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Study on the Synthetic Process of Calcium Borate

C.E. Cao[1,2] , Y.J. Wang[1], N.Z. Zheng[2], C.H. Xiong[2] and H.R Shen [2]

[1] Material college of South China University of Technology, Guangzhou 510640, China
[2] Material college of Jingdezhen Ceramic Institute, Jingdezhen 333001, China

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Abstract. Calcium borate used for non-pollution flux of ceramic decoration materials is synthesized by using boric acid and calcium carbonate as raw materials. The effects of reaction temperature, concentration, time, pH value and additive agent on synthesis of calcium borate are studied. The synthesized products are characterized by using DTA, XRD, TEM and SEM. The results show that the better conditions are: synthesis temperature is 80-100°C, the proportion of boric acid and water is 0.26 ~ 0.42 to 1(mol), the proportion of calcium carbonate and boric acid is 0.09-0.15 to 1(mol), the pH value is 5 ~ 7, reaction time is 3hs. The synthetic calcium borate is non-crystalline with particle size of 0.1 ~ 0.2 μm, when being calcinated at 300°C, the main crystal phase is $CaO{\cdot}3B_2O_3{\cdot}4H_2O$.

Introduction

As a new kind of chemical material, Calcium borate is widely used in glass, enamel and ceramic industries. As a replacement of boric acid, borax and natural magnesium boride mineral, calcium borate can reduce the volatilization of boric oxide and prevent alkali metal ion and impurity constituent from introducing. Up to now, boron oxide is introduced from boric acid, borax, natural magnesium boride mineral or imported Turkey calcium borate [1], because there is no calcium borate mineral in China to mine commercially. But natural calcium borate mineral cannot be used directly in non-alkali glass, fine glaze and flux of on-glaze decoration pigment due to the impurity constituent, so it must be purified before using.

The alkali-boron-silicate system is chosen in the research of leadless glaze and flux. Boron oxide, as main flux with other alkalis and flux, replaces lead completely, which is solving the problem of lead release and resuming the status of Chinese porcelain export [2]. Boric acid and borax are used in the procession of glaze and flux to meet the demand of boron. As it is well known, boric acid has much chemical combined water that causes large loss and much pollution when fused; it also erodes furnace; furthermore, the combined water cannot be excluded completely when fused. When boric acid is used for glaze and pigment, the fused flux can also separate out bubble, which affects the quality of products. Boric acid is poisonous to human tissue, and will gradually poison human body when inhaled frequently [3]. On the other hand, in processing leadless glaze and flux, feldspar is still the main flux constituent, the content of alkali metal (K, Na) in feldspar can meet the need of pre-scription, so it is not advisable to use boric acid in this processing. Natural magnesium borate mineral contains high quantity of magnesium and iron oxide impurity, it is unsuitable for the flux of on-glaze decoration pigment and transparent colored glaze, otherwise it makes glaze crystallized, opacifying, and affects glaze color. As an important constituent in glaze and flux, calcium is introduced in the form of calcium carbonate (natural limestone, calcite), when heated up to ~ 900°C, the carbon dioxide decomposed from calcium carbonate makes products present much defect. It shows that it is a valuable job for the producer of leadless glaze and flux to synthesize calcium borate in advance.

At present, calcium borate is on the way to be researched and developed in China [1,4]. To synthesize boride directly from the boron mineral on industrial scale, the binary calcium biborate ($CaO{\cdot}B_2O_3{\cdot}nH_2O$) is obtained , that is calcium biborate. Our test shows that boride products on sale are mostly calcium biborate ($CaO{\cdot}B_2O_3{\cdot}2H_2O$), in which the content of boron oxide and calcium oxide is about 40%, 38% respectively, not suitable for leadless glaze and flux use. Also it is not

economical to synthesize calcium biborate with boric acid. In the study, writer take a new kind of synthesis method [4], using boric acid and calcium carbonate, to synthesize calcium and boron compounds suitable for leadless glaze and flux.

Experimental

Materials. Boric acid (H_3BO_3) and calcium carbonate ($CaCO_3$) are used as raw materials with industrial purity, hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) are used to adjust pH value, CMC as a disperser to adjust slurry and calcium chloride ($CaCl_2$) as an additive to advance the reaction.

Experiment instruments. Calcium borate is synthesized with water bath under the condition of constant temperature. The synthesizing state of calcium borate powder is studied by using differential thermal analysis (DTA); the qualitative analysis of the synthesized powder and calcinated sample is done by using X-ray diffraction (XRD); the shape and the size of the synthesized powder and the appearance of the calcinated sample are observed with scanning electron microscope (SEM) and transmission electron microscope (TEM).

