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Effect of Cr_2O_3 on the formation of C_3S in $3CaO:1SiO_2:xCr_2O_3$ system

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Abstract

Specimens of tricalcium silicate (C_3S) containing 0.5, 1, 1.5, 2, 4, and 5 wt.% Cr_2O_3 were prepared by repeated firing of a mix containing $CaCO_3$ and quartz in 3:1 stoichiometric ratio along with varying concentrations of Cr_2O_3 at 1450°C. The final products were investigated using chemical analysis, XRD, OM, and scanning electron microscope (SEM) with EDAX. It has been found that there is a formation of $CaCrO_4$ compound. The triclinic form of pure C_3S is retained with Cr_2O_3 up to 2%. Introduction of 4–5% Cr_2O_3 converts it to the monoclinic form. Cr_2O_3 is soluble in C_3S up to 1.56% at 1450°C. Cr_2O_3 improves the crystal size of C_3S up to 1% only. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: C_3S; Cr_2O_3; $CaCrO_4$; Polymorphs; Solubility

1. Introduction

Chromium has been reported to replace calcium, silicon, or both in chromium doped tricalcium silicate (C_3S) [1–3]. Different authors have reported the limit of solubility at 0.9% [4], 1.368% [3], 1.4% [5], 1.5% [6], 1.7% [1], and 2% [2] of Cr_2O_3 mass percentage of C_3S solid solution, at various temperatures. Solubility at 1450°C has not been reported. Much attention has not been paid to the investigation of the chromium compounds, e.g. calcium chromate, a compound considered as a corrosion inhibitor [7], formed in the system CaO-SiO_2-Cr_2O_3 at 1450°C.

Present investigations aim at finding the solubility of Cr_2O_3 in C_3S at the temperature of formation of C_3S, i.e. 1450°C and study the various polymorphs stabilized at this temperature, to look into the distribution of Cr in the phases, and formation of chromium compounds in the CaO-SiO-Cr_2O_3 system.

2. Experimental

2.1. Preparation of specimens

Pure C_3S and its solid solutions with chromium were made exactly under identical conditions by repeated firing of calcium carbonate and quartz in the stoichiometric ratio of 3:1 in presence of varying amounts of Cr_2O_3 from 0.5 to 5 wt.% of C_3S at 1450°C. All the materials used were of analytical reagent grade. Calcium carbonate and quartz were ground to a fine powder and homogenized with Cr_2O_3 in anhydrous acetone. The dried mass was pressed into pellets of 10-mm diameter by applying a pressure of 5000 kg/cm^2 using a hydraulic press and fired at 1450°C for 4 h in a platinum dish in an electric furnace. The sintered pellets were ground to pass 63-μm sieve and reformed into pellets and fired again at 1450°C for 4 h. Samples were cooled at room temperature at ~27°C. This process was repeated until free lime was reduced to <0.1% in pure C_3S. The final products were examined by chemical analysis, XRD, OM, and scanning electron microscope (SEM) with EDAX.

2.2. Chemical analysis

Free lime was estimated in the final products using ethylene glycol method [8].

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2.3. XRD analysis

Specimens of pure and Cr_2O_3-doped C_3S were powdered to pass 45-μm sieve and studied on the Regaku Rad Max system with wide-angle horizontal goniometer and graphite monochromator using CuKα radiations.

2.4. Optical microscopy

The polished sections of the specimens etched with hydrofluoric acid were examined under a Zeiss Polarizing Microscope for qualitative determination of the phases.

2.5. Electron microscopy

SEM and EDAX studies were carried out on a Philips SEM 515 with EDAX PV 9900 for the study of microstructural features, limit of incorporation of Cr_2O_3 into C_3S and its distribution in the phases.

3. Results and discussion

3.1. Chemical analysis

3.1.1. Free lime

Results of free lime in the final products as determined by the ethylene glycol method have been presented in Table 1. The results indicate that there is very little release of free lime up to 1.5% addition of Cr_2O_3. Specimen containing 2% Cr_2O_3 has 0.79% CaO_f. This indicates that Cr_2O_3 gets into solid solution of C_3S up to 1.5%. Beyond 1.5% Cr_2O_3, there seems a partial decomposition of C_3S, resulting in the release of lime. This is supported by the work of Boikova who reported that the limiting solid solution of Cr_2O_3 in C_3S, contained only 1.5 wt.% Cr_2O_3 at 1500°C. If Cr_2O_3 content exceeds 2 wt.%, there occurs the decomposition of the solid solutions with the formation of free CaO and dicalcium silicate stabilized by Cr_2O_3. With increasing Cr_2O_3 content in the mixture, the amount of solid solution $3CaOSiO_2$ with Cr_2O_3 decreases, and at more than 5 wt.% Cr_2O_3, no formation of the solid solution is observed [6].

