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Effect of Zinc Oxide and Copper Oxide on the Formation of C_3S in $3CaO:1SiO_2:xCu(Zn)$ System†

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Application of isothermal calcination method for metal oxide with different mineral C_3S formation system was reported. Results showed that the addition of metal oxide was helpful for the synthesis of C_3S, provides for the mineral C_3S formation liquid, increased the amount of liquid phase. When the single or double metal ions was added to C_3S, multiphase body presents the model of T, R and M, respectively.

Keywords: Solid state reaction, Multiphase, Metal oxide.

INTRODUCTION

High gelling Portland cement clinker is the key to the preparation of high performance cement components, it not only play strength, but also play an important role on cement mixed material activity excitation, C_3S is the most gel phase. The content and activity improvement of C_3S certainly give clinker high gelling property[1]. But if the content of C_3S in clinker was increased, the ease of burning of clinker was worse. Sintering temperature and sintering time were increased. The formation of C_3S is a chemical reaction in the highest temperature of clinker burning process. The improvement of C_3S formation dynamics, means that the clinker burning ease was improved[2]. The overall impact of metal ions on the properties of clinker could be summarized to two aspects, (i) the liquid properties was changed, including decreaseing initial formation temperature, changing liquid viscosity and surface tension, the liquid is the important C_3S formation environmental factors. (ii) through the solid solution effect, the thermal stability of clinker minerals would be changed, the addition ions was reacted with calcium and silicon, resulting in the clinker burning ease changed. Many scholars had done much work on the clinker burning ease[3-7].

In this paper, the CuO and ZnO were added on the formation of C_3S, the application of isothermal calcination method for metal ions with different mineral C_3S formation system was discussed.

EXPERIMENTAL

All chemicals used in our experiments were purchased and used as received without further purification.

In a typical procedure, a certain amount of $CaCO_3$ and SiO_2 with the design of the mineral composition were grinded in a mortar to homogeneous samples. Then the sample was calcined at 1400 ºC for 90 min, the final sample was obtained with the high temperature cooling to room temperature quickly.

Characterization: X-Ray powder diffraction patterns (XRD) of the products were obtained on a Japan Rigaku Dmax-gA rotation anode X-ray diffractometer equipped with graphite monochromatized CuK_α radiation ($\lambda = 1.54178$ Å). The field-emission scanning electron microscope (FE-SEM) measurements were carried out with a field-emission microscope (JEOL, 7500B) operated at an acceleration voltage of 10 kV.

RESULTS AND DISCUSSION

Effect of C_3S with different content of ZnO and CuO: The XRD of C_3S samples with different content of ZnO and CuO was shown in Fig. 1, respectively.

The XRD of C_3S samples with adding different content of both ZnO and CuO was shown in Fig. 2, respectively and the content of ZnO and CuO was shown in Table-1:

Figs. 1 and 2 showed that a small amount of SiO_2 and CaO was not reacted. When the metal was added, it is propitious to promote the reaction adding metal ions, reducing the amount of reactants. But it couldn't clear the problem.

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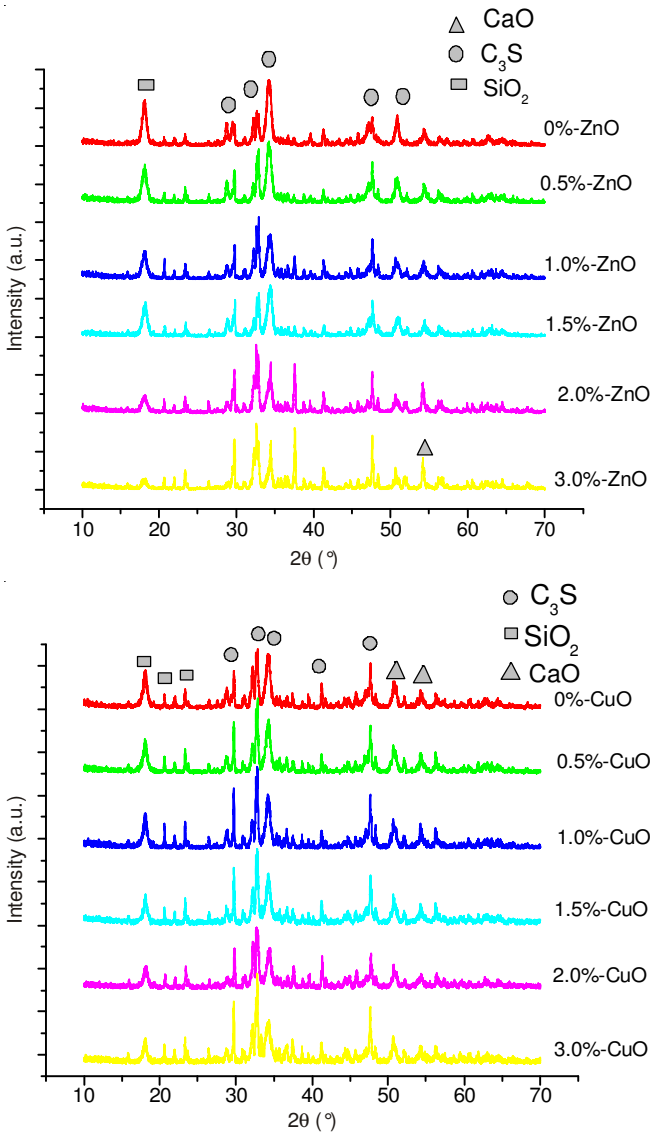

