Emissivity of Titanium Oxide Powder Coating & Its Structure

by H. Kanematsu*, N. Wada, & T. Oki

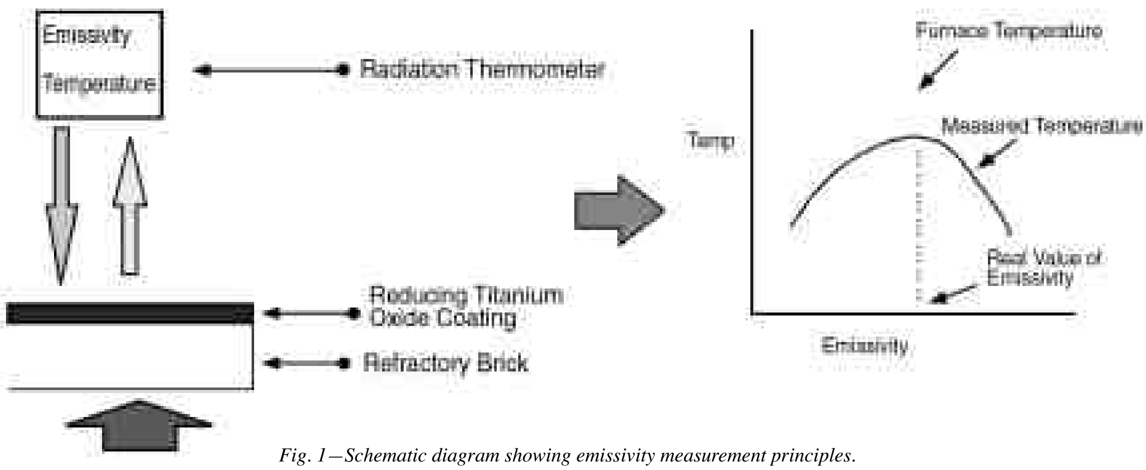

Fig. 1—Schematic diagram showing emissivity measurement principles.

The concepts of energy and resource conservation are very important every technical field. A great amount of energy is saved when the heat efficiency of industrial furnaces is increased. To this end, the application of highly emissive powder coatings, such as silicon carbide or chromites, on furnace walls, has been successful to date. However, silicon carbide doesn't work well at temperatures above 800°C (1472°F), while chromite is not environmentally friendly, because of the hexavalent chromium factor. Therefore, we focused on titanium oxide as an alternative and investigated the relation between emissivity and redox behavior.

Resources and energy conservation have recently come under close scrutiny because of environmental issues. The Kyoto Protocol and other worldwide environmental policies now require increased energy efficiency in heating furnaces, steel converters and the like and decreased green house emissions from the use of fossil fuels.

With such considerations in mind, the following materials research topics are likely to be pursued: (1) the development of materials to lower the use ratio of fossil fuels, (2) the development of materials inhibiting the production of green house gases (CO_2) or decomposing them, (3) environmentally friendly materials free from hazardous elements such as lead or chromium. Therefore, the development of high emissivity coating materials for industrial furnaces must also take these considerations into account.

High emissivity coatings[1] are often applied to the inner walls of industrial furnaces to increase heat and energy efficiency. Silicon carbide and chromite coatings are well known.[2] Silicon carbide works well at temperatures below 800°C (1472°F). However, the absorption and emission of energy decrease very rapidly above this temperature. On the other hand, the chromite coating lacks the high absorption or emission properties of silicon carbide. Further, hexavalent chromium ions, hazardous to the environment, may be produced during the process. In considering alternatives, therefore, we examined the relation of emissivity to the structural change at high temperatures for titanium oxide, and considered its applicability to industrial furnace coatings.

Nuts & Bolts: What This Paper Means to You

Instead of discussing a process, this paper deals with the properties of a sintered powder coating application. Energy and resource conservation are very important today. Considerable energy is saved when the heat efficiency of industrial furnaces is increased. To this end, the application of highly emissive powder coatings (such as silicon carbide or chromites) on furnace walls, has been successful. However, silicon carbide doesn't work well at temperatures above 800°C (1472°F), while chromite is not environmentally friendly, because of the hexavalent chromium factor. Therefore, we focused on titanium oxide as an alternative and investigated the relationship between its emissivity and structure.

