論文 A Study on the Strength and Grindability of Granulated Copper Smelting Slag Produced by Water Quenching*

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The strength and grindability of copper smelting slag produced by water quenching have been investigated in the framework of single particle crushing and corrective grinding tests. X-ray diffraction analysis clearly indicated that the slag samples are the mixture of glassy and crystalline components, such as fayalite and magnetite. The amount of crystalline component of as-quenched samples increases as the particle size increases. The particle compressive strength of 10 ~ 20 μ m diameter particles of a sample mainly composed of glassy component appears to be almost twice as high as that of a sample including a large amount of crystalline components.

KEY WORDS: Copper Smelting, Slag Particle Compressive Strength, Grindability, X-ray Diffraction

1. Introduction

The recycling of industrial waste to useful products is strongly requested for saving our limited natural resources. In this sense, the water-quenched copper smelting slags have recently received attention as a polishing sand for the maintenance of many industrial facilities. Thus, the measurements of basic physical properties such as strength and grindability are necessary for wider applications of this granulated slag. However, little attention has been paid to water-quenched copper smelting slag.

Copper smelting slag mainly consists of fayalite[Fe₂SiO₄] and magnetite[Fe₃O₄] with a glassy matrix. The phase compositions of these types of slag, which depend on the quenching condition such as cooling temperature and pressure, are directly related to their physical properties of the present interest. Therefore, this paper describes the first results on the strength and grindability of the water-quenched copper smelting slags coupled with phase characterization by means of X-ray diffraction.

2. Experimental Apparatus and Procedures

The copper smelting slag samples produced by water quenching used in this work were taken from the Saganoseki Smelter of Nippon Mining Co., Ltd. Chemical compositions of the slag samples are given in Table 1 together with Bond's work index determined by the standard ball milling method. The size distribution of slag samples is shown in Fig. 1. The photo-micrographs of the polished sections of the present slag samples (Fig. 2) clearly indicate that needle-like fayalite and square-like magnetite crystals exist with the glassy matrix and their percentages correspond to the original sample size. It

Table 1 Chemical composition and Bond's work index of the copper smelting slag produced by water quenching.

Chemical composition	mass %
Cu	0.59
Fe	38.50
Si	9.80
Pb	0.15
Zn	1.32
As	0.09
Sb	0.04
Bond's work index	21.0 kWh/t

is also worth mentioning that the small amounts of spherical copper and copper sulfide are randomly observed in these sections. Therefore, the original granulated slag samples were sieved and classified into the following nine fractions: over 4000 μ m, 3360 ~ 4000 μ m, 2380 ~ 3360 μ m, 1680 ~ 2380 μ m, 1190 ~ 1680 μ m, 840 ~ 1190 μ m, 710 ~ 840 μ m, 250 ~ 710 μ m and under 250 μ m.

Strength measurements of the slag samples were carried out by using a compression testing machine for a small size particle, which enables us to vary compressive load and deformation from 0 to 9.8×10^{-1} N and 0 to 5 μ m, respectively. The size of a single slag particle in the strength measurement was kept constant between 10 and 20 μ m in diameter which is determined by micro-mesh sieves. The loading rate was kept constant at 6.27×10^{-3} N/s so as to be an ordinary loading rate during the measurements of particle compressive strength, so that the single particle fracture is made within a few minute. When a particle is compressed between two parallel platens, the strength of a single particle can be estimated from particle compressive strength, St , defined by the following equation.¹⁾

$$St = 2.8 P / (\pi d^2) \quad \dots\dots\dots (1)$$

Where, P is the fracture load and d the initial distance between the two parallel platens when a particle is beginning to be

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Fig. 1 Particle size distribution of the original slag samples.

Fig. 2 Photo-micrographs of polished sections of the present slag samples. (A) over 4000 μm (B) 1680 ~ 2380 μm

compressed. Strain energy, E , stored in a particle until the fracture starts is defined in the following form.

$$E = \int_0^d P dA \quad \dots\dots\dots (2)$$

Where in Eq.(2), A is the deformation of a specimen. The value of E is estimated from the compression test. For the relationship between St and E , the following equation can be derived from the theory of the materials dynamics.²⁾

$$E/M = 0.897^{2/3} \rho^{-1} [(1-\nu_1^2)/Y_1 + (1-\nu_2^2)/Y_2]^{2/3} St^{5/3} \quad \dots\dots\dots (3)$$

Where, M is the mass of specimen, ρ the density of a sample, ν the Poisson's ratio, Y the Young's modulus. Subscripts 1 and 2 denote a specimen and platens, respectively.

