Journal of Ceramic Processing Research. Vol. 9, No. 5, pp. 544~548 (2008)

J O U R N A L O F
Ceramic Processing Research

Effect of a glass addition on the ceramic layer prepared by a thermite reaction under a centrifugal force

Minh-Tung Le[a], Cheol-Gi Kim[a], Yang-Kyu Ahn[b] and Hun-Saeng Chung[b,*]

[a]*Department of Material Science & Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, Korea.*
[b]*Department of Chemistry, Konyang University, 119 Daehak-ro, Nonsan, Chungnam 320-711, Korea.*

A ceramic layer was produced on a steel pipe inner surface by a centrifugal thermite process. A powdery mixture of ferric oxide and aluminum was used with the glass whose major compositions were SiO_2, Na_2O, CaO, and MgO. The ceramic layer consisted of the crystalline structures of corundum (α-Al_2O_3) and hercynite ($FeAl_2O_4$). The amorphous phases of $Ca_3Al_2(SiO_4)_3$, $MgFeAlO_4$ and $NaAlSiO_4$ in the ceramic layer were found to be responsible for a significant improvement of the dense structure. The glass addition increased the density of the ceramic layer from 2.9 g/cm^3 to 3.6 g/cm^3 and the hardness from 1,450 to 1,800 Hv.

Key words: Centrifugal thermite process, Ceramic lining, Thermite reaction, Glass.

Introduction

With the advantages of large exothermic heat, local ignition and self-sustaining combustion, the thermite reaction has become one of the most important branches of self-propagation high temperature systhesis(SHS). It has been developed to synthesize ceramic and metal composites, and especially to manufacture ceramic-lined steel pipes under a centrifugal field [1, 2]. The centrifugal thermite (C-T) process has been proposed and investigated as a simple, rapid, and economical method for forming a ceramic lining layer on the inner surface of a pipe [1-3]. Products of this process have been utilized as conduits for cement, oil, and coal slurries [4]. The preparation of ceramic lined pipes by the centrifugal thermite process is based on the reaction between Fe_2O_3 and Al:

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2\ Fe \qquad \Delta H = -836\ kJ \quad (1)$$

When a thermite mixture is filled in a steel pipe and is ignited to combust, the molten ceramic (Al_2O_3) and metal (Fe) from the exothermic reaction can be separated in layers by virtue of their density difference under a centrifugal force. Therefore, there is a ceramic layer on the innermost side and an intermediate iron layer between the ceramic layer and steel pipe surface. The ceramic layer which is composed of the FeO-Al_2O_3 (hercynite) crystalline structure plays an important role in improving the mechanical properties of the ceramic layer, such as its toughness and thermal shock resistance [5]. However, the application of the thermite process for the ceramic lining of pipes without the use of additives holds some demerits, mostly due to the formation of large pores within the layer causing a structure of low density. Various additives such as SiO_2, $Na_2B_4O_7$, MgO, CrO_3, etc. have been used to solve this problem [5-7]. A SiO_2-Na_2O-CaO glass could be a candidate to be used as an additive to improve the fluidity of the melt at high temperatures from the thermite reaction.

In the present studies, the glass was added to a Fe_2O_3 and Al mixture, mixed, and ignited. A ceramic lining on the steel pipe surface was formed by the centrifugal thermite process. The density, hardness, and microstructures of the ceramic layer were studied along with the densification process.

Experimental procedure

A mixture of thermite material was prepared by stoichiometrically mixing aluminum powder (< 100 μm with average size 39 μm, 99.7% purity, Alcoa Brazil) and ferric oxide powder (< 5 μm with average size 1.6 μm, ≥ 99.0% purity, EWIC Korea). The glass powder 12 μm in average size provided by Kukyoung G&M Company, Korea, was used as an additive. The composition of the glass presented in Table 1 was determined by a chemical method, ICP-AES (Jobin-Yon, JY38 Plus, France), and AAS (AAnalyst 400, PerkinElmer, USA). The glass consists of SiO_2, Na_2O, CaO, and MgO, as major components along with Al_2O_3, Fe_2O_3, and CeO as minor constituents.