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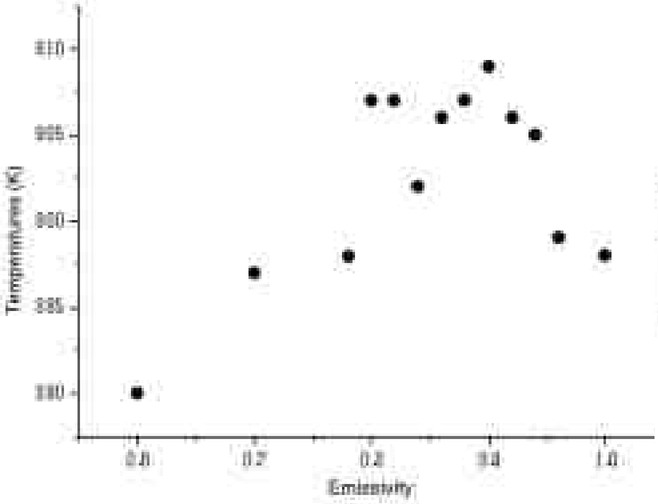

Fig. 2—Correlation between emissivity and surface temperature—titania powder coating (Furnace temperature = 650°C (1202°F).

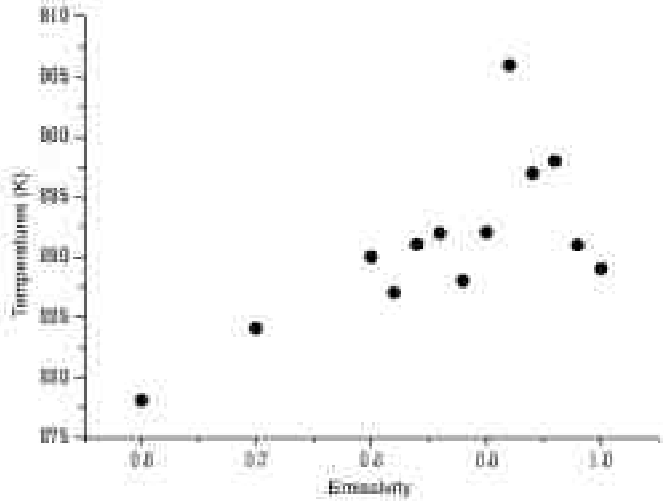

Fig. 3—Correlation between emissivity and surface temperature—titania powder coating (Furnace temperature = 950°C (1742°F).

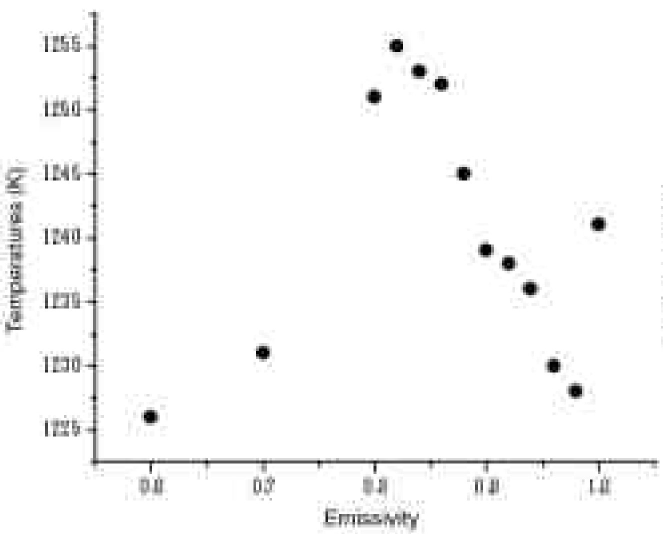

Fig. 4—Correlation between emissivity and surface temperature—titania powder coating (Furnace temperature = 1350°C (2462°F).