Fig. 1. XRD of C_3S samples with different content of ZnO (above) and CuO (below)

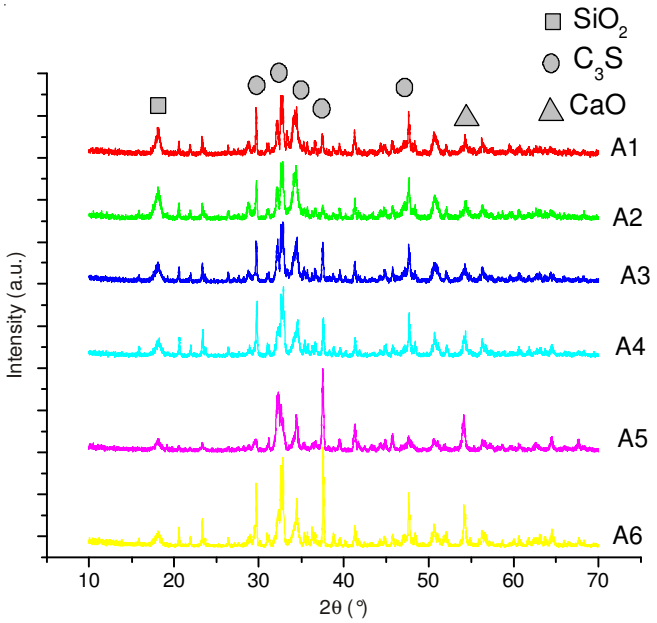

Fig. 2. XRD of C_3S samples with different content of both ZnO and CuO combined

TABLE-1
DIFFERENT CONTENT OF ZnO AND CuO

Sample	A1	A2	A3	A4	A5	A6
w (CuO) (%)	0.0	0.5	1.0	1.5	2.0	3.0
w (ZnO) (%)	3.0	2.0	1.5	1.0	0.5	0.0

C_3S is the main cement clinker mineral. There were seven kinds of pure C_3S crystal type, three kinds of italic type (T), three kinds of single crystal italic type (M) and one kind of oblique six-party crystal shape (R)[8]. When heated, these crystals are mutual conversion was shown in Fig. 3:

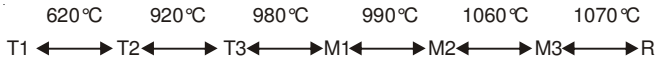

Fig. 3. Crystal structure transition temperature

Literature showed that, different C_3S crystal in 2θ from 32 to 33° and from 51 to 52° had different peak shape. T multiphase peak shape in 2θ from 32 to 33° and from 51 to 52° had obvious multiple branches, however, M multiphase peak shape in 2θ from 32 to 33° and from 51 to 52° had only one or two.

Combined with the literature[8], the main characteristic of C_3S peak application with different metal oxide content in 2θ from 32 to 33° and from 51 to 52° was shown by application of full spectrum.

Tricalcium silicate type polycrystalline phase peak with ZnO: The main characteristic of C_3S peak with different content ZnO in 2θ from 32 to 33° and from 51 to 52° was shown in Fig. 4.

