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Preparation of the Mixture of MHSH and HMB Whiskers by Hydro-thermal Method in the Mother liquor of Boric acid Production

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Abstract: The mixture of whiskers of magnesium hydroxide sulfate hydrate(MHSH) and hydrated magnesium borate (HMB) were prepared by hydro-thermal method in the mother liquor of boric acid production, the composition of the products were $5Mg(OH)_2 \cdot MgSO_4 \cdot 2H_2O$ and $MgB_6O_{10} \cdot 5H_2O$ confirmed by XRD testing. The dehydration analysis indicated that continuous steps of dehydration have promised an application in the flame retardant reinforced material have broad prospects.
Keywords: magnesium hydroxide sulfate hydrate, hydrated magnesium borate, whisker, hydro-thermal method, mother liquor, boric acid.

Introduction

Large amounts of magnesium sulfate and a small amount of boric acid existed in the boric acid mother liquor production. As a useful treatment technology, magnesium sulfate heptahydrate can be obtained by using the method of crystallization and used as boric magnesium fertilizer. Even so, how to use of the boric acid mother liquor production has been a high value-added industrial problems to be solved in particular and strict environmental requirements[1-3]. The MgO-$MgSO_4$-H_2O or alkaline substances-$MgSO_4$-H_2O system has been the subject for numerous investigations in the past few decades because several magnesium hydroxide sulfate hydrate(MHSH) have been shown as promising materials, recently, some MHSH fibers or whiskers were proved to be well suited as an additive for resin, filler, filter medium, or reinforcements of polymers and plastics[4-9]. The $MgCl$-H_3BO_3-$NaOH$ or $MgNO_3$-$NaBH$-H_2O system has been used for making the hydrated magnesium borate(HMB) whiskers, one of the most promising application of the products is as precursor for the formation of anhydrous magnesium borates, which possess excellent mechanical properties and have applications in antiwear additives, thermoluminescence phosphor, ferroelastic materials and electronic ceramics, hydrothermal technology has emerged as a thriving method for the synthesis of nanostructures in the past decades because of its energy savings, better control of nucleation and shape, and lower temperature of operation,etc[10-16]. The MgO-$MgSO_4$-H_3BO_3-H_2O system has been established in this paper according to the composition of the boric acid mother liquor production, and the mixture whiskers of MHSH and HMB were prepared simultaneously by hydro-thermal method, the results can provided the basis for high value-added application of the boric acid mother liquor production.

Experimental

The mixture of sample of MHSH and HMB were synthesized by the hydrothermal method, all reactants were analytically pure, 2.024g magnesium oxide powder was dissolved in 40ml distilled water, then 1.2g anhydrous magnesium sulfate and 0.038g boric acid was putted respectively into the beaker, after until completely dissolved, the solution were placed into a Teflon-lined autoclave of 50ml capacity. Then, the autoclave was filled with aqueous up to 80% of the total volume. The autoclave was sealed into a stainless steel tank, and maintained at 200℃ for 16h without shaking or stirring. After the autoclave was cooled to room temperature naturally, the white mixture of sample was filtered, the precipitate was washed with distilled water and absolute ethanol for several times, and then dried in a vacuum at 60℃ for 4h.finally, the sample was obtained.

Results and discussion

The SEM image and the yield of the sample with molar ration changing from 1:1 to 1:6, of magnesium sulfate and magnesium oxide under the condition of the molar ratio of anhydrous magnesium sulfate and boric acid were maintained at 1:1 were shown in figure 1 and figure 2 respectively. It can be seen in figure 1 that the image of the samples was needle-like in a, together in with in b, whisker and flocculence in c, typical fiber bundle in d, sheet structure flocculence and needle like in e, hairchested fiber bundle in f, and the yield of sample increased with the molar ratio of magnesium sulfate and magnesium oxide decreased from 1:1 to 1:4.34, then decreased at 1:5, increased at 1:6 in figure 2 respectively. The formation of HMSH was easy then HMB under thermal condition according to the known reaction process, the increase of magnesium oxide reacted with them successfully, so much so that magnesium hydrate created under excessive magnesium oxide which the variation trend of samples yield reflected in figure 2.

