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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect of Mechanical Activation of Magnesia-Ferriferous Slags in Carbon Dioxide on Their Properties

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Abstract—Effect of the mechanochemical activation of magnesia-ferriferous slags in air and in carbon dioxide on their binding properties and the strength of samples, including those produced in fabrication of slag-alkaline binders was studied. Data on the composition of newly formed substances, furnished by scanning electron microscopy and X-ray fluorescence microanalysis, are presented.

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The aim of this study was to make a comparative analysis of the influence exerted by mechanical activation (MA) in a centrifugal-planetary mill of magnesia-ferriferous slags formed in nonferrous metallurgy on their binding properties in relation to the following parameters: (1) type of a medium (air, carbon dioxide), (2) presence of an activator (soluble glass), (3) specific surface area of the slag, and (4) duration of hardening under standard conditions.

Previously, the binding properties of magnesia-ferriferous slags from Kola mining-and-smelting company have been studied in the case of their normal hardening without activators in relation to the time and medium of grinding (air, CO_2) in ball and vibration mills [1, 2]. As expected, the strength of samples obtained without active additives was low. Samples produced from ground slags formed at Pechenganikel' combine had a compression strength not exceeding 4 MPa. At the same time, the strength of a magnesia-ferriferous slag ground to a specific surface area of 570 $m^2 kg^{-1}$ in a ball mill in the atmosphere of CO_2 was 3.5 MPa at hardening durations of 28 days and more, whereas a similar parameter of a slag ground in air was as low as 0.3 MPa [2]. The centrifugal-planetary mill was chosen in the present study because this mill, being the most energy-intensive apparatus, provides the maximum mechanochemical effect and thereby makes it possible to clearly elucidate the effect of various factors and, in particular, the MA medium on the strength of slag samples, including those contained in a slag-alkaline binder (SAB).

It was found in [3–7] that metallurgical slags from Pechenganikel' combine are hardened in standard conditions under alkaline activation. The components of SAB are finely ground granulated slag and soluble liquid glass. It was shown that a key factor in SAB hardening is the content of Na_2O as the most active part of soluble glass. To obtain the maximum strength, it is necessary to satisfy the following conditions: Na_2O content 3–5% (relative to the mass of finely ground slag in SAB), liquid glass modulus 1.5–2.0, water-to-slag ratio W/S 0.20–0.23 [4]. The increased activity of sodium liquid glass in hardening reactions at a silica modulus of 1.5–2.0 is presumably due to the specific structure of the Na silicate solution, which is confirmed by dilatometric data [5]. The effect of MA, including the medium of MA, on the SAB strength has not been studied previously.

A necessary condition for hardening of a composite into SAB is the ability of the surface of the active component to interact with the alkaline component to give hydrosilicates. It is known that the reactivity of the surface layers of powder particles can be markedly changed by MA [8–11]. A possible important factor that affects the state of the surface of a material being

dispersed is the gas medium in which the grinding is performed. It has been found previously that a prolonged grinding of Ca,Mg-containing silicates is accompanied by absorption of large amounts (>10 wt %) of atmospheric CO_2 by these materials [12]. The carbonization effect is enhanced in the case of MA in a purely CO_2 atmosphere [13, 14]. It should be noted that a deep mechanically induced interaction of silicates with carbon dioxide is not accompanied, contrary to expectations, by formation of calcite, magnesite, and other carbonate materials. Under the influence of a mechanical activation, CO_2 molecules penetrate into the bulk of a structurally disordered silicate matrix to give distorted carbonate groups. As a result, not only the structure, but also the chemical composition of outer layers of particles directly involved in hydration reactions are strongly modified.

EXPERIMENTAL

The mechanochemical activation was carried out in an AGO-2 laboratory centrifugal-planetary mill at a centrifugal factor of 40 g. Steel balls 8 mm in diameter served as milling bodies. The ratio between the masses of the balls and a sample being ground was 10. In grinding of samples in the atmosphere of CO_2, the mill drums were filled prior to an experiment with carbon dioxide from a cylinder, with air whose density is 1.5 times lower than that of CO_2 being displaced. The procedure of drum filling with CO_2 was repeated every 30 s of MA. Prior to the drum filling with carbon dioxide, the reaction mass was agitated. The specific surface area was measured using the air-permeability method. An X-ray phase analysis was made on a DRON-2 diffractometer ($Cu_{K\alpha}$ radiation). The content of CO_2 in the samples was determined by the volumetric method with an AN-7529 analyzer as follows. A weighed portion of a sample was calcined in a furnace at 1200°C. The carbon dioxide evolved in the process was absorbed in an electrochemical cell by a strontium chloride solution, which caused its acidification. The resulting solution was neutralized by passing a current through the cell, via reduction of hydrogen ions. The content of CO_2 was found from the quantity of electricity required for the neutralization.

