Effects of additives Si on casting structure of ceramic liner produced by a centrifugal–thermit process

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In order to control the quality of ceramic layer produced by a centrifugal–thermit process, effects of the amount of additives Si on phase constituents and casting structure of the layer are studied. The results show that silicon is mainly distributed over the matrix phase of the inner part of the layer, and the matrix belongs to a spinel "solid solution" having many Si^{4+} ions replacing Al^{3+}. Because of its low melting point, the fluidity of liquid ceramic and thus the surface quality are improved. However, the effect of silicon is not always positive, since the dissolution of Si^{4+} ions enlarges the temperature range of freezing, thus it increases the tendency of "constitutional supercooling" and facilitates the development of equiaxed zone. In addition, with increasing silicon content the viscosity of liquid ceramic will increase as well. All these factors make the liquid feeding more difficult and lead to poor surface quality and high porosity of the layer. The changes in casting structure with various Si contents are discussed from the above point of view.

1. Introduction

The thermite reactions have been widely utilized in engineering practice for a long time (for example, welding of rails and preparation of alloys, etc). Because of the large amount of heat generated from the reaction, the resultants are often melted; thus the alumina, commonly referred to as slag, can be separated and removed from resultants of the reaction, and only metallic phases are used as the desired products. Recently, thermite reactions have been reintroduced with the development of the newly emerged SHS (self-propagating high temperature synthesis) technology [1]; one of the applications is the centrifugal–thermite coating process. In this process, a powdered thermite mixture (such as Al–Fe$_2$O$_3$) is first packed into a rotating pipe, and the reactants will be uniformly distributed against the inner wall of the pipe. The reaction is then initiated by ignition. The centrifugal force exerted on the reactants facilitates the separation of the melted metallic phase from the alumina and the expulsion of trapped and impurity gases. Due to its higher density, the metal phase is forced to touch the inner surface of the pipe, and the alumina forms an inward ceramic layer which provides a good resistance to wear and corrosion. Up to now, much of the research work of the process has been carried out by Odawara and his coworkers [2–5]. They studied the effects of parameters such as centrifugal force and environmental pressure, on the quality of the lined layer, measured the mechanical behaviour and thermal shock resistance of the composite pipe, and thus justified the feasibility of the process.

The preparation of metal–ceramic composite pipe with this method is very attractive due to its simplicity of technology and equipment, and its low consumption of energy, especially because there is no other reliable and simple method for producing ceramic lined pipe. It seems that the principle of this technology is simple; however, it is very difficult to obtain a satisfactory product, since the nature of the process is very complex, involving the chemical reaction, melting of the resultants and the separation and solidification of liquid under centrifugal force. In particular, all these processes are completed in a very short time interval, so the quality control of the product is rather difficult. One of the problems is its poor surface quality and high porosity of the ceramic layer. In order to improve the quality, adding additives, such as SiO$_2$ or Si, to the reactants has been proposed [6], and it is believed that the additives can increase the fluidity of liquid phase, thus decreasing the porosity and improving the quality of the layer surface. The mechanism of improving quality with additives is not yet clear, and the knowledge available from sintering can not be directly applied to the SHS thermit process, in which the ceramic product is obtained through solidification. In this paper, effects of amount of additives on phase constituents and cast structure of the layer were systematically studied, so as to gain an insight into the formation of ceramic layer through centrifugal–thermit process and the function of additives. This might be useful in improving the quality of coating layer.

2. Experimental procedure

The chemical, pure Fe$_2$O$_3$, 200 mesh Al powder and 200 mesh Si powder were used as the thermite

TABLE I Composition of reactant mixture

No.	Total mass (g)	Fe_2O_3:(Al + Si) (g/g)	Fe_2O_3 (g)	Al (g)	Si (g)
1			203	64	3
2	270	3:1	204	60	8
3			204	55	13

reactants. To study the effect of Si additives on phase constituents and structures of the ceramic layer, the amount of Si was varied, while the total mass of reactants and the mass ratio of Fe_2O_3 to reducing agents (Al + Si) were kept nearly constant as indicated in Table I.