Fig. 4 showed without ZnO, the form of C_3S was T type multiphase body and when the content of ZnO was 0.5, 1.0 and 1.5 %, the peak type bifurcate in 2θ from 32 to 33° reduced, with the increase of ZnO content, two bifurcation phenomenon gradually became clear, C_3S existed in R type multiphase body. When the ZnO content was 2.0 and 3.0 %, the typical peak M type multiphase body in 2θ from 32 to 33° is same to the literature. Although the peak type in 2θ from 51 to 52° still was a fork, which is shown that a forked peak type is also a form of M peak type in 2θ from 51 to 52° in the literature[9].

Tricalcium silicate type polycrystalline phase peak with CuO: The main characteristic of C_3S peak with different content CuO in 2θ from 32 to 33° and from 51 to 52° was shown in Fig. 5.

Fig. 5 showed the content of CuO was 0, 1 and 2 %, the form of C_3S was T type multiphase body, when the content is 0.5 %, the peak type bifurcate in 2θ from 32 to 33° reduced, with the increase of ZnO content, two bifurcation phenomenon gradually became clear, C_3S exists in R type multiphase body. When the CuO content was 3 %, the typical peak M type multiphase body in 2θ from 32 to 33° was same to the literature[9].

Tricalcium silicate type polycrystalline phase peak with both ZnO and CuO: The main characteristic of C_3S peak with different content both ZnO and CuO in 2θ from 32 to 33° and from 51 to 52° was shown in Fig. 6.

Fig. 6 showed the content of ZnO and CuO was 0.5 %, 2.0 %, the form of C_3S was R type multiphase body, doped with other content, C_3S exists in M type multiphase body.

