

Research Article

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Effect of Basicity on Precipitation of Spinel Crystals in a $\text{CaO-SiO}_2\text{-MgO-Cr}_2\text{O}_3\text{-FeO}$ System

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Abstract: The comprehensive utilization of stainless steel slag is one of major problems to be solved at “green steelworks”. Precipitation of spinel crystals can effectively detoxify residue. The effect of basicity defined by $\omega(\text{CaO})/\omega(\text{SiO}_2)$ ratio on precipitation of spinel crystals in a $\text{CaO-SiO}_2\text{-MgO-Cr}_2\text{O}_3\text{-8 wt% FeO}$ system has been determined with such tools as FactSage 7.1, SEM-EDS, IPP 6.0 and XRD. The FactSage 7.1 results showed that the rate of spinel phase enrichment with chromium was about 98% for the system basicity less than 1.4 and about 78% above this value. The precipitation of solid particles in solution appeared to be significantly influenced by basicity. With its increase the solid phase grew, the liquid one reduced, the particle diffusion was limited, and the growth of spinel crystals was inhibited. The spinel crystal size increased rapidly with decrease of basicity. When basicity increased from 0.6 up to 1.0, the crystal size decreased sharply from 12.30 μm down to 6.22 μm , and the reduction constituted as much as 49.43%. When basicity increased from 1.0 up to 2.2, the spinel crystal size moderately decreased from 6.22 μm down to 4.47 μm . Therefore, reduction of basicity is conducive to spinel crystal enrichment with chromium what appears to be a key factor to control basicity at detoxification of the chromium-containing steel slag.

Keywords: stainless steel slag; precipitation; basicity; detoxification; crystal size

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1 Introduction

Stainless steel is widely used because of its excellent corrosion resistance. China's crude stainless steel output in 2018 appeared to be 26.7068 million tons, with increase 0.9331 million tons (3.62%) compared to the level 25.7737 million tons in 2017. China's stainless steel demand is expected to grow further in the next three years [1]. Stainless steel slag is a by-product of stainless steel production and constitutes 15-20% of output of the crude stainless steel [2]. If the metal recovery residue is not detoxified, such a heavy metal as Cr in the stainless steel slag has the leaching risk into the soil and groundwater with accumulation of slag in the slag yard [3]. Moreover, there are a lot of research world-wide on detoxification of stainless steel residue. It is generally believed that the reduction and solidification methods are those most suitable for detoxification. The former is aimed to reduce the content of Cr in a slag by adding the reducing agent at high temperature to reduce the risk of leaching Cr [4, 5], whereas the latter is related to handling the stainless steel slag as raw material to make a permeable subgrade brick, cement and glass-ceramics, so that Cr can be sealed within a glass phase or chromium-rich spinel crystals [6–8]. In view of both economic benefits and amount of residue accumulated, usage of residue in building materials meets the requirements of green production at steelworks.

The structure of a spinel crystal is stable, and its oxidation resistance is good. Our previous work [9] shows that 8 wt% FeO in the system can promote formation of spinel crystals. Upon adjusting a composition of the stainless steel slag, its leaching is much lower than the permissible level according to the national leaching toxicity standard HJ/T 299-2007, and FeO can promote formation of the chromium-rich spinel crystal $(\text{MgFe})(\text{FeAlCr})_2\text{O}_4$ [10, 11]. The precipitation behavior of spinel crystals can be represented by the nucleation and growth processes. A ki-

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Table 1: Chemical composition of the samples, g.

| No. | CaO | SiO ₂ | MgO | Cr ₂ O ₃ | FeO | CaO%/SiO ₂ % |
|-----|-------|------------------|------|--------------------------------|------|-------------------------|
| D1 | 29.25 | 48.75 | 8.00 | 6.00 | 8.00 | 0.60 |
| D2 | 39.00 | 39.00 | 8.00 | 6.00 | 8.00 | 1.00 |
| D3 | 42.55 | 35.45 | 8.00 | 6.00 | 8.00 | 1.20 |
| D4 | 45.50 | 32.50 | 8.00 | 6.00 | 8.00 | 1.40 |
| D5 | 50.14 | 27.86 | 8.00 | 6.00 | 8.00 | 1.80 |
| D6 | 52.00 | 26.00 | 8.00 | 6.00 | 8.00 | 2.00 |
| D7 | 53.63 | 24.38 | 8.00 | 6.00 | 8.00 | 2.20 |

