

The formation of Cr(VI) compound at the interface between metal and heat-insulating material and the approach to prevent the formation by sol-gel process

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Most heating apparatuses include Cr-containing metals and heat-insulating materials that are often placed in contact with each other. It was observed that hexavalent chromium [Cr(VI)] oxide occurred at the contact interface between Cr-containing metals and heat-insulating materials at elevated temperatures. Yellowish reaction products were confirmed on the contact surfaces of the heat-insulating materials and were identified as Cr(VI) compounds. The effect of heat-treatment temperature, time and metal Cr content on the amount of Cr(VI) was investigated. The amount of Cr(VI) compound increased as the heat-treatment temperature, time and metal Cr content increased. The compounds that occurred as a result of the reaction were CaCrO_4 and Na_2CrO_4 for heat-insulating materials containing Ca and Na, respectively. The sol-gel coating technique was used to prevent the formation of Cr(VI) compounds. Al_2O_3 -based coating films were formed on the surfaces of SUS304 metals by a dipping process. The coated metals were placed on the heat-insulating materials and these specimens were heat-treated at 873 K for 5,000 h. As a result, the formation of Cr(VI) was almost completely prevented by the coating film. It was concluded that the Al_2O_3 -based coating films effectively suppressed the diffusion of Cr.

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1. Introduction

Chromium is abundantly present in nature. The most common forms are trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium and the latter is mainly produced by industrial processes such as electroplating, glass and ceramics manufacturing, mining and metallurgy.¹⁾⁻³⁾

Cr(VI) compounds are toxic, carcinogenic and mutagenic in humans and animals. The noxiousness of Cr(VI) compounds is caused by its strong oxidation power and can result in various diseases. Accordingly, it is important that the Cr(VI) compounds produced in industrial processes should be reduction-treated and prevented from dispersing outside. It is also necessary to develop technology to prevent the formation of Cr(VI) compounds.⁴⁾⁻⁸⁾

Most heating apparatuses such as incinerators, high-temperature reactors and melting furnaces include Cr-containing metals and heat-insulating materials (insulators). As Cr-containing metals have high thermal resistance, they are commonly used in high-temperature environments. With respect to insulators, Ca-Si-O-based compounds are widely used due to their high thermal resistance, low thermal conductivity and low cost.⁹⁾ In many cases, the insulators are placed in contact with the metals in the heating apparatuses.

It was found that Cr(VI) oxide occurred at the contact interfaces between the metals and insulators at elevated temperatures.¹⁰⁾ Namely, yellowish reaction products were observed on the contact surfaces of the insulators and were identified as Cr(VI) oxides. There are few reports about this phenomenon and

there is no quantitative data on the formation of Cr(VI) oxides in this situation. The relationship between the amount of Cr(VI) and the surrounding conditions should be clarified, and technology to prevent the formation of Cr(VI) oxides should be developed.

One approach is to use Ca-free insulators. Ca-free insulators consisting of high-purity alumina or mullite are commercially available,^{11),12)} but they are much more expensive than Ca-Si-O-based compounds. Therefore, insulators consisting of Ca-Si-O are widely used especially in the field of large-scale heating apparatuses. Another approach is to use Cr-free super alloys such as Ni- or Co-based alloys,¹³⁾ but these too are expensive and so their use is limited.

A unique and practical solution is the sol-gel coating process, in which a ceramic precursor solution is coated onto a substrate metal and is subsequently decomposed by heat treatment. It is a simple process applicable to large and complex contact interfaces.¹⁴⁾⁻¹⁸⁾

This study quantitatively estimated the formation of Cr(VI) oxides at the contact interfaces between metals and insulators at elevated temperatures. Furthermore, the sol-gel coating process for preventing such formation was investigated.

2. Experimental procedure

2.1 Specimens

Table 1 shows the composition of the metals used in this experiment. JIS STPA22 (ASTM A335-P12), JIS STPA24 (ASTM A335-P22), JIS STPA28 used for thermal power plant (ASTM A213-P91) and JIS SUS304 (ASTM A312 TP304) were used. The compositions of STPA22, STPA24 and SUS304 were obtained from the inspection certificates supplied by the producer

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Table 1. Composition of metals used in this experiment

Metal	Cr	Ni	Mo	Mn	Si	C	S	P	V	Nb	Al	Co	Ti	Fe
STPA 22	0.91	—	0.48	0.45	0.24	0.12	0.003	0.009	—	—	—	—	—	Val.
STPA 24	2.05	—	0.91	0.37	0.25	0.11	0.005	0.015	—	—	—	—	—	89
STPA 28*	8.5	0.08	0.92	0.44	0.37	—	—	—	0.21	0.09	—	—	—	Val.
SUS304	18.2	8.09	—	0.85	0.27	0.06	0.003	0.024	—	—	—	—	—	Val.

