Physical Properties of Ceramic Layer Prepared by SHS in Centrifugal Field

Jaeryeong Lee¹, M. T. Le²,³ and H. S. Chung²

¹Department Geosystem Engineering, Kangwon National University, Chuncheon, Kangwon-do 200-701, Korea
²Division Minerals and Materials Processing, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Korea
³Department Materials Science and Engineering, Chungnam National University, Daejeon 305-764, Korea

The self-propagating reaction under centrifugal force has been proposed for the ceramic coating on a hollow body. When a SHS or thermit mixture is filled in a steel pipe and ignited to combust, a molten ceramic and metal from exothermic combustion reaction can be separated in layers by virtue of their density difference under centrifugal force. Consequently, there are a ceramic layer at the innermost side and an intermediate iron layer between the ceramic layer and steel pipe inner surface. The reaction formula of the Fe₃O₄-Al system is as follows: \( \text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} \), \( \Delta H = -836 \text{kJ/mol} \).

The centrifugal SHS process is effective technique to make a thick ceramic lining layer (>1 mm) on the inner surface of pipe. As the result, the lined pipe is expected to have advantages of wear-, corrosion-, thermal shock-, and mechanical shock resistance. Especially, the discrete gradient of composition, high density, and the mosaic-typed microstructure in the lining layer are determinative factors to improve durability against sever operating environment. To prepare the lining with these properties mentioned above, many researches have been carried out with the change of conditions in the centrifugal SHS process.

The mixture was input into a carbon steel pipe with an inner diameter of 54 mm and a wall thickness of 3 mm. The length of the pipe is 300 mm. The pipe together with reactant was settled at a horizontal centrifuge rotating about its axis. The rotation speed was adjusted to 110 G (G: the acceleration due to gravity), and the mixture was ignited with a tungsten filament as its end. After the completion of reaction, rotation was continued for a few minutes to cool the composite pipe.

The pieces of the ceramic layer (1 mm × 1 mm size) were taken out for SEM observation (JSM-6380LA, JEOL). The density of the ceramic layer is measured by the Archimedes method. The phase composition of the ceramic layer is identified by X-ray diffraction (Rotaflex Ru-200B Cu Ka, Rigaku). Its hardness is measured by the Vickers method (Hardness tester, MVK-E, Akashi).

3. Results and Discussion

3.1 Composition

Typical X-ray diffraction patterns of the ceramic layers prepared by the centrifugal SHS process are shown in Fig. 1. Major intensity peaks of corundum (α-Al₂O₃) and hercynite (FeAl₂O₄) only appear and other crystal forms are not detected. The mixture was investigated with the change of filling ratio (thermit mixture, Fe₂O₃ and Al) and the addition of silica. The apparent density and hardness of the ceramic layer were improved from 2.9 g/cm³ to 3.7 g/cm³ and 1,700 Hv with the effect of additive, silica.

Fig. 1 XRD pattern of ceramic layers prepared at 40% filling ratio (a) without quartz (b) with 4% quartz.
detected. It is also found that there are essentially the same XRD patterns between two ceramic layers synthesized (a) with and (b) without the addition of quartz.

Interestingly, any specific signs of silicon-based crystals are not found in Fig. 1(b). In other words, it is believed that the introduction of quartz mainly contributed to the formation of amorphous silicates in the ceramic layer even though there are some possibilities of the silicon inclusion in the corundum and hercynite structures.

In addition, any intensity peaks of iron metal are not seen in the Figure. It indicates that iron is well segregated from the ceramic layer by centrifugation, which is also confirmed under a scanning electron microscope.

3.2 Apparent density and hardness

While the centrifugal machine rotates at a preset revolution, a tunnel forms in the thermit powder mixture bulk filled in a steel pipe. After the ignition, the combustion reaction propagates throughout the tunnel in a few seconds. The molten material produced at over 3,000°C by the exothermic combustion will move very quickly towards the steel pipe surface. Despite a strong centrifugal force, some gases evolved may not escape from the melt and lower the density of the ceramic layer, since solidification process in the course of cooling takes place very quickly.

Figures 2 and 3 show apparent densities of the ceramic specimens prepared at different experimental conditions. The filling ratio herein refers to the ratio of the weight of the thermit material filled in a steel pipe to the weight of the steel pipe.

In Fig. 2, the apparent densities range from 2.8 to 3.0 g/cm³ for the ceramic layers prepared at the filling ratios in the 20–50% range without a silica additive, while 3.6–3.75 g/cm³ for the ones with 4% silica in the thermit mixtures. Herein, a rotation speed is set at 2,000 rpm which is sufficient for the dense layer.

In Fig. 3, the apparent densities range from 2.8 to 3.0 g/cm³ for the ceramic layers prepared at the filling ratios in the 20–50% range without a silica additive, while 3.6–3.75 g/cm³ for the ones with 4% silica in the thermit mixtures. Herein, a rotation speed is set at 2,000 rpm which is sufficient for the dense layer.