Experiment procedure. Through exploratory experiments and experiment optimization, the technological parameters such as the mol proportion range of boric acid to water and that of calcium carbonate to boric acid, the pH value and the reaction temperature as well as the reaction time are confirmed. The reaction is processed in the beaker. Reactant materials are added gradually to help complete the reaction and the slurry stirred during the whole processing. The synthesized slurry is filtered right after reaction, washed with hot distilled water, and dried at the temperature of 100°C.

Results and discussion

Determination of synthesis processing with DTA. The characters of DTA of boric acid and calcium carbonate can be obtained. All DTA curves of powder synthesized are almost the same, in which dewatering temperature is between 220-320°C, while recrystallizing temperature of the non-crystal is about 680°C. The larger the exothermic peak is, the morel the quantity of the synthesized product will be. The synthesis process can be estimated according to the shape of the exothermic peak, and better technological parameters can also be chosen. The experimental condition for DTA is as follows: dropping speed is 4mm/min, intensifying speed is 20°C/min, temperature quantity is 50mV, thermo differential quantity is 250 μV. A large amount of experimental results show that DTA is the easy and useful analytical method to study synthesis of Calcium Borate.

Exploratory experiment. According to the isotherm figure, pH value and the relation between temperature and solid state composition of the system CaO-B_2O_3-H_2O [3]. 8 Exploratory prescriptions are listed in table 1 (pH value is 8-9, and reaction time is 2 hours).

The DTA curves suggest that prescription 8 has a large exothermic peak. Further experiments are carried out with prescription 8 to determine the better parameters.

Table 1 Prescription composition and reaction temperature

Prescription	H_3BO_3:H_2O(mol)	$CaCO_3$: H_3BO_3(mol)	Temperature(°C)
1	0.26	0.10	70
2	0.26	0.11	80
3	0.26	0.12	90
4	0.26	0.13	100
5	0.33	0.10	70
6	0.33	0.11	80
7	0.33	0.12	90
8	0.33	0.13	100

Optimization of reaction time and temperature. The reaction time is 1h, 2hs, 3hs respectively with the same composition of prescription 8. The DTA curves indicate the powder synthesized with 3h has a large exothermic peak. Then further experiments are carried out with the same time of 3hs, the temperature is 70°, 80°, 90°, 100°C respectively. The DTA curves indicate the powder synthesized with 70°C has a small exothermic peak. So the reaction temperature is confirmed at 90°C, because when the temperature is 100°C, the slurry begins to boil and makes the reactants go out.

Effect of reactants concentration. The mol proportion of boric acid to water and that of calcium carbonate to boric acid are studied respectively. We need excessive boric acid react with calcium carbonate (product synthesized is $CaO{\cdot}3B_2O_3{\cdot}nH_2O$), so in prescription the quantity of boric acid is more than its solubility. The solubility of boric acid increases when temperature rises. Boric acid can more dissolve at the chosen temperature of 90°C. The solubility of calcium carbonate reduces as temperature rises. When the temperature goes to 60°C, calcium carbonate almost cannot dissolve. So the reactants are added in 3 times in order to let them react completely. The first time some quantity of reactants is added (boric acid 26% of its total, calcium carbonate 4% of its total) in the beaker, stirred and heated to 60°C, the remainder reactants are added for 2 times in 10 min, then heated to 90°C and stirred for 3h. In this way, the exothermic peak of the powder synthesized is much larger than that of the powder synthesized with adding reactants once only. The proportion of boric acid to water and calcium carbonate to boric acid is 0.26-0.42 : 1, 0.09-0.15 : 1 respectively. In this proportion range exothermic peak can be obtained, the main crystal phase of the synthesized product is $CaO{\cdot}3B_2O_3{\cdot}4H_2O$. The small amount of $CaO{\cdot}3B_2O_3{\cdot}5H_2O$ has been produced owing to the result of both evaporation and addition of water. After cross and single experiments, the best technological parameters are: the proportion of boric acid to water is 0.38 and the proportion of calcium carbonate to boric acid is 0.13.

Effects of additives and pH value. The slurry becomes thicker while calcium carbonate reacts with boric acid, which is not beneficial to reaction. The effect of disperser is studied. The result shows that the better disperser is low polymerization degree CMC whose dose is 0.1%. The pH value of the slurry apparently influences the reaction product. Therefore, in the study hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) are used to adjust the pH value. Because boric acid is weak acid without addition of regulating agent, the pH value of slurry is 6-7, and the main crystal phase synthesized is $CaO{\cdot}3B_2O_3{\cdot}4H_2O$. When ammonium hydroxide (NH_4OH) is added into the slurry, the pH value is over 10, and the main crystal phase synthesized is calcium borate ($CaO{\cdot}B_2O_3{\cdot}2H_2O$), there is ammonium borate deposite in mother solution. After adding hydrochloric acid (HCl), the pH value of the slurry is 4-5, then calcium borate synthesized begins to be decomposed by hydrochloric acid (HCl) and separates out boric acid, there is no exothermic peak in DTA curve of the sample. Calcium chloric ($CaCl_2$) is a neutral salt, so when it is added to the slurry, the pH value is 5-6, calcium ion (Ca^{2+}) increases and chloric ion (Cl^-) makes boric acid dissociate, which is beneficial to the reaction. When the other parameters are the same, DTA result shows that product with addition of calcium chloric has much larger exothermic peak. But the amount of Ca^{2+} added must be noticed, or $2CaO{\cdot}3B_2O_3{\cdot}H_2O$ may be formed.

