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APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS TO DETERMINE THE INFLUENCE OF THE THERMAL HISTORY ON THE DEGREE OF VITRIFICATION IN THE SYSTEM $CaO–MgO–SiO_2$

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Diopside, $CaO.MgO.2SiO_2$, and glasses of the same stoichiometry are fundamental phases in non-ferrous slags. Samples of this composition, prepared from the melt at different cooling rates, were examined via DTA and IR spectra. A correlation was found between the degree of vitrification and the magnitude of the exothermic effect at around 870 °C. The same dependence exists for some slags. No exotherm was observed for well-crystallized samples. The reactivity with water was assigned to the glass content.

The glass content of a slag, an important factor determining its hydraulic properties [1], can be determined by X-ray diffraction [2, 3] or by scanning electron microscopy [4]. The properties of slags also depend on the fineness and the cooling rate [5]. According to some investigators, differential thermal analysis is a sensitive and fast method for determination of the glass contents of slags.

In this work, we synthesized compositions in the system $CaO–MgO–SiO_2$ at different cooling rates. The chemical compositions of the samples corresponded to diopside ($CaO \cdot MgO \cdot 2SiO_2$), which is one of the fundamental phases in non-ferrous slag. The effects of the thermal history on the glass content and hydraulic properties are discussed.

Experimental

Glasses of the composition $CaO \cdot MgO \cdot 2SiO_2$ were obtained at different cooling rates, as shown in Fig. 1 (water-quenching and air quenching). $CaCO_3$, $MgCO_3$ and SiO_2 were used as chemical reagents for these syntheses, which were carried out in Pt crucibles. Glasses were ground to have a Blaine's surface area of about 400 $m^2 \cdot kg^{-1}$. All synthesized glasses were autoclaved at 200° for 72 h and then investigated by IR spectroscopy and X-ray diffraction (XRD).

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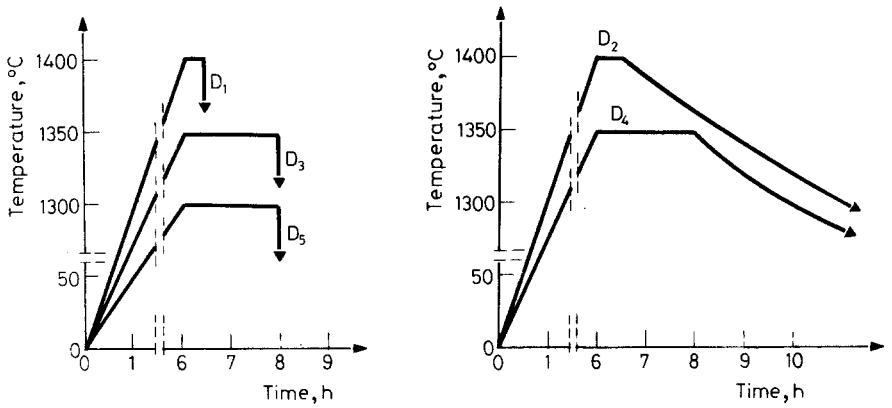

Fig. 1 Heating and cooling schedule for preparation of samples:
D_1, D_3, D_5 water-quenching
D_2, D_4 air coding

Results and discussion

The effects of the thermal history on the structures and hydraulic properties of the synthesized samples were confirmed by IR and DTA methods (Figs 2 and 3). The highest degree of vitrification in the system $CaO–MgO–SiO_2$ was found for sample D_1. As shown in Fig. 2, intense IR bands were detected in its spectrum. IR and