netic condition is the key factor affecting crystallization of a slag system. The viscosity of a liquid slag increases with increase of its basicity that is not conducive to diffusion of particles [12]. Furthermore, the existence of calcium orthosilicate accelerates leaching of Cr [13]. Hence, it is necessary to study the effect of basicity on the precipitation behavior of spinel crystals in the modified slag system. On the one hand, the mechanism of spinel crystal precipitation with a synergetic effect of both factors can be clarified. On the other hand, optimal parameters can be found to promote usage of spinel crystals when processing the stainless steel slag what also provides a feasible comprehensive utilization of its accumulated heaps.

2 Experimental

Based on principles of metallurgical thermodynamics and mineralogy, the solidification process was calculated for the CaO-SiO₂-MgO-Cr₂O₃-8 wt%FeO slag system with FactSage 7.1 to study the theoretical basis of formation of chromium spinel in the stainless steel slag. The sample composition is shown in Table 1. Chemical reagents CaO, SiO₂, MgO, Cr₂O₃, FeC₂O₄·2H₂O and H₃BO₃ are the analytical reagents.

Thus, FeO was to be replaced by ferrous oxalate, and 0.2 wt% H₃BO₃ was added to prevent disintegration because of the slag composition [14]. After precise weighing with electronic control and sieving the slag 4-6 times (the sieve aperture used in the experiment was equal to 0.5 mm), it was grinded by a powder sample machine to be fully mixed. 100 g of the mixture in a molybdenum crucible was melted in a high temperature carbon tube furnace according to a special temperature regime (in the nitrogen atmosphere with a 10°C/min heating rate up to 1550°C after holding for 30 minutes). A sample of this synthetic slag was obtained by water quenching. The slag samples and resins were transformed into scanning elec-

tron microscopy (SEM) samples with an inlaying machine. Upon polishing and spraying, their micro-morphology was observed by means of scanning electron microscopy, and EDS was used to study the features of micro-area composition, element linear and map distribution. Upon grinding a suitable amount of slag samples, a mineral composition analysis was carried out by means of XRD. Photos collected by SEM were scanned with the Image-Pro Plus 6.0 (IPP 6.0) image analysis software to determine the particle size of spinel crystals in the samples. The effect of basicity on the spinel precipitation behavior in the CaO-SiO₂-MgO-Cr₂O₃-8 wt% FeO system was studied thereby.

FactSage7.1 was applied to simulate the phase transformation and precipitation of the spinel phase during solidification of molten slag. The specific setting conditions are shown as follows.

Database: FactPS, FToxide, FSstel;

Compound setting: idea gas, pure solid;

Solution phase setting: FToxid-SLAGA, FToxid-SPINA, FToxid-MeO_A, FToxid-bC2SA, FToxid-aC2SA, FToxid-Mel_A.

The FToxid-SLAGA was set as the target phase of Scheil-Gulliver Cooling. The setting temperature was 2000°C and the solidification step was 10°C. The calculation process terminated automatically when the target phase completely disappeared. The results were exported in picture and edited by FactSage7.1.

3 Results and Discussion

3.1 Effect of basicity on the precipitation behavior of spinel crystals

Figure 1 shows that the spinel crystal represents indeed a high temperature precipitation phase. The number next to the curve indicates the basicity of the sample. When basicity of the slag is equal to 0.6, the initial spinel precipita-

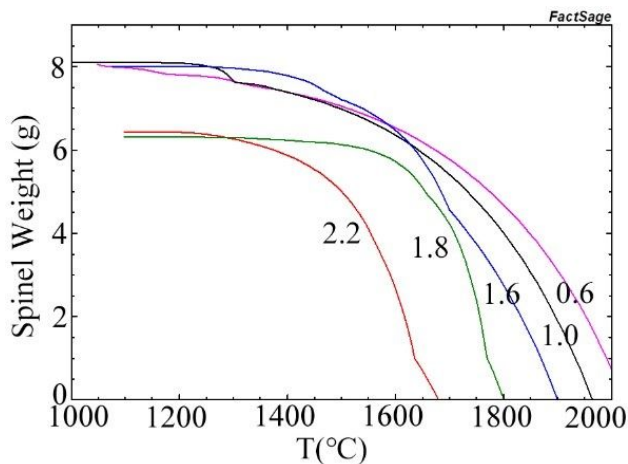


Figure 1: Effect of temperature on the spinel crystals weight.