Results of the test. The TEM photo of the powder that is synthesized under the best condition is shown in Fig 1, with particle size of 0.1-0.2 μm, XRD graph of the powder is shown in Fig 2 (a), which mostly is amorphous particles with a little peak of $CaO{\cdot}3B_2O_3{\cdot}4H_2O$. DTA curve is shown in Fig 3, endothermic peak is at about 220 and 320°C, which corresponds to the dewatering of the powder, exothermic peak is at 680°C, which corresponds to the recrystallization of amorphous. Plate–like or pillar-like crystal druse is produced when the powder is calcined at 700°C. After the calcination, the sample appears loose and breakable due to loss of water, the pores and the loose structure can be observed by means of SEM. The XRD graph of the particle calcined at 300°C is shown in Fig 2 (b) where the main crystal phase is $CaO{\cdot}3B_2O_3{\cdot}4H_2O$, but there is also a little $CaO{\cdot}3B_2O_3{\cdot}5H_2O$.

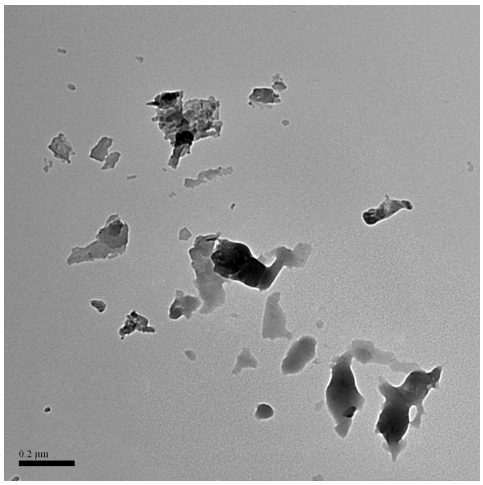

Fig.1 The TEM photo of the powder

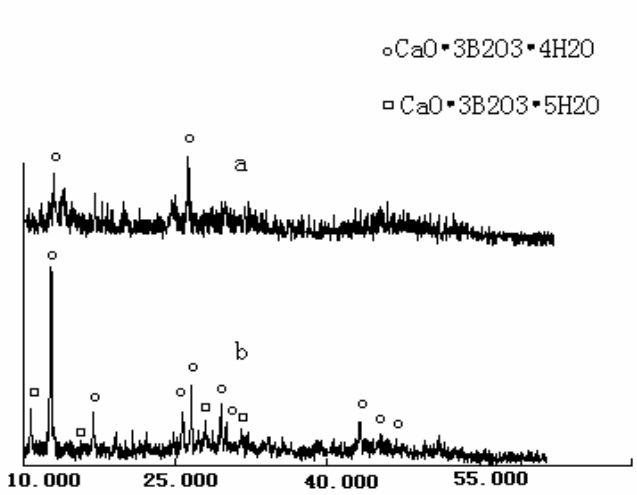

Fig.2 The XRD graph of the powder

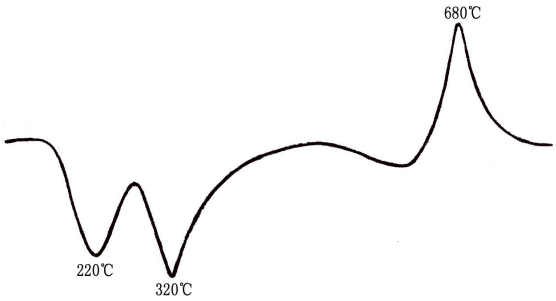

Fig.3 The DTA curve of the powder

Conclusion

Calcium borate manufactured in this study is amorphous with particle size of 0.1-0.2 μm, after calcind at 300°C, the main crystal phase is $CaO{\cdot}3B_2O_3{\cdot}4H_2O$. The technological parameters are: synthesis temperature is at 80-100°C, in particular at 90°C; the proportion of boric acid to water is 0.26-0.42:1, in particular at 0.38:1; the proportion of calcium carbonate to boric acid is 0.09-0.15:1, in particular 0.13:1; pH value of the slurry is 5-7; reactive time is 3hs. The result shows that DTA is the easy and useful analysis method studying synthesis of calcium borate. Adding reactants in several times makes reactants react fully. It is beneficial to reaction that CMC and calcium chloric are used as additives.

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