Effect of heat treatment on structure and mechanical properties of basalt fibers and its application for fabrication Cu based composite

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Abstract

This paper firstly presents an experimental investigation of the effects of heat treatment temperatures and atmosphere on the tensile strength and structure of basalt fibers. The results show that the basalt fibers after heat treatment in air (200–600 °C) have the characteristics of amorphous state due to the oxidation of Fe$^{2+}$ into Fe$^{3+}$. On the contrary, the vacuum heat treatment induces the crystallization of basalt fibers. The reason is that the Fe$^{2+}$ cations can act as network modifiers and the Fe$^{3+}$ can participate in and enhance glass network. Furthermore, the single fiber strength of basalt fiber decreases with the increase of heat treatment temperature. However, the single fiber strength of basalt fibers after vacuum heat treatment is about 3 times that of basalt fibers after air heat treatment. On this foundation, basalt fibers were used for fabrication of copper matrix composites by spark plasma sintering (SPS) and hot press sintering (HPS) for the first time. The results exhibit that the strength of basalt fibers reinforced copper matrix composites prepared by SPS is 276 MPa, which are higher than that by HPS (192 MPa) due to fast heating rate and short holding time.

1. Introduction

Basalt fibers were made by high-speed drawing of platinum-rhodium alloy wire drawing leakage plate after melting of basalt at 1450 °C ~ 1500 °C [1]. Basalt fibers have excellent mechanical properties, high temperature resistance and thermal stability [2]. At present, basalt fibers have been applied as aerospace materials, polymer matrix composite materials, friction materials, heat insulation materials and filter materials, and with the deepening of research there is a broader application prospect [3]. Basalt fibers are ideal substitutes for aramid fibers, carbon fibers and other high performance fibers [4].

One important application of basalt fibers is as the reinforcing phase of composites [5, 6]. Lopresto et al [7] investigated the physical and mechanical properties of polyurethane matrix filled with short basalt fibers. Lv et al [8] revealed the effect of basalt fibers on the deformation capacities and damage mechanism of resin matrix. Sim [9] studied the effect of basalt fibers on the mechanical and deformation properties of concrete. Yan et al [10] explored the effect of basalt fibers on the cracking resistance of microbond asphalt macadam. Ding et al [11] obtained fully dense continuous basalt fibers (CBF) reinforced Al-Si composite by vacuum pressure infiltration at 660 °C and 10 MPa pressure for 10 min. The flexural strength of composites reached 201–213 MPa. Yang et al [12] studied the influences of basalt fiber content on mechanical properties of basalt fiber reinforced aluminum matrix composites. The dynamic compressive yield strength and ultimate compressive strength of 10 wt% Bf/Al composite are 280 MPa and 330 MPa, increasing by 150 MPa and 160 MPa compared with the pure aluminum. Vannan et al found that the tensile strength of short basalt fibers reinforced Al alloy composites increased from 175 MPa to 215 MPa with the increase in Cu coated reinforcement content from 0–10%. However, to the best of our knowledge, basalt fibers are rarely applied in copper matrix composites.

Cu has excellent thermal properties and good machinability, but poor mechanical properties [13, 14]. So, it is often necessary to add reinforcing phase, such as particles, fibers, etc. Among various reinforcing materials,
fibers have high strength, high specific modulus, and excellent fatigue resistance and are easily dispersed in the copper matrix \[15, 16\]. Basalt fibers exhibit better mechanical performance than glass fibers, lower prices than carbon fibers, and are the most cost-effective type of high-tech fiber. Therefore, the basalt fibers reinforced copper matrix composites was prepared, and the microstructure and tensile strength of the composite were studied.

2. Experiment

The basalt fibers used in this experiment were provided by Jilin huayang department material research and development Co. Ltd. The SEM image, TEM image and EDS pattern (Position 1 of figure 1(a)) of basalt fibers are exhibited in figure 1. As can be seen from figure 1(a), the basalt fibers surface is smooth and the diameter of basalt fibers is about 12 μm. The selected area electron diffraction pattern shown in figure 1(b) confirms the amorphous nature of original basalt fibers. In addition, the basalt fibers are composed of O, Si, Al, Fe, Ca, Na, Mg and Ti according to the EDS result (figure 1(c)).

The basalt fibers were heated to 200 ~600 °C at a speed of 10 °C min \(^{-1}\) in air and vacuum (10\(^{-4}\) Pa) for 30 min, and then cooled to room temperature. After that, the microstructure and elemental composition of basalt fibers were researched by scanning electron microscope (SEM, Gemini Supra 40, Zeiss, Germany) equipped with an energy dispersive x-ray spectroscopy (EDS). The phase composition was determined by selected area electron diffraction using transmission electron microscope (TEM, JEM-2000DX, JEOL, Japan). The TEM specimens were prepared by milling the basalt fibers into powder with a diameter of about 200 ~500 nm. The Fourier transforms infrared spectrometer (FTIR, PE-SP100, PerkinElmer, USA) was used to collect infrared spectra of the powder samples in the range 500 ~4000 cm \(^{-1}\). The powders of basalt fibers were mixed with KBr which is binder, to prepare disc-shaped samples by using a tablet machine for FTIR studies. The tensile strength of the single basalt fiber was investigated by electronic single fibers strength tester (XQ-2, 2022).
Shanghai New fibers Instrument, China). At least five specimens were used to obtain the average strength for each experimental condition.