The feedstock materials were mixed for 1 hour in a barrier mixer. A carbon steel pipe 300 mm long with an inner diameter of 54 mm and a wall thickness of 3 mm was mounted in a centrifuge reactor. The mixture was filled into the steel pipe with a 40% filling ratio. The filling ratio

Table 1. Composition of glass

Compound	Na_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	CeO	Others
Content (wt%)	12.1	9.12	3.24	66.7	1.18	0.34	0.05	7.27

* Corresponding author:
Tel: +82-41-730-5585
Fax: +82-41-730-5762
E mail: hsc2490@konyang.ac.kr

herein refers to the ratio of the weight of the thermite mixture filled in the steel pipe to the weight of the steel pipe. A part of the sample powder was ignited to start the thermite reaction with an electrically heated coiled tungsten wire 0.5 mm in diameter. The centrifugal force of the system was set at 120 g. After completion of the reaction, the centrifuge machine was allowed to rotate for 10 more minutes until the reactor body cooled down.

A piece of the sample was taken out from the ceramic layer of the pipe and mounted in thermosetting plastics, and then ground and polished with different particle size diamond powders for scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopic (EDX), (JEOL JSM-6380LA) analysis. The phase composition of the ceramic layer was identified by X-ray diffraction (XRD, Rotaflex Ru-200B CuKα, Rigaku). Its hardness was measured by the Vickers method (Hardness Tester, MVK-E, Akashi).

Results and Discussion

Density and hardness

The thermite powder mixture was filled in the steel pipe and pressed against the inner wall by centrifugal force and ignited. After the ignition, the combustion propagated throughout the thermite tunnel within a few seconds. The molten material produced at over 3,000 °C by exothermic combustion moved towards the steel pipe surface.

Despite the strong centrifugal force, some gases evolved could not escape from the melt and lowered the ceramic layer density, since the solidification process takes place very quickly. In the Al-Fe_2O_3 system, the density of the ceramic layer was very low at 2.9 g/cm^3. A significant number of pores were observed in the ceramic layer.

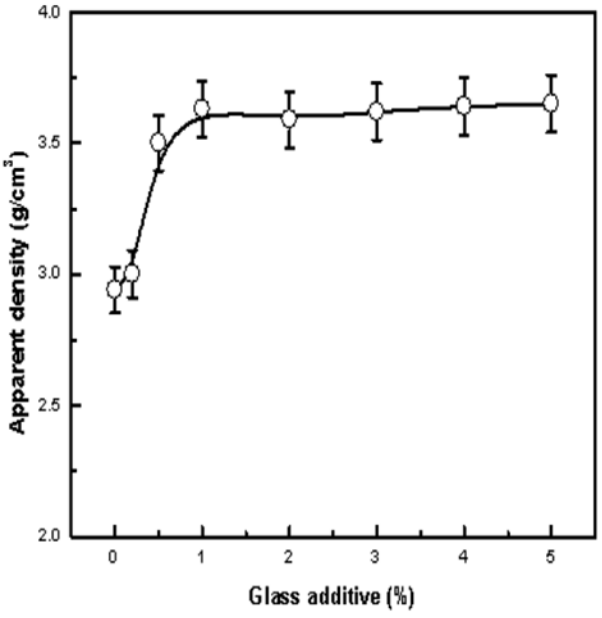

Fig. 1. Effect of glass addition on ceramic layer density at a 40% filling ratio and with 120 g centrifugal force

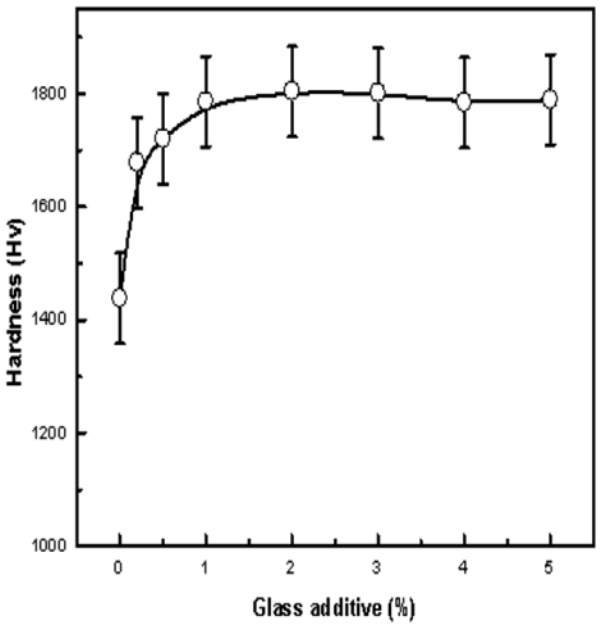

Fig. 2. Effect of glass addition on ceramic layer hardness at a 40% filling ratio and with 120 g centrifugal force.

