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Mechanical properties of Cu-based composites reinforced by carbon nanotubes ①

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Abstract: Cu-based composites reinforced by 0 % ~ 25 % (volume fraction) carbon nanotubes were prepared. The fracture behaviors and the rolling properties of the composites and the effects of the volume fraction of the carbon nanotubes were studied. The experimental results show that the fracture toughness of the composites is related to the pulling-out and bridging of the carbon nanotubes in the fracture process. With the volume fraction of the carbon nanotubes increasing, the Vicker's hardness and the compactness of the composites increase first and then decrease. The peaks of the hardness and the compactness occur at 12 % ~ 15 % of volume fraction of carbon nanotubes. Some proper ratio of rolling reduction benefits to the comprehensive mechanical properties of the composites.

Key words: Cu-matrix composites; carbon nanotubes; nanotubes content; fracture behavior; rolling
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1 INTRODUCTION

Because of their strength, high elastic modulus, large ratio of slenderness (100 ~ 1 000) and wear resistance, the discovery of the carbon nanotubes has drawn great attentions[1~3]. They show great potential as fiber reinforcements. Tsinghua University has successfully applied them to the surface laser coating of the ductile iron[4,5]. However, the reports about the uses of the nanotubes as fiber reinforcement of composites cannot be found yet. Considering the wide applications of the carbon fibers-reinforced Cu-based composites(C/Cu)[6,7], it is expected that the C/Cu composites will be brought into full play in high strength, low expansion, good heat and electric conduction and excellent wear resistance by replacing the carbon fibers with the carbon nanotubes[8]. This paper aims to study the fracture behaviors and the rolling properties of the Cu-based composites reinforced by the carbon nanotubes and the effects of the volume fraction of the carbon nanotubes.

2 EXPERIMENTAL

The carbon nanotubes were prepared by the thermal decomposition of acetylene catalyzed by cobalt. They were treated by chemical nickeling, and then were mixed with copper powder (0.070 mm) by ball milling for 60 min, cold pressed at 355 MPa, sintered at 850 ℃ in vacuum, straightly rolled or 0.5 mm Cu-sheathed rolled with a ratio of rolling reduction per rolling of 30 %, and annealed at 550 ℃ in vacuum[9]. The prepared composites were spark eroded into

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specimens. The metallographs and compactness were observed by optical microscopy, the distributions of the nanotubes and the fractographs were determined by scanning electron microscopy. The Vicker's hardness was measured at a load of 49 N for 15 s. The density was decided by the weight method and the compactness by the Archimedean method (the precision of the balance used is 0.1 mg).

3 RESULTS AND DISCUSSION

3.1 Fracture behaviors of composites

The experimental results show that the Vicker's hardness of the composites tested is 115 ~ 125, and the compactness is 92 % ~ 98 %. The SEM fractographs in Fig.1 indicate that the carbon nanotubes are homogeneously distributed and do not adhere to each other very often, and that there occur pulling-out and bridging on the fractographs, and the fractures propagate along the direction of the initial cracks. Therefore, the main fracture mechanism of the composites is pulling-out of the fibers[10]. The low-magnification SEM fractographs in Fig.2 show the typical shearing lip and fracture dimples. Therefore the fracture of the composites is ductile, ruptured through the aggregation of the micropores. The rolling tests show that the composites can reach a deformation of 50 % ~ 60 % and have good isotropy of mechanical properties compared with the conventional carbon fibers-reinforced Cu-based composites.