Electrolytic Cu powder (purity > 99.9 wt%) and short basalt fibers (length: 2 mm) were used for fabricating the basalt fibers reinforced copper matrix composites. 1.5 wt% basalt fiber was used to prepare the composites in this paper. To improve the interface binding between basalt fibers and Cu, the basalt fibers were coated with copper using electroless plating before sintering. The SEM image of copper-plated basalt fiber is shown in figure 2. The composition of the electroless bath is given in table 1 and the plating thickness is about 2 μm.

The basalt fibers and copper powder was mixed by a planetary ball mill at a rotational speed of 150 rpm for milling times of 6 h. The mixtures were cold compacted by plate vulcanizer at a load of 200 MPa to achieve a green specimen. Then, the specimens were sintered by spark plasma sintering (SPS) and hot pressing sintering (HPS) using the same vacuum (10⁻⁴ Pa), sintering temperature (600 °C), pressure (30 MPa) and furnace cooling. The temperature-time curves of these two methods are shown in figure 3. The SEM was used to observe microstructure and fracture morphology of the composites. The strength of composites was measured by a universal testing machine (Model 1186, Instron, USA) with a cross-head speed of 0.6 mm min⁻¹ at room temperature. The dimension of the tensile specimen is shown in figure 4.

3. Results and discussion

3.1. Micromorphology of basalt fibers

3.1.1. SEM analysis

Figure 5 is the SEM images of the surface of the basalt fibers after heat treatment at 200 ∼600 °C in different atmospheres. Figure 6 shows the element distribution across the red line singed in figures 5(f)–(g). As the temperature of heat treatment increases, the surface of the fibers becomes smooth gradually. This is because the sizing agent on the surface of the fibers is decomposed and volatilized at high temperature [17, 18]. The sizing agent is a multi-component aqueous solution or aqueous emulsion composed of binder, coupling agent, surfactant, antistatic agent and other solutes. Sizing agent plays a vital role in improving and protecting the performance and quality of the raw silk. However, as shown in figure 6, the EDS analysis of basalt fibers shows that the content of Fe on the surface of the treated fibers in air is about 3 times that in vacuum, and its distribution is extremely uneven. This indicates that ferrous oxide in basalt fibers can migrate to the fibers surface during heat treatment in the air.
3.1.2. TEM analysis
Figure 7 exhibits the selected area diffraction (SAD) patterns of basalt fibers after heat treatment in different temperature and atmosphere. The basalt fibers after heat treatment at 200 ~ 600 °C in air shows the characteristics of amorphous state (figures 7(a), (c) and (e)). On the contrary, the heat treatment in vacuum induces the crystallization of basalt fibers (figures 7(b), (d) and (f)). Moreover, the type and content of crystalline phases depend on the temperature of heat treatment. After heat treatment at 200 °C, the crystalline phase can be identified as CaO according to the SAD pattern (figure 7(b)). When the temperature of heat treatment is increased to 400 °C, CaO and a small amount of CaFeO$_2$ can be formed (figure 7(d)). Furthermore, the CaFeO$_2$ becomes main crystalline phase after heat treatment at 600 °C (figure 7(f)). During heat treatment in air the Fe$^{2+}$ can be oxidized to form Fe$^{3+}$. It is believed that Fe$^{2+}$ cations act as network modifiers with octahedral coordination, which can weaken structure of the glass and promote the crystallization. On the contrary, Fe$^{3+}$ ions can participate in the formation of glass network in the form of [FeO$_4$]$^{19}$ [19]. As a result, the heat treatment in air leads to the increase of Fe$^{3+}$ ions, which improve glass forming ability. The heat treatment in vacuum remains more Fe$^{2+}$ ions, which destroys the network structure of glass and promotes the crystallization of fibers.

3.1.3. IR analysis
The fingerprint region of infrared spectrum contains detailed molecular structure information. As can be seen from the infrared spectrum in figure 8, the strongest infrared absorption peak appears at 1002 cm$^{-1}$, which indicates the existence of Si-O$_{ab}$ bond in the fibers (table 2) [20]. There are two weak absorption peaks at...
Figure 5. SEM images of basalt fibers after heat treatment in different temperature, (a), (b) 200 °C, (c), (d) 400 °C, (e), (f) 600 °C and atmosphere, (a), (c), (e) air, (b), (d), (f) vacuum.

