Titanium Oxide Powder Coating for High Emissivity

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The concept of energy and resource conservation are very important for every technical field. A great amount of energy is saved when the heat efficiency for industrial furnaces is increased. For this purpose, high emissive powder coating on furnace walls, such as silicon carbide, chromite etc., have been used so far. However, silicon carbide doesn=t work well at relatively high temperatures over 900"K, while chromite is not environmentally friendly because of the production of hexavalent chromium. Therefore, we focused on titanium oxide and investigated the relation between emissivity and redox behavior.

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1. INTRODUCTION

Saving resources and energy has come under close scrutiny recently, being related to environmental issues. The establishment of related technology in different fields of science and technology is required very urgently. We can reasonably expect that saving energy in industrial furnaces will lead not only to economical benefits like cost reduction, but also to saving global resources and protection of the environment.

High emissivity coating(1) is often applied to the inner wall of industrial furnaces to increase heat and energy efficiency. Silicon carbide and chromite are well known components of coating film(2). The former works well at temperatures lower than 1073"K(800"C , 1472"F). However, the absorption and emission of energy decrease very rapidly at temperatures higher than 1073K(800"C, 1472"F). On the other hand, the chromite coating doesn=t have as high an absorption or emission. Also hexavalent chromium ions, hazardous to the environment, may be produced in the process. Therefore, we examined the relation of emissivity and the structural change at high temperatures for titanium oxide, and discussed its applicability to the coating for industrial furnaces.

EXPERIMENTAL

Specimens used in this experiment were titanium oxide powder heated in a reducing atmosphere. Usually, titanium oxide like rutile, anastase etc. absorbs visible light and is almost transparent. However, once it is heated at high temperatures in a reducing atmosphere and cooled back to room temperature, it turns black, since oxygen atoms break out of the titanium oxide lattice. The non-stoichiometric titanium oxide produced through heating in a reducing atmosphere like hydrogen is called >Reduced titanium oxide=(3), (4). Some inorganic oxides like P_2O_5 or Na_2O as bond was mixed with the >reduced titanium oxide= to some extent and the mixed powder was suspended in water. This specimen was our starting material. The suspension was painted on refractory bricks and dried in 21.6ks (6hrs) at room temperature. Then they were heated to 423"K(150"C, 302"F) in 21.6ks (6hrs) in an electric furnace (Yamato FP31). For reference, conventional high emissivity coating material composed of chromite was painted on the refractory bricks and dried in the same way. The thickness of all these coatings were adjusted to 1mm (3.94H10^{-2} inch).

Firstly, the emissivity of specimens was measured by using a radiation thermometer (Chino, IR-AH), as follows. Each specimen (a refractory brick with one side painted by reduced titanium oxide) whose dimension was 110mmH110mmH 60mm (4.33 inch × 4.33 inch × 2.36 inch) was placed in a furnace (Koyo-Lindberg, 1700"C-box furnace 51314), so that the painted side was parallel to the vertical cover of the furnace. The radiation thermometer was set at the same horizontal line of the specimens in the furnace and at the distance where the radiation thermometer was focalized. The specimens were then heated. When the furnace reached the prescribed temperatures, the vertical cover of the furnace was opened and the temperatures on the surface of specimens were immediately measured by the radiation thermometer to which each emissivity was input in advance. The procedure was repeated at every 100"K from 923"K(650"C, 1202"F) to 1623"K (1350"C, 2462"F). For each measurement, the temperature of the specimen=s surface was plotted against the input emissivity. The emissivity at the maximum temperature measured for a specimen=s surface closest to the furnace temperature was fixed as the real emissivity for each furnace temperature. The emissivity of all these specimens was measured at a wavelength of 0.65ìm. The procedure to determine the emissivity at each furnace temperature is explained schematically in Fig.1.

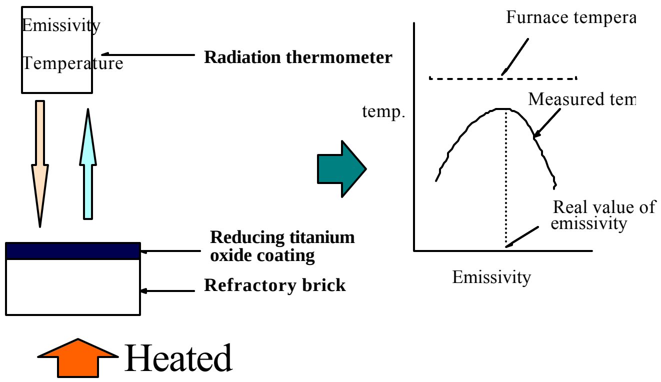

Fig.1 Schematic illustration measurement principle.