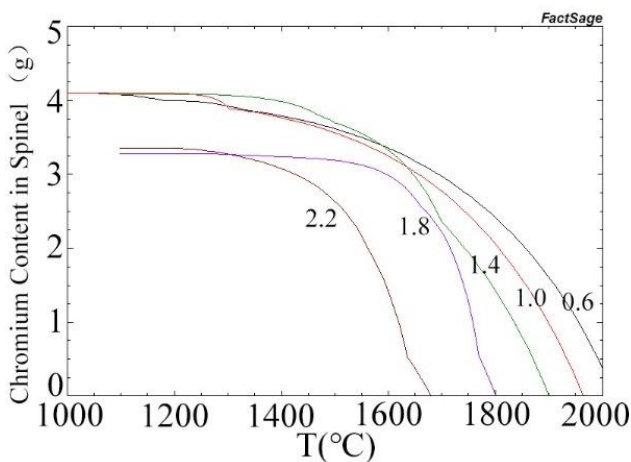


Figure 2: Effect of basicity on chromium content in spinel solid solution.

tion temperature is greater than 2000°C . The temperature range of rapid crystallization is narrow, and the crystallization rate slows down gradually with decrease of temperature until the spinel crystals completely precipitate, and the weight of spinel crystals remains constant (a plateau area). Concentration of CaO increases with increase of basicity that promotes formation of calcium silicate with a high melting point. Viscosity of the slag increases correspondingly, and the diffusion rate of particles in the slag slows down. Therefore, the spinel crystal precipitation process is faster in the slags of higher basicity (1.8, 2.2), and the weights of the spinel crystals are greater than those of the lower-basicity slags. Final weight of the spinel crystal is about 6.25 g for slag basicity 1.8 or 2.2 and grows up to about 8.05 g for basicities 0.6, 1.0, or 1.4. As it is shown in Figure 2, the content of chromium in the spinel crystals can be obtained to calculate the enrichment rate (the

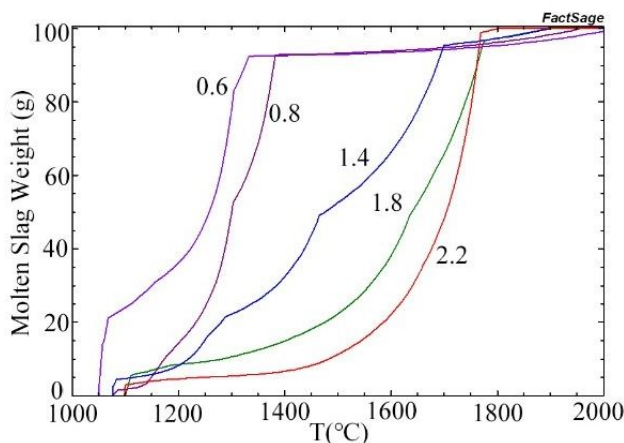


Figure 3: Residual liquid phase changed with the basicity during the solidification process

ratio of the chromium content in the spinel crystal to total chromium content in the slag). The enrichment rate is about 78% at basicity 1.8 or 2.2 and 98% at basicities 0.6, 1.0 or 1.4. According to the FactSage 7.1 calculations, the slag with low basicity is propitious to formation of the spinel crystals and to their enrichment chromium.

As it can be seen in Figure 3, the liquid phase ratio of the $\text{CaO-SiO}_2\text{-MgO-Cr}_2\text{O}_3\text{-8 wt\% FeO}$ system is negatively correlated with basicity of a molten slag with weight less than about 95 g. A large number of crystals began to precipitate below 1300°C with basicity of samples less than 1.0. At these basicities, the liquid phase ratio remains about 90% for temperatures greater than 1300°C . For the samples with high basicity ($B=2.2$), a large number of crystals were precipitated at 1700°C , and the proportion of a residual liquid phase was less than 40%. This implies that increase of basicity promotes precipitation of a large number of silicate phases with a high melting point.