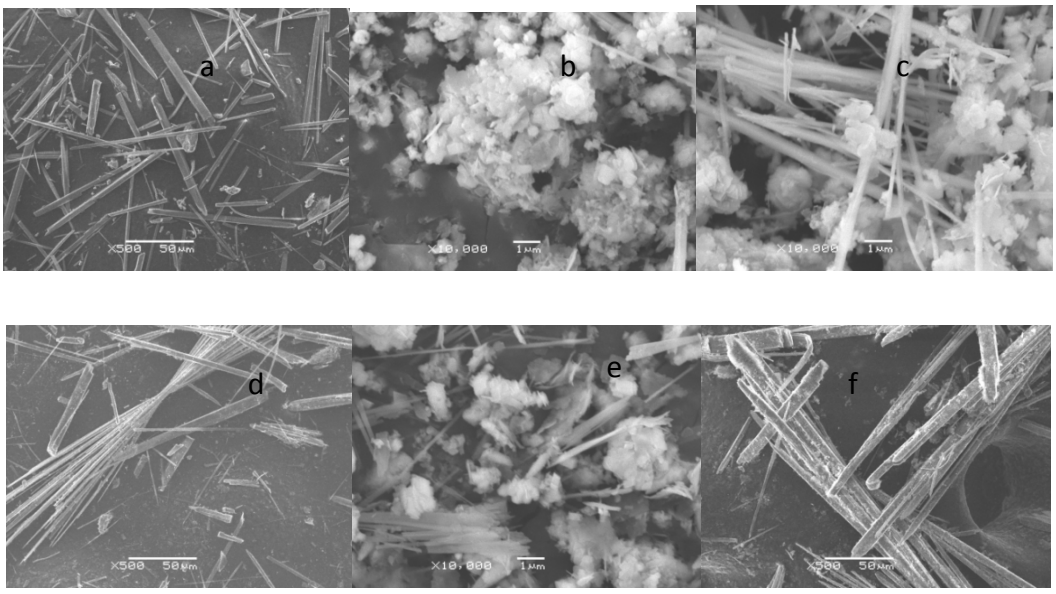

Figure 1: SEM image of samples with different molar ratio of magnesium sulfate and magnesium oxide
Molar ratio: a, 1:1, b, 1:2, c, 1:3,d, 1:4.34, e, 1:5, f, 1;6

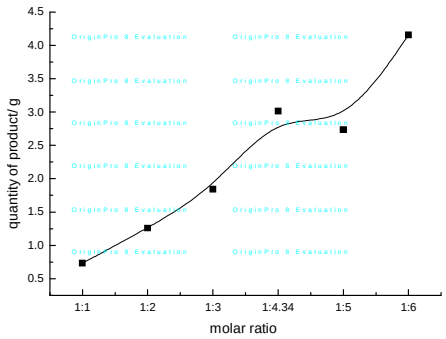

Figure 2: yield of samples with different molar ratio of magnesium sulfate and magnesium oxide

The SEM image and the yield of the sample as the molar ratio of boric acid and magnesium oxide was increased to 1, 2 and 4times respectively were shown in figure3 and figure4 under the condition of the molar ratio of magnesium sulfate and magnesium oxide was maintained at 1:5, It can be seen in figure3 that the image of samples changed from mixture of needle-like and sheet structure flocculence to hairchested fiber bundle in a, b and c, and the yield of the product increased firstly and then decreased in figure4. The pH value and concentration of Mg^{2+} ions in the solution increased with the the molar ratio of boric acid and magnesium oxide was increased to 1, 2 and 4times respectively, it was in favour of the formation of typical hairchested fiber bundle magnesium hydroxide sulfate hydrate whisker relative to magnesium borate. Even some formation of magnesium hydroxide and the quantity of product increased and decreased in figure4 relatively.

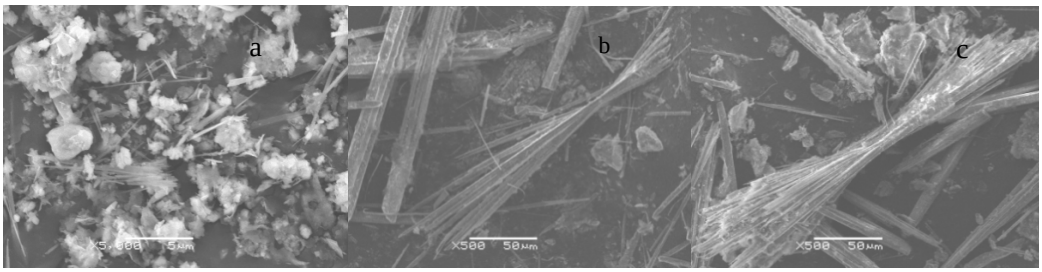

Figure 3: SEM image of samples with different molar ratio of boric acid and magnesium oxide
Times of molar ratio: a, 1, b, 2, c, 4

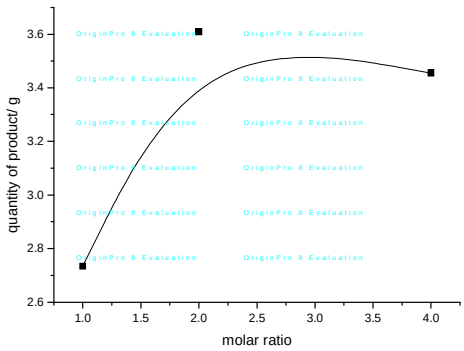

Figure 4: yield of product with different molar ratio of boric acid and magnesium oxide

The SEM image of the samples was shown in figure5 as scale-up to 2 to 4times simultaneously. It can be seen obviously that large amount of magnesium hydroxide sulfate hydrate whisker have been formed then magnesium borate as the molar ratio of magnesium sulfate, boric acid, and magnesium oxide increased 2 to 4times.

