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New concept cracking tubes for ethylene plant in a petrochemical industry

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Alumina-forming materials are next generation materials used in petrochemical industry for ethylene cracking tubes. Carbon deposited on internal surface of the cracking tube in the process of thermal cracking of hydrocarbon during operation causes material degradation problem due to significant carburization and blockage caused by decrease of the tube inner diameter. Therefore, authors developed the technology to form dense alumina film with high purity on the internal surface of cracking tubes by alloy composition and optimizing of the generation of oxide film for material protection. This material has the ability to generate a stable aluminum film at high temperatures, it also possesses far greater resistance to oxidation and carburization. Tests performed in the recent years by domestic and international petrochemical manufacturers with actual furnaces confirmed excellent performance of the material and it is focus of attention from the industry.

***Keywords**: Ethylene, Cracking tube, Carbon, Alumina, Thermal decomposition, Oxide film*

1. Introduction

The cracking tubes for the ethylene plant in a petrochemical industry are used in high temperature condition of more than 1000°C. During the operation, coke formation occurs at tube inside by thermal cracking of hydrocarbon. This coke formation at high temperature causes carburization at tube material. Therefore, the heat-resistant alloys that have good oxidation resistance and carburization resistance are applied as cracking tube material. Generally, a chromium oxide film to be formed on the surface during operation prevents carburization of base metal, but a chromium oxide film isn't stable in the severe high temperature. Therefore, we focused on an aluminum oxide film which is more stable at the severe condition. Based on the results of the experiment, we have developed the new concept cracking tube that generate a high purity alumina oxide film on the inside surface.

In addition to the investigation of the oxide film produced on the test material described above, its oxidation resistance and carburization resistance were evaluated and good results were observed.

2. Experimental method

2.1 Material under test

The composition of conventional cracking tube material is 35Cr-45Ni. On the other hand, development material is 25Cr-35Ni-Al. Authors tested materials 35AF and 45A shown in the table 1. Samples were manufactured by using a centrifugal casting process, and test sample was taken for analysis from the thick central part of the casted body. Chemical composition analysis was performed by using a spark optical emission spectrometer.

Table 1 Component of the material(mass%)

	C	Cr	Ni	Al	Fe	other
Development material (35AF)	0.4/0.6	22/28	29/37	2.0/4.0	Bal.	Add
Conventional material (35Cr-45Ni：45A)	0.4/0.6	30/35	40/46	＜0.5	Bal.	—

2.2 Oxide film analysis

Analysis of the components and composition of the oxide film produced on test material was performed by observation of its cross-section with using EPMA. To identify internal structure of the sample it was analyzed from surface to the center using a XDR method.

2.3 Oxidation resistance test

To evaluate the oxidation characteristics sample was subjected to 10 hours cyclic oxidation tests. During the cyclic oxidation test sample was heated from room temperature to 1050°C in air atmosphere, subjected to 10 hours hold and cooled to the room temperature using air cooling. This process was repeated 50 times. Evalution based on weight change measurement and surface observation.

2.4 Carburization resistance test

Carburizing properties were evaluated using gas carburizing tests.During the gas carburization test sample was held in a mixed CH_4 and H_2 atmosphere in a gas ring furnace at 980°C for 200 hours, and carbon weight increase on outer surface of the sample was measured in arbitrary points.

3. Test results and considerations

3.1 Oxide film analysis

Film observation results are shown on the Figs 1, 2. The result of mapping analysis by EPMA conducted to determine the composition of the oxide film showed that oxide film on the surface of the conventional material based from Cr oxide, while the oxide film on the developed material contained Al oxide (Fig. 1). Further results of XRD measurements showed that the oxide film of the new material composed from α-alumina (Fig. 2).

It can be surmised that for each of the oxide films the generated oxide film is grown by internal diffusion of oxygen. Thus, we can suppose that because α-alumina oxide is denser than Cr oxide, it suppresses the internal diffusion of oxygen, and alumina oxide film became thinner.