3.2. XRD study

Specimens of pure and doped C_3S were subjected to the X-ray diffraction analysis. The various polymorphs detected in the specimens have been presented in Fig. 1 and Table 2. Specimens doped with Cr_2O_3 up to 2% indicate mainly the presence of C_3S. Specimens containing 4% and 5% Cr_2O_3 show the presence of C_3S, C_2S, CaO_f, and $CaCrO_4$. In the 5% Cr_2O_3 specimen, peaks having *d* values of 3.61 and 1.85 Å indicate the presence of $CaCrO_4$ (Fig. 2).

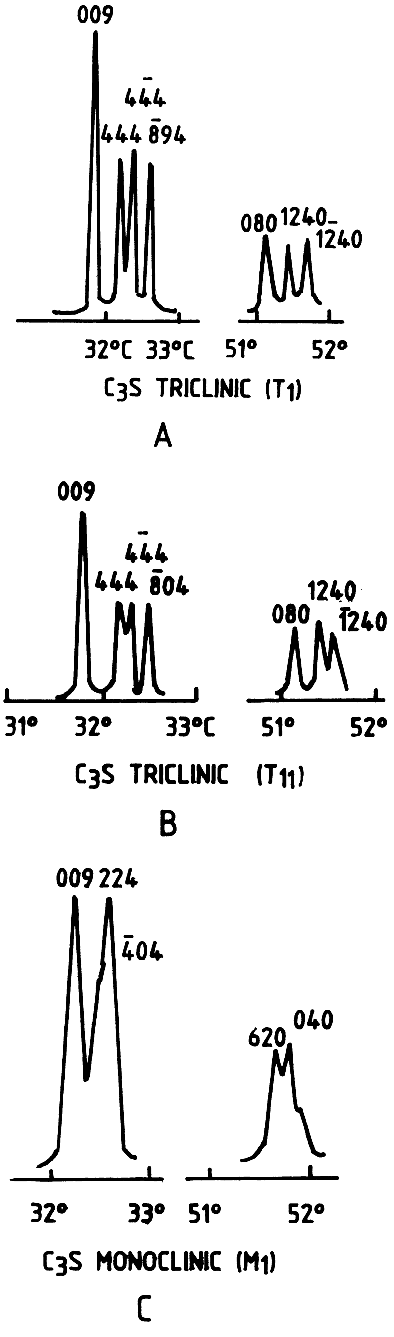

Fig. 1. (A) C_3S with 0.5% Cr_2O_3; (B) 2% Cr_2O_3; (C) 5% Cr_2O_3.

Table 1
CaO_f/% Cr_2O_3

Cr_2O_3	0	0.5	1	1.5	2	4	5
CaO_f	0.07	0.10	0.20	0.25	0.79	1.87	2.56

Table 2
Polymorphs of C_3S with varying percentage of Cr_2O_3

Sakurai et al. [1]	Enculescu [9]	This study
0–1.4% T_I	0.5% M_I	0–0.5% T_I
1.4–1.7% T_{II}	2.0% M_I	1–2.0% T_{II}
–	–	4–5.0% M_I