The weighted reactants were blended with a ball mill and dried thoroughly at $120\,°C$, then the dried reactants were loosely packed into a carbon steel pipe with an outer diameter of 72.5 mm and a wall thickness of 4.5 mm. The length of the pipe is 100 mm. The carbon steel pipe together with reactants were put into a horizontal centrifuge rotating about its axis. The rotation speed of the pipe was gradually increased to yield 200 g, so as to keep the reactants adhering closely to the inner wall of the pipe. An acetylene torch was used to initiate the thermite reaction and the exothermic reaction was almost instantaneously completed. After completing the reaction, rotation was continued for a few minutes to cool the composite pipe, then the phase constituents and structures of the ceramic layer were studied by X-ray diffraction (XRD, CuK_α), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

3. Experimental results
3.1. Macroscopic structures
The cross-sections of the three samples of composite pipe are shown in Fig. 1. It is obvious that the ceramics and metallic phase are well separated and the intermediate iron layer has been welded with the steel pipe. Thus an integrated ceramic lined steel pipe is formed. The smoothness of the inner surface is slightly different for the three samples and the surface of sample No. 2 seems the most acceptable.

The cast structures of ceramic layer of the three samples are presented in Fig. 2. Sample No. 1, which contains < 1% silicon, basically consists of a columnar dendritic zone normal to the wall, and many interdendritic pores exist near the inward layer. As the silicon content increases, besides the columnar zone, a randomly orientated equiaxed crystal zone appears in the inner region of the ceramic layer, meanwhile many isolated pores can be seen in the equiaxed zone. The thickness of the equiaxed zone increases with increasing silicon content. In addition, the structure and pores also become coarse.

3.2. XRD pattern
The ceramic layer was ground into a powdery sample, then the XRD analysis was carried out to study their phase constituents. The patterns for
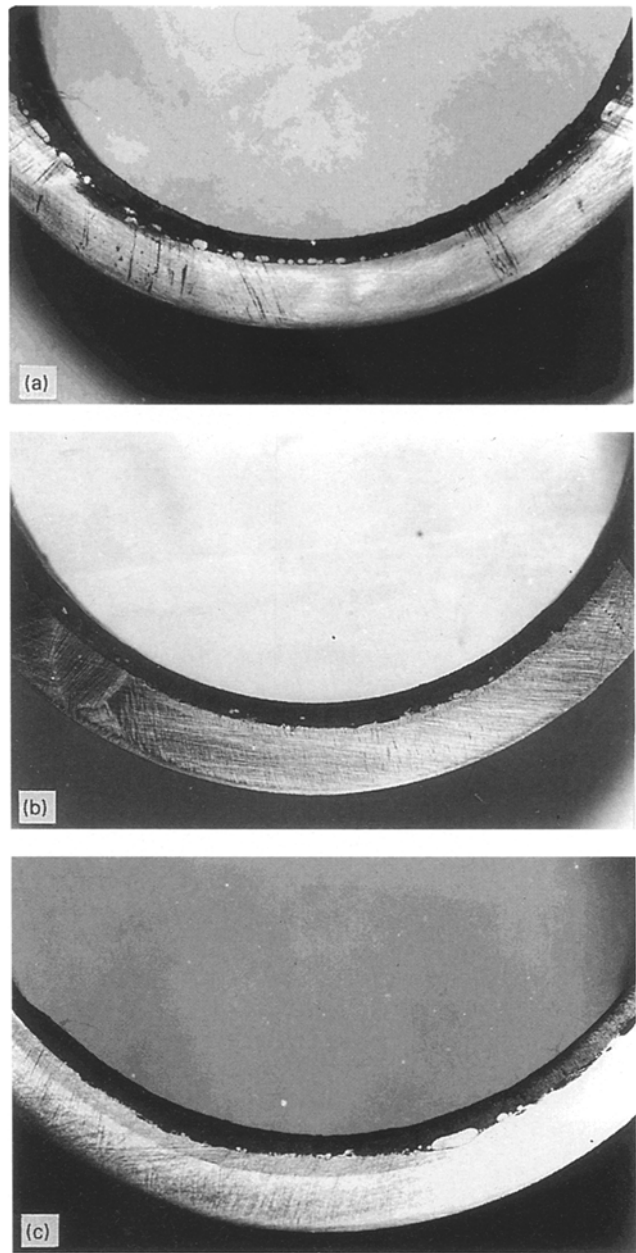

