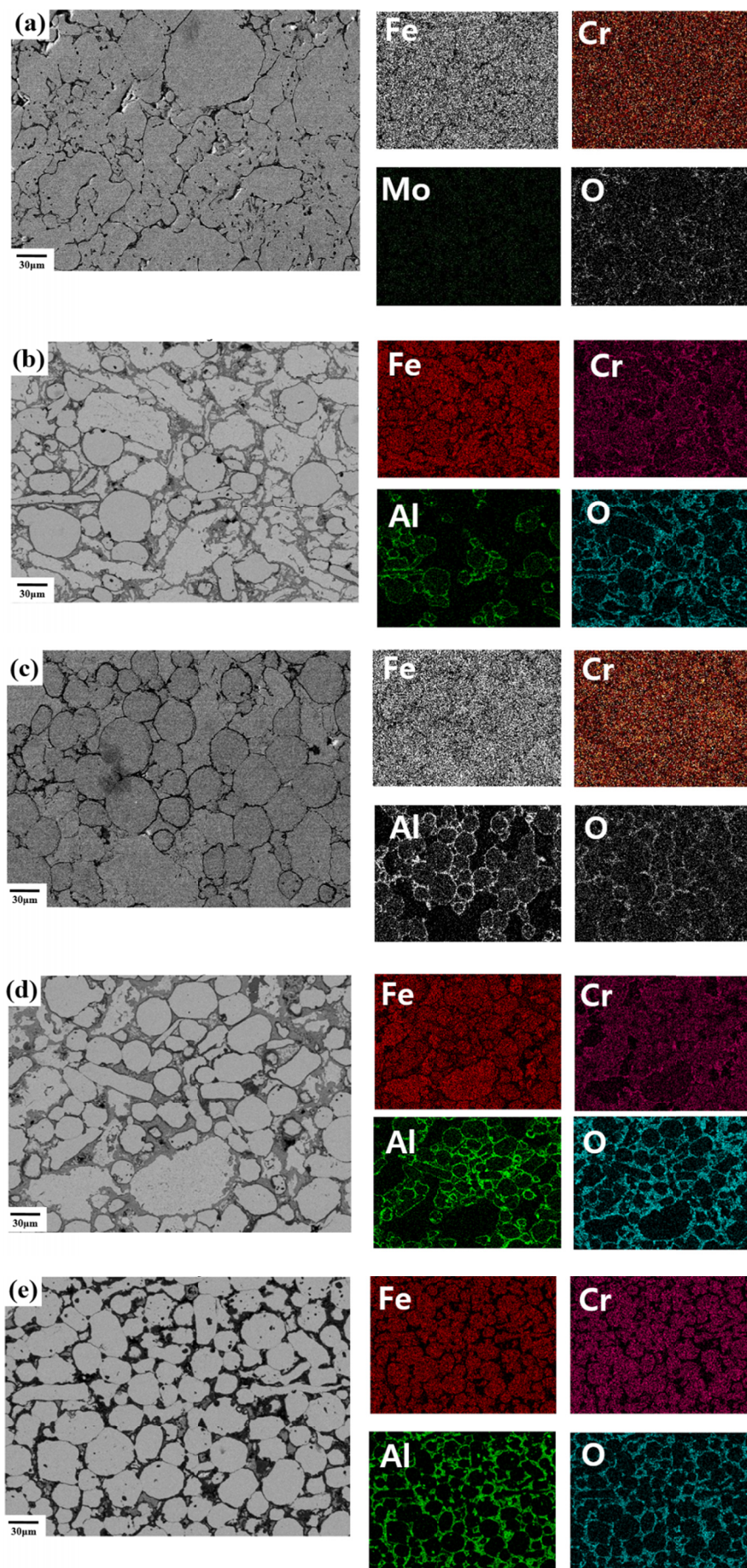


Fig. 5. EDS mapping results of specimens after 210hr exposure at 950°C in air: (a) 434L, (b) 434L (0.75) + FeCrAlloy (0.25), (c) 434L (0.5) + FeCrAlloy(0.5), (d) 434L (0.25) + FeCrAlloy (0.75) and (e) FeCrAlloy

The high value of electrical resistivity were observed initially decreased after the initial oxidation time of 60 hrs, because the sintering was gradually proceeded with the flow of oxidation time. Comparing with the XRD results, the electrical resistivity values were high in sequence as a lot of the oxide peaks were observed. In case of 434L only, the sufficient oxidation resistance and electrical resistivity could not be obtained because the oxide scales on the particle surface were not formed. Similar to this, the development of protective scale on the surface obtained the excellent oxidation resistance but electrical resistance effect was little due to the small amount of oxidation of Fecraloy as shown Fig. 4 (e). Resulting from the oxidation weight increase of 434L is higher than that of Fecraloy, it is considered that 434L has the higher oxidation tendency. Therefore the 434L particles were oxidized selectively in case of 434L mixed with Fecraloy, Fe-Cr and Cr oxides were generated primarily. Even if the destruction of the oxide layer occurs, it was able to maintain stable protective scale due to the formation of  $Al_2O_3$ . Whereby the formation of Fe-Cr oxides on grain boundary, the electrical resistivity was obtained by interrupting the current flow through the particle. It seems that the high value of electrical resistivity is indicated because a lot of oxides such as  $Al_2O_3$  and Fe-Cr oxides were formed.

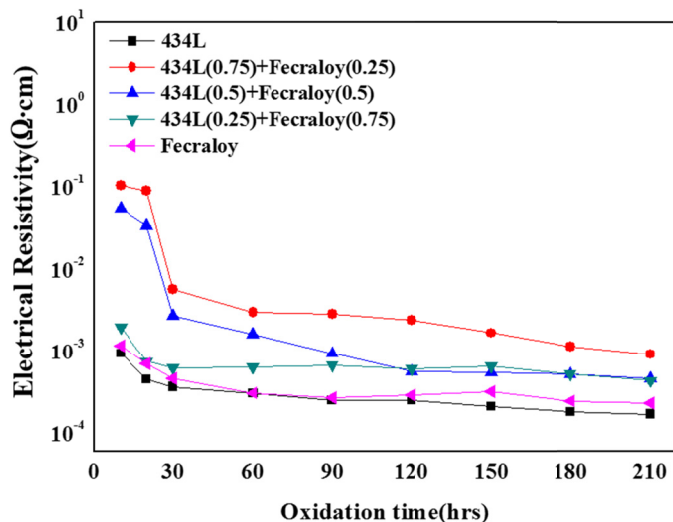


Fig. 6. Electrical resistivity of 434L mixed with Fecraloy specimens after oxidation tests at 950°C for 210 hrs in air

#### 4. Conclusions

The weight change ratio decreased in case of the addition of Fecraloy compared with the 434L, and Fecraloy has lower oxidation tendency than 434L. It could be considered that the addition of Fecraloy effects better oxidation resistance by the formation of the stable at high-temperature and protective  $Al_2O_3$  scale on the particle surface from EDS results. When STS434L was mixed with the Fecraloy powder, the high-temperature electrical resistivity increased by forming composite oxides such as Fe-Cr, Cr and Al oxides in grain boundary.

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