Corrective grinding of the slag samples was made using an alumina tumbling ball mill. The geometrical sizes of the mill are 140 mm in inner diameter and 140 mm in depth. The mass of the grinding media (alumina ball: 20 mm ϕ) and slag

samples were kept constant at 1100g and 100g, respectively. The rotational speed of the mill was kept at 89 rpm, which corresponds to 75% of the critical speed.

Grindability of the slag samples was determined from the particle size analysis using the JIS standard sieves, the micro-mesh sieves and the particle size analyzer; SA-CP2 (Shimadzu Co., Ltd.). Quartz was also used in the grinding experiment in comparison with the data of the slag. The properties of the quartz can be quoted from the previous papers.³⁾⁴⁾

3. Experimental Results and Discussion

3.1 X-ray diffraction analysis

The slag samples were crushed and sieved under 25 μm and X-ray diffraction profiles were measured by Cu $K\alpha$ radiation with a singly-bent pyrolytic graphite monochromator in a diffracted beam in range from $2\theta = 20^\circ \sim 50^\circ$, where θ is a half of an angle between incident and diffracted beams. As a typical example, Fig. 3 shows the X-ray diffraction patterns of granulated slags with six different categories; over 4000 μm , 2380 ~ 3360 μm , 1680 ~ 2380 μm , 840 ~ 1190 μm , 710 ~ 840 μm and under 250 μm . The diffraction patterns of fayalite and magnetite included in the granulated slag samples agree well with the JCPDS cards 34-178 and 19-629, respectively. It is clearly detected that the amount of crystalline components gradually decreases as the size of the slag samples decreases and the sample, whose size lies between 710 and 1190 μm , is considered to be a glassy component only. This fact can be explained by the assumption that the cooling rate of the smaller particle of the slag samples is much faster than that of the larger ones. It is, however, noted that a small

Fig. 3 X-ray diffraction patterns of the water quenched copper smelting slags for various sample sizes.

amount of crystalline component is detected in the smallest samples with the particle size under $250\mu\text{m}$. It may be quite feasible to conclude that the smallest sample of this size is likely to be a mixture of the original as-quenched slag and the fractured products of the larger particles including a considerable amount of crystalline components. The different state of these slag samples is well attributed to the variation of the grindability, which will be described in the later section.

3.2 Strength

Fig. 4 gives a typical load and deformation curve of a single slag particle sieved from 10 to $20\mu\text{m}$ (the mean diameter: $15\mu\text{m}$). Fig. 5 shows the relationship between St and E/M for the granulated slag samples with its original granulated particle size over $4000\mu\text{m}$ and $710 \sim 1000\mu\text{m}$, as an example. As can be seen in Fig. 5, the fracture of a single slag particle is classified into the brittle mode by finding good agreement in the gradient between the experimental data and theoretical values (Eq.(3)) expressed by the solid lines, although the experimental results are widely scattered in certain positions. Fig. 6 gives variation of St and E/M of a single slag particle sieved

Fig. 4 Typical load and deformation curve of a single particle having a $15\mu\text{m}$ mean diameter. ($d_0 = 840 \sim 1190\mu\text{m}$)

Fig. 5 Relationship between the particle compressive strength and the specific fracture energy obtained from the compression of a single slag particle having a $15\mu\text{m}$ mean diameter.

Fig. 6 Variation of the particle compressive strength, the specific fracture energy and density with the original size of slag samples.

from 10 to $20\mu\text{m}$ together with the density of granulated slags as a function of the original granulated particle size, d_0 . In Fig. 6, the data of quartz with the same particle size ($15\mu\text{m}$) are also indicated for comparison.⁵⁾ Similar correlations are well recognized in both quantities of St and E/M . Furthermore, the mean values of St and E/M of the particles formed mainly by the glassy component were found to be much greater than those of the particles composed of crystalline components. Especially, a drastic change is observed in the mean value of strength at the vicinity of the particle size of $1500\mu\text{m}$. This is consistent with the X-ray diffraction results (Fig. 3) indicating a different combination of the glassy and crystalline components with respect to the respective particle size. Comparing the results of St and E/M with those of quartz, the strength of glassy slag is equivalent to that of quartz. However, E/M of the present slag samples is smaller than that of quartz. This may be due to the difference in the mechanical properties such as Young's modulus and Poisson's ratio between these two materials. Consequently, the higher strength of the slag samples with a large amount of the glassy component is appreciated in comparison with the strength of the samples with a large amount of crystalline component. Regarding to the data on the density of granulated slags, which were measured by the Archimedes' method with toluene, it was found that the density of the slag samples with a crystalline structure is higher than the glassy structure case. It may be also noted that the density varies almost inversely as a function of the original size of slag samples in comparison with the results of St and E/M .