Figure 1 Cross section of the three pipes. (a) Sample No. 1; (b) sample No. 2; (c) sample No. 3.

samples No. 1 and No. 3 are shown in Fig. 3(a, b), and the main phases of both samples are α-Al_2O_3 and $FeAl_2O_4$. However, some differences do exist. (1) The relative amounts of the two main phases are different, the amount of α-Al_2O_3 reduces significantly with the increase in silicon content. (2) It looks as if many new peaks emerge on the XRD pattern for sample No. 3, but all of them cannot be identified with the XRD cards of binary and ternary compounds of Al_2O_3–SiO_2–FeO system. Careful examination reveals that all the new peaks appear on the right side of the $FeAl_2O_4$ peaks, and form groups of peaks along with the peak of $FeAl_2O_4$. (3) For sample No. 3 a small amount of new phase FeO appears, and the peak intensity of SiO_2 increases slightly.

3.3. SEM and EDS analysis
Structures in the columnar zone for the three samples under SEM are shown in Fig. 4(a, b, c), while structures

Figure 3 X-ray diffraction pattern for (a) sample No. 1, (b) sample No. 3. $\triangle$ α-Al_2O_3; $\bigcirc$ $FeAl_2O_4$; $\square$ SiO_2; 0 FeO.
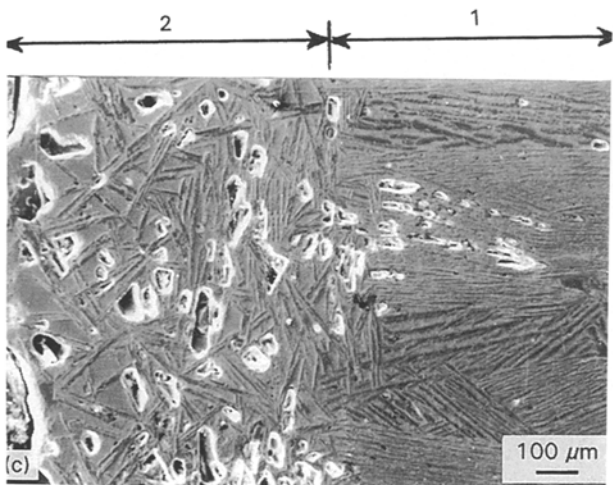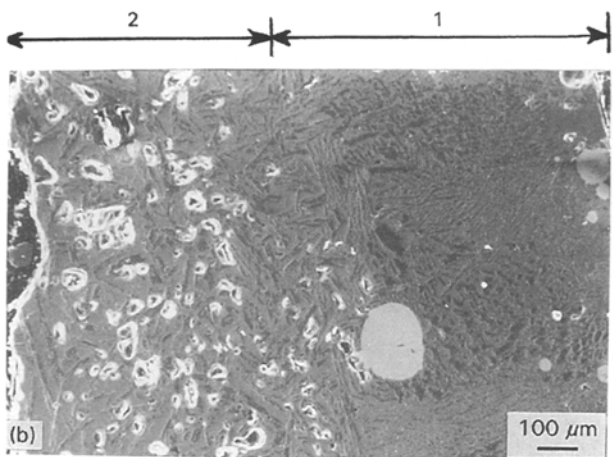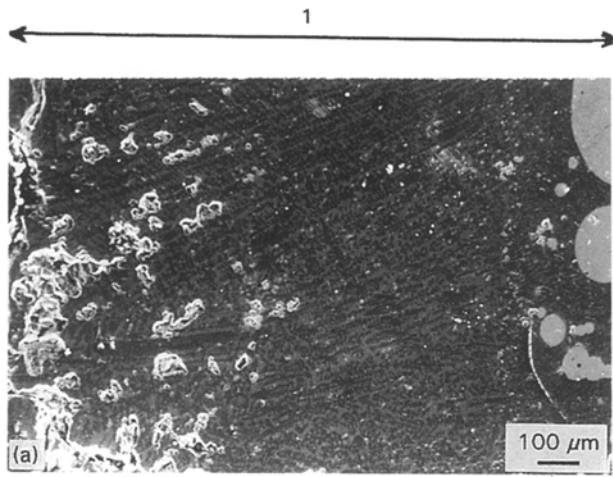