Backscattered-electron (SEM) images of parts of the polished surface of preparations were obtained with a LEO-1450 scanning electron microscope. A diagnostics and an X-ray fluorescence microanalysis of the phases observed were performed with a ROENTEC energy-dispersion detector, an attachment to the scanning electron microscope.

Samples with dimensions of 1.41 × 1.41 × 1.41 cm were fabricated from a normal-thickness paste produced from ground slags to determine their binding properties in the absence of an activator. The samples were hardened under humid conditions at a temperature of 20–22°C. In a study of SAB, identical cubes were fabricated with consideration of the optimal conditions described above: 5% Na_2O (relative to the mass of a finely ground slag in SAB), liquid glass modulus 1.5, W/S 0.23.

The mineral composition of slags from Pechenganikel' combine is dominated by a magnesia-ferriferous glass (95–98 wt %); the amount of the crystalline phase (skeletal crystals of olivine) is 2–5 wt %, and that of ore minerals, 1–3 wt %. The chemical composition of the

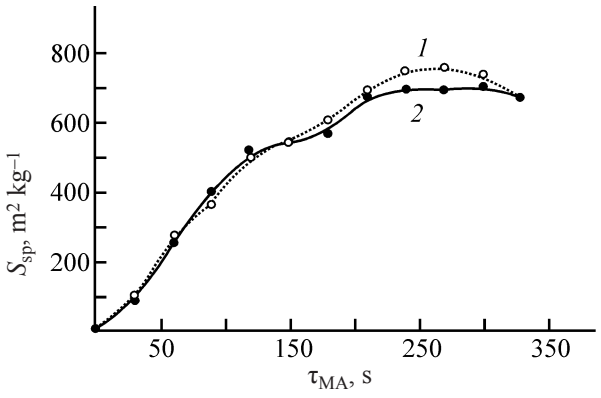

Fig. 1. Specific surface area S_{sp} of the slag vs. the MA duration τ_{MA} in an AGO-2 centrifugal-planetary mill in (*1*) air and (*2*) CO_2.

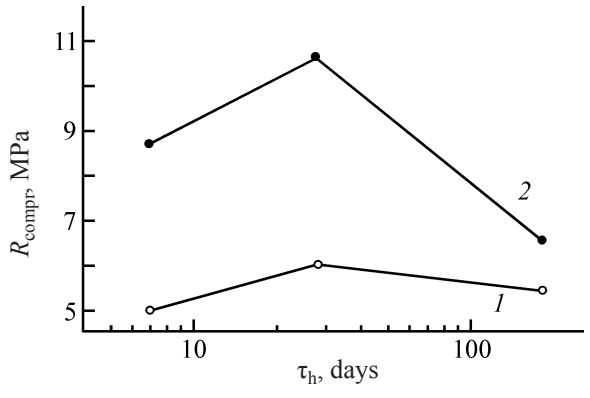

Fig. 2. Compression strength R_{compr} of slag samples obtained without an activator vs. the hardening duration τ_h. S_{sp} (m^2 kg^{-1}): (*1*) 670 (air) and (*2*) 690 (CO_2).

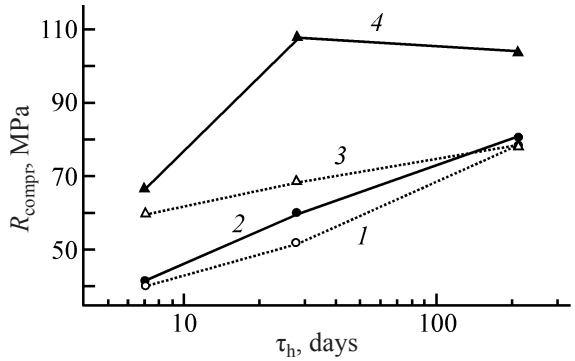

Fig. 3. Compression strength R_{compr} of SAB samples vs. the hardening duration τ_h. S_{sp} (m^2 kg^{-1}) (*1*) 410, (*2*) 450, (*3*) 750, and (*4*) 730. MA medium: (*1, 3*) air and (*2, 4*) CO_2.