3.3 Grindability

The results of size distribution of the fractured fragments of the granulated slag having particle sizes of $2380 \sim 3360\mu\text{m}$

Fig. 7 Particle size distributions of ground products of slag samples by a tumbling ball mill at various grinding times.

and 590 ~ 710 μm by the tumbling ball mill are shown in Fig. 7. The numerical values of 5, 10, 20, 40 and 90 in this figure denote the grinding time [min]. In the case of the larger particle size shown in Fig. 7(a), the slope of the straight lines on the part of fine particle range remarkably decreases as the grinding time increases. On the contrary, no significant change is detected in the slope of the straight lines for smaller particle size shown in Fig. 7(b) except for the results of 90 min. This implies that the smaller particles of granulated slag can not be easily ground in comparison with the larger ones.

Fig. 8 Variation of reduction ratio with the grinding time for copper smelting slags and quartz.

Fig. 9 Cumulative fraction retained on the stated screen size as a function of the grinding time for three sizes of slag samples.

Fig. 8 indicates the reduction ratio, r , defined by (d_0/d_{50}) as a function of the grinding time for three particle sizes of the granulated slag together with the results of quartz with the particle size ranging from 710 to 840 μm . The reduction ratio is known to correspond to the grindability. It is generally said that the larger the reduction ratio of a sample becomes, the easier the sample is able to be ground when the grinding energies input in samples are equivalent. As shown in Fig. 8, better grindability is found in the slag samples having a larger particle size which involve a large amount of crystalline components, compared with smaller particle size consisting mainly of glassy component. However, the grindability of the slag sample is much lower than that of quartz.

The cumulative fraction, R , retained on the stated screen size for the slag samples with three different particle sizes is given in Fig. 9 as a function of the grinding time. The fractional rate of breakage, k , can be determined from the gradient of each curve in Fig. 9, depending on the grinding time.⁶⁾ The value of k in two cases of 1680 ~ 2380 μm and 3360 ~ 4760 μm shows a remarkable change with an increase in the grinding time in the initial grinding stage within a few minutes. This contrasts with the smaller particle size of 420 ~ 590 μm . On the other hand, in the long grinding time region, the gradient of the two curves for the cases of 1680 ~ 2380 μm and 3360 ~ 4760 μm , apparently becomes smaller than that for the 420 ~ 590 μm case. This may be attributed to the production of a large amount of fine particles during long grinding of the slag samples with the crystalline components.

4. Concluding Remarks

The strength and grindability of copper smelting slags produced by water quenching were tested together with the X-ray diffraction analysis. The following conclusions of this study could be made:

- (1) The granulated slag is found to be the mixture of crystalline and glassy components, amounts of which are closely related to the original particle size.
- (2) The reduction ratio of a slag sample with a large amount

of crystalline component is almost twice as large as that of a slag sample mainly composed of a glassy component. This result is well attributed to the single particle strength measurements.

- (3) The density of the slag samples varies almost inversely in comparison with the results of the single particle strength measurements.
- (4) The granulated slag samples in this work are not easily ground in comparison with quartz.

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Nomenclature

d	: distance between two parallel platens when a particle is beginning to be compressed	[m]
d_0	: original particle size	[μm]
d_{50}	: particle size passed 50% of ground particles	[μm]
D	: cumulative fraction passing	[—]

E	: fracture energy	[J]
E/M	: specific fracture energy	[J/kg]
k	: fractional rate of breakage	[min^{-1}]
M	: mass of a specimen	[kg]
P	: fracture load	[N]
r	: reduction ratio	[—]
R	: cumulative fraction retained	[—]
St	: particle compressive strength	[Pa]
t	: grinding time	[min]
Y	: Young's modulus	[Pa]
W_i	: Bond's work index	[kWh/t]
2θ	: Bragg's angle	[°]
Δ	: deformation of a specimen	[m]
ρ	: density of a sample	[kg/m^3]
ν	: Poisson's ratio	[—]

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銅製錬水砕スラグの強度と破砕性

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銅製錬工程において大量に排出されるシリケート系水砕スラグについて、X線回折法等によるキャラクタリゼーションを行うとともに、同水砕スラグの強度と破砕性について、単粒子破砕ならびに集合粉砕の立場から実験的に検討を行った。まず、X線回折結果では、生成粒度約1.5mm以上の粗粒子はFayalite, Magnetiteの結晶質を多く含み、粒子径が小さくなるに伴いガラス質構造となっていることがわかった。この結果を踏まえて、生成粒度毎の粒子から10~20 μm (平均粒子径15 μm)の粒子を作製し、その強度を測定した結果、細粒子 (ガラス質) の強度は粗粒子

(結晶質)のその約2倍となっていること等がわかった。また、ボールミルによる粉砕実験では、細粒子の粉砕比 (粉砕前粒度 / 粉砕後粒度) は粗粒子のその約 (1/2) となっている等、粗粒子は細粒子に比較して破砕されやすいことがわかった。

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