Figure 2 Cast structure of ceramic layers for (a) sample No. 1; (b) sample No. 2; (c) sample No. 3. Zone 1; columnar dendritic crystals; Zone 2; equiaxed crystals.

in the equiaxed zone of samples No. 2 and No. 3 are shown in Fig. 5(a, b). It can be seen from their contrasts that they consist primarily of three phases, which are labelled 1, 2, 3 on the micrographs. Results of EDS analysis for these three phases are listed in Table II (the light element O cannot be detected here). According to these results together with their morphology it can be concluded that the coarse dark crystals (phase 1), containing a small amount of iron but no silicon are α-Al_2O_3 which freeze at first. Then light

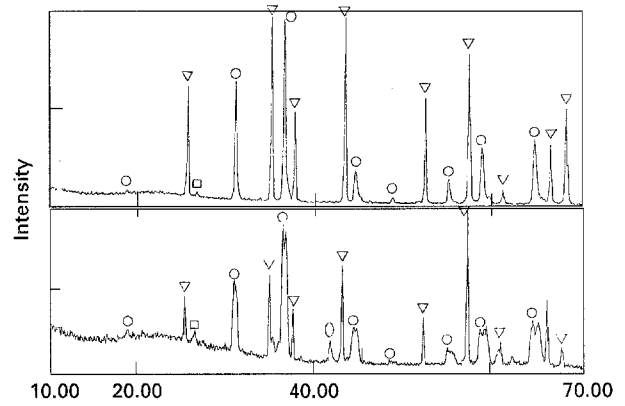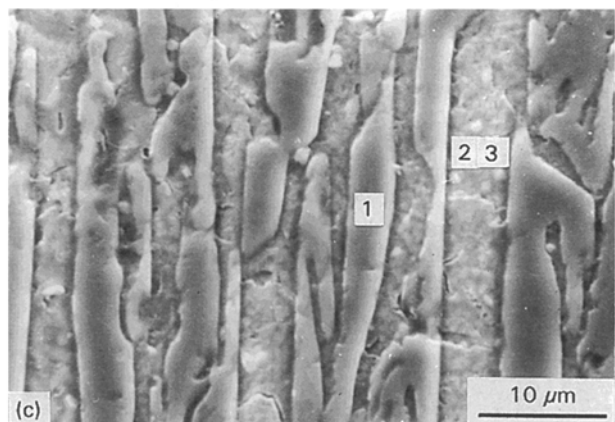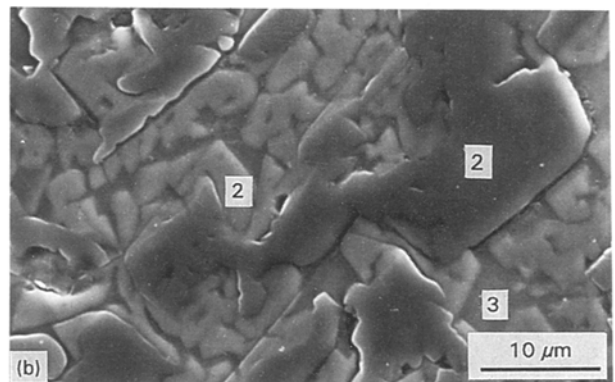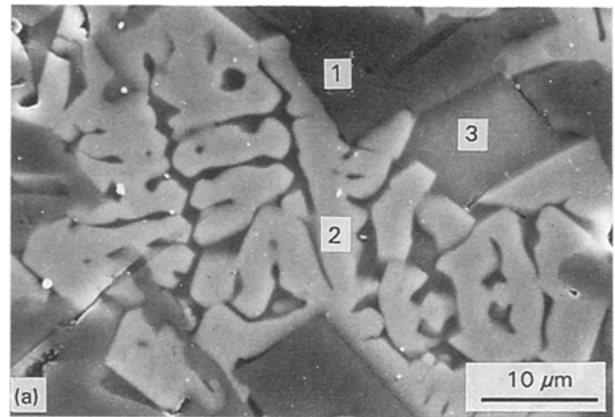Figure 4 Microstructures in the columnar zone for (a) sample No. 1; (b) sample No. 2; (c) sample No. 3.
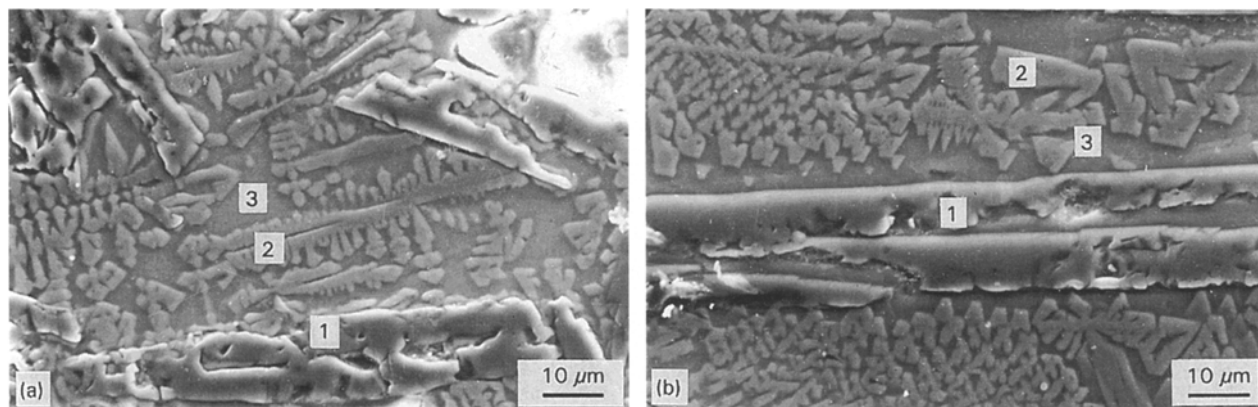
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Figure 5 Microstructures in the equiaxed zone for (a) sample No. 2; (b) sample No. 3.

TABLE II Relative amount (at.%) of Al, Si, Fe in phases 1, 2, 3 measured from EDS

		Columnar zone			Equiaxed zone		
		Phase 1	Phase 2	Phase 3	Phase 1	Phase 2	Phase 3
1	Al	99.69	65.19	76.16			
	Si	0.0	0.0	18.49			
	Fe	0.31	34.81	5.31			
2	Al	99.27	52.27[a]	70.98[a]	99.32	58.66	18.44
	Si	0.0	6.81[a]	15.13[a]	0.0	5.40	44.68
	Fe	0.73	40.92[a]	13.91[a]	0.68	35.94	36.88
3	Al	98.90		60.02	99.40	63.70	20.62
	Si	0.0		4.02	0.0	1.53	45.66