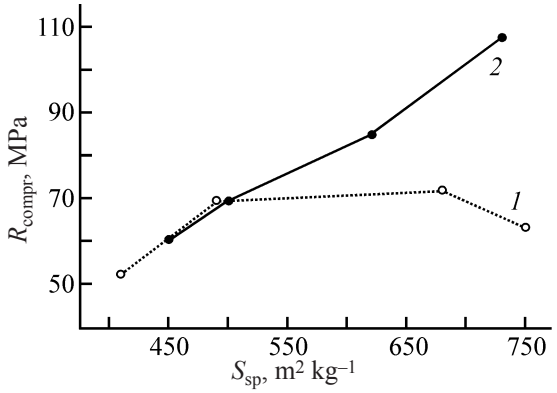

Fig. 4. Compression strength R_{compr} of SAB samples with an age of 28 days vs. the specific surface area S_{sp} of the slag. MA medium: (*1, 3*) air and (*2, 4*) CO_2.

slags is as follows (wt %): SiO_2 40.88, Al_2O_3 6.90, FeO 35.40, CaO 2.65, MgO 10.71, ($Na_2O + K_2O$) 2.1, S 0.71, and trace amounts of Fe_2O_3.

Data on the specific surface area S_{sp} of the slag are shown in Fig. 1 in relation to the duration of MA in an AGO-2 centrifugal-planetary mill in air and in the atmosphere of CO_2. At treatment durations shorter than 150 s, S_{sp} is almost insensitive to the MA medium; further, dispersion becomes more effective in air, in agreement with the data previously obtained for the ball mill [2]. The decrease in S_{sp} upon an MA in CO_2 may be due both to enhancement of the molecular-dense aggregation of particles and to an increase in the plasticity of the material as a result of CO_2 absorption by outer layers of slag grains. According to analytical data, the CO_2 content of the slag upon 330 s of MA in carbon dioxide is 0.50 wt %. A similar value for MA in air is 0.20 wt %.

Chemical composition of new formations in SAB according to the results of an X-ray fluorescence microanalysis (with H_2O disregarded)

Component	Content, wt %			
	in a crack	between grains	spherical inclusions	between grains
	grinding medium			
	CO_2			air
CO_2	19.1	16.1	16.9	8.3
MgO	7.8	6.8	9.4	7.8
SiO_2	41.2	41.2	40.1	41.8
FeO	16.2	22.7	16.9	25.7
$A1_2O_3$	6.0	5.8	7.0	8.3
CaO	4.6	2.7	2.2	2.8
Na_2O	3.4	2.9	6.3	3.5
K_2O	1.1	0.91	0.75	0.84
TiO_2	0.70	0.81	0.52	0.79

For the two MA media, $S_{sp} \approx 700$ m^2 kg^{-1}; data on the compression strength R_{compr} of activator-free slag samples are presented in Fig. 2 in relation to the hardening duration. It can be clearly seen that the MA in carbon dioxide yields higher strength samples at all hardening durations. During the first 28 days, the strength increases for both grinding media, and after that it starts to decrease, i.e., there occurs the so-called "temporal decrease in strength." The absolute values of the compression strength are several times those obtained with a ball mill [2], but the maximum value of R_{compr} does not exceed 11 MPa (Fig. 2).

Figure 3 shows dependences of the R_{compr} of SAB samples on the hardening duration for specific surface areas of the slag of approximately 400 and 700 m^2 kg^{-1}. The same tendency is observed, if samples with comparable values of S_{sp} are examined: the atmosphere of carbon dioxide as an MA medium intensifies hydration processes. Data on the R_{compr} of SAB samples with an age of 28 days, presented in Fig. 4 in relation to the specific surface of the slag, indicate that the positive influence of CO_2 becomes more pronounced as the degree of dispersion increases. It should be noted that the strength of SAB samples obtained with the MA of the slag in CO_2 reaches values of 100–110 MPa (Figs. 3, 4).

Figures 5 and 6 show typical SEM images of polished surfaces of samples obtained in SAB hardening. Morphological characteristics of samples produced from