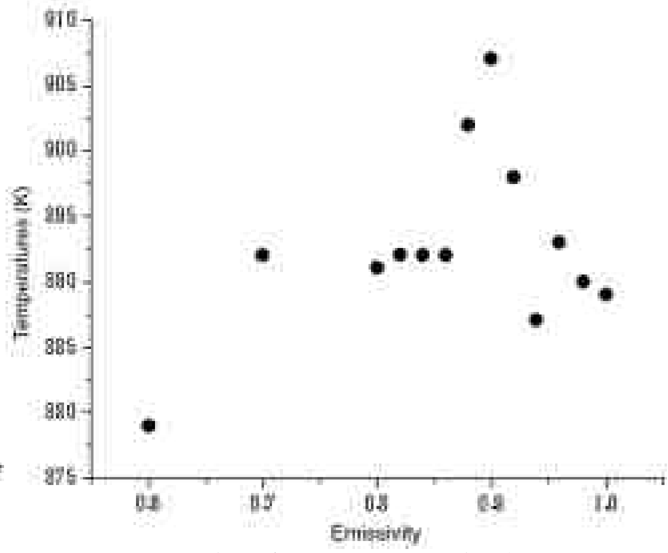

Fig. 5—Correlation between emissivity and surface temperature—chromite coating (Furnace temperature = 650°C (1202°F).

Experimental

Specimens used in this work consisted of titanium oxide powder heated in a reducing atmosphere. Usually, titanium oxide, like rutile or anastase, absorbs visible light and is almost transparent. However, once it is heated at high temperature 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] Certain inorganic oxides such as P_2O_5 or Na_2O were used as bonding agents and mixed with the "reduced titanium oxide." The mixed powder was suspended in water. This was our starting material. The suspension was painted on refractory bricks and dried for six hours at room temperature. They were then heated to 150°C (302°F) for six hours in an electric furnace. For a reference, a conventional high emissivity chromite coating was painted on other refractory bricks and dried in the same way. The thickness of all these coatings was 1 mm (39.4 mils).

The emissivity at each temperature was measured by using a radiation thermometer, shown schematically in Fig. 1. Each specimen (a refractory brick with one side painted with reduced titanium oxide) whose dimension was 11 x 11 x 6 cm (4.33 x 4.33 x 2.36 in.) was placed in a furnace such that the painted side was parallel to the vertical cover of the furnace. The radiation thermometer was set on the same horizontal plane as the specimens in the furnace and at the distance where the radiation thermometer was focused. The specimens were then heated. When the furnace reached the prescribed temperature, the vertical cover of the furnace was opened and the temperature on the surface of the specimens was immediately measured by the radiation thermometer to which each emissivity value was input in advance. The procedure was repeated at intervals of 100 Celsius degrees (C°) from 650°C to 1350°C (1202°F to 2462°F). For each measurement, the surface temperature was plotted versus the input emissivity. The emissivity at the maximum temperature measured for a specimen surface closest to the furnace temperature was fixed as the real emissivity for each furnace temperature. The emissivity of all specimens was measured at a wavelength of 0.65 μm.

The structure of the coating was determined by x-ray diffraction (XRD). Reduced titanium oxide was coated on another refractory brick, 10 x 10 x 5 cm (3.94 x 3.94 x 1.97 in.). All were heated in the same electric furnace. At intervals of 100 C° from 650°C to 1350°C (1202°F to 2462°F), the specimen was removed from the furnace, cooled in air and analyzed by XRD. The X-ray voltage

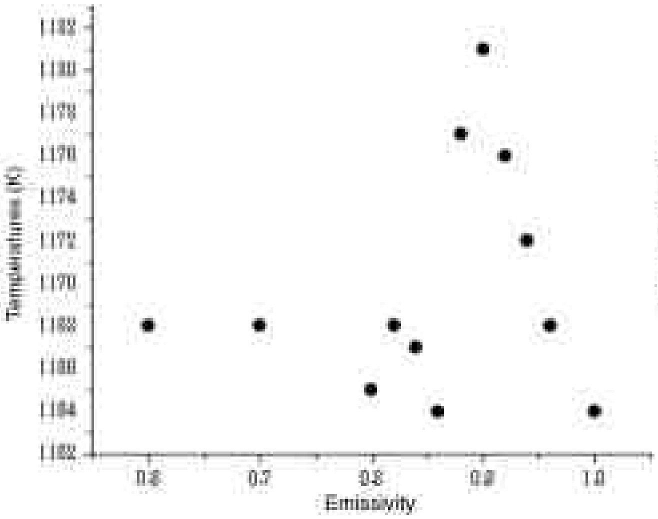

Fig. 6—Correlation between emissivity and surface temperature—chromite coating (Furnace temperature = 950°C (1742°F).