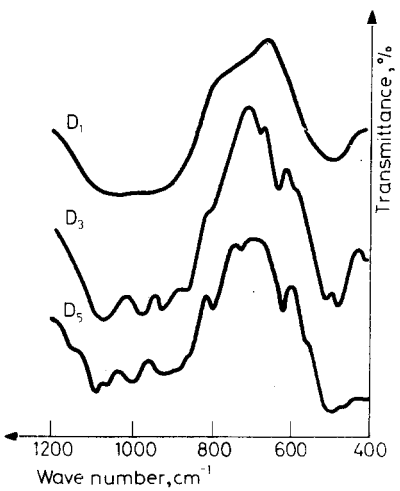

Fig. 2 IR spectra of quenched samples

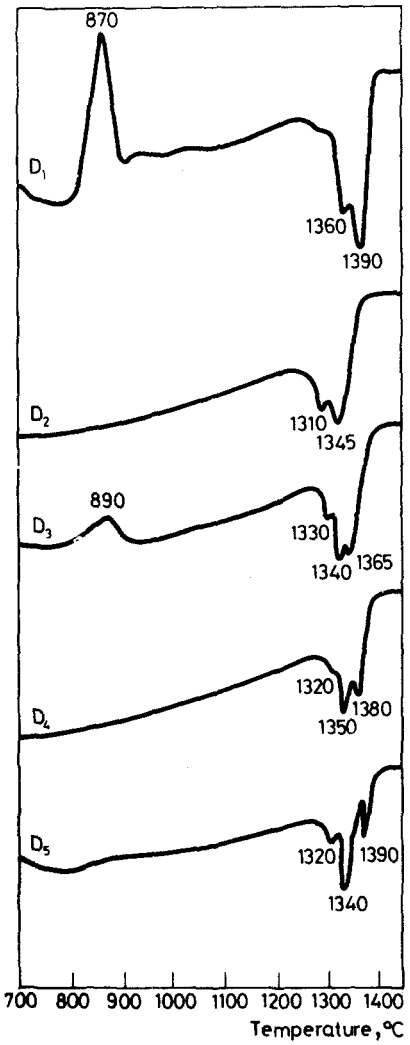

Fig. 3 DTA curves of:
quenched samples (D_1, D_3, D_5)
slowly-cooled samples (D_2, D_4)

XRD investigations indicated a low degree of crystalline order in water-quenched samples. Examinations of synthesized samples by means of DTA showed that endothermic effects occurred in the temperature range 1300–1400°. Exothermic peaks at about 880° were observed only for the vitreous samples D_1 and D_3.

A similar dependence was found in the examined slags. Microscopic investigations of non-ferrous slag showed a glass content of 85–90%. Upon DTA,

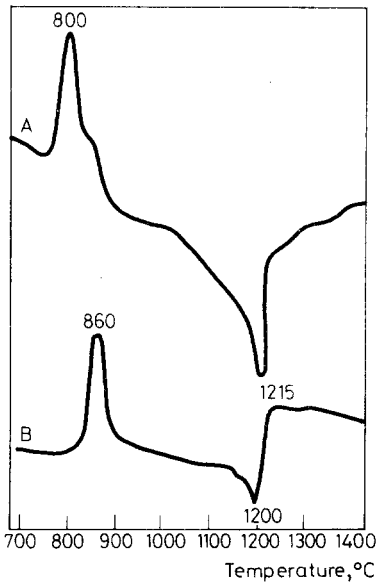

Fig. 4 DTA curves of non-ferrous slags

these slags gave exothermic peaks at 800° and at 860°. Furthermore, the DTA curves of slags heated at 1000° for 1 h and then slowly cooled to allow crystallization did not exhibit any exothermic effect. These results indicate a correlation between the magnitude of the exothermic effect at about 870° and the degree of vitrification of slag samples.

Samples D_1, D_2, D_3, D_4 and D_5 were treated under hydrothermal conditions at 200° for 72 h, and then investigated by XRD. The greatest reactivity was found in vitreous phases (specimens D_1 and D_3). XRD revealed the highest amounts of hydrates in well vitrified samples.

As concerns the reaction with water, vitrified phases displayed a greater activity than well-crystallized phases with the same overall composition.

References

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Zusammenfassung — Diopsid $CaO.MgO.2SiO_2$ und Gläser dieser Zusammensetzung sind wesentliche Bestandteile von Schlacken der Nichteisenmetallurgie. Aus der Schmelze mit verschiedenen Abkühlungsgeschwindigkeiten präparierte Proben dieser Zusammensetzung wurden durch DTA und IR-Spektroskopie untersucht. Zwischen dem Glasgehalt und der Grösse des exothermen Effekts bei 870 °C wurde ein Zusammenhang gefunden. Die gleiche Abhängigkeit besteht bei einigen Schlacken. Gut kristallisierte Proben zeigen keinen exothermen Effekt. Die Reaktivität mit Wasser wird ebenfalls dem Glasgehalt zugeschrieben.

Резюме — Диопсид $CaO.MgO.2SiO_2$ и стекла того же самого стехиометрического состава являются основными продуктами шлаков цветной металлургии. Образцы с таким составом, полученные из расплавов при различных скоростях охлаждения, были исследованы методом ДТА и ИК спектроскопии. Установлена корреляция между степенью стеклования и значением экзотермического эффекта около 870°. Аналогичные зависимости существуют и в некоторых шлаках. В хорошо кристаллизующихся образцах не наблюдалось экзотермических эффектов. Реакционная способность образцов с водой обусловлена наличием стекла.