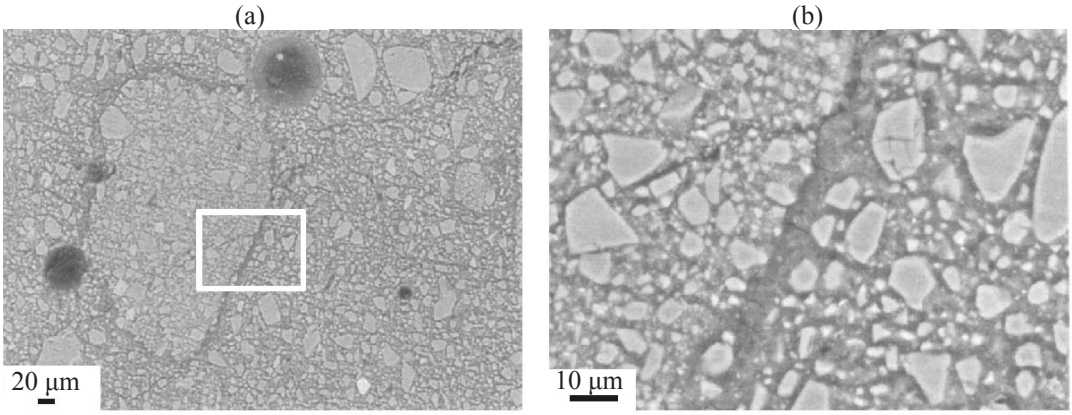

Fig. 5. SEM images of hardened SAB samples based on a slag ground in carbon dioxide. Fig. 5b shows the fragment denoted by the rectangle in Fig. 5a.

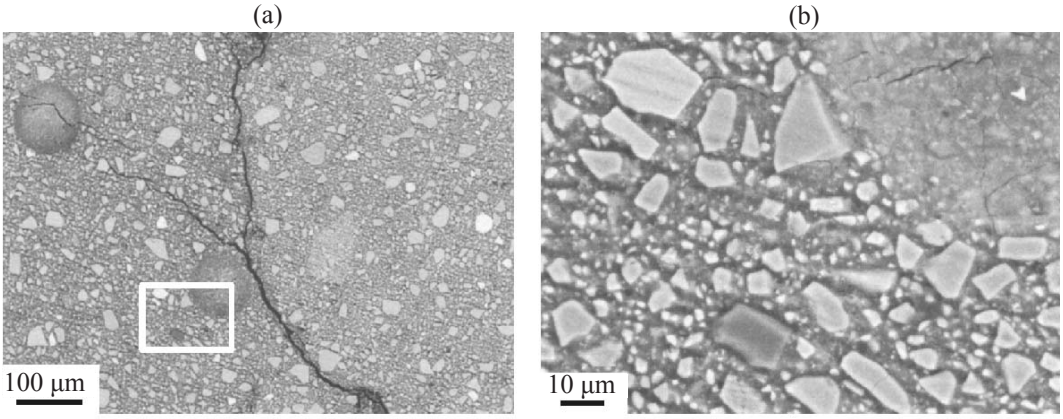

Fig. 6. SEM images of hardened SAB samples based on a slag ground in air. Fig. 6b shows the fragment denoted by the rectangle in Fig. 6a.

a slag ground in carbon dioxide (Fig. 5) and in air (Fig. 6) are similar. Together with polydisperse irregularly shaped slag particles distributed in the bulk of the hardened cement phase (dark background), it also contains spherical formations 30–200 μm in diameter (Figs. 5a, 6a). The spherical inclusions presumably appear upon the following processes. In placement of the mixture into molds, air bubbles penetrate into the bulk of samples. The resulting pores are gradually filled with the liquid phase containing slag microparticles, which then solidifies. The presence of slag microparticles in the spheres is clearly seen in Fig. 6a. It should be noted that the formation of spherical pores in hardening of SABs based on magnesia-ferriferous slags was previously noted in [7].

It was of interest to find out how the atmosphere in which the slag is ground affects the composition of new formations in SAB hardening. According to XPA data, the new formations have a colloidal or a concealed-crystalline structure, in agreement with the results of [7]. The table lists the averaged composition of the new formations in SAB, found by X-ray fluorescence microanalysis, without regard for water for samples produced by slag grinding in carbon dioxide and in air. The analysis was made at points in the intergrain space, in cracks filled by the cement phase, and in spherical inclusions. It follows from the data in the table that, with CO_2 used as the grinding medium, the compositions of the newly formed substance at these points are, on the whole, close. The main distinction of the composition of the newly formed substance for a slag ground in air is the substantially lower content of carbonate groups. According to the data obtained, it is 2–2.5 times lower than that for samples produced by grinding in carbon dioxide (see table). This indicates that, as a result of interaction with liquid glass, carbon dioxide absorbed in grinding by outer layers of slag particles to give carbonate ions passes into the new

formations. It should also be noted that, with water and CO_2 disregarded, the composition of the new formations is close to similar data obtain in [7] by chemical analysis (no analysis for CO_2 was made in [7]).

CONCLUSIONS

(1) It was found that a preliminary mechanical activation in the atmosphere of carbon dioxide, compared with that in air, makes the sample strength higher, including the case of synthesis of slag-alkaline binders.

(2) A mechanism by which absorbed carbon dioxide affects properties of a slag-alkaline binder via interaction of a liquid glass solution with the outer carbonized layer was suggested.

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