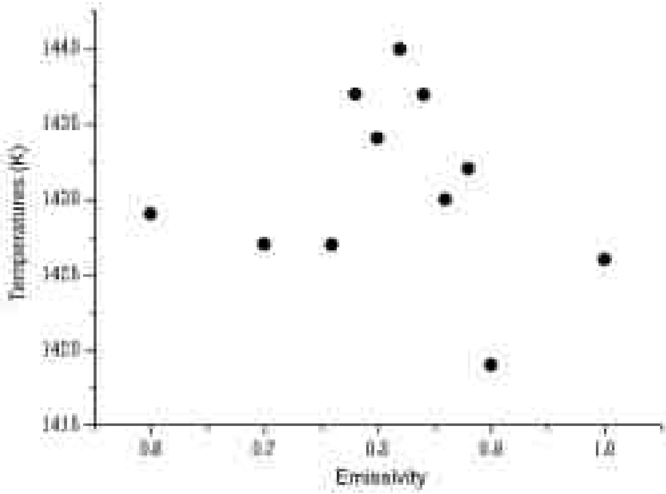

Fig. 7—Correlation between emissivity and surface temperature—chromite coating (Furnace temperature = 1350°C (2462°F).

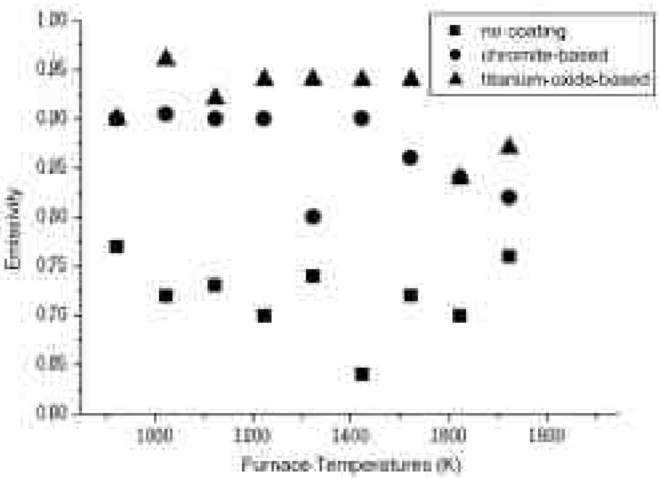

Fig. 8—Emissivity of different coatings.

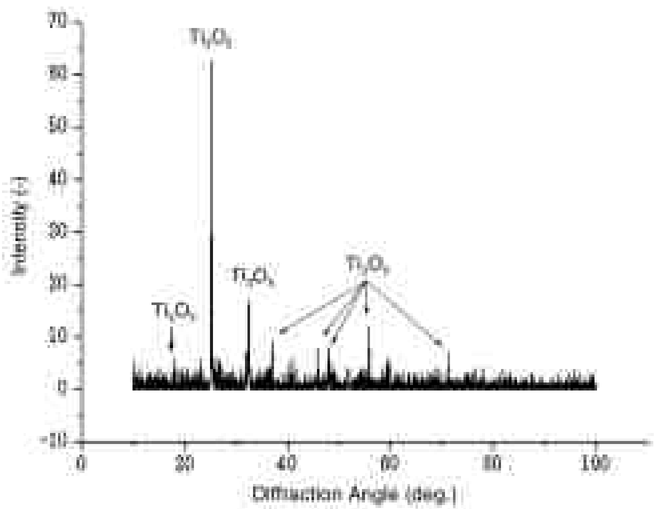

Fig. 9—X-ray diffraction results for reducing titanium oxide.

and current for the measurement were 40 kV and 20 mA, respectively. Copper was used as the electrode and a monochrometer was used. The diffraction was measured at 2ℵangles from 10° to 100°.