3.2 Effect of basicity on the spinel crystal size

SEM was used to scan the microstructure of samples with different basicities as shown in Figure 4. The slag ($B=0.6$) is composed by three distinct mineral phases: a spinel crystal, diopside ($\text{CaMgSi}_2\text{O}_6$) and a silicate matrix, what appears to be consistent with the XRD-observations (Figure 5). Except the spinel crystals, some other crystals are embedded in the silicate matrix because of physical and chemical constraints related to samples in Figures 4b to 4d.

Figure 4 also shows that the spinel crystal size in different slag samples is significantly different. This is con-

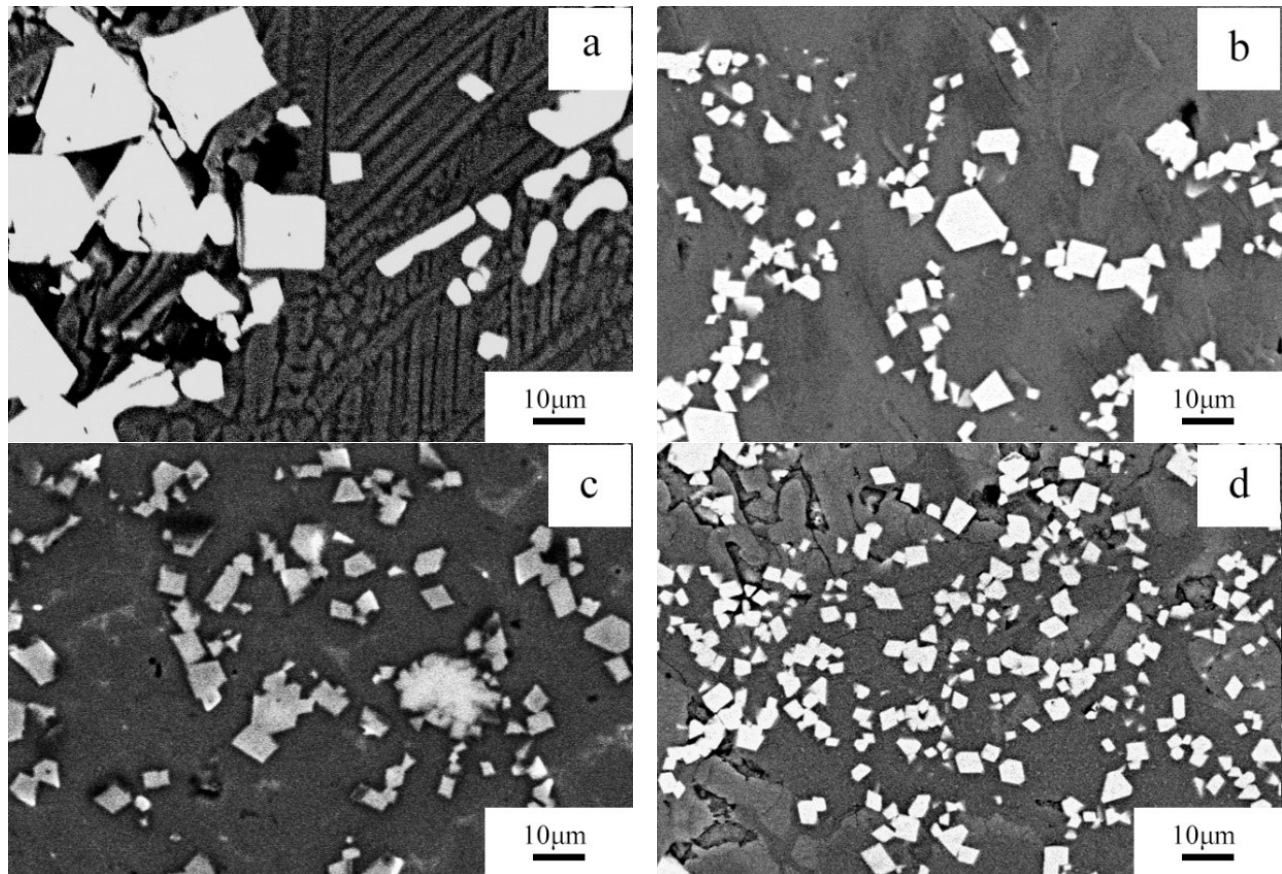


Figure 4: Microstructure of the samples at different basicities (a-0.6, b-1.0, c-1.4, d-1.8).