The structure of the coating was identified by X-ray Diffraction Analysis (XRD). Reduced titanium oxide was coated on another refractory brick. The dimension was 10mm (3.94inch) H10mm (3.94inch), and the thickness was 5mm (1.97inch). All of them were heated in the same electric furnace. At every 100"C from 923"K (650"C, 1202"F) to 1623"K (1350"C, 2462"F), the specimen was taken out from the furnace, cooled in air and analyzed by XRD apparatus (Rigaku, RINT2100). X-ray voltage and current for the measurement were 40kV and 20mA, respectively. Copper was used as the electrode and a monochrometer was used. The diffraction was measured at the angles 2è from 10" to 100".

RESULTS AND DISCUSSION

The relation between emissivity and temperature of the specimens at different temperatures was measured by radiation thermometer. Fig.2 shows the results at the furnace temperature of 923"K (650"C, 1202"F). The abscissa axis corresponds to emissivity and the vertical to the temperatures measured by radiation thermometer. The temperatures on the vertical axis show the measured values for the surface of the specimens, when a certain value for emissivity was postulated and entered into the radiation thermometer. The experimental results were plotted in the emissivity-temperature plane. The real value for emissivity was assumed to correspond to temperatures close to the furnace temperature. The result in Fig.2 shows the relation has bimodal peaks. However, the maximum peak was found at the

emissivity of -0.9V. Fig.3 shows results measured at the furnace temperature of 1223"K (950"C, 1742"F). The maximum peak of the real value of emissivity for the surface of the specimen was 0.92 higher than that at 923"K (650"C, 1202"F). On the other hand, the result at 1623"K (1350"C, 2462"F) shown in Fig.4 indicates that the maximum peak (0.82) moved in the direction of lower emissivity. These series of results indicate that the emissivity of titanium oxide powder coating ranged from 0.82-0.92 at temperatures from 923"K (650"C, 1202"F) to 1623"K (1350"C,

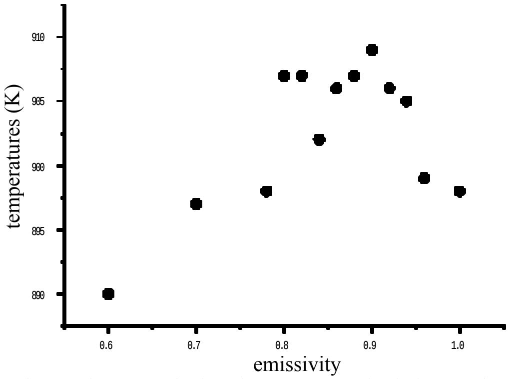

Fig.2 The correlation between emissivity and temperatures of the specimen's surface
(Furnace temperature: 923K, titanium oxide powder coating)

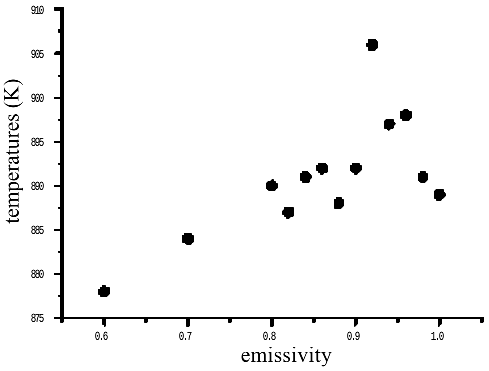

Fig.3 The correlation between emissivity and temperatures of the specimen's surface
(Furnace temperature: 1223K, titanium oxide powder coating)

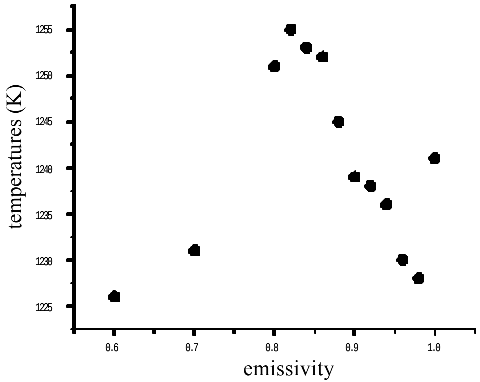

Fig.4 The correlation between emissivity and temperatures of the specimen's surface
Furnace temperature: 1623K, titanium oxide powder coating)