JIS STPA22 (ASTM A335-P12), JIS STPA24 (ASTM A335-P22), JIS STPA28* (ASTM A213-P91), JIS SUS304 (ASTM A312-TP304) mass %

*Used for thermal power plant

Table 2. Composition of heat-insulating materials (insulators) used in this experiment

Insulator	Type	SiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CO ₃	SO ₄
(A)	Block	48	35	0.38	0.34	0.31	0.94	1.4	0.3	21	0.1
(B)	Coating & Self-Curing	30	36	11	0.15	<0.1	3.9	0.51	0.13	21	1.1
(C)	Block	75	0.49	0.1	7.3	3.1	9.4	0.7	0.1	4.1	<0.1

mass %

and that of STPA28 was obtained from the analysis by X-ray fluorescence (Rigaku Corp., RIX3001). Cr content of STPA22, STPA24, STPA28 and SUS304 was 0.91, 2.0, 8.5 and 18.2%, respectively.

Table 2 shows the composition of the insulators used in this experiment. These insulators were dried and ground to powder for the chemical analysis. In the case of CO₃ and SO₄, the powder was analyzed by the infrared absorption method using a high-frequency induction furnace (Horiba, Ltd., EMIA920V2). For Na₂O and K₂O, the powder was dissolved in nitric-hydrofluoric acid and analyzed by plasma emission spectrometry (Seiko Instruments Inc., SPS3100HVUV/SII). Here, nitric-hydrofluoric acid was prepared by mixing 10 ml nitric acid (46%) and 10 ml hydrofluoric acid (61%), which was then diluted to 100 ml with water. For the other constitutions, the powder was dissolved in alkaline solution and analyzed by plasma emission spectrometry. The alkaline solution was prepared by mixing Na₂CO₃ and Na₂B₄O₇ (Na₂CO₃:Na₂B₄O₇ = 3:1 in weight) and then 4 g of the mixture was melted and diluted to 500 ml with water.

Insulator (A) is a block type mainly composed of CaO-SiO₂ (Nihon Keikaku Corp., Keikaku Ace Super Silica). The bulk density, which was measured by weight and dimensions after heat-treatment at 773 K for 1 h, was around 0.18 Mg/m³ in the case of insulator (A). Insulator (B) is a self-curing type coating (Sakai Sangyo Corp., Howaitoragu). It is also mainly composed of CaO-SiO₂ and includes MgO and Al₂O₃. The bulk density was around 1.22 Mg/m³. The block type insulator (C) is mainly composed of SiO₂ and includes Na₂O, K₂O and Al₂O₃ (Fuji Perlite Co., Ltd., Water-repellent Perlite). The bulk density was around 0.19 Mg/m³. Insulator (C) with negligibly low Ca content was used as the reference in this experiment.

The metals and insulators used in this experiment were both rectangular solids. The specimen size was 30 × 30 × 5 mm for the metal and 30 × 30 × 10 mm for the insulator. The maximum height Rz of the surface roughness for the metal was 3 μm. For the insulators, the surfaces were sliced by a metal cutter.

2.2 Reaction test

Figure 1 shows the method of setting the specimens for the reaction test. Metal containing Cr was placed on the insulator and fixed lightly with fiber yarn mainly composed of Al₂O₃ to prevent slippage. The stress applied on the interface between the metal and insulator was the dead weight of the metal, approximately 40 kg/m². The specimens were heat-treated at different temper-

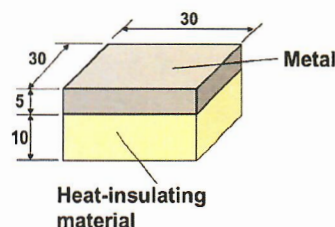


Fig. 1. Setting method of specimens for reaction test.

atures in air.

After the heat-treatment, the contact surfaces of the insulators were scraped off by the metal cutter. Approximately 0.2 g of powder scraped off from the insulator was placed in a beaker to which 20 ml of water was added. The mixture of powder and water was heat-treated at 373 K for 30 min to elute Cr(VI). After the heat-treatment, the mixture was filtered using filter paper. The amount of Cr(VI) in the solution was analyzed by diphenyl-carbazide absorption photometry (Hitachi, Ltd., U-1900). The amount of Cr(VI) was converted to weight per unit area (mg/m²).

The total amount of Cr was also analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES; Shimadzu Corp., ICPS-8000) for the same powder. As there was no significant difference between the amount of Cr(VI) and the total Cr, it was considered that all the Cr which formed was Cr(VI) and it was completely dissolved by the above process. When Cr(VI) is formed, yellowish color peculiar to Cr(VI) is confirmed and this coloration phenomenon is very sensitive. This coloration phenomenon was only on the insulator side and not accepted on the metal side at all. Therefore, the amount of Cr(VI) on the insulator side was analyzed in this paper.

The powders scraped off from the contact surfaces of the insulators were crushed by a mortar and analyzed by X-ray diffraction apparatus (Rigaku Corp., RINT2200) to identify the crystal phases. The powder from inside the insulator was also analyzed by X-ray diffraction apparatus for reference. The amount of powder analyzed by X-ray diffraction apparatus was around 100 mg.

2.3 Sol-gel coating

The sol-gel coating process was used to form thin films on the surfaces of the metal specimens.