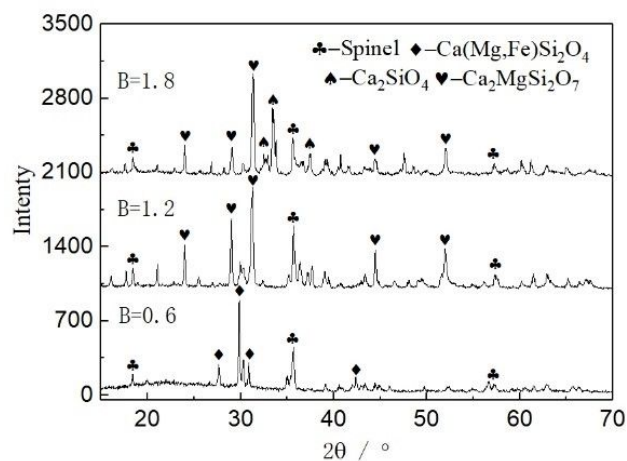


Figure 5: XRD diffraction patterns of the samples.

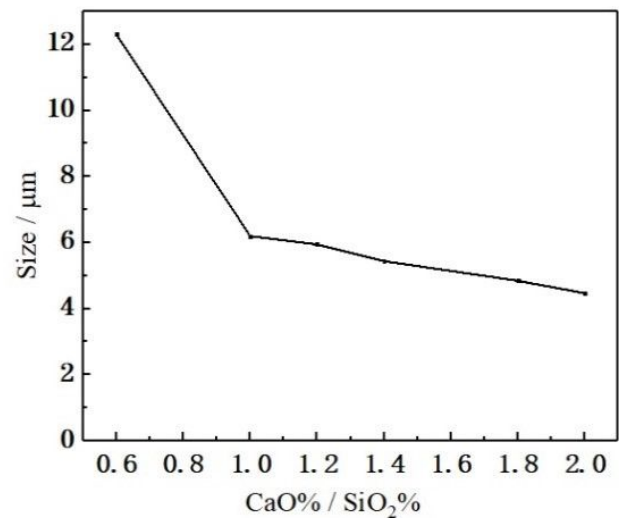


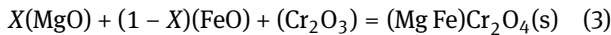
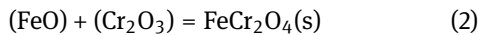
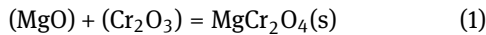
Figure 6: Effect of basicity on the size of spinel crystals.

firmed by the results of analysis with the IPP 6.0 software (Figure 6). The spinel crystal size is negatively correlated with the slag basicity. Basicity 1.0 is a critical value for the two different trends, and the spinel crystal size increases rapidly with decrease of basicity when the latter is lower

than 1.0. There is a great drop in the spinel crystal size from 12.30 μm down to 6.22 μm that constitutes 49.43% when basicity increases from 0.6 up to 1.0. The curve trend is mod-

erate, the spinel crystal size decreases from 6.22 μm down to 4.47 μm as basicity increases from 1.0 up to 2.2. When the slag basicity is equal to 0.6, the slag system possesses the lowest viscosity and the highest diffusion rate of particles. The spinel crystal size is the largest one after heat preservation for 30 minutes.

According to the results of thermodynamic analysis, the spinel crystal represents a high temperature stable phase of a high chemical stability. Its precipitation is conditioned by dissolution of MgO, FeO and Cr₂O₃ in the molten slag (Eq. 1-3). When a crystal nucleates in the melt, the solute atoms in the neighboring area are likely to rapidly diffuse to the nucleus of the precipitated phase, but they are expected to be depleted soon. After that, the solute atoms in the matrix are first to enter the crystal interface due to the bulk diffusion maintaining the phase transformation process and to move then to a core of the precipitated phase due to interface diffusion what makes the core to grow continuously. The composition of the spinel crystal is obviously different from that of the slag. The growth rate of the spinel crystal depends on the long-range diffusion of solute atoms. The long-range diffusion of particles in the slag plays an important role in a continuous growth of spinel crystals.



