Precipitation and Growth of V-concentrating Phase in Synthetic V-bearing Steelmaking Slag

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The precipitation and growth of V-concentrating phase are implemented in the synthetic V-bearing steelmaking slag based on the composition of factory slag from the Masteel Co. X-ray diffraction (XRD) and scanning electron microscopy (SEM), with energy dispersive X-ray spectrometer (EDX) are used to investigate the slag after heat treatment and to determine the temperature at which crystallization of V-concentrating phase is initiated. It is demonstrated Whitlockite with a high content of V2O5 (called V-concentrating phase) nucleates homogeneously and heterogeneously at 1 623–1 598 K. When emplaced holding time at 1 548 K, the crystals of V-concentrating phase grow with increasing of the holding time using crystal size distribution theory (CSD). Observation of the microstructures and crystallite-size data indicates that the precipitation of V-concentrating phase proceeds via three different mechanisms: nucleation, growth, and coalescence of grains of V-concentrating phase.

KEY WORDS: V-bearing steelmaking slag; V-concentrating phase; crystal growth; crystal size distribution.

1. Introduction

China obtains vanadium from mining and refining operations in its Sichuan and Anhui provinces.1,2 There is always a large amount of vanadium discarded in the form of steel-making slag. In China, more than 14.07 million tons of steel-making slag are generated every year,3 and most are cast aside without recovering the some valuable resources such as vanadium it contains. It is a urgent matter to develop novel methods to treat the steel-making slags to realize their intrinsic value. The concentration of vanadium in some Chinese steel-making slags, however, is not high enough to use as a vanadium resource, and it is considered to be a harmful by-product of steel-making.4–6 Crystal nucleation and growth studies are important to investigate the crystallization of casting mold slag,7,8 so it can be used to study the crystallization of V-concentrating phase in the V-bearing slag. Therefore, when vanadium precipitates in some Chinese steel-making slags, however, is not high enough to use as a vanadium resource, and it is considered to be a harmful by-product of steel-making.4–6 Crystal nucleation and growth studies are important to investigate the crystallization of casting mold slag,7,8 so it can be used to study the crystallization of V-concentrating phase in the V-bearing slag. Therefore, when vanadium precipitates in some steel-making slag, it can be selectively recycled from slag.9 A consistent number of studies have been dealing with the recycling of industrial residues based on selective enrichment, such as Ti-bearing blast-furnace slag for Ti and B-bearing slag for B.10,11

It is well known that on cooling a melt, overall crystallization can occur by a combination of nucleation and growth. Also, crystal nucleation can occur homogeneously or heterogeneously.12,13 Steelmaking slag with vanadium, after undercooling from melts, will experience crystallization to a degree that largely depends on the crystallization temperature and aging time, among other parameters, such as chemical composition. Cooling and its process with time during crystallization of a melt are the main factors controlling the texture of solidified slag.

For a given slag composition, crystalline textures bear important information on the temperature history. The goal of this study is to investigate the crystallization process of the synthetic V-bearing steelwork slag and to determine the crystallization temperature of V-concentrating phase. In order to correct the slag chemical composition and to promote the crystallization of V-concentrating phase, Al2O3 was added into the slag. With the crystallization temperature, we can choose a proper thermal process to investigate the growth of V-concentrating phase using crystal size distribution (CSD).

2. Experimental Procedure

200 g of master slag were prepared from analytical grade CaO, MgO, Al2O3, SiO2, NH4VO3 and (NH4)2HPO4. All reagents were carefully weighed and completely mixed. This mixture, placed in an alumina crucible, was melted at 1 823 K for 30 min in a furnace with heating elements of MoSi2. The melts were quenched by pouring on a steel plates. Then the as-quenched slag was crushed carefully using an agate mortar and pestle. The slag composition was based on the practical steel-making slags. After added by another 20 wt% Al2O3 in the batch, the chemical composition of the synthetic slag was shown in Table 1.