Figure 2 shows the procedure for preparing the films by the sol-gel process. The surfaces of SUS304 metal specimens were

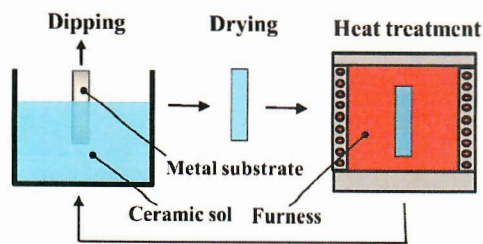


Fig. 2. Procedure for preparing films.

washed with acetone. The specimens were dipped in the ceramic sol and then extracted at a constant speed (5 mm/s). The ceramic sol consisted of pseudoboehmite powder, 3-glycidoxypropyltrimethoxysilane ($C_9H_{20}O_5Si$), water and methanol where the ratio of pseudoboehmite powder (as Al_2O_3), $C_9H_{20}O_5Si$ (as SiO_2), water and methanol was 6.3:1.5:59.7:28 in weight, respectively (Kawaken Fine Chemicals Co., Ltd., CSA-110AD). $C_9H_{20}O_5Si$ was added to improve the adhesion of the coating film to the metal substrate.¹⁹⁾

After drying at room temperature, the coated metal specimens were heat-treated and uniform ceramic films were formed on the surfaces of the metal specimens by the decomposition of the ceramic precursor. The thickness of the film was controlled by the number of repetitions of the above operations. Here, the specimens were dipped and heat-treated three times. The heat-treatment conditions were 773 K for 10 min in the first two times and the last time was 873 K for 10 min. The heat-treatment temperature was determined based on the thermogravimetric analysis (TG) data of the ceramic sol. The coated metal specimens were placed on the insulator and heat-treated at 873 K for different lengths of time in air. The amount of Cr(VI) that occurred on the contact surfaces of the insulators was estimated by the same method as for the non-coated specimens described above.

The coated metal specimen was analyzed by low incidence X-ray diffraction (Philips Corp., X'PERT MRD) and the constituent phases were identified. The instrument was operated in a step-scan mode in increments of $0.01^\circ 2\theta$, and counts were accumulated for 0.5 s at each step. The generator voltage was 45 kV and the tube current was 40 mA. The angle of incidence was set to 1.5° . After the reaction test, the coated surfaces of the metal specimens were sliced and the cross sections were padded with a resin. After curing the resin, the cross section was polished. The vicinity of the coating films was milled by argon ions (Jeol Ltd., SM-09010). The microstructures in the vicinity of the coating films were observed by a field emission scanning electron microscope (FE-SEM; Jeol Ltd., 6700F) and analyzed by electron probe microanalyzer (EPMA; Jeol Ltd., JXA 8500F). Furthermore, the cross section of the vicinity of the coating film was cut to $0.2\ \mu m$ by a focused ion beam (FIB; Hitachi Hi-Technologies Corp., FB-2100), then scanning transmission electron microscopy (STEM; Hitachi Hi-Technologies Corp., HD-2000) images and energy dispersive spectroscopy (EDS; Thermo Fisher Scientific K.K., Noran System Seven) mapping were observed.

3. Results and discussion

3.1 Estimation of formation of Cr(VI)

Figure 3 shows the relationship between the Cr content of the metal and the amount of Cr(VI) that occurred at 773 and 873 K after 5,000 h of heat-treatment. The metals used for the experiment were STPA22, STPA24, STPA28 and SUS304. Cr content of these metals was 0.91, 2.0, 8.5 and 18.2%, respectively. Insulator (A) mainly composed of $CaO-SiO_2$ was used for all

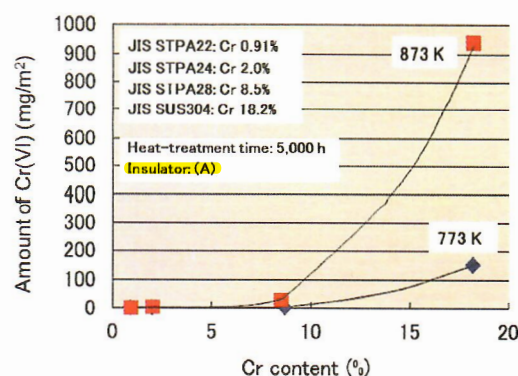


Fig. 3. Relationship between Cr content of metal and amount of Cr(VI) that occurred at 773 and 873 K after 5,000 h.

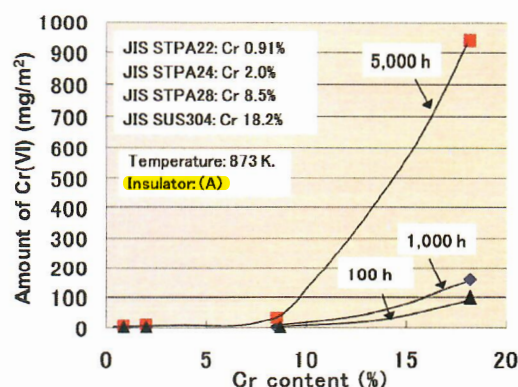


Fig. 4. Relationship between Cr content of metal and amount of Cr(VI) that occurred at 873 K for different heat-treatment times.

experiments. The amount of Cr(VI) that occurred with the specimens using metal with less than 8.5% Cr was minute and that for the specimens using metal with 18.2% Cr was $150\ mg/m^2$ at 773 K and $940\ mg/m^2$ at 873 K. The amount of Cr(VI) sharply increased at above 8.5% Cr content for both cases at 773 and 873 K. It was considered that the amount of Cr(VI) that occurred by heat-treatment was strongly influenced by the Cr content in the metals and the heat-treatment temperature.