Figure 6. Distribution of Fe element across the red line signed in figure 5 (f)–(g).
2850 cm$^{-1}$ and 2920 cm$^{-1}$. These two weak peaks correspond to some impurities attached to the surface of basalt fibers [21]. At 3434 cm$^{-1}$, it is the Fe-O antisymmetric absorption peak of Fe$_2$O$_3$. As can be seen from curve a - d in figure 8, the area of absorption peak at 3434 cm$^{-1}$ has an increasing trend, which can be attributed to the oxidation of Fe$^{2+}$. However, it can be seen from curve e, f and g in figure 8, the content of Fe$^{3+}$ is basically unchanged due to heat treatment in vacuum atmosphere.

3.2. Mechanical properties of basalt fibers

Figure 9 is the single fiber strength of basalt fibers after heat treatment in different condition. It can be seen from figure 9 that the single fiber strength of basalt fibers gradually decreases with the increase of heat treatment temperature. Similar phenomena can be found in previous works [22–24]. Akhlaghi et al [25] found that the
single fiber strength of basalt fibers deteriorates gradually with the increase of holding time and temperature of heat treatment. The strength of basalt fibers decreased from 1500 MPa to 322 MPa when the heat treatment temperature increased from 300 °C to 600 °C. Chen et al.[26] found that the single fiber strength of basalt fibers decreases with the increase of temperature in different atmospheres. The strength of basalt fibers in argon atmosphere is obviously better than that in air atmosphere. However, no vacuum atmosphere was used during heat treatment in previous studies. In this work, the single fiber strength of basalt fibers after vacuum heat
treatment is about 3 times that of basalt fibers after air heat treatment. So, the single fiber strength of basalt fibers can be better retained after vacuum heat treatment. This difference can be attributed to the following two aspects. On one hand, it can be seen from figure 6 that the content of Fe on the surface of basalt fibers is significantly enhanced after the process of air heat treatment. The diffusion of iron ion during heat treatment may lead to surface defects \[27, 28\]. On the other hand, the basalt fibers in the vacuum atmosphere have low crystallization temperature. It is well known that the crystallization is conducive to improve the strength of the silicate material \[29\]. After heat treatment in vacuum, the strength of the fiber is still higher than that of copper, so basalt fibers can be used in copper matrix composites.

3.3. Basalt fibers reinforced copper matrix composites

In order to further explore the application of basalt fibers in composites. According to the previous experiments, 1.5 wt% basalt fibers reinforced copper matrix composites were prepared by HPS and SPS. Figure 10 shows the SEM images of the composite prepared by SPS and HPS. These two sintering methods exhibit similar microstructure characteristics. No cracks, pores and obvious agglomeration of basalt fibers were formed in the basalt fibers reinforced copper matrix composites. Figure 11 is the tensile stress-strain curve of the basalt fibers reinforced copper matrix composites. The tensile strength and elongation of the composite prepared by traditional HPS is 192 MPa and 9%, respectively. However, the tensile strength and elongation can be increased

![Figure 10. SEM images of composites prepared by different sintering methods, (a) SPS, (b) HPS.](image1)

![Figure 11. Stress-strain curves from tensile testing of composites.](image2)
to 276 MPa and 17% by using the novel SPS. The strength of pure copper prepared by SPS and HPS is about 210 MPa and 202 MPa, which is consistent with previous works [30]. Therefore, the addition of basalt fibers is effective to improve the mechanical properties of copper. Figure 12 shows the SEM images of fracture surface of composites fabricated by different sintering method. The pull-out of fibers can be found on the surface of the samples prepared by SPS, which indicates that the basalt fibers maintain excellent mechanical properties. By contrary, fracture of basalt fibers can be observed on the surface of the samples prepared by HPS, which demonstrate the low strength of basalt fibers. For HPS, slow heating rate and long holding time deteriorate obviously the strength of basalt fibers, and then lead to low mechanical properties of composites.

4. Conclusion

The effect of heat treatment on structure and tensile strength basalt fibers were analyzed. The application of basalt fibers for fabricating copper matrix composites was studied. The main conclusions were as follows:

(1) As the temperature of heat treatment increases, the surface of the basalt fibers becomes smooth gradually due to the volatilization of sizing agent.

(2) During heat treatment in air, $\text{Fe}^{2+}$ as network modifier can be oxidized into $\text{Fe}^{3+}$, which cause the fibers to maintain the amorphous structure. On the contrary, the vacuum heat treatment induces the crystallization of basalt fibers because of the weakening of the glass network by $\text{Fe}^{2+}$.

(3) The strength of basalt fibers after vacuum heat treatment is higher than that after air heat treatment. The air heat treatment may cause more serious surface defects and the vacuum heat treatment can improve the strength of basalt fibers by crystallization.

(4) The tensile strength and elongation of basalt fibers reinforced copper matrix composites prepared by SPS is higher than that by HPS due to fast heating rate and short holding time. At the same time, the tensile strength is increased by 32% compared to copper.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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