The crystallization temperature of V-concentrating phase was determined in a separate kinetic study. A tube furnace heated with MoSi2 heating elements was used for the experiments. Temperature of the furnace was controlled by a
Shimaden SR-53 programmable temperature controller (± 1 K). 4×10^5 g of the crushed slag were placed in four alumina crucibles and heated to the liquid state at 1 803 K in air. After an isothermal period of 30 min, cooling experiments were performed from the isotropic melt at cooling rate of 3 K/min to the crystallization temperature of 1 623 K, 1 598 K, 1 573 K and 1 548 K. At each run temperature, one of the four crucibles was quickly withdrawn from the furnace and quenched in the oil-cooled quenching chamber.

Growth experiment was chosen at 1 548 K according to the crystallization temperature V-concentrating phase. The charge was first melted and held at 1 803 K for 30 min, then cooled at 3 K/min to 1 548 K, at which the charge was held for 30–750 min before quenched in air.

Quenched samples were cut using a low speed diamond saw. The samples were then ground with 600–1000 grit SiC paper, and finally polished to 1 μm using diamond paste. The microstructures were observed using a scanning electron microscope (Philips XL30) operated at 20 kV. The SEM was equipped with an Energy Dispersion X-ray Spectroscopy (EDX or EDS) unit (EDAX DX4i) that allowed compositional measurements to be done. The identification of the precipitated crystalline phases was performed by powder X-ray diffractometer (Rigaku D/max-r) using Cu Kα radiation in 2θ range from 10° to 70°.

3. Results and Discussion

3.1. Crystallization Temperature of V-concentrating Phase

Figure 1 shows the X-ray pattern of slag powder samples quenched at a temperature range of 1 548–1 623 K. Well-defined peaks are observed in the X-ray pattern, typical of material with well-ordered crystalline phases which are: (i) gehlenite, (Ca₂Al₂SiO₇) (JCDPS 20-0199) and (ii) grossite, (CaAl₄O₇) (JCDPS 23-1037). Gehlenite and grossite are important solid solution series. EDX analysis results given in Table 2 show that chemical elements found in the gehlenite crystal are Ca, Al, Si, Fe and P with atomic ratio: Ca : (Al + Fe) : (Si + P) ≈ 2 : 2 : 1. We assume that Fe and P occupy part of the sites of Al and Si in the gehlenite structure, respectively. In grossite crystal, the atomic ratio of Ca : (Al + Fe) is close to 1 : 4, also, Fe occupies parts of the sites of Al in the grossite structure to form solid solution. So, the microanalysis are in agreement with the phases gehlenite and grossite identified by XRD.

The backscattered electron (BSE) image (shown in Fig. 2(c)) shows a phase separation from groundmass B and the onset of new crystallization of dendrite-like grains. At 1 573 K and 1 548 K, the dendrite-like grains grow into larger elongated grains (marked by A in Figs. 2(a) and 2(b)). A-phase contains Ca, P, O, V and some small amount of Al, Fe, Si with Ca : (P + V + Si) = 1.55 : 1 analysed by EDX (see Table 2), so we speculate that A-phase is whitlockite (Ca₅(PO₄)₂) enriched in vanadium, containing as much as 14.90 wt% (6.8×10²/182×2×10²/7.5×60+12×12 = 12×36×156×6.8×182×2×160) of V₂O₅. The whitlockite (Ca₅(PO₄)₂) (JCDPS 09-0169) phase is confirmed in X-ray diffraction pattern as shown in Fig. 1. At 1 548 K×300 min, not only whitlockite phase becomes purer with a smaller amount of Al, Fe, Si, but also the content of V₂O₅ reaches to 23.87 wt%. So, whitlockite (Ca₅(PO₄)₂) phase enriched in very high amount of vanadium, it will be called V-concentrating phase. As a result of above quenching experiments and BSE observations, we can determine that V-concentrating phase nucleated between 1 623 K and 1 598 K.