Results & Discussion

The relation between emissivity and temperature of the specimens at different temperatures was measured by the radiation thermometer. Figure 2 shows the results at the furnace temperature of 650°C (1202°F). The x-axis corresponds to emissivity and the y-axis reflects the surface temperatures. 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 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 -0.9 V. Figure 3 shows results measured at the furnace temperature of 950°C (1742°F). The maximum peak of the real value of emissivity was 0.92 higher than at 650°C (1202°F). On the other hand, the result at 1350°C (2462°F) shown in Fig. 4 indicates that the maximum peak (0.82) moved in the direction of lower emissivity. These results indicate that the emissivity of titanium oxide powder coating ranged from 0.82 to 0.92 at temperatures from 650°C to 1350°C (1202°F to 2462°F), and emissivity decreased with increasing temperature.

We anticipated that the emissivity of the titanium oxide powder coating would be higher than that of the conventional coating. Accordingly, we investigated the emissivity of a chromite-based powder coating by the same procedure. Figure 5 shows the results at a furnace temperature of 650°C (1202°F) for the chromite-based coating. The maximum emissivity peak was 0.9, almost the same as for the titanium powder. Figure 6 shows the results at the furnace temperature of 950°C (1742°F). The maximum peak was located at a lower emissivity value than that in Fig. 5. The emissivity at 950°C (1742°F) was lower than that at 650°C (1202°F). Figure 7 shows the correlation between the emissivity and temperature at the furnace temperature of 1350°C (2462°F). The maximum emissivity was 0.8, lower than the results shown in both Figs. 5 and 6. These results for chromite-based coating indicate that the emissivity was lower than that of titanium oxide in the temperature range from 650°C to 1350°C (1202°F to 2462°F). These results also show that the emissivity of the chromite-based coating decreased faster with increasing temperature than did the titanium oxide coating.

The emissivity of all these specimens titanium oxide coating, chromite coating and uncoated refractory bricks was measured at temperatures from 650°C to 1450°C (1202°F to 2642°F), as shown in Fig. 8. Both the titanium oxide and chromite coating emissivity values were higher than that of the uncoated refractory brick. This indicates that both materials were appropriate for high emissivity coatings for industrial furnaces. Compared with chromite, the titanium oxide coating had a higher emissivity over the entire range of temperatures. Since chromite-based coatings have already been used in practice, the result is highly significant for future applications. The emissivity for both coatings decreased at temperatures over 1227°C (2240°F). However, the decrease of emissivity for the titanium oxide coating occurred at higher temperatures than that for the chromite-based coating.

We considered the reasons why the titanium oxide coating was so highly emissive and at the higher temperatures, relative to the chromite coating, by examining the changes in the structure of the titanium oxide coating with temperature by x-ray diffraction.

Figure 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 800°C (1472°F). 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:

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

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

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

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

Figure 10 shows the XRD results for the reducing titanium oxide heated to 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 2ℵ= 26°was present, suggesting that Ti_3O_5 was still stable, and contributed to the high emissivity of the specimen at this temperature.

Figure 11 shows the XRD results for the reducing titanium oxide heated to 950°C (1742°F). Although Ti_3O_5 was still found in the spectrum, titanium dioxide, TiO_2 was present. In this study, heating was carried out in the electric furnace with no regulation of the atmosphere. Therefore, the specimens could be oxidized by the ambient oxygen in the furnace. At 950°C (1742°F), oxidation of Ti_3O_5 occurred to some extent.

Figure 12 shows the XRD results for the specimen heated to 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 2ℵvalues of 28° and 53°, as well as other angles.

All of these XRD results explain why the specimen exhibited relatively high emissivity at higher temperatures, when compared with chromite-based coating and the substrate refractory bricks. The existence of Ti_3O_5 was the key reason for this high emissivity. Even though it was oxidized and to some extent changed to TiO_2, the Ti_3O_5 was relatively stable at higher temperatures. We presume that the oxygen deficiency in the crystal lattice of titanium oxide could not be completely filled through the re-oxidizing process at the higher temperatures. We also presume that there are many oxygen deficient sites in the specimens, leading to the high emissivity at relatively higher temperatures.