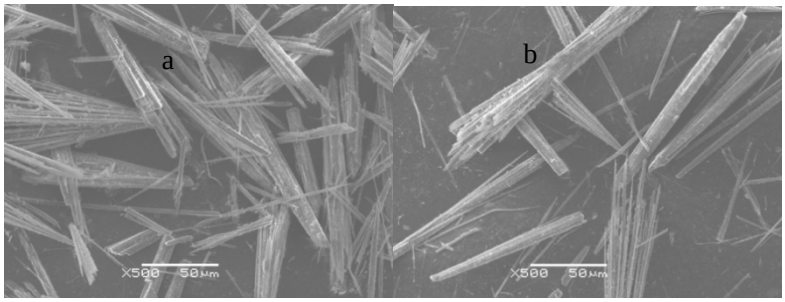

Figure 5: SEM image of samples with different molar ratio
Times of molar ratio: a, 2, b, 4

The XRD diagram of the mixture of magnesium hydroxide sulfate hydrate whisker and magnesium borate was shown in figure 6, the result indicated in figure6 that the diffraction peak at 31.589、37.933、48.859 as A was identical with the structure of orthogonal magnesium hydroxide sulfate hydrate ($5Mg(OH)_2 \cdot MgSO_4 \cdot 2H_2O$) and at

25.913、29.756、47.305 as B was identical with the structure of orthogonal magnesium borate ($MgB_6O_{10}\cdot 5H_2O$) in the standard samples cards（JCPDS 33-0859）

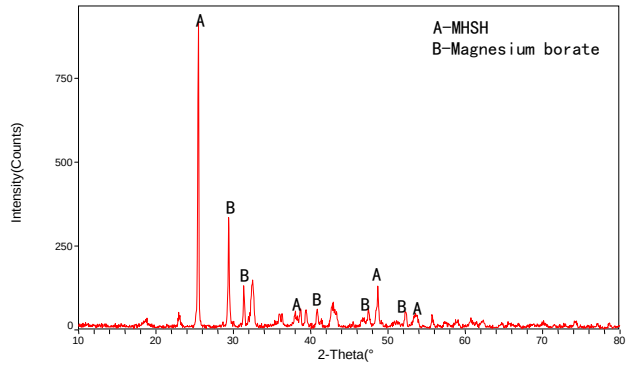

Figure 6: XRD diagram of the mixture of sample

The TG diagram of the mixture of magnesium hydroxide sulfate hydrate whisker and magnesium borate was shown in figure7, it can be seen that it was continuous steps of dehydration to the mixture at temperature between 360℃ and 760℃, the weight loss of the mixture was 6.04%, 17.92%, and 3.84% with the step between360℃ and 480℃ , 480℃ and 670℃, and 670℃ and 760℃, it can be predicted that the characteristics of multistage decomposition dehydration，and the fibrous structure can be used as an additive in flame or fire retardant, and reinforcement of plastic and rubber et.al.

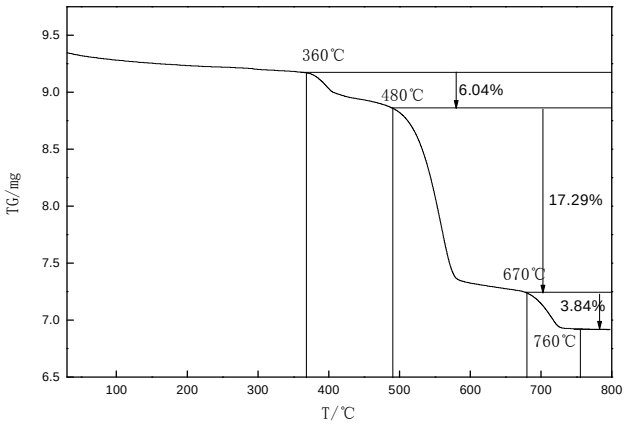

Figure 7: TG diagram of the mixture of samples

Conclusion

1 The mixture of whiskers of magnesium hydroxide sulfate hydrate and hydrated magnesium borate were prepared by hydro-thermal method in the mother liquor of boric acid production.

2 The procudts were $5Mg(OH)_2\cdot MgSO_4\cdot 2H_2O$ and $MgB_6O_{10}\cdot 5H_2O$ confirmed by XRD testing.

3 The multistage decomposition dehydration and the fibrous structure indicate that it has predicted application in the flame retardant reinforced material.

4 It provided the basis for high value-added utilization of the mother liquor of boric acid production.

Acknowledgements

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