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is the innermost ceramic layer exposed. In the micrographs taken in the mode of back scattered electron diffraction, the grey phase is corundum ($\alpha$-Al$_2$O$_3$) and the white one between the $\alpha$-Al$_2$O$_3$ phases is FeAl$_2$O$_4$. The black images in the specimens indicate pores. A distinct feature can be observed: the grain size of corundum becomes larger as the image point moves towards the open side, and as the filling ratio increases.

An adiabatic combustion temperature of the thermit reaction between Fe$_2$O$_3$ and Al is about 3,480°C which is much higher than the melting temperatures of corundum ($T_m = 2,030^\circ$C) and iron ($T_m = 1,536^\circ$C). After the reaction completes, the molten corundum and iron separate each other under centrifugal force.

Most of the generated heat releases to open environment through the circumference of steel pipe and thus the temperature gradient mainly directs along the radius of the pipe. Within about 20 seconds after completing the reaction, the temperature in the thermit layer drops very quickly down to 1,000°C at which most of major solidification processes are believed to stop. Therefore, the size and shape of grains within the ceramic layer will significantly vary, depending upon their locations.

As for the ceramic layer, corundum nucleates first upon cooling down and grows towards the liquid phase since the melting temperature of corundum is higher than that of FeAl$_2$O$_4$ ($T_m = 1,780^\circ$C). Then, it is believed that FeAl$_2$O$_4$ preferably begins to form on the boundary of $\alpha$-Al$_2$O$_3$ grains. As shown in Fig. 5, the corundum grains on the inner side of the layer as well as at the higher filling ratio of the thermit mixture are larger than in other conditions, which is due to keeping temperature high longer.

There is a band of very fine equiaxed grains of corundum near the inner edge of the ceramic layer as shown on the left side of the images in Fig. 5(a-1) and 5(b-1), which is seemingly caused by rapid heat dissipation through the steel pipe wall. In addition, it can be seen that corundum grains grow in columnar shape towards the inner part right after the equiaxed grain band nearly along the radial direction of heat conduction during the prolonged time of cooling.

Figure 5(a-2) and Figure 5(b-2) show the SEM images of the ceramic layers in the middle. Corundum grains in Fig. 5(a-2) clearly show columnar shape with high aspect ratio, but they in Fig. 5(b-2) are larger in size and less columnar in shape, which can be explained with cooling rate differences. Furthermore, it is noted that the SEM images of
the open surface of the ceramic layers in Fig. 5(a-3) and Fig. 5(b-3) show large and irregular shape corundum grains. This is thought that corundum grains first grow in the melt state and then are sintered for further enlargement at low cooling rates.

3.4 Microstructure with quartz

According to Fig. 6, micrographs of the ceramic layers prepared with the thermit mixtures containing different amounts of quartz, it is noticed that the microstructures with and without quartz are quite different each other. As shown in Fig. 6(a) for the case of no quartz, corundum grains in irregularly granulated shape with large pores are common even though dendritic ones are occasionally found. However, dense microstructure of the layers with dendritic grains is dominantly formed as shown in Fig. 6(b)–6(d) with a small amount of quartz, which is well agreed with the density measurements of Fig. 2. It is also noted in the photos that the dendritic structure of alumina becomes finer with the increase of the SiO₂ addition.

After the combustion reaction completes, the temperature of molten products cools down. However, it is expected that a low melting or solidification temperature of the silicate amorphous composition formed from the SiO₂-Al₂O₃-FeO system certainly keeps its liquid phase state for a long time in the course of cooling, providing a great effect on the produced grains growth and the ceramic layer microstructure under centrifugal force.

Any XRD intensity peaks of silicon or silicate crystal are not found as shown in Fig. 1. In other words, silicon based compounds exist most likely in an amorphous form. Therefore, it is believed that they enhance the fluidity of the melt, promoting the arrangement of Al₂O₃ and FeAl₂O₄ crystalline minerals and the exclusion of evolved gases in the ceramic layer.

4. Conclusions

A steel pipe inner surface can be densely ceramic-lined by the SHS process with aluminum, iron oxide and quartz in a steel pipe rotating under centrifugal force. The ceramic layer is mainly composed of α-Al₂O₃ and FeAl₂O₄ crystalline materials. The size of corundum grains becomes larger towards the pipe innermost side with higher filling of thermit mixtures. Amorphous materials produced by the addition of quartz to the SHS mixture enhance the fluidity of the melt, resulting in highly dense ceramic layer in conjunction with dendritic structure formation of corundum. The apparent density and hardness of the ceramic layer are 2.9 g/cm³ and 1,430 Hv without the quartz additive, while they are 3.7 g/cm³ and 1,700 Hv with it, respectively.

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REFERENCES