It is interesting to see in the Figs. 2(c) and 2(d) that the

![Fig. 1. XRD patterns of quenched samples from different temperature.](image-url)

Figure 1. XRD patterns of quenched samples from different temperature.

| Table 1. Chemical composition of phases in slag by EDX (%). |
|----------------------------------|
| Elmt   | 1573K×30min | 1548K×300min | 1573K×30min |
| CaO    | 34.67       | 37.88        | 39.75       |
| SiO₂   | 11.50       | 19.51        | 43.89       |
| MgO    | 3.20        | 3.65         | 10.89       |
| Al₂O₃  | 20.60       | 1.22         | -           |
| V₂O₅   | 2.50        | 1.12         | -           |
| P₂O₅   | 2.40        | 1.88         | -           |

| Elmt | 1573K×30min | 1548K×300min | 1573K×30min |
|------|-------------|--------------|-------------|
| O    | 34.67       | 37.88        | 39.75       |
| Mg   | -           | 1.03         | -           |
| Al   | 2.58        | 19.51        | 43.89       |
| Si   | 4.75        | 3.65         | 10.89       |
| P    | 12.13       | 1.12         | -           |
| Ca   | 36.73       | 19.30        | 12.92       |
| V    | 6.80        | 1.88         | -           |
| Fe   | 2.35        | 15.64        | 3.44        |

- element is not detected
V-concentrating phase can both nucleate at the boundaries of matrix and gehlenite or grossite and in the interior of matrix. It means that there exist two kinds of nucleation, i.e., heterogeneous nucleation and homogeneous nucleation.

Several important differences can be drawn between phases crystallizing from a liquid and phases crystallizing in a complete solid. During metamorphism, heterogeneous nucleation may dominate because solid–solid surface energies are low and dislocations, or grain boundaries, are abundant. In contrast, homogeneous nucleation from a melt requires the overstepping of an energy barrier. According to the classical nucleation theory, heterogeneous nucleation of V-concentrating phase can be more easily produced than homogeneous nucleation, from Fig. 2(d) dendrites of V-concentrating phase are formed on the particle surfaces of gehlenite and geossite, representing heterogeneous nucleation. Whereas, from Fig. 2(c) dendrites which are formed in the matrix represents homogeneous nucleation. So, when undercooled from melts, heterogeneous nucleation of V-concentrating phase is assumed to form more early than homogeneous nucleation.

The crystallization process of V-concentrating phase is helped by the presence of another addition of Al$_2$O$_3$. The possible reason is that Al$_2$O$_3$ has been considered an effective nucleating agent in the crystallization process of gehlenite and grossite, thus P$_2$O$_5$ and V$_2$O$_5$ in the matrix have high potential to be precipitated into whitlockite from the matrix (phase B). In Magang steelmaking slag adding 10% of SiO$_2$, three main mineral components: dicalcium silicate, calcium ferrite and wustite are found, and vanadium distributes in calcium ferrite and the vanadium concentrating phase consisting mainly of CaO, SiO$_2$, V$_2$O$_5$ and P$_2$O$_5$ or Iron Oxide. Comparily, Al$_2$O$_3$ added is effective to concentrate vanadium of the slag in the only one phase, the whitlockite, but the mechanism is not understood clearly yet and waiting for more research in detail.

### 3.2. Growth of V-concentrating Phase

The basic precept of CSD analysis is that easily measured parameters such as crystal size, crystal number and other crystal population characteristics can be related to rates of crystal nucleation and growth. A detailed description of the CSD theory was given by Randolph and Larson and its application to igneous processes was documented by Marsh and Cashman. The CSD method was applied as described in Burkhard.

When we use CSD theory to analysis growth of V-concentrating phase in the slag, only a brief summary is given here.

The number of crystals of a given size ($L$) per unit volume is a function of the size. This function is called population density $n(L)$ and can be described as

$$n(L) = \frac{N_V}{dL} \exp \left( - \frac{L}{G\tau} \right)$$

where $N_V$ is the total number of crystals per unit volume smaller than $L$. Population density is exponentially related to crystal size ($L$) and for a steady state system can be simply assumed as

$$n = n^0 \exp \left( - \frac{L}{G\tau} \right)$$

If the frequency in $n$ is plotted versus the bin size $L$, the slope of the resulting curve corresponds to $1/G\tau$ ($G$= growth rate and $\tau$=growth time), and $\ln(n^0)$ to the number of crystals of zero size, i.e., the number of nuclei.