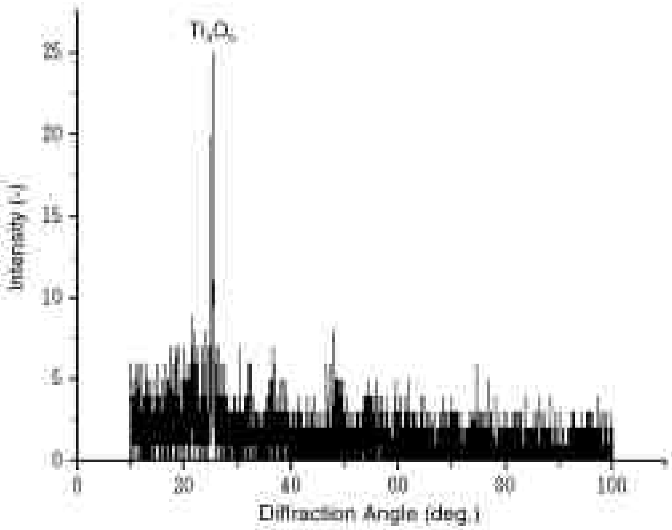

Fig. 10—X-ray diffraction results for titanium oxide coating heated at 650°C (1202°F).

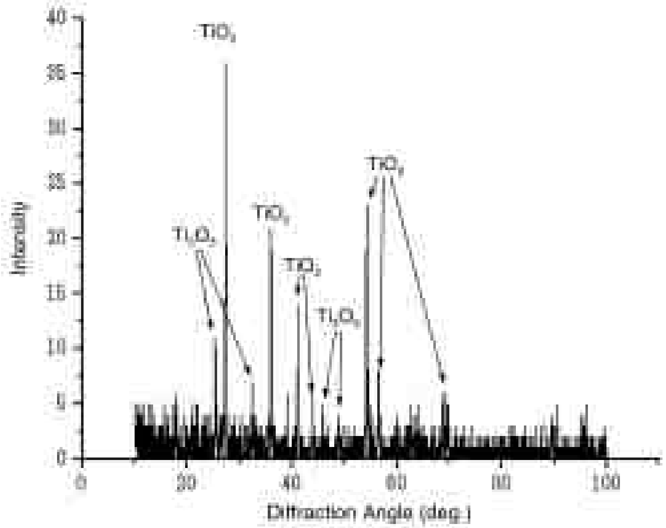

Fig. 11—X-ray diffraction results for titanium oxide coating heated at 850°C (1562°F).

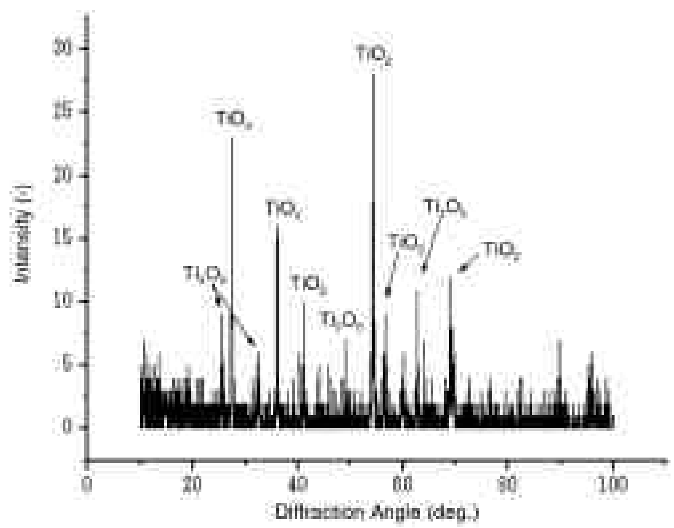

Fig. 12—X-ray diffraction results for titanium oxide coating heated at 1250°C (2282°F).

Regarding 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. It will ensure that the heat retaining properties of such 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 to the conventional chromite-based coating, the titanium oxide coating had a higher emissivity at temperatures from 650°C to 1450°C (1202°F to 2642°F). The high emissivity was maintained, even at higher temperatures. X-ray diffraction indicated that the starting material was mainly composed of Ti_3O_5 which was still found at higher temperatures. Ti_3O_5 played a key role in the high emissivity of the reducing titanium oxide coating. In our experiments, 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 did not produce a significant decrease of emissivity. From the practical viewpoint, the industrial furnace often has a reducing atmosphere, therefore, high Ti_3O_5 content should be maintained and will be stable at higher temperatures.

Acknowledgement

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