Size R of a spinel crystal in the slag can be expressed by Eq. 4 [15] according to which the crystal size in a precipitated melt depends mainly on the particles diffusion coefficient D in the melt. As it follows from the Stokes-Einstein equation (Eq. 5), the diffusion coefficient itself is determined by temperature, particle size and melt viscosity [15]:

$$R = \left[\frac{2(c_0 - c_M)}{c_N - c_M} D t \right]^{\frac{1}{2}}, \quad (4)$$

$$D = \frac{k_B T}{3\pi d \mu}, \quad (5)$$

where c_0 is average concentration of particles in the slag, c_M is concentration of particles at the crystal interface from the slag side, c_N is concentration of particles at the crystal interface from the crystal side, t is the slag treatment time, d denotes a particle's diameter, μ is melt viscosity, T is absolute temperature, and k_B is the Boltzmann constant.

According to the slag molecular theory, the diffusion velocities of the (FeO), (MgO) and (Cr₂O₃) particles in the melt are closely related to viscosity of the stable slag at some temperature. On the basis of thermodynamic analysis of solidification of the CaO-SiO₂-MgO-Cr₂O₃-8 wt% FeO system, the slag system studied in this paper is to be considered as heterogeneous. Viscosity can be expressed as a function of liquid viscosity η_0 in a two-phase melt containing solid precipitates (Eq. 6) [16]:

$$\eta = \eta_0(1 + 2.5f), \quad (6)$$

where f is bulk concentration of suspended solid particles in the liquid phase.

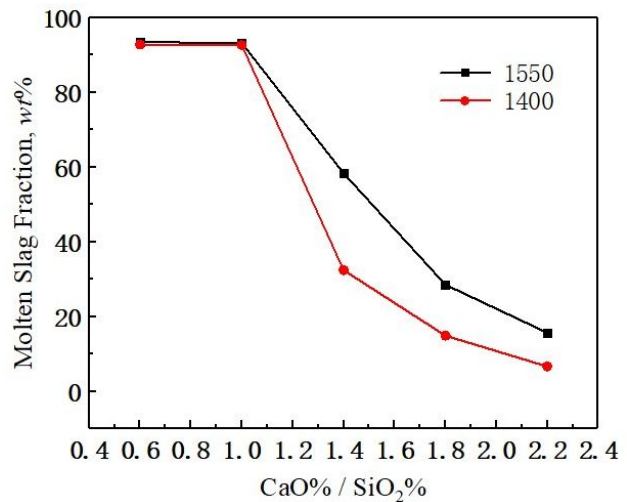


Figure 7: Relationship between the mass ratio of residual liquid phase and basicity at 1400°C and 1550°C.

According to the results of theoretical analysis (Figure 7), basicity has a crucial influence on precipitation of solid particles in the liquid phase. The portion of a residual liquid in the slag decreases from 93.51% down to 15.67% when basicity increases from 0.6 up to 2.2 at 1550°C, and decreases from 92.82% down to 6.65% when basicity increases from 0.6 up to 2.2 at 1400°C. Increase of basicity promotes precipitation of crystals while the amount of the liquid phase is being greatly reduced, diffusion of particles restricted and growth of crystals restrained. Furthermore, as it is shown in Figure 7, D7 which is $\omega(\text{CaO})/\omega(\text{SiO}_2)$ ratio of 2.2 contains only 15.67% liquid phase at 1550°C. Spinel crystals are hardly to grow through particle diffusion during the cooling process even if spinel nuclei are being formed.

4 Conclusion

The effect of basicity on precipitation of spinel crystals in the CaO-SiO₂-MgO-Cr₂O₃-8 wt% FeO slag system has been determined using the FactSage 7.1, SEM-EDS, IPP 6.0 and XRD tools. The results are to be summarized as follows.

- (1) The FactSage 7.1 results show that as basicity is lower than 1.4 the rate of slag enrichment with chromium is about 98%, and when basicity is greater than 1.4, the enrichment rate is about 78%. Excessive basicity is not conducive to the precipitation of spinel crystals and affects the enrichment rate therein.
- (2) As basicity of the slag is less than 1.0, the spinel crystal size increases rapidly with decrease of basicity. There is a great drop in the spinel crystal size from 12.30 μm down to 6.22 μm that constitutes 49.43% when basicity increases from 0.6 up to 1.0. The curve trend is moderate, the spinel crystal size decreases from 6.22 μm down to 4.47 μm as basicity increases from 1.0 up to 2.2.
- (3) Due to the particle diffusion, a lower basicity and viscosity are beneficial to the growth of spinel crystals.

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