Investigations on oxidation resistance of phase change materials for heat storage

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Abstract. Antioxidant graphite was prepared from Al(H2PO4)3 solution by solution impregnation method. The as-prepared antioxidant graphite was further compounded with phase change materials for heat storage depending upon the form-stable technique. SEM with EDS analyses were used to characterize both the morphology and microstructure of the impregnated graphite while DSC were used to measure thermal properties of the composite. The results showed that the best impregnation mass ratio of Al(H2PO4)3 to graphite should be 2:1~3:1. In this case, the obtained composite heat storage material can realize certain oxidation resistance and obtain good heat storage performance after thermal cycling.

1. Introduction
Research on heat storage materials is one of the important strategies to solve energy problems. Graphite processes high thermal conductivity and is regarded as good additive, which is often used to compound with phase change materials for heat storage to improve their thermal performance. But it is well known that the additive graphite will be oxidized at the temperature higher than 450°C, which greatly limits its applications in high temperature heat storage materials [1-2]. Many researchers have been reported their investigations on the oxidation resistance of graphite materials, among which the solution impregnation is regarded as an effective way to improve the oxidation resistance of graphite materials at high temperature. For example, in 1997, T. DuRKI, A. PER proved the mixed acid solution of phenolic resin and boron can increase the oxidation stability of the sample surface [3]; Manocha et. al adopted the silica sol and SiOC sol as medium to impregnate C/C composites. After effective impregnation and heat treatment, C/C composites can show good antioxidant effect at temperatures above 1000°C [4]; In 2002, Wei-ming Lu et. al pretreated graphite materials with ozone and then impregnated them with phosphoric acid and dissolved aluminum hydroxide for the first time. Their results suggested the oxidation resistance of carbon can be improved significantly [5]. In this study, the additive graphite was first treated by solution impregnation method and then mixed with phase change materials using form-stable technique for improving high-temperature oxidation resistance of phase change materials for heat storage. It is no doubt that the related research has far reaching significance in the application of high temperature phase change materials. Our studies suggested graphite treated by solution impregnation technique has certain practical significance for the high temperature application of phase change materials.
2. Experiment

2.1. Experimental material

Materials used in the experiment include graphite (purity ≥99%, flake size ≤30μm), Na₂CO₃ (GR, purity ≥99.9%), K₂CO₃ (GR, purity ≥99.5%), MgO (AR, purity ≥99.9%), H₃BO₃ (AR, purity ≥99.5%), Al(H₃PO₄)₃ (AR, 50% w/w). The composition of the immersion liquid is shown in Table 1 while the composition of each component in the obtained composite phase change heat storage material is shown in Table 2.

| The number of Impregnation solution | solvent            | solute               | the amount of solvent | The amount of solute |
|-------------------------------------|--------------------|----------------------|-----------------------|---------------------|
| 1                                   | H₂O                | H₃BO₃               | 80ml                  | 5g                  |
| 2                                   | Al(H₃PO₄)₃+H₂O     | H₃BO₃               | 40ml+40ml             | 5g                  |
| 3                                   | Al(H₃PO₄)₃+H₂O     | -                   | 40ml+40ml             | -                   |
| 4                                   | Al(H₃PO₄)₃+H₂O     | H₃BO₃               | 40ml+40ml             | 20g                 |
| 5 (Initial sample)                  | -                  | -                   | -                     | -                   |

Table 1 Composition of impregnating solution

| Na₂CO₃ | K₂CO₃ | MgO | MG (Modified graphite) |
|--------|-------|-----|------------------------|
| 28.6   | 26.4  | 35  | 10                     |

Table 2 Chemical composition of heat storage material (wt%)

2.2. Sample preparation

Graphite with a weight of 4g were first added to the impregnation solutions presented in table 1, then the obtained solutions were mixed and heated at the impregnated temperature of 70°C. After effective mixture, the solutions were finally dried in an oven at 120°C. Before mixing with Na₂CO₃-K₂CO₃ eutectic salt and MgO, these dried samples were put into alumina crucible and heat treated in muffle furnace and then cooled to room temperature. The corresponding calcinations technique is described in Fig.1(a). Fig.1(b) is the sintering procedure for fabricating phase transition heat storage materials. A typical preparation route for heat storage materials is all the materials including eutectic salt, the impregnated products and MgO etc. were mixed together and pressed into a die with a diameter of 12.6mm, and further sintered according to techniques shown in Fig.1(b).