Glass powder was added to the Al-Fe_2O_3 mixture, and a ceramic layer was produced on the steel pipe surface by the centrifugal thermite process. The ceramic density change as a function of the amount of the glass powder added is depicted in Fig. 1 The glass addition notably improved the degree of densification of the ceramic. The density increased from 2.9 g/cm^3 to 3.6 g/cm^3 with increasing glass additions, but remained unchanged in the 1-5% range of the addition.

The Vickers hardness of the ceramic layer specimens prepared was measured with a 50-kg load and the results are shown in Fig. 2 The ceramic layer had a hardness of 1,450 Hv with no glass addition, but the hardness abruptly increased to 1,800 Hv with a 1% addition and remained unchanged with the further additions. It is thought that the sharp increase in both density and hardness was caused by the change of the layer microstructure during the solidification period.

Crystalline phases

X-ray diffraction patterns of the ceramic layer formed without and with a glass addition are shown in Fig. 3 Major intensity peaks of corundum (α-Al_2O_3) and hercynite ($FeAl_2O_4$) clearly appeared in both the patterns, and essentially no difference could be found in the layer synthesized (a) without the glass addition and (b) with an addition of 4% glass. However, the intensities were found to be somewhat stronger with the glass-added specimen than that without it.

After the completion of the thermite reaction, the melt fluidity would be enhanced by the glass addition and be kept longer compared to the case of no glass addition. The fluidity is believed to have an important role in the formation

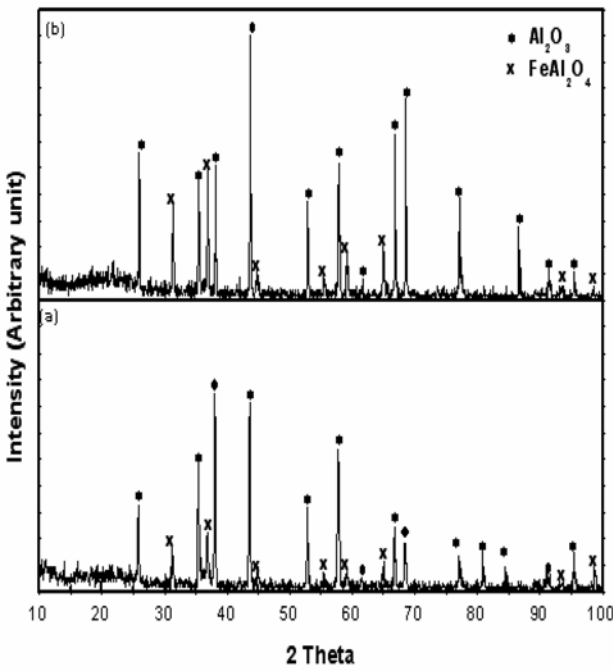

Fig. 3. XRD patterns of ceramic layers prepared at a 40% filling ratio and with 120 g centrifugal force, (a) without glass; (b) with 4% glass.

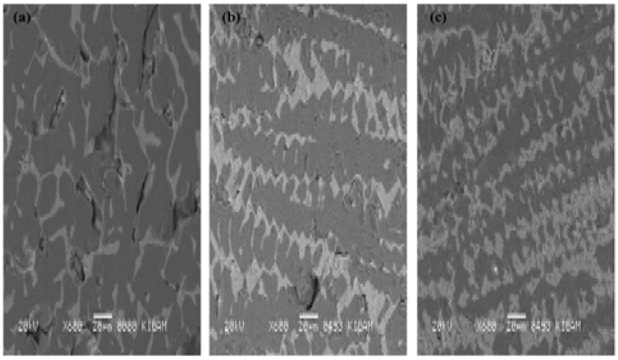

Fig. 4. Micrographs of ceramic layers at a 40% filling ratio and 120 g centrifugal force, with (a) 0%; (b) 1%; (c) 5% of glass additive.

of the ceramic layer microstructure. In other words, the crystal nucleation and growth would be more active with low viscous melts rather than with high ones. This will be mentioned in the later sections.