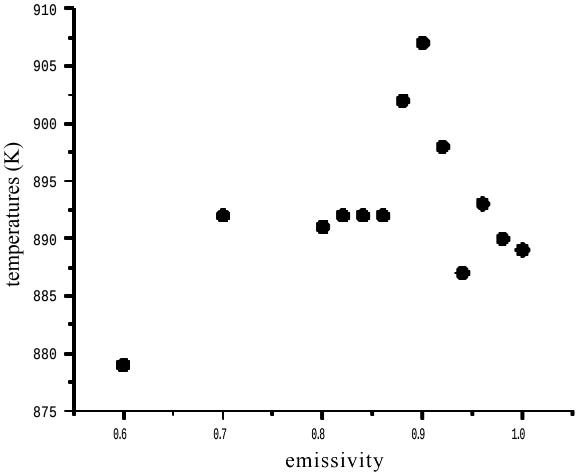

Fig.5 The correlation between emissivity and temperatures for chromite coating.
Furnace temperature: 923K)

2462"F), and emissivity decreased with an increase in temperature.

We suspect that the emissivity of titanium oxide powder coating is relatively higher than the conventional coating. We investigated the emissivity of chromite base powder coating by the same procedure. Fig.5 shows the results at the furnace temperature of 923"K (650"C, 1202"F) for the chromite based coating. The maximum peak of emissivity was 0.9, almost the same as titanium powder. On the other hand, Fig.6 shows the results at the furnace temperature of 1223"K (950"C, 1742"F). The maximum peak was located at the lower emissivity than that in Fig.5. It indicates that the emissivity at the furnace temperature of 1223"K (950"C, 1742"F) is lower than that at 923"K. Fig.7 shows the correlation between the emissivity and temperature at the furnace temperature of 1623"K (1350"C, 2462"F). The maximum peak of emissivity was 0.8, lower than both Fig.5 and Fig.6. These results for chromite-based coating indicate that the emissivity is relatively lower than that of titanium oxide power coating in the temperature range from 923"K (650"C, 1202"F) to 1623"K (1350"C, 2462"F). These results also suggest that the emissivity of chromite-based coating decreased with an increase of temperature more remarkably than that of titanium oxide coating.

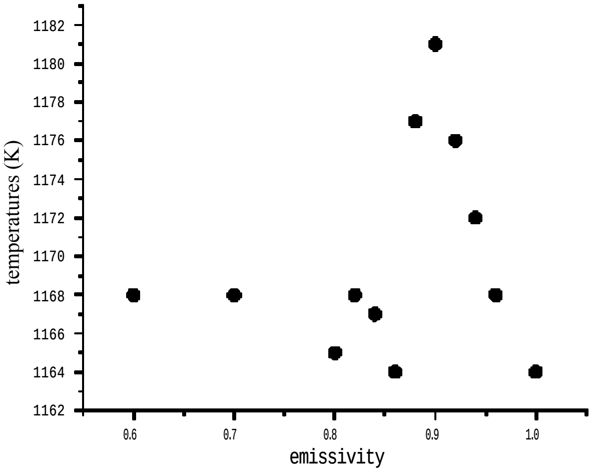

Fig.6 The correlation between emissivity and temperatures for chromite coating.
(furnace temperature: 1223K)

The emissivity of all these specimens including titanium oxide coating, chromite coating and refractory bricks as substrate was measured at temperatures from 923"K to 1723"K, as shown in Fig.8. Both titanium oxide coating and chromite coating were higher than the refractory brick as substrate. It indicates that both materials are applicable as high emissivity coating for industrial furnaces. Compared with chromite, titanium oxide coating had higher emissivity in the entire range of temperatures. Since the chromite-based coating has been utilized as practical high emissivity coating material so far, the result is highly significant for future applications. The emissivity for both coatings decreased at temperatures over 1500"K. However, the decrease of emissivity for titanium oxide coating was at higher temperatures than that of chromite-based coating.

We investigated the reasons why the titanium oxide coating is so highly emissive and at relatively higher temperatures by examining the structure of titanium oxide coating as it changes with temperatures by X-ray Diffraction Analysis (XRD).

Fig. 9 shows the result of XRD for titanium oxide coating after drying. It was derived from titanium oxide powder (TiO_2) through heating in a reducing atmosphere at 1073"K. The figure shows that the starting material was Ti_3O_5, suggesting that TiO_2 changed to Ti_3O_5 through the heating process in a reducing atmosphere. Generally, the stoichiometric compound, TiO_2 loses its oxygen atoms$^{(5)}$ through light energy as follows:

$$TiO_2\,(\text{rutile}) \xrightarrow{\text{Light energy}} TiO_{2\text{-}X} + (x/2)O_2 \qquad (1)$$

Therefore, it has attracted attention as a photocatalyst. However, titanium dioxide, TiO_2 can be also reduced by thermal energy.