[a] The data are not exact because the dimensions of phases are close to that of the electron beam spot.

coloured dendritic crystals (phase 2), containing small amounts of silicon, freeze in the gap of α-Al_2O_3, and it seems that their compositions are close to $FeAl_2O_4$. Finally matrix phase (phase 3), which is silicon-rich oxide, particularly within the equiaxed zone, freezes.
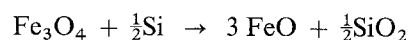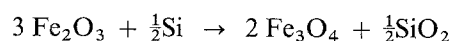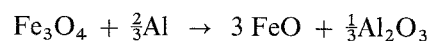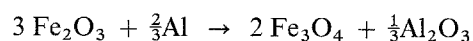
4. Discussion
4.1. Phase constituents of the ceramic liner
It is known that the ceramic liner obtained by thermit reaction is composed of two phases–α-Al_2O_3 and $FeAl_2O_4$ [3], but the effect of additives Si on the phase constituents has not yet been studied. Data in Table II show that when silicon is added, except the α-Al_2O_3, the other two phases all contain Al, Fe and Si. Referring to phase diagrams [7], there are two ternary oxides $Fe_3Al_2(SiO_4)_3$ and $Fe_2Al_4Si_3O_{18}$. Unfortunately, none of them can be detected on the XRD pattern, and the compositions of phases 2 and 3 presented in Table II are not in accordance with the stoichiometry of the above chemical formula, therefore, it is believed that they have not been obtained in the layer.

Careful analysis of the compositions of phases 2 and 3 shows that even though their compositions vary with the amount of silicon added and with the distance from the surface, the iron content in phases 2 and 3 almost remain unchanged and equal to 34–37%, and the sum of Al and Si remains at 63–66%. So the ratio of (Al + Si) at.% to Fe is around

2 : 1. If we consider "groups of peaks" appearing on the XRD pattern, it is reasonable to assume that phases 2 and 3 have the same crystal structure and both belong to the $FeAl_2O_4$ spinel. The composition of phase 2 is rather close to the typical $FeAl_2O_4$, while phase 3 (matrix phase) has more Si^{4+} ions replacing Al^{3+} ions; thus a "solid solution" of Si^{4+} dissolved into $FeAl_2O_4$ is formed. In order to maintain electrical neutrality, each three Si^{4+} ion must replace four Al^{3+} ions, leaving one vacant lattice site. Therefore, the interplanar distances vary with the silicon content, but all are lower than that of typical $FeAl_2O_4$ spinel, thus several small peaks appear on the right side of the peak of $FeAl_2O_4$ (the direction of decreasing interplanar distance).

According to free energy of oxide formation, it is assumed that when Al and Si are employed as reducing agents, the following reactions should occur

$$3\,Fe_2O_3 + \tfrac{2}{3}Al \rightarrow 2\,Fe_3O_4 + \tfrac{1}{3}Al_2O_3$$

$$Fe_3O_4 + \tfrac{2}{3}Al \rightarrow 3\,FeO + \tfrac{1}{3}Al_2O_3$$

$$3\,Fe_2O_3 + \tfrac{1}{2}Si \rightarrow 2\,Fe_3O_4 + \tfrac{1}{2}SiO_2$$

$$Fe_3O_4 + \tfrac{1}{2}Si \rightarrow 3\,FeO + \tfrac{1}{2}SiO_2$$

If the above reactions do occur, SiO_2 should react with FeO and Al_2O_3, and thus yield many binary and ternary oxides. However, experimental results imply that most of the silicon does not take part in the thermit reaction, but dissolves into the phase of

FeAl$_2$O$_4$. We are not sure whether it is caused by the thermodynamic conditions or dynamic factors. No matter what the origin, it decreases the effective amount of reducing agent, and thus affects the completeness of the reaction for sample No. 3. The variation of phase constituent with increasing silicon content, as shown in Fig. 3, confirms the incompleteness of the reaction.