Since the V-concentrating phase precipitated after gehenite and grossite, the size distributions are measured in number per unit areas on a gehenite- and grossite- and vesicle-free basis, and a conversion has to be made to number per...
unit volume by raising the number measured per unit area to the 3/2 power.\(^{16}\)

\[ N_{v} = \left( \frac{N_{A}}{A} \right)^{1.5} \] ..........................(3)

The number of V-concentrating phase per unit area is measured using NIH Image on the BSE photographs (Fig. 3 as an example).

Considering calculation of Brandeis and Jaupart,\(^{18}\) the mean crystal size \((L_{D})\) have a relation with growth rate and nucleation rate as following:

\[ L_{D} = \left( \frac{1}{n_{0}} \right)^{1/4} \] ..........................(4)

Raw data for the CSD were obtained by back-scattered electron (BSE) imaging methods. In a second step, we calculated the area of the particles with the help of image-analysis tools (NIH-Image public domain software, U.S. National Institute of Health). We then calculated a one-dimensional length from the area, by using the equation:

\[ L = \sqrt{\frac{\text{area}}{\pi}} \] ..........................(5)

The one-dimensional length \((L)\) is the diameter of a circle with the equivalent area as the crystal.\(^{19}\) Table 3 presents the measurements and results of V-concentrating phase of run products yielded by different isothermal time at 1 548 K.

At 1 548 K, with holding time between 30 and 750 min, intercept \(\ln n_{0}\) greatly decreases from 19.478 to 17.083 mm\(^{-2}\) (Table 3), corresponding to an increase in the value of \(G\) (CSD slopes change from steep to swallow), suggesting extensive grain growth from 7.67 to 13.97 \(\mu m\).

When solid particles with a range of crystal size are dispersed throughout a melt, the average crystal size will increase over time by a process called Ostwald ripening. During coarsening, crystals with radii less than a critical radius \(r^{*}\) will shrink, while crystals with \(r > r^{*}\) will grow. The value of \(r^{*}\) increases with the time, so that some crystals may grow early but then shrink when \(r^{*}\) exceeds their radii \((r < r^{*})\). If annealing time is short, the nucleation rate is high. Conversely, long annealing time result in the dissolution of crystals below the critical radius \(r^{*}\) and growth of crystals larger than \(r^{*}\), resulting in a decrease of \(N_{A}\) and population density \(n^{0}\). Higgins\(^{20}\) investigated anorthosite by textural coarsening and attributed the linear CSD values to result from linearly increasing undercooling. In Ostwald ripening, small crystals are resorbed, whereas larger crystals grow from both material recycled by the resorption of crystals smaller than the critical size and the new material brought in by the circulating magmatic fluids. Cashman and Ferry.\(^{21}\) interpreted that grain growth with later loss of small crystals was due to annealing.

As discussed above, coarsening of V-concentrating phase is primarily through a process of dissolution-precipitation in the presence of fluids (XRD suggesting the existence of glass in Fig. 1).

However, Ostwald ripening was not the only V-concentrating phase growth mechanism. During coarsening of V-concentrating phase, V-concentrating phase crystals migrate with mobile grain boundaries, in many cases encountering other grossite crystals with which they restrictively grow between elongated grossite grains. Run products from the sets of experiments show clear textural evidence of growth by coalescence, such as necking and irregular composite crystals with multiple branches (Fig. 3).

4. Conclusions

The synthetic V-bearing steelmaking slag was prepared by the melt-quenching process and crystallization process was applied. During the solidification of the slag, both gehlenite and grossite are the two former precipitating phases and a high percent of vanadium can be enriched in \(\text{Ca}_3(\text{PO}_4)_2\) phase with 23.87 wt% \(\text{V}_2\text{O}_5\). When undercooled from melts to 1 598–1 623 K, \(\text{Ca}_3(\text{PO}_4)_2\) phase can nucleate homogeneously and heterogeneously. At 1 548 K, with isothermal holding time, CSD slopes change from steep to swallow, indicating that V-concentrating phase grows by Ostwald ripening and coalescence.