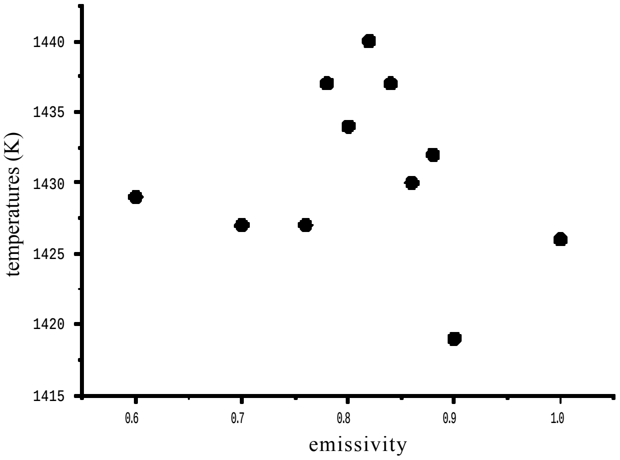

Fig.7 The correlation between emissivity and temperatures for chromite coating. (furnace temperature:1623K)

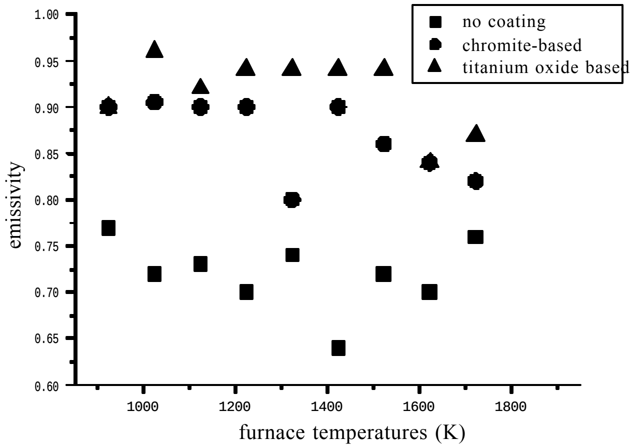

Fig.8 Emissivity of different coatings.

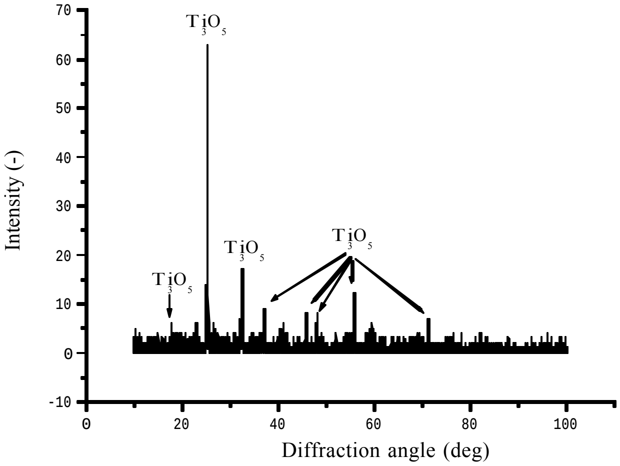

Fig.9 XRD for reducing titanium oxide.

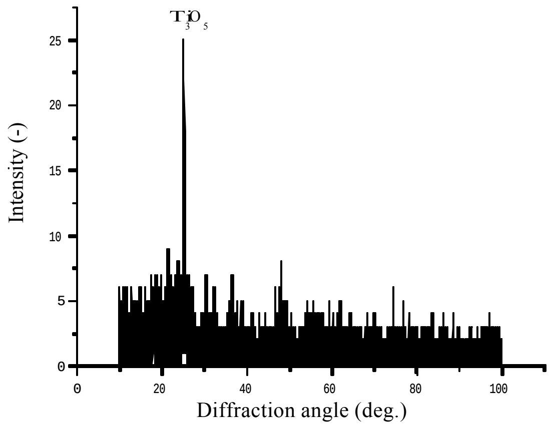

Fig.10 XRD for titanium oxide coating heated at 923K

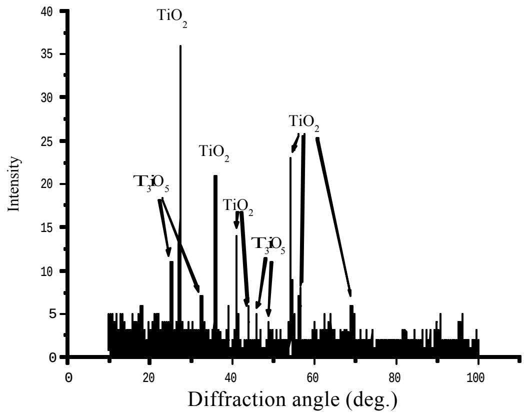

Fig.11 XRD for titanium oxide coating heated at 1123K.