Microstructure

The microstructures of the ceramic layers observed by SEM are shown in Fig. 4 The micrographs taken with back scattered electrons show gray-colored phases of α-Al_2O_3 and lighter-colored phases of $FeAl_2O_4$. The gray grain-shaped

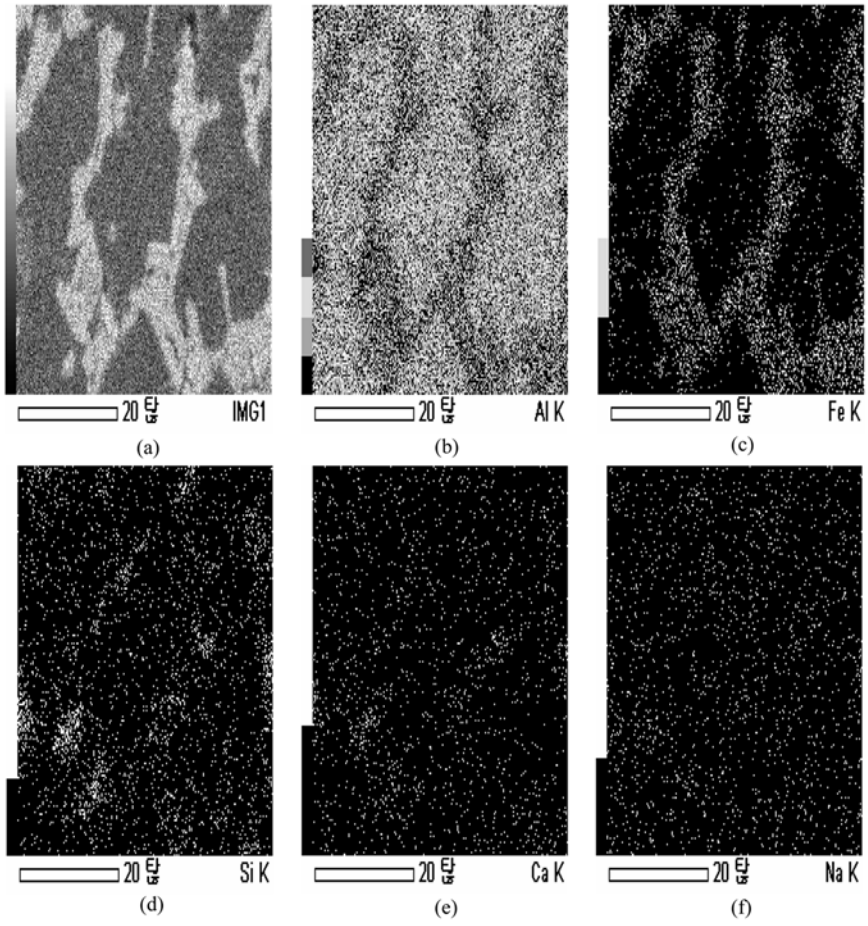

Fig. 5. EDX maps for a ceramic layer prepared with a 4% glass addition, a 40% filling ratio and 120 g centrifugal force.

α-Al_2O_3 are surrounded by spinel-like structured $FeAl_2O_4$. In Fig. 4(a), without a glass addition, alumina grains are distributed in the ceramic layer along with large dark pores. Because the melting temperature of α-Al_2O_3 (2,054 °C) is higher than $FeAl_2O_4$ (1,780 °C), alumina seems to nucleate and grow first. Then, $FeAl_2O_4$ gets solidified and crystallized on the already formed α-Al_2O_3 grains.

The temperature gradient through the melt layer by the quick heat release through the pipe outer surface has been known to cause the formation of dentritic structured grains in the direction of heat conduction. A dense microstructure of the ceramic layer is dominant with an increase of glass additions as shown in Fig. 4(b, c). It was also noticed in the micrographs that the dendritic structure becomes finer with an increase in the addition of the glass. This fineness is presumed to come from the increased amount of flowing material and its enhanced fluidity.

The melting temperature of glass in the range 1,400-1,600 °C [8] retains the liquid phase for a long time, and provides a large effect on the growth of crystal grains as well as their structure in the melt. In the absence of the glass, the large pores are clearly observed in the lighter-colored phases in Fig. 4(a), but the glass addition leads to a significant decrease in the pores with an increment of lighter-colored phases as noticed in Fig. 4(b) and 4(c). Herein, the lighter-colored phases in the ceramic layer are likely to be composed of some form of amorphous materials along with hercynite crystals. Therefore, it can be said that the dense structure of ceramic layer formed by the glass addition certainly results in the increase of its density and hardness.

Non-crystalline phases

Figure 5 shows EDX elemental maps along with SEM micrographs for the ceramic layers. Highly concentrated aluminum is clearly detected in the dark colored phases being considered as α-Al_2O_3 grains in Fig. 5(b). Element of iron lies heavily between the alumina grains as seen in Fig. 5(c) and this likely forms the $FeAl_2O_4$ crystal structure according to the XRD data of Fig. 3.