Figure 4 shows the relationship between the Cr content in the metal and the amount of Cr(VI) that occurred at 873 K for different heat-treatment times. Insulator (A) mainly composed of $CaO-SiO_2$ was used for all experiments. The amount of Cr(VI) that occurred with the specimens using metal with less than 8.5% Cr was minute and that for the specimens using metal with 18.2% Cr was 100, 160 and $940\ mg/m^2$ for 100, 1,000 and 5,000 h of heat-treatment time, respectively. This also shows that the amount of Cr(VI) that occurred at the contact interface by the heat-treatment was strongly influenced by the Cr content of the metal and a critical point existed at around a little less than 10% Cr content. It was considered that heat-treatment time also strongly influenced the amount of Cr(VI).

Figure 5 shows the visual appearance of the contact interfaces of the insulators before and after the reaction test for the combination of SUS304 and insulator (A) heat-treated at 873 K for 1,000 h. A yellowish substance was observed on the surface of the insulator after the reaction test. The amount of Cr(VI) that occurred at the contact interface was $160\ mg/m^2$. It was suggested that Cr(VI) occurred by the diffusion of Cr from the metal to the insulator.

The reaction products on the insulators were analyzed. **Figure 6** shows the results of the X-ray diffraction analysis for the contact surface of the insulator and inside the insulator for the combination of SUS304 and insulator (A) heat-treated at 873 K for 1,000 h. The insulator inside was composed of CaSiO₃, Ca₂SiO₄ and Ca₈Si₅O₁₈. On the other hand, CaCrO₄ crystalline phase was detected for the contact surface of the insulator in addition to CaSiO₃, which originated from the substrate of the insulator. It was considered that the yellowish substance was CaCrO₄, which is one of the Cr(VI) compounds. It was suggested that the Cr in the metal diffused to the surface of the metal and formed Cr oxide, and CaCrO₄ was formed by the reaction between the Cr oxide and the insulator. Accordingly, the reaction between the metal and the insulator can be explained by the following equation.

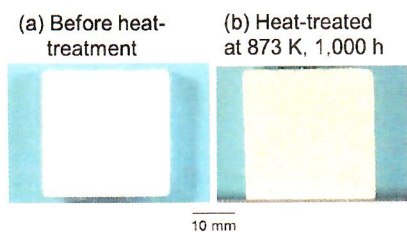
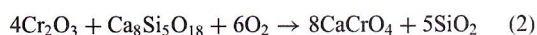
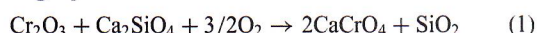
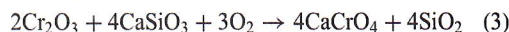


Fig. 5. Visual appearance of insulator contact face before and after the reaction test for the combination of SUS304 and insulator (A) heat-treated at 873 K for 1,000 h.

In addition to the above, some of the CaSiO₃ might have reacted with Cr₂O₃ as described below.



Apparently, reactions (1) and (2) occurred prior to reaction (3). According to the above equation, SiO₂ will occur in all cases. However, no SiO₂ crystalline phases were detected in the X-ray diffraction chart. It was suggested that the SiO₂ amorphous phase was formed in the above equation as the heat-treatment temperature was considerably low.

The influence of the insulator composition on the amount of Cr(VI) was evaluated. **Figure 7** shows the relationship between the heat-treatment time and the amount of Cr(VI) that occurred at 773 K for the combination of SUS304 and insulator (A), (B) and (C), respectively. In all cases, the amount of Cr(VI) increased as the heat-treatment time increased and there was no prominent difference between the combinations using insulator (A) and (B). However, the amount of Cr(VI) that occurred with the combination of SUS304 and insulator (C) was much greater compared to the others. Insulators (A) and (B) are mainly composed of CaO-SiO₂ and insulator (C) is mainly composed of SiO₂ and includes Na₂O, K₂O and Al₂O₃.

Figure 8 shows that the results of the X-ray diffraction analysis for the contact interface of the insulator for the combination of SUS304 on insulator (C) and the insulator inside heat-treated at 773 K for 5,000 h. The insulator inside was composed of SiO₂ (quartz) and NaAlSi₃O₈. In addition to these crystalline peaks, a broad peak was observed between 15 and 30° and it was considered that insulator (C) included a large amount of amorphous phase. On the other hand, Na₂CrO₄ crystalline phase was detected in addition to SiO₂, NaAlSi₃O₈ and amorphous phase at