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![Fig. 3. BSE images of run sample with 750 min isothermal holding at 1 548 K.](image)

| Isothermal holding time at 1548K (s) | Number of grains | Area (\(\mu m^2\)) | Slope (1/G\(\tau\)) | Intercept (ln(n\(0\))) | \(R^2\) | \(L_D (\mu m)\) | Bin interval (\(\mu m\)) |
|-------------------------------------|----------------|-----------------|-------------------|---------------------|-------|----------------|---------------------|
| 1800                                | 1462           | 0.0475          | -459.16           | 19.478             | 0.893 | 7.67           | 0.67-14.89          |
| 3600                                | 1536           | 0.04385         | -396.28           | 19.043             | 0.838 | 8.56           | 0.67-14.67          |
| 10800                               | 607            | 0.0295          | -362.3            | 17.613             | 0.758 | 12.24          | 0.67-14.97          |
| 45000                               | 467            | 0.018           | -253.51           | 17.084             | 0.667 | 13.97          | 0.67-18.48          |
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REFERENCES
1) H. Preblinger: Steel Res., 73 (2002), 522.
2) R. R. Moskalyk and A. M. Alfantazi: Miner. Eng., 16 (2003), 793.
3) H. T. Shen and E. Fornberg: Waste Manage., 23 (2003), 933.
4) L. Yu, L. S. Li and Y. C. Dong: The Global Symp. on Recycling, Waste Treatment and Clean Technology (REWAS'04), TMS, Warrendale, PA, (2004), 2235.
5) L. Yu, Y. C. Dong and L. S. Li: Proc. of 5th Int. Symp. on Waste Processing and Recycling in Mineral and Metallurgical Industries [COM 2004], CIM, Hamilton, Ontario, Canada, (2004), 309.
6) F. Y. Zhang, L. H. Wen and Y. Z. Sheng: Steel Res., 73 (2002), 428.
7) K. Yoshiaki, C. E. Cicutti and A. W. Cramb: ISIJ Int., 38 (1998), 357.
8) C. Orrling, S. Sridhar and A. W. Cramb: ISIJ Int., 40 (2000), 877.
9) Z. T. Sui, L. Zhang, T. P. Lou, G. Q. Li and H. S. Chen: Yazawa Int. Symp.: Metall. and Mater. Process. Principles and Technologies; Materials Processing Fundamentals and New Technologies, TMS, Warrendale, PA, (2003), 681.
10) Y. H. Li, T. P. Lou, Y. H. Xia and Z. T. Sui: J. Mater. Sci., 35 (2000), 5635.
11) Z. T. Sui, P. X. Zhang and C. Yamauchi: Acta Mater., 47 (1999), 1337.
12) A. A. Cabral, V. M. Fokin, E. D. Zanotto and C. R. Chinaglia: J. Non-Cryst. Solids, 330 (2003), 174.
13) Y. Park and B. Hanson: J. Volcanol. Geotherm. Res., 90 (1999), 103.
14) A. D. Randolph and M. A. Larson: Theory of Particulate Processes, 2nd Ed., Academic Press, New York, (1988), 251.
15) B. D. Marsh: Contrib. Mineral. Petrol., 99 (1988), 277.
16) K. V. Cashman: Contrib. Mineral. Petrol., 113 (1992), 126.
17) D. J. M. Burkhard: Contrib. Mineral. Petrol., 142 (2002), 724.
18) G. Brandeis and C. Jaupart: Contrib. Mineral. Petrol., 96 (1987), 24.
19) R. Heilbronner and D. Bruhn: J. Struct. Geol., 20 (1998), 695.
20) M. D. Higgins: J. Petrol., 42 (1998), 1307.
21) K. V. Cashman and J. M. Ferry: Contrib. Mineral. Petrol., 99 (1988), 401.