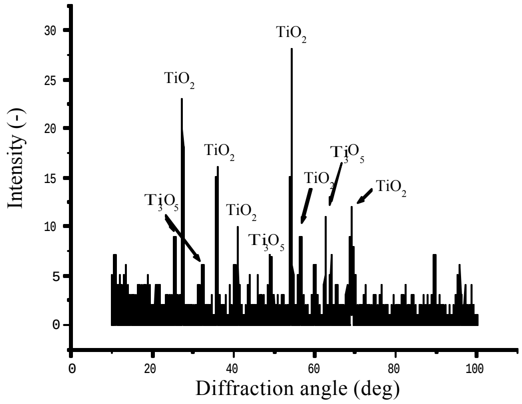

Fig.12 XRD for titanium oxide coating heated at 1523K.

$$TiO_2\,\text{(rutile)} \xrightarrow{\text{Thermal energy}} TiO_{2-X} + (x/2)O_2 \qquad (2)$$

Therefore, the reduced titanium oxide, Ti_3O_5 was formed as the starting material for our study. As mentioned already, the starting material was black, even though the rutile was generally transparent. It can be explained by the high emissivity of the reducing titanium oxide, Ti_3O_5.

Fig.10 shows the XRD for the reducing titanium oxide heated to 923"K (650"C, 1202"F). Background interference was high and the spectrum obtained in this case was unclear. However, the characteristic peak for Ti_3O_5 found at approximately 26 " was present, suggesting that Ti_3O_5 was still stable, and contributed to the high emissivity of the specimen at this temperature.

Fig.11 shows the result of XRD for the reducing titanium oxide heated to 1223"K (950"C, 1742"F). Even though Ti_3O_5 was still found in the spectrum, titanium dioxide, TiO_2 was present. The heating was carried out in the electric furnace without any regulation of atmosphere in our study. Therefore, the specimens were able to be oxidized by the ambient oxygen in the furnace. At the temperature of 1223"K (950"C, 1742"F), oxidation of Ti_3O_5 occurred to some extent.

Fig.12 shows the XRD for the specimen heated to 1523"K (1250"C, 2282"F). Ti_3O_5 was present, suggesting that Ti_3O_5 was still stable at such a high temperature, even under the oxidizing atmosphere. However, characteristics peaks for titanium dioxide (TiO_2) were found at both 28" and 53", as well as other angles.

All of these XRD results explain why the specimen had the relatively high emissivity at higher temperatures, compared with chromite-based coating and the substrate refractory bricks. The existence of Ti_3O_5 was the key reason for the high emissivity of the specimen. Even though it was oxidized and changed to TiO_2 to some extent, Ti_3O_5 was relatively stable at higher temperatures. We presume that the oxygen deficiency in the crystal lattice of titanium oxide is unable to be filled with fully through the re-oxidizing process at higher temperatures. We also presume that there are many oxygen deficient sites in the specimens, which lead to the high emissivity at relatively higher temperatures.

Regarding the application of the coating to practical industrial furnaces, such as blast furnace or oil plants, the percentage and partial pressure of oxygen are usually much lower than those in our experiment. Therefore, the stability of Ti_3O_5, which plays a key role in high emissivity, will be much higher. Itt will ensure the heat retaining property of industrial furnaces will save energy, leading to cost reduction.

CONCLUSIONS

We investigated the emissivity of the reducing titanium oxide coating and the change in structure with temperature change by X-ray Diffraction Analysis. Compared with the conventional chromite- based coating, titanium oxide coating had higher emissivity at temperatures from 923"K (650"C, 1202"F) to 1723"K (1450"C, 2642"F). The high emissivity was maintained, even at higher temperatures. X-ray Diffraction Analysis indicated that the starting material was mainly composed of Ti_3O_5 and was still found even at higher temperatures. Ti_3O_5 played a key role in the high emissivity of the reducing titanium oxide coating. In our experiment, the atmosphere was not regulated through the heating process in the electric furnace. Therefore, the specimens were oxidized to some extent and TiO_2 was produced. However, it didn=t lead to a significant decrease of emissivity. From the practical viewpoint, the industrial furnace often has a reducing atmosphere, therefore, Ti_3O_5 will be maintained in higher percentages and will be much more stable at higher temperatures.

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