N. A. TOROPOV, B. V. VOLKONSKII, and V. I. SADKOV

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N. A. TOROPOV, B. V. VOLKONSKII, and V. I. SADKOV

ON THE QUESTION OF THE POLYMORPHISM OF DICALCIUM SILICATE

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Dicalcium silicate is one of the principal minerals of Portland-cement clinker. Therefore, the question of studying the process of polymorphic transformations of dicalcium silicate has always attracted the attention of many investigators.

The polymorphic transformations of dicalcium silicate have been studied by various methods: the petrographic method, in which differences in the modifications were established from optical constants; the X-ray method; dynamic methods, or the method of heating and cooling curves; and, finally, the static method, or the method of instantaneous cooling– "quenching."

Dicalcium silicate was at one time identified in three modifications: α, β, and γ. Subsequently, a number of investigators indicated the existence also of β'- and α'-modifications of dicalcium silicate.

Bredig ([1]) considers that, alongside the α-modification C_2S, isomorphous with α-K_2SO_4, there also exists α'-$2CaO \cdot SiO_2$, isomorphous with the rhombic form of β-K_2SO_4 and stable in the range between the high-temperature α-form and 850°. F. I. Vasenin ([2]), using the method of heating and cooling curves, established the existence of a C_2S form which he assigns to β'-C_2S. Later, Tromel and Möller ([3]) also noted the existence of α'-C_2S. Saalfeld ([4]), in his work, likewise confirms the existence of α'-C_2S.

Interesting data are given by Metzger ([5]). He considers generally accepted the opinion that C_2S is present in Portland-cement clinker exclusively in the form of β-C_2S or α-C_2S. A similar point of view was supported by Nurse ([6]) in 1952 in his report at the International Congress on the Chemistry of Cement in London. However, he noted the possibility of the presence also of the α'-modification. The modeling method proposed by Goldschmidt ([7]) consists in using the low-melting system NaF—BeF_2 as a model of the system CaO—SiO_2. These studies were continued by Tilley ([8]). The results obtained by him coincide to a considerable extent with the above-mentioned results of direct studies of C_2S; thus, for example, in Na_2BeF_4–a model for C_2S–there appears, as the stable modification at the highest temperature, a hexagonal crystal lattice which, like α-C_2S, has a structure of the Na_2SO_4 type.

Fig. 1. Ionization X-ray diffraction patterns of five polymorphic modifications of dicalcium silicate. A —α-modification, —α'-modification, —β'-modification, —β-modification, —γ-modification

Figure 1: Fig. 1. Ionization X-ray diffraction patterns of five polymorphic modifications of dicalcium silicate. A —α-modification, —α'-modification, —β'-modification, —β-modification, —γ-modification

In studying the polymorphism of dicalcium silicate, we applied the method of high-temperature ionization X-ray patterns. On a high-temperature ionization X-ray structural apparatus we were able to follow the process of polymorphic transformations of dicalcium silicate, to establish the temperature limits of these transformations, to reveal the β'- and α'-modifications of dicalcium silicate, and to obtain their X-ray characteristics. As the starting material we took, according to the previously established classification, the γ-modification of dicalcium silicate.

Upon heating the γ-modification of C_2S to 760°, it has a crystal lattice characterized by three strong diffraction maxima, which have interplanar-spacing values $d/n = 3.00$ Å; 2.73 Å; 1.90 Å, and corresponding intensities $I/I_1 = 100, 53$, and 41. At a temperature of 760° the lattice of the γ-modification begins to change, and in the temperature interval from 760° to 900° the β-modification of dicalcium silicate is recorded; its lattice, as is known, has two characteristic strong diffraction maxima: 2.77 and 2.73 Å, and corresponding intensities $I/I_1 = 100$ and 92.

Fig. 1. Ionization X-ray diffraction patterns of five polymorphic modifications of dicalcium silicate.
A —α-modification, —α'-modification, —β'-modification, —β-modification, —γ-modification.

Then, at a temperature of 900° the β-modification of dicalcium silicate passes into a modification designated by us as β'. This modification exists up to a temperature of 1230° and has the following X-ray characteristic for the brightest diffraction maxima: $d/n = 2.80$ Å; 2.75 Å; 2.27 Å; 1.97 Å; 1.608 Å; 1.401 Å, and corresponding intensities $I/I_2 = 100, 74, 22, 22, 28$, and 28.

With an increase in temperature to 1230° we again observe a rearrangement of the crystal lattice of dicalcium silicate, and in this temperature interval a special structure is recorded, which we assign to the α'-modification of dicalcium silicate.

The α'-modification of dicalcium silicate has an X-ray characteristic of the principal diffraction maxima with the following values of d/n: 2.83 Å; 2.30 Å and 1.62 Å, with corresponding intensities I/I_1: 100, 18, and 23.

When the temperature is raised above 1420°, the lattice of the α'-modification of dicalcium silicate passes into the known high-temperature α-modification.

On cooling, the same transitions of the polymorphic modifications are observed in the reverse order.

The temperature boundary of the transition of the β'-modification into the β-modification shifts toward lower temperatures to 650°, while the temperature of the transition of the β-modification into the γ-modification shifts to 450°.

Table 1

β'-Modification	β'-Modification	α'-Modification	α'-Modification
d/n, Å	I/I_1	d/n, Å	I/I_1
2.80	100	2.83	100
2.75	74	2.44	9
2.40	11	2.36	4
2.27	22	2.30	18
2.08	6	2.109	4
1.974	22	2.034	4
1.783	6	1.993	4
1.608	28	1.626	23
1.577	6	1.413	14
1.401	28		
1.195	11		

The ionization X-ray diffraction method used made it possible, by direct recording of ionization X-ray diffraction patterns at high temperatures, to establish the existence of β'- and α'-modifications of dicalcium···

silicate and to obtain their X-ray characteristics (Fig. 1).

Table 1 gives the numerical values of the diffraction maxima and their intensities, and the interplanar spacings in the crystal lattice of the β'- and α'-modifications of dicalcium silicate.

All-Union Scientific Research
Institute "Giprocement"

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Note: Figure translations are in progress. See original paper for figures.