2.3. Tests and characterization methods

The oxidation weight loss of the as-prepared heat storage materials was measured using an electronic balance (METTLERTOLEDO ML204). SEM combined with EDS (SU1080) were used to observe and analyze the possible microstructure evolutions of both the composite and coated graphite. DSC (STA 449) were used to measure the cycled thermal stability of heat storage materials.
2.4. Results and discussion

Dependence of the oxidation weight losses obtained under various conditions on the holding times is shown in Fig. 2. It was reported that boric acid could be changed into B$_2$O$_3$ after dehydration. The formed B$_2$O$_3$ would become glass melt with low volatility, high viscosity and strong adhesion at high temperature. Therefore, it can adhere to the active sites of graphite to protect graphite from oxidation [6].

However, Fig. 2 suggests that the mass loss rate of the sample impregnated with high concentration boric acid solution alone is obviously higher than the untreated sample. The increased weight loss rates might be due to the following two reasons:

1) Few H$_3$BO$_3$ molecules and acid ions in the solution resulting from the lower solubility of H$_3$BO$_3$ cannot be inserted into the graphite layer effectively.

2) Part of the substance in the antioxidants will be lost due to the condensation reaction occurrence or volatilization.

The results in Fig.2 also indicate that the weight loss rates of all the samples obtained by impregnation with aluminum dihydrogen phosphate solution became decreased obviously. Aluminum dihydrogen phosphate can be converted to Al(PO)$_3$ at 300 ℃, and further polymerized into aluminum metaphosphate, which usually becomes mesh-like shape and further plays a role of protection for graphite from oxidation[7]. Obviously, the best impregnation result can be achieved in aluminum dihydrogen phosphate.

SEM observations on the samples with different impregnation ratios of aluminum dihydrogen phosphate and graphite are given in Fig.3.
It can be seen from Fig.3 that the graphite flakes tend to become thicker due to the presence of the coating layer with the increased aluminum dihydrogen phosphate ratios. The increased thickness of the coating layer can reach the maximum value between 2:1 and 3:1. Therefore, it is reasonably concluded that the optimum ratio of aluminum dihydrogen phosphate to graphite should be between 2:1 and 3:1. For further proving this, the point scanning were carried out and the results were given in Fig.3. The point scanning data in Fig.3 revealed only part of the graphite in the sample is effectively coated in the case of the impregnation ratio of 2:1, as marked by point A shown in Fig.3 (d). The other part of the graphite isn’t coated successfully, as shown in point B in figure (d). For the samples with the impregnation ratio of 3:1, the point scanning results suggested these samples could be effectively coated, as marked by points C and D shown in Fig.3 (e). These results further confirmed that the optimum impregnation ratio of aluminum dihydrogen phosphate to graphite is 2:1 ~ 3:1.

![Figure 4 line scanning analysis on the cross-section of the sample (a) and DSC curves of the samples with various thermal cycle numbers(b)](image)

Fig. 4 (a) shows the line scanning results on the cross-section of composite phase change material fabricated using the impregnated sample 3 (as shown in Fig.2) and Fig. 4 (b) is the DSC curves of the same sample with various thermal cycles. It can be seen that the average strength of C on the fracture surface of the sample doped with impregnated sample 3 is 22.85, which indicates good oxidation resistance. Meanwhile, almost unchanged values in latent heat suggest the stable thermal performance of the samples.

3. Conclusion
In this study, aluminum dihydrogen phosphate was used to impregnate flake graphite samples for the first time, and the optimum impregnation ratio was obtained as follows: the mass ratio of aluminum dihydrogen phosphate to graphite was 2:1 to 3:1. The impregnated graphite was combined with phase change material for achieving better oxidation resistance. The results show that the sample has good oxidation resistance and excellent thermal cycle stability.

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