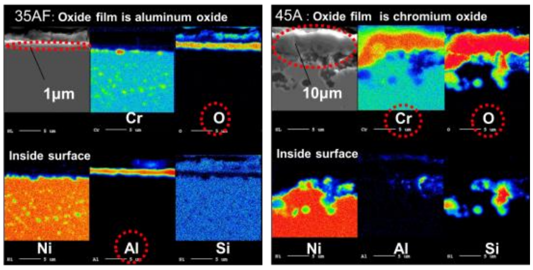

Fig.1 Cross-sectional observation of the oxide film

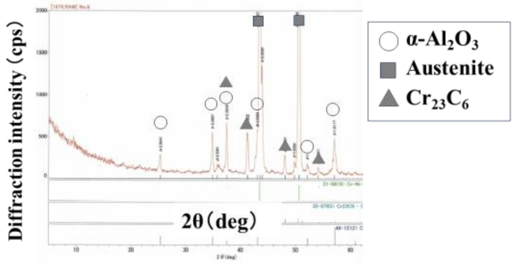

Fig.2 XRD diffraction results of the oxide film

3.2 Oxidation resistance test

Cyclyic oxidation test results are shown on the Figs 3. Even though the significant decrease in the weight of the conventional material was observed, in the newly developed material a little weight increase was detected. From the appearance of test samples, conventional material exhibited peeling of the oxide film, but new material showed almost no peeling. We considered the peeling mechanism as follows. First, the oxide film is swelled by intermittent oxidation. Next, on cooling, a shock on the oxide film is given due to a difference in thermal stress of the base material. These occurs repeatedly, and the oxide film is peeling.

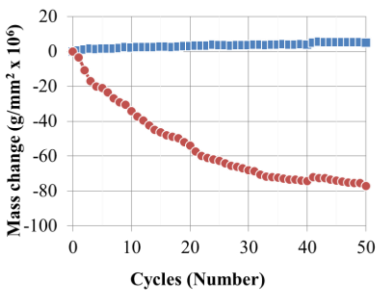

Fig.3 Results of cyclic oxidation test

3.3 Carburization resistance test

Carburization resistance test results are shown on the Figs 4. From the results of gas carburizing test, while the conventional material showed carburization from the surface, in the developed material almost no carburization was found (Fig. 4). It can be explained that because Cr oxide film generated on surface of the conventional material is less dense than the Al oxide film produced on surface of the developed material, carbon penetrates the Cr oxide which causes carburization. Because Al oxide prevents carbon penetration, carburization does not occur. Additionally, whereas in move severe conditions carburization in the conventional material accelerated, in new material carburization speed did not change.

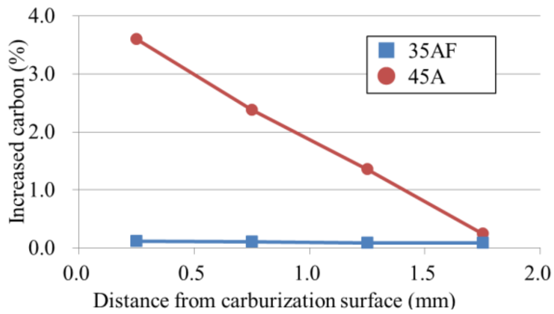

Fig.4 Results of gas carburization test

4. Conclusion

By analyzing the oxide film generated on the internal surface of cracking tubes and performing oxidation resistance and carburizing resistance tests, the following results were obtained.

(1) From the observation of the oxide film generated on the developed material, the film was identified as α-alumina by XRD measurements.

(2) Oxidation test results showed that Cr oxide film on conventional material becomes unstable at the high temperature exhibiting swelling and peeling. On the other hand, Al oxide film on the developed material showed almost no peeling and kept stability at the high temperature.

(3) Carburization test results showed that Al oxide film produced on the developed material performs well at the test temperature and indicates much less carburization comparing to Cr oxide film generated on the conventional material.