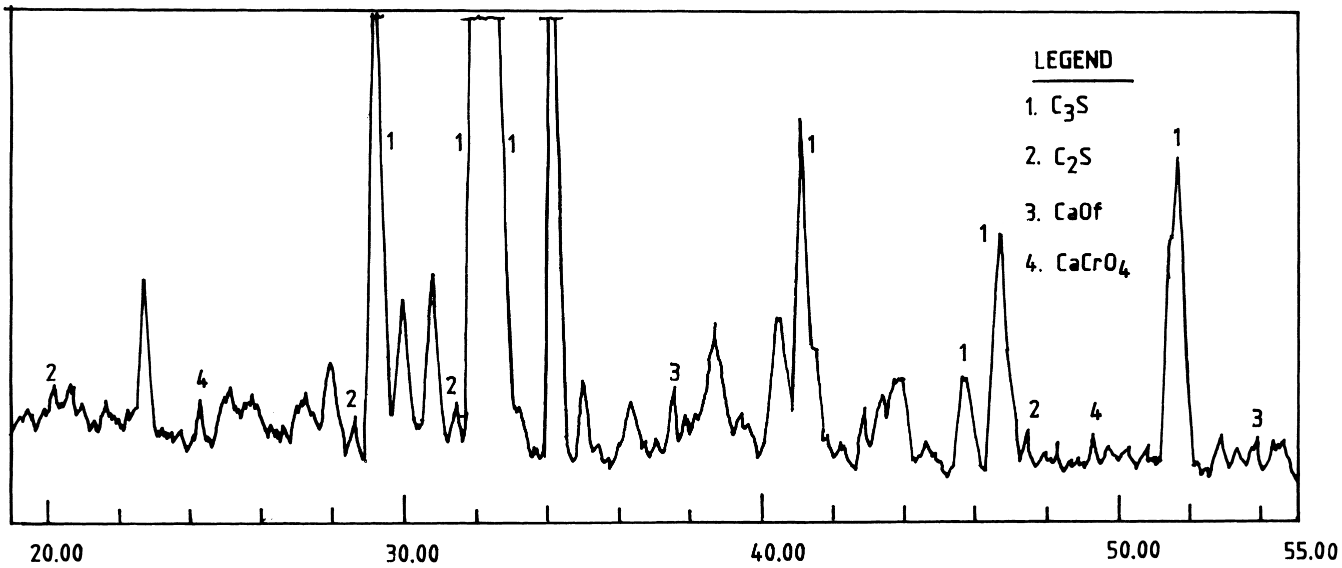

Fig. 2. C_3S with 5% Cr_2O_3.

Enculescu [9] found $2CaOSiO_2$, Cr_2O_3, and calcium chromate ($CaCrO_4$) in samples doped with 4% and 8% Cr_2O_3 by XRD. It is reported that the solid solutions of C_3S with Cr_2O_3 may be described by the formula:

$$(Ca_{3-x}Cr_x)(Si_{1-y}Cr_y)O_{5-z}.$$

3.3. Microscopy

3.3.1. Optical microscopy

The crystal size of the specimens was observed in the final products, and results are presented in Table 3 along with the results of the other authors. It has been observed that there is an increase of the size of the C_3S with the introduction of Cr_2O_3 up to 2% only. The size is maximum at 1% Cr_2O_3 level. It starts diminishing beyond 2% Cr_2O_3, in comparison to the pure C_3S. Butt et al. [4], however, observed that the crystal size of alite decreased beyond 0.5% Cr_2O_3 (Table 3).

3.3.2. Electron microscopy

Specimens containing Cr_2O_3 (0.5–5%) were analyzed under a scanning electron microscope and EDAX including electron probe X-ray mapping to determine the distribution of Cr. Specimens containing Cr_2O_3 up to 1.5% exhibit the presence of C_3S. C_3S with 2% Cr_2O_3 displays mainly the presence of C_3S, along with very small amount of C_2S and free lime. Specimens with 4% and 5% Cr_2O_3 exhibit C_3S, C_2S, and free CaO. The elemental distribution for Cr X-ray

Table 3
Size of C_3S crystals (μm/% Cr_2O_3)

Author	Percentage of Cr_2O_3	Crystal size of C_3S/alite			Specimen
		Minimum	Maximum	Average	
This study	0	5	35	14	C_3S
	0.5	7	40	20	
	1.0	10	70	35	
	2.0	15	65	30	
	4.0	2	25	10	
	5.0	4	20	10	
Butt et al. [4]	0	8	30	–	Clinker
	0.5	15	100	–	
	1.0	5	40	–	
	1.5	5	40	–	
	2.0	10	50	–	
Kurdowski [10]	0	–	–	17.9	Clinker
	0.2	–	–	19.6	
	0.4	–	–	23.2	

