SYNTHETIC WOLLASTONITE FROM DIATOMITE AND CARBONATE WASTE

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1. INTRODUCTION

Wollastonite is widely used in ceramic production because it reduces the shrinkage of the products, increases their strength and provides for rapid firing of the bodies (< 30 min) [1]. Wollastonite is obtained industrially through: reaction in a solid phase; melting of schists in a glass furnace; sedimentation of solution and through hydrothermal synthesis [2].

2. EXPERIMENT AND DISCUSSION

For our investigations, the wollastonite was obtained from diatomite and carbonate waste by crystallization of melts, respectively of glass and by a solid state reaction. The mixtures for wollastonite contain (in mass %): 35-45 diatomite and 55-65 carbonate waste from sugar production. Diatomite from General Toshevo (Bulgaria) is characterized by fine porosity, high adhesion and dispersion. It consists almost solely of diatomaceous frames. In the form of admixtures, there are some small quantities of clay substance (0.443 nm); calcite (0.303 nm) and quartz (0.334 nm). Diatomite has the following chemical composition (in mass %): 83.60 SiO_2; 5.56 Al_2O_3; 2.13 Fe_2O_3; 0.85 CaO; 0.80 MgO; 0.59 Na_2O; 0.84 K_2O; 5.63 L.O.I. The DTA curve of diatomite has an endoeffect in the interval 50-150oC with a maximum at 90°C and mass loss due to the TG-curve is 5.60 mass %.

Carbonate waste from sugar production in Kameno (Bulgaria) consists of fine dispersed calcite (0.303 nm) with specific surface 2372 m^2/kg and particle distribution: fraction > 60 μm – 0.5%; fraction 60-10 μm – 95.0% and fraction <10 μm – 4.5%. The carbonate waste has an endoeffect in the interval 700-880oC with a maximum at 840°C and mass loss 47 mass % L.O.I. Some negligible admixtures of quartz, clay and organic substances are contained.

Wollastonite is obtained at crystallization from the melt after mixture melting at 1450°C -1 h and subsequent isothermal crystallization of glass at 1200oC – 30 min. The quantity of wollastonite (pseudowollastonite - $Ca_3Si_3O_9$ – 0.322-0.197-0.281 nm) is maximum at a correlation of CaO/Si_2O in glasses of 1:1 or approximately this value. In a proportion of CaO/Si_2O <1, the quantity of wollastonite decreases and that of the glass increases, but when CaO/Si_2O >1, glass quantity decreases and gehlenite (0.285 nm) appears. The optimal content of the components in the mixtures is 40 diatomite and 60 carbonate waste in mass %. The combination of fluxes, which appear to be a basic raw material for wollastonite, reduces the melting temperature of the mixtures, contributes advantages for homogenization of the melts, and increases the crystallization ability of the glasses.

An important disadvantage of the method described for wollastonite preparation consists in the formation and growth of crystals at temperatures that are 200-250°C higher than that of glass maturation. This disadvantage of the wollastonite glasses – to have strong deformation at the crystallization temperature is avoided by introducing 2 mass parts CaF_2, acting as a crystallization catalyst. Glasses an optimum content of components: 40 mass % diatomite, 60 mass % carbonate waste and 2 mass parts CaF_2, do not show deformation at isothermal crystallization of glasses at 1200oC for 30 min. The explanation lies in the forming of crystal nuclei or small crystals from cuspidine $Ca_4Si_2O_7F_2$ (0.306 nm) in the moment of melting spill, that form a crystal frame keeping glasses from deforming at the next thermal treatment.

Solid phase synthesis of wollastonite has been performed from the above-mentioned composition of mixtures (in mass %): 35-45 diatomite and 55-65 carbonate waste. Mixtures underwent homogenization and milling in a porcelain ball mill, after which they were tempered and fired at 1000°C for 1 h. The fired tablets were milled again and homogenized, formed in tablets and subjected to second firing at 1200°C for 1 h. The product obtained after firing twice consisted of almost solely of wollastonite (pseudowollastonite - $Ca_3Si_3O_9$) - about 95%. Quartz and gehlenite were present as admixtures. The average sizes of the wollastonite crystals were in the range of 1 -3 μm. The interplane distances (d) and the relative intensity (I/I_1) of wollastonite, compared with those of pseudowollastonite using ASTM-card 19-248 are given in Table 1.

N	Wollastonite		Pseudowollastonite 19-248		N	Wollastonite		Pseudowollastonite 19-248	
	d. nm	I/I_1.%	d. nm	I/I_1.%		d. nm	I/I_1.%	d. nm	I/I_1.%
1	0.563	13	0.567	60	9	0.199	34	0.208	70
2	0.433	9	0.437	50	10	0.197	72	0.197	100
3	0.341	32	0.342	70	11	0.183	12	0.183	60
4	0.321	100	0.322	100	12	0.171	7	0.171	30
5	0.274	70	0.281	70	13	0.168	10	0.168	30
6	0.245	25	0.245	70	14	0.161	9	0.162	30
7	0.232	65	0.235	30	15	0.147	12	0.148	50
8	0.204	55	0.204	30	16	0.140	5	0.140	30

Table 1. Interplane distances (d) and relative intensity (I/I_1) of wollastonite

3. CONCLUSION

Wollastonite has been obtained (pseudowollastonite - $Ca_3Si_3O_9$) applying glass and ceramic technology from mixtures with composition (in mass %): 35-45 diatomite and 55-65 carbonate waste from the production of sugar. At the optimum mixture components content: 40 mass % diatomite and 60 mass % carbonate waste, the yield of wollastonite was about 95 %. The average sizes of wollastonite crystals were in the range of 1-3 μm.

REFERENCES

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