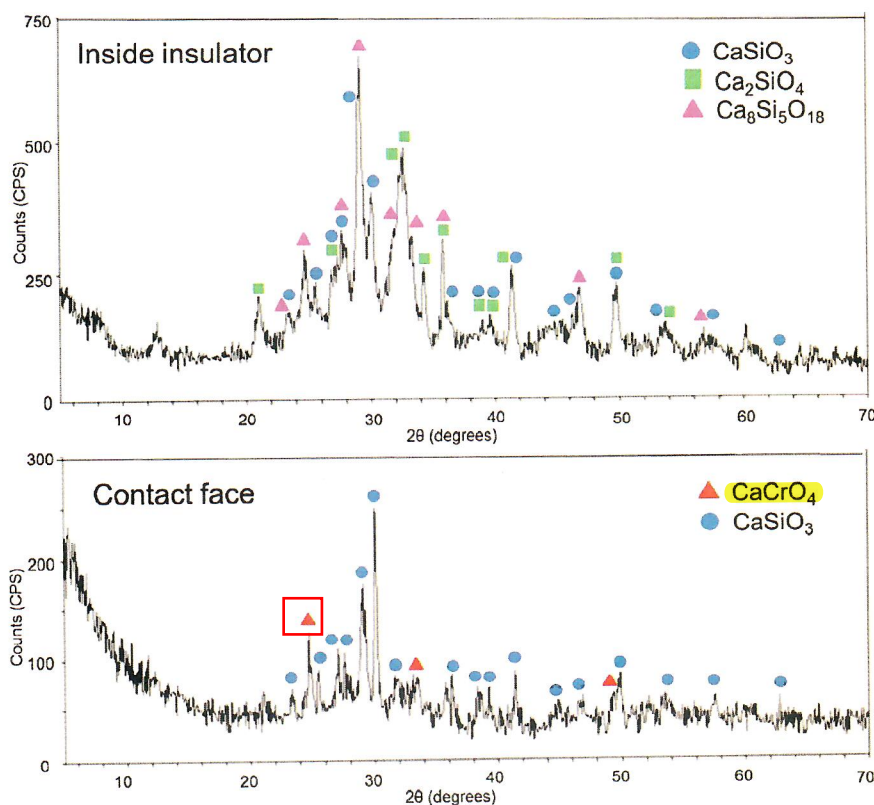


Fig. 6. Results of X-ray diffraction analysis for insulator inside and contact surface of insulator for the combination of SUS304 and insulator (A) heat-treated at 873 K for 1,000 h.

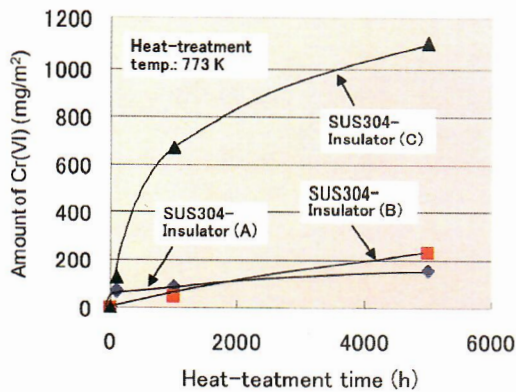


Fig. 7. Relationship between heat-treatment time and amount of Cr(VI) that occurred at 773 K for the combination of SUS304 and insulator (A), insulator (B) and insulator (C).

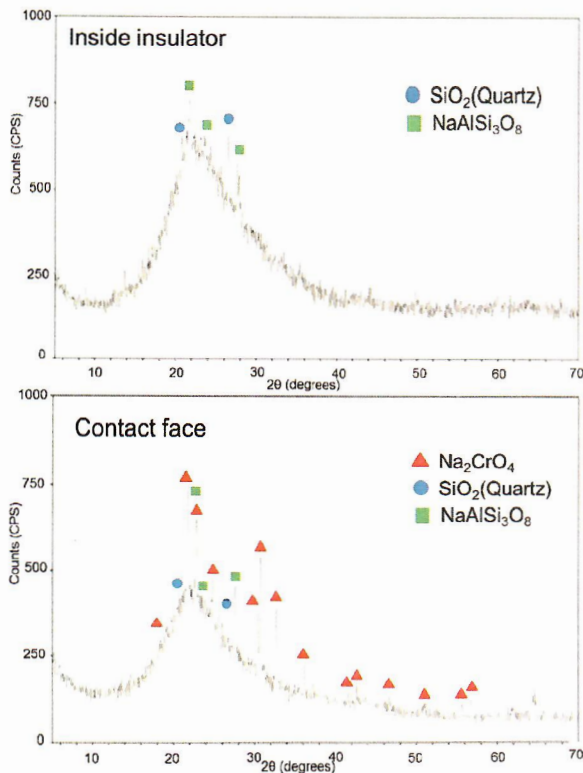
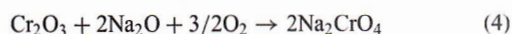


Fig. 8. Results of X-ray diffraction analysis for insulator inside and contact surface of insulator for the combination of SUS304 and insulator (C) at 773 K for 5,000 h.

the contact interface. Therefore, it was concluded that the Cr(VI) compound that occurred at the contact interface of insulator (C) was Na₂CrO₄. Accordingly, the reaction between the metal and the insulator (C) can be explained by the following equation.



Cr(VI) occurred not only for the insulator containing calcium (Ca) but also for that containing Na. However, the content of Na in insulator (C) was 7.3%. On the other hand, the content of Ca in insulators (A) and (B) was 35 and 36%, respectively. The difference between the amount of Cr(VI) that occurred with insulator (C) and that with insulator (A) and (B) could not be explained by the alkaline content.