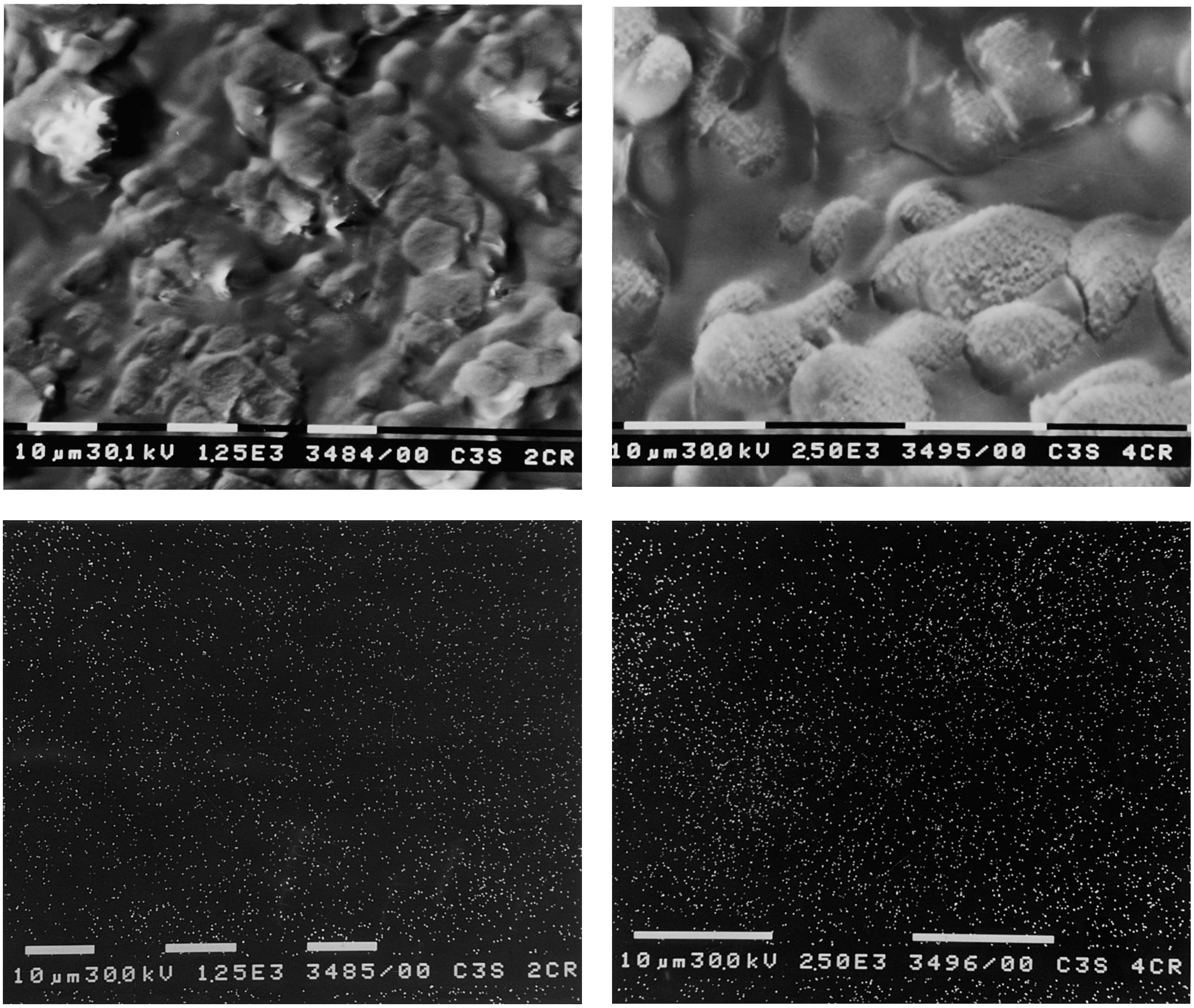

Fig. 3. Distribution of Cr. C_3S with 2% Cr_2O_3 (A–C); C_3S with 4% Cr_2O_3 (B–D).

mapping indicate that Cr_2O_3 is mainly located in the C_3S up to 1.5%. In the specimen with 2% Cr_2O_3, it is mostly distributed in C_3S, which is the dominated phase. Individual grains of C_2S in the 2% Cr_2O_3 specimen, when subjected to EDAX analysis also indicated the presence of Cr_2O_3.

In the specimens with 4% and 5% Cr_2O_3, it is mainly located in C_2S. Micrographs are presented in Fig. 3. EDAX analysis showed C_3S to contain up to 1.56 wt.% Cr_2O_3 (average of five point counts in each frame, for 10 frames), indicating the limit of incorporation to be 1.56% at 1450°C. This is also supported by the results of chemical analysis (Section 3.1 and Table 1). Formation of any chromium compound has not been detected probably because of the less amount. Solubility of Cr_2O_3 in C_3S has been reported in Table 4 along with that reported by the other authors.

4. Conclusions

1. Cr_2O_3 goes into solid solution of C_3S up to 1.56 wt.% at 1450°C.
2. Beyond the solubility limit at 1450°C, there is a partial decomposition of C_3S and $CaCrO_4$ is formed.
3. C_3S remains triclinic with Cr_2O_3 up to 2%. Concentrations of 4% Cr_2O_3 and above transform it into the monoclinic form.

Table 4
Solubility of Cr_2O_3 in C_3S (wt.%)

This study (1450°C)	Firens and Verhaegen [3] (1350°C)	Sychev and Korneev [2] (1500°C)	Boikova [6] (1500°C)	Sakurai et al. [1] (1550°C)	Woermann et al. [5] (1550°C)
1.56	1.368	2.0	1.50	1.70	1.40

4. Cr_2O_3 improves the crystal size of C_3S up to 2%. Crystal size is maximum with 1% Cr_2O_3.

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