The major elements of the glass such as silicon, calcium, and sodium are found in the approximate region of the iron even though they are sparsely distributed as seen in Fig. 5(d), 5(e), and 5(f), respectively. These elements are expected to be present in the form of oxides. However, any evidence of these compounds in a crystalline form was not found in the XRD data as shown in Fig. 3 Therefore, the compounds in this area are likely to be in non-crystalline state. In other words, it may be considered that oxide materials with low melting temperatures exist between the crystalline grains of Al_2O_3 and $FeAl_2O_4$.

To identify the composition of an amorphous phase in the ceramic layer, heat treatment was carried out for specimens of 1.5 cm × 2 cm in an electric furnace at 1,200 °C for 4 hours. The X-ray pattern for the heat treated specimen is shown in Fig. 6 Compared to the data in Fig. 3 beside α-Al_2O_3 and $FeAl_2O_4$, new crystalline phases of $Ca_3Al_2(SiO_4)_3$, $MgFeAlO_4$ and $NaAlSiO_4$ are found. Possibly, they are the compounds which can lower the melting temperature, resulting in enhancing the melt fluidity for a long time during the cooling and easing the structural rearrangement of the ceramic layer.

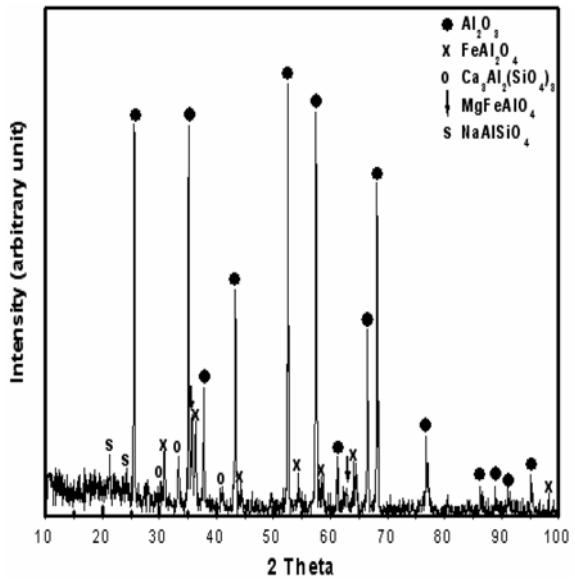

Fig. 6. XRD patterns of a ceramic layer prepared with a 4% glass addition, a 40% filling ratio and 120 g centrifugal force after heat treatment at 1,200 °C.

Conclusions

A ceramic layer on a steel pipe inner surface was produced by the thermite process under a centrifugal force. A thermite mixture of ferric oxide and aluminum was used along with glass powder as an additive.

The addition of glass produced a highly dense structure in the ceramic layer compared with the one without it. The dendritic crystalline structure of α-Al_2O_3 and $FeAl_2O_4$ was well developed in the vertical direction to the pipe surface and it became finer with an increase in the amount of the glass.

The apparent density and hardness of the ceramic layer were significantly improved in the presence of the glass. Its density increased from 2.9 to 3.6 g/cm^3 and the hardness from 1,450 to 1,800 Hv.

The glass addition improved the fluidity of the thermite mixture melt and promoted the arrangement of the layer structure to a dense state. The amorphous phases of $Ca_3Al_2(SiO_4)_3$, $MgFeAlO_4$ and $NaAlSiO_4$ in the ceramic layer responsible for the enhanced melt fluidity.

References

1. Odawara, U.S. Pat. No. 4363832 (1982).
2. Odawara and J. Ikeuchi, Jpn. Inst. Met., Sendai, 45, (1981) 316-321.
3. Eiji Miyazaki and Odawara, Processing by centrifugation, Edited by Regel and Wilcox Kluwer Acadamic /Plenum Puplishers, New York, (2001) 213-222.
4. ShuGe Zhang, XiaoXin Zhou and DongHao Qian, Inter. J. SHS. 11[2] (2002) 219-227.

5. Odawara, Key Eng. Mater, 122-124. (1996) 463-476.
6. Zhonge Du, Hanguang Fu, Hanfeng Fu and Qiang Xiao, Mater. Lett., 59 (2005) 1853-1858.
7. Jaeryong Lee, M.T. Le and H.S. Chung, Mater. Trans. 48 (2007) 2960-2963.
8. World Book Encyclopedia 2000 ed. Chicago, IL. World Book Inc. (2000) 215