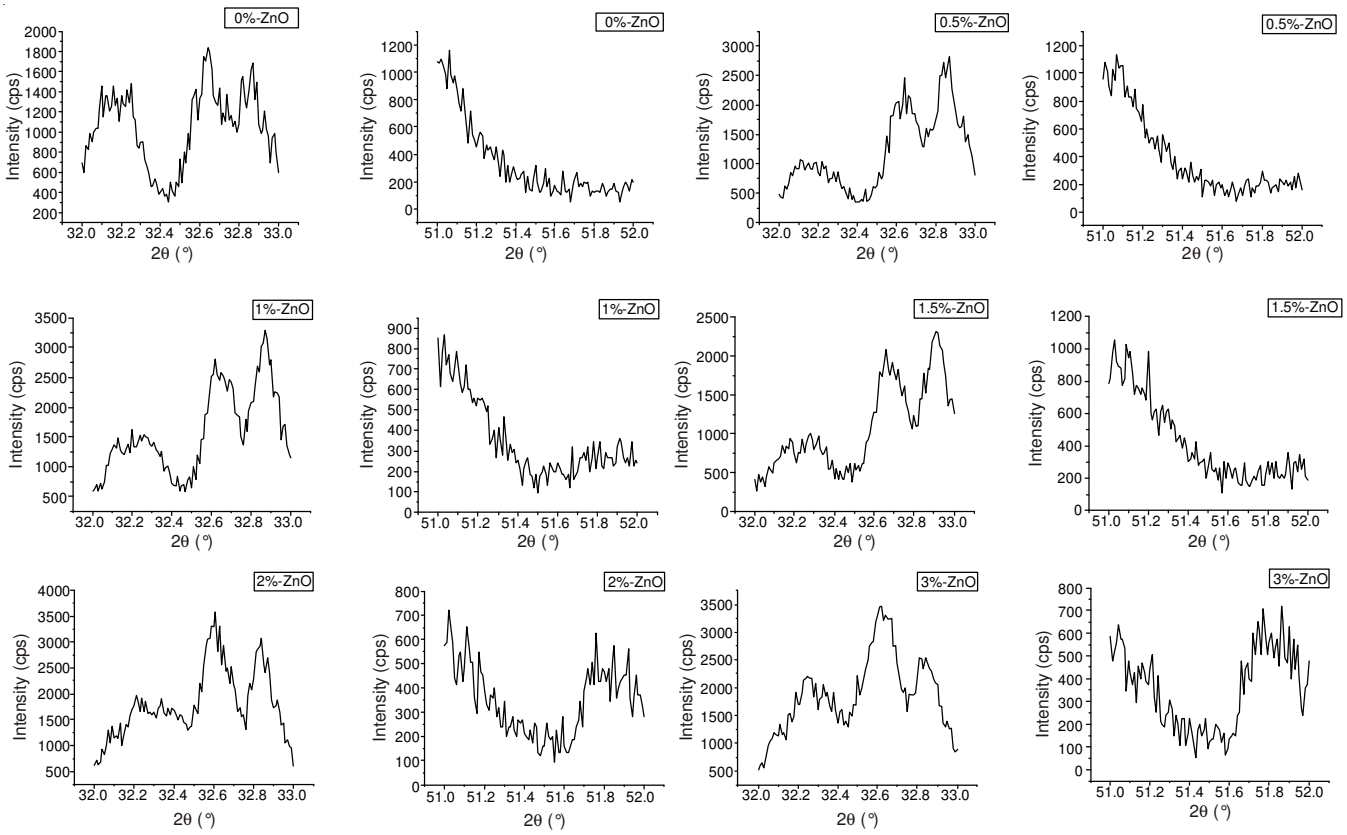

Fig. 4. Doped with different content ZnO

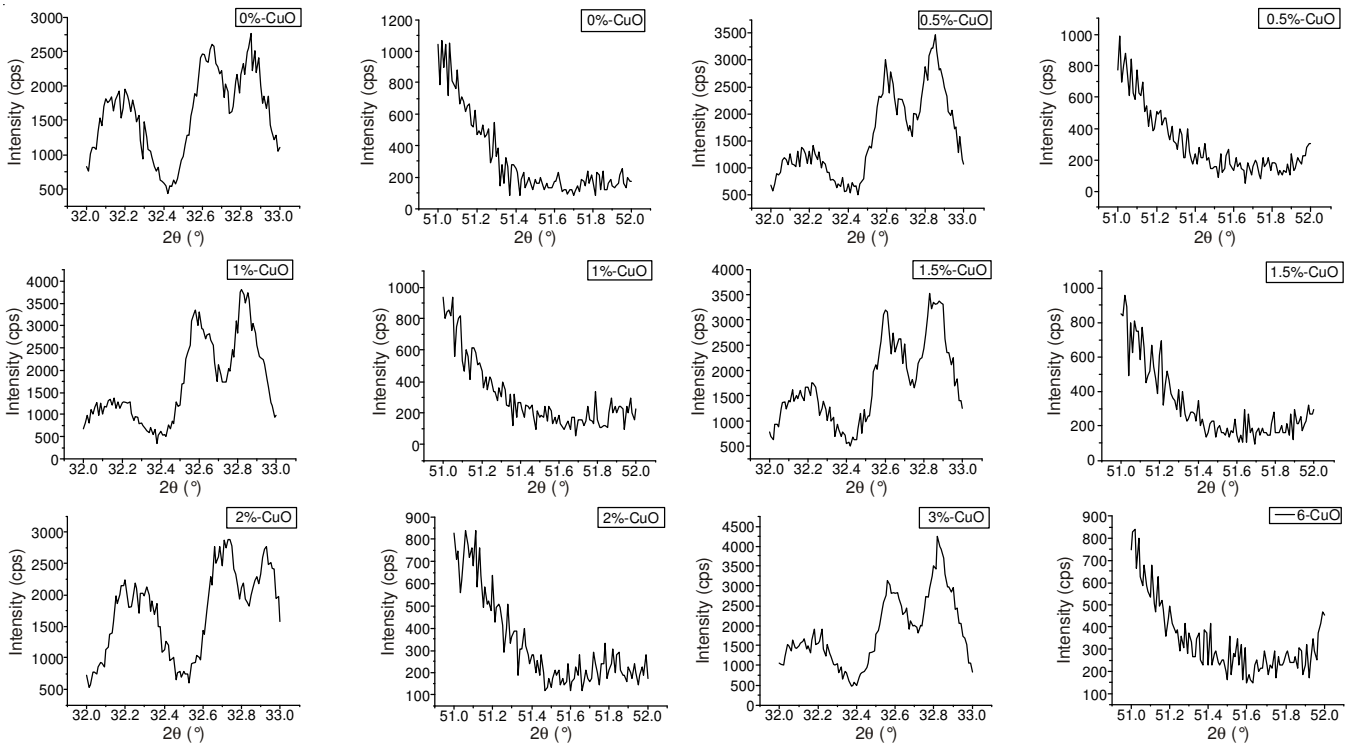

Fig. 5. Doped with different content CuO

Conclusion

Application of isothermal calcination method for metal oxide ZnO and CuO with different mineral C_3S formation system was discussed. Results showed that the addition of metal oxide is helpful for the synthesis of C_3S. When the ZnO content was 2 and 3 %, the CuO content was 3 %, the form of C_3S was M type multiphase body. When composite doped with ZnO and CuO, the content of ZnO and CuO is 3, 2, 1.5, 1, 0, 0, 0.5, 1, 1.5 and 3 %, respectively, the form of C_3S was M type multiphase body.