4.2. Casting structures of ceramic liner

To the authors' knowledge, the study of solidification of ceramics, especially under the effect of centrifugal force, has not yet been reported. Here, the principle of solidification of metals is used to analyse the casting structure of the ceramic layer. The process of centrifugal–thermit coating is very complicated. It involves a thermite reaction, melting of the resultants by reaction heat, and freezing due to heat loss to the environment through the pipe wall. Additives Si affect not only the reaction heat, but also the composition of resultants, thus changing the solidification characteristics and final structure. The effects of silicon can be discussed as follows.

As the high melting Al$_2$O$_3$ freezes, the silicon will be rejected to the liquid phase ahead of the solid–liquid interface since Si cannot dissolve in alumina, which leads to progressive enrichment of the silicon in the remaining liquid, and finally the silicon is mainly distributed over the matrix phase 3 of the inner part of the layer. It is well known that solute atoms usually lower the freezing point of solid solutions, so the same phenomenon is expected to occur when silicon dissolves into FeAl$_2$O$_4$ spinel, and then its fluidity will be improved. It is worthwhile pointing out, however, that the effect of silicon is not always positive. Dissolved silicon ions increase the temperature range of freezing, thus increasing the tendency of "constitutional supercooling" ahead of freezing interface, consequently facilitating the development of an equiaxed zone and making feeding more difficult. In addition, although the freezing point of the spinel is lowered by the dissolution of Si^{4+} ions, cations could increase the viscosity of the liquid, because of the composition dependence of viscosity [8, 9], which will of course also play a negative role on freezing.

The double-faced effect of the silicon has a significant influence on the quality of the final product. As it contains no silicon or a small amount of silicon (sample No. 1), the reaction heat is relatively larger, which is favourable to the maintaining of a positive temperature gradient, and thus facilitates the growing of a well-oriented columnar zone against the direction of heat flow. However, the higher freezing point of the liquid deteriorates its feeding ability, so many interdendritic pores appear, which make the surface quality poor. As the silicon content increases, the reaction heat decreases, which flattens the temperature gradient under the same cooling conditions, thus increasing the possibility of a nucleus forming in the equiaxed zone. From Fig. 2 it is clear that the porosity does not decrease for higher silicon content, which indicates that the feeding ability of the liquid phase is not improved monotonically with increasing silicon content. Interestingly, as shown in Fig. 2, the structure in the equiaxed zone becomes coarser with increasing silicon content although the reaction heat might decrease. This change can be attributed to the increase in viscosity of the liquid, then the nucleation rate and growth rate of solidification are lowered and a coarser structure will be obtained. The rough surface of sample No. 3 is probably caused by the bad feeding and the coarse structures.

5. Conclusions

1. When a small amount of silicon is added to the thermite reactants, only a well-oriented columnar structure is obtained and many interdendritic pores are found. If the amount of silicon increases, an equiaxed zone emerges in addition to the columnar zone, and the thickness of the equiaxed zone increases with silicon content.
2. SEM micrographs show that the microstructures of the ceramic layer consist of three phases – coarse α-Al$_2$O$_3$, fine dendritic crystals and matrix phase. EDS results show that the silicon is mainly distributed over the matrix phase of the equiaxed zone.
3. The main phases of the ceramic layer are α-Al$_2$O$_3$ and FeAl$_2$O$_4$ spinel, but for higher silicon content the amount of α-Al$_2$O$_3$ reduces significantly and a new crystal having the same structure as spinel but with lower interplanar distance obviously exists.
4. The silicon has a double-faced effect on the quality of ceramic layer. The positive effect is to lower the freezing point, thus to improve the fluidity and decrease the porosity. The negative effect is to facilitate the development of equiaxed zone and the viscosity will increase; these factors make the liquid feeding more difficult.

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