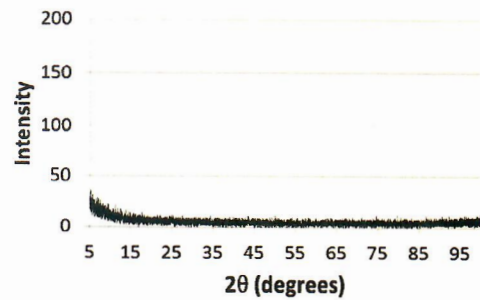


Fig. 9. Low incident angle X-ray diffraction chart for Al₂O₃-based coating film formed on SUS304 substrate heat-treated at 873 K for 10 min.

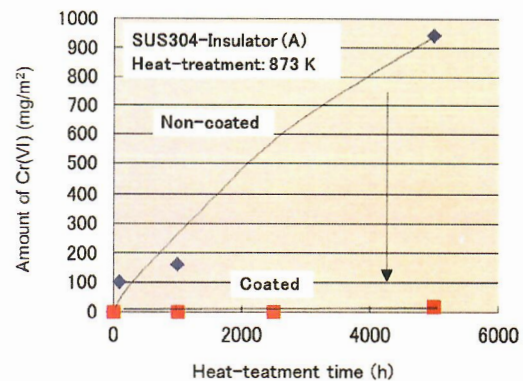


Fig. 10. Relationship between heat-treatment time and amount of Cr(VI) that occurred at 873 K for the combination of coated SUS304 and insulator (A) and the combination of non-coated SUS304 and insulator (A).

The following possibility was suggested. The amorphous phase included Na and Na in the amorphous phase was more active than Ca in the calcium silicate crystal phase. Hence, the amount of Cr(VI) that occurred with insulator (C) was much greater than that with insulators (A) and (B). However, we need to obtain additional data to explain the phenomenon.

Above discussion was based on the solid-state reactions. Stearns et al. reported that the evaporation of Cr₂O₃ in O₂ atmospheres is caused by the following reaction.²⁰⁾



Caplan et al. investigated the evaporation of Cr₂O₃ at high temperatures and his data showed that the evaporation rates of Cr₂O₃ at temperatures below 1273 K are negligibly small.^{21),22)} Therefore, it was suggested that the evaporation of Cr₂O₃ in this study was small enough as heat-treatment temperature in this work was below 873 K.

3.2 Preventing the formation of Cr(VI)

The sol-gel coating process was applied to prevent Cr(VI) formation. Al₂O₃-based sol was used for the coating process. A silicon coupling agent (C₉H₂₀O₅Si) was added to improve the adhesion of the coating film to the metal substrate.

Figure 9 shows the results of low incident angle X-ray diffraction analysis for the Al₂O₃-based coating film formed on SUS304 substrate heat-treated at 873 K for 10 min. Clear crystal phases were not detected and it was suggested that the coating film consisted of amorphous phase. Yamaguchi et al. reported that alkoxide-derived boehmite gel heat-treated at 803 K showed an

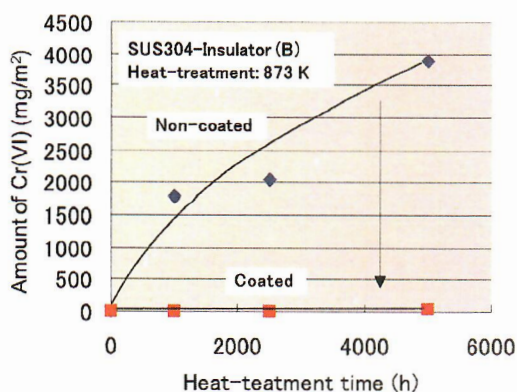


Fig. 11. Relationship between heat-treatment time and amount of Cr(VI) that occurred at 873 K for the combination of coated SUS304 and insulator (B) and the combination of non-coated SUS304 and insulator (B).

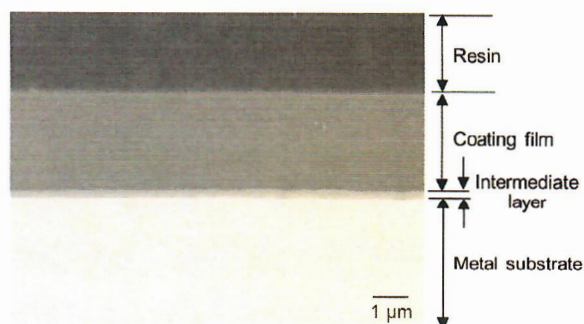


Fig. 12. Backscattered electron image of cross section for metal specimen after reaction test for the combination of coated SUS304 and insulator (B) heat-treated at 873 K for 2,500 h.