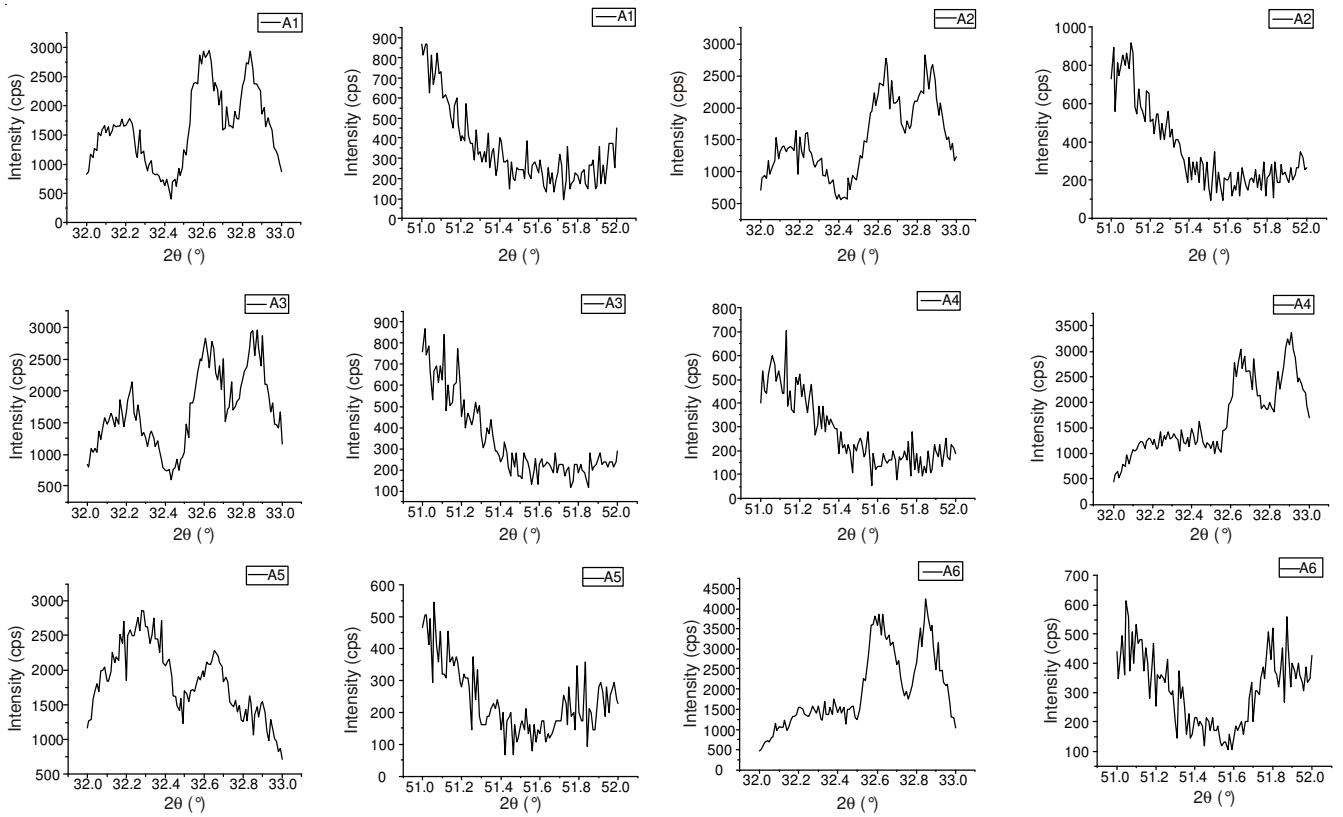

Fig. 6. Doped with different content both ZnO and CuO combined

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