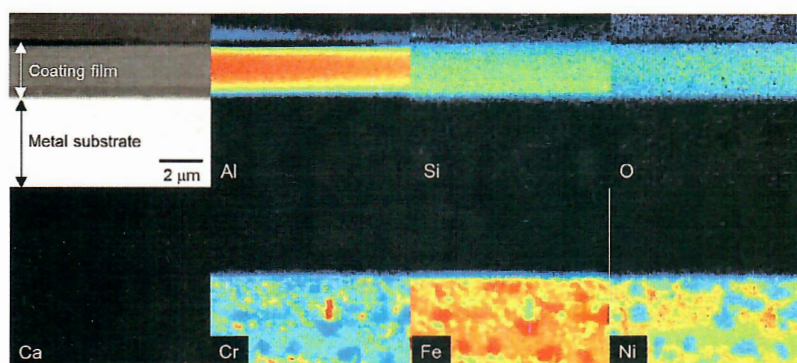


Fig. 13. EPMA analysis for cross section of metal specimen after reaction test for the combination of coated SUS304 and insulator (B) heat-treated at 873 K for 2,500 h.

amorphous phase and changed to γ -Al₂O₃ at 1008 K.²³⁾ On the other hand, Keysar et al. investigated the heat-treatment change of alkoxide-derived boehmite aerogel and concluded that the aerogel heat-treated at 873 K showed η -Al₂O₃ and changed to θ -Al₂O₃ at 1473 K.²⁴⁾ It is possible that the presence of SiO₂ prevented the crystallization of Al₂O₃ in our experiment.

The reaction test was performed to estimate the effect of coating film using SUS304 metal coated by Al₂O₃-based coating film. **Figure 10** shows the relationship between the heat-treatment time and the amount of Cr(VI) that occurred at 873 K for the combination of coated SUS304 and insulator (A) and the combination of non-coated SUS304 and insulator (A). For the combination of non-coated SUS304 and insulator (A), the amount of Cr(VI) increased as the heat-treatment time increased and the amount of Cr(VI) was 940 mg/m² for 5,000 h of heat-treatment. On the contrary, for the combination of coated SUS304 and insulator (A), the amount of Cr(VI) was negligible for all heat-treatment times. The formation of Cr(VI) was almost completely prevented by the coating film.

Figure 11 shows the relationship between heat-treatment time and the amount of Cr(VI) that occurred at 873 K for the combination of coated SUS304 and insulator (B) and the combination of non-coated SUS304 and insulator (B). The results were the same as for the combination using insulator (A). The amount of Cr(VI) increased as the heat-treatment time increased and the amount of Cr(VI) was 3,890 mg/m² for 5,000 h of heat-treatment. On the contrary, for the combination of coated SUS304 and

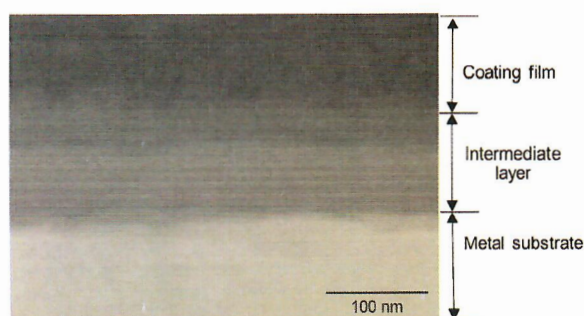


Fig. 14. HAADF-STEM image of cross section of metal specimen after reaction test for the combination of coated SUS304 and insulator (B) heat-treated at 873 K for 2,500 h.

insulator (B), the amount Cr(VI) was negligible for all heat-treatment times. The formation of Cr(VI) was almost completely prevented by the coating film. It was concluded that Al₂O₃-based coating film was effective for preventing the diffusion of Cr from the metal to the insulator and the formation of Cr(VI) compounds.

Figure 12 shows the backscattered electron image of the cross section for the metal specimen after the reaction test for the combination of coated SUS304 and insulator (B) heat-treated at 873 K for 2,500 h. The film thickness was 3–4 µm and no gaps were observed at the interface between the coating film and metal

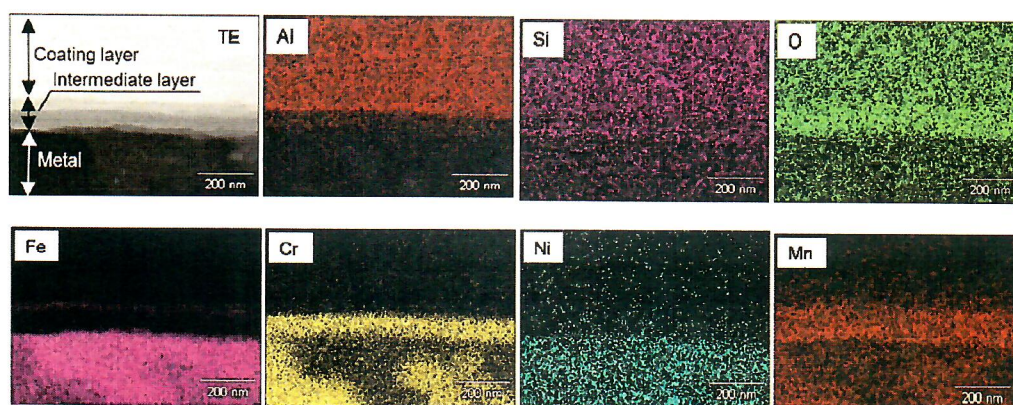


Fig. 15. EDS mapping of cross section of metal specimen after reaction test for the combination of coated SUS304 and insulator (B) heat-treated at 873 K for 2,500 h.

substrate. However, an approximately 0.1 μm intermediate layer was observed between the coating film and metal substrate. **Figure 13** shows the EMPA analysis for the same specimen. Al, Si and O elements were detected in the coating film and were dispersed uniformly in the film. It was also observed that Cr did not diffuse deeply within the film. At the interface between the metal and coating film, there was a layer containing Si and O, but no Al. The distributions of Si and O completely matched each other. It was also observed that a Cr-rich and Fe-poor thin layer had formed on the top of the metal area, and that Ni had partially segregated at this layer. Therefore, it was suggested that the intermediate layer consisted of mainly Cr, Si and O. This conjecture was supported by the fact that the electron reflectance of the intermediate layer corresponding to the average atomic weight was intermediate between that of the coating film and the metal substrate. Ca segregation was not detected and the detected signal was weak. It was considered that Ca diffusion from insulator was negligible. Details on the intermediate layer were not obtained by this analysis.

To investigate the intermediate layer in more detail, STEM observation was carried out. **Figure 14** shows an HAADF-STEM image in the vicinity of the coating film after the reaction test for the combination of coated SUS304 and insulator (B) heat-treated at 873 K for 2,500 h. The thickness of the intermediate layer was approximately 0.1 μm , and the layer consisted of two portions. The electron beam transmittance of both portions corresponding to the average atomic weight was close, suggesting that the composition of both portions of the layer was similar. **Figure 15** shows EDS mapping of the same specimen. The following results were obtained by this mapping. Al element hardly existed in the intermediate layer. Si and O uniformly existed in the layer. Fe and Ni hardly existed in the intermediate layer. Cr and Mn existed in the layer. A notable fact is that Cr was concentrated in the metal side of the intermediate layer, whereas Mn was uniformly dispersed over the entire layer. Namely, it was considered that the intermediate layer mainly consisted of Cr, Mn, Si and O. In addition, the metal side of the intermediate layer consisted of Cr, Mn, Si and O and the Al_2O_3 -based coating film side of this layer consisted of mainly Mn, Si and O. This distribution analysis can explain the fact that the intermediate layer consists of two layers as observed in the HAADF-STEM image. In any case, the intermediate layer was formed as a result of the diffusion of Cr, Mn, Si and O during heat-treatment in the reaction test. These observations confirmed that the Al_2O_3 -based coating film was effective for preventing the diffusion of Cr and the occurrence of

Cr(VI) compounds.

4. Conclusions

It was observed that Cr(VI) oxides occurred at the contact interfaces between metals and insulators at elevated temperatures. Yellowish reaction products were confirmed in the contact faces between Cr-containing metals and insulators and were identified as Cr(VI) oxides. The amount of Cr(VI) increased as the metal Cr content, heat-treatment temperature, and heat-treatment time increased. The compounds that occurred as a result of the reaction were CaCrO_4 and Na_2CrO_4 for heat-insulating materials containing Ca and Na, respectively.

The sol-gel coating process was used to prevent Cr(VI) oxides in the combination of SUS304 metal and the insulator mainly composed of Ca-Si-O. Al_2O_3 -based coating film was formed on the surfaces of metals by dipping process. It was observed that the formation of Cr(VI) was almost completely prevented by the Al_2O_3 -based coating film. It was concluded that the Al_2O_3 -based coating film was effective for suppressing the diffusion of Cr from the metal to the insulator.

References

- 1) C. C. Liu, M. K. Wang, C. S. Chiou, Y. S. Li, Y. A. Lin and S. S. Huang, *Ind. Eng. Chem. Res.*, 45, 8891–8899 (2006).
- 2) L. Dupont and E. Guillon, *Environ. Sci. Technol.*, 37, 4235–4241 (2003).
- 3) H. M. H. Gad, A. M. A. Hasan, M. A. Mahmoud and T. F. Mohammed, *International Journal of Sci. & Eng. Res.*, 5, 1796–1800 (2014).
- 4) V. K. Gupta, D. Pathania, S. Sharma and P. Singh, *J. Colloid Interface Sci.*, 401, 125–132 (2013).
- 5) H. M. H. Gad, H. A. Omar, M. H. Khalil and M. R. Hassan, *Journal of American Science*, 9, 95–106 (2013).
- 6) F. Venditti, A. Ceglie, G. Palazzo, G. Colafemmina and F. Lopez, *J. Colloid Interface Sci.*, 310, 353–361 (2007).
- 7) S. X. Li, Y. Q. Lian, J. F. Mai, J. X. Tan, S. J. Hu, W. Q. Xia and W. W. Duan, *Adv. Mater.*, 433–440, 793–797 (2012).
- 8) E. A. Ayuso, A. G. Sanchez and X. Querol, *J. Hazard. Mater.*, 142, 191–198 (2007).
- 9) Q. Zheng and W. Wang, *Br. Ceram. Trans.*, 99, 187–190 (2000).
- 10) A. Sayano, H. Kanno, S. Inagaki, M. Takahashi and M. Yoshida, Proc. IUMRS-ICA 2014, Aug. 24–30, Fukuoka, Japan, D4-P26-018 (2014).
- 11) J. Roy, N. Bandyopadhyay, S. Das and S. Maitra, *J. Eng. Sci. & Tech. Rev.*, 3, 136–141 (2010).
- 12) R. Kumar, V. Prabhakar and J. Saini, *International Journal of*