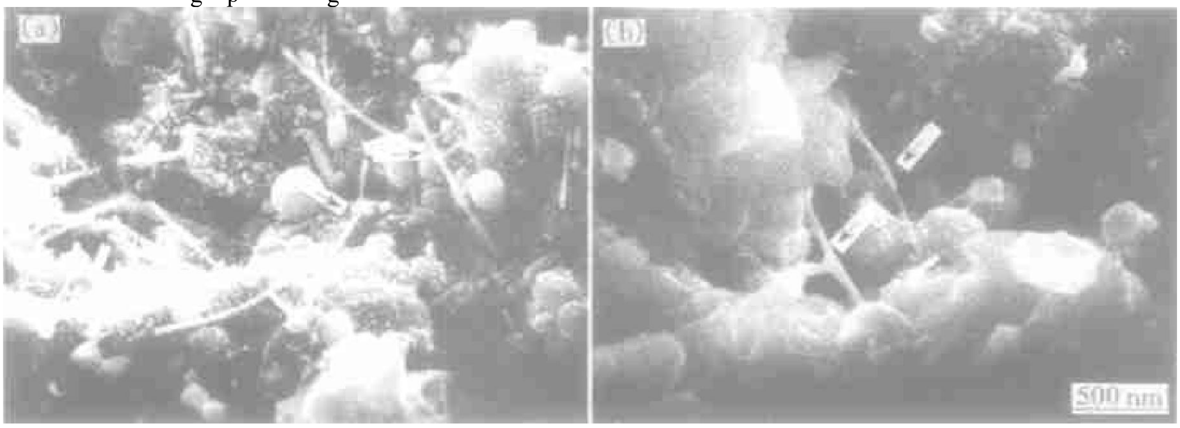

Fig.1 SEM fractographs of carbon nanotubes-reinforced Cu-based composite
(a) —Pulling-out of carbon nanotubes; (b) —Bridging of carbon nanotubes

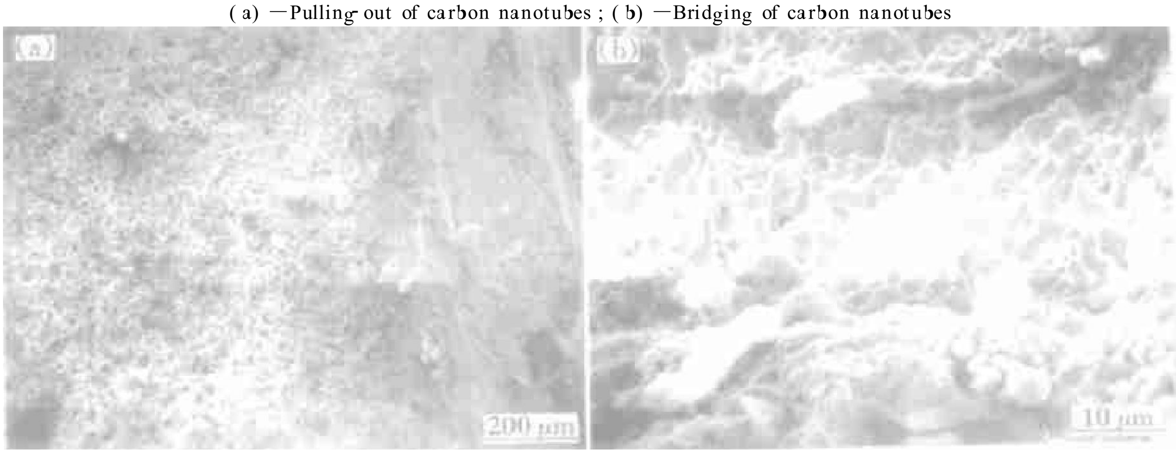

Fig.2 SEM fractographs of carbon nanotubes-reinforced Cu-based composite
(a) —Low-magnification SEM morphology; (b) —Dimples on fracture surface

Compared with the other fracture mechanisms, much more work must be consumed in the fiber pulling-out mechamism, therefore the critical energy disspation ratio for the crack propagation is large. And the fiber bridging shields effect of the cracks reduces the stress intensity factors at the crack tips, as a result the propagation ratio of the cracks are slowed down. So the fracture toughness is high. In addition, when the cracks propagate in the copper matrix, there occur plastic deformations at the crack tips with large stress concentrations owing to copper plasticity, which leads to the passivation of the crack tips. Thus the stress concentrations are relaxed and a great amount of energy is absorbed, finally the propagation of the cracks is impeded.

3.2 Effects of content of carbon nanotubes on Vicker's hardness compactness of composites

The content of the carbon nanotubes has significant effects on the Vicker's hardness and the compactness of the composites. It can be seen from Fig.3(a) that the Vicker's hardness (HV) increases with increasing volume fraction (φ_f) of the nanotubes, and when $\varphi_f = 12\%$, HV reaches the peak value, then decreases with inceeasing content of the nanotubes. Fig.3(b) indicates that the compactness (d_r) of the composites increases progressively with increasing volume fraction of the carbon nanotubes and reaches the peak value at 12%, then decreases with the further increase of the content of the nanotubes. With regards to the Vicker's hardness and the compactness of the composites, the optimum volume fraction of the carbon nanotubes is about 12%.

In view of the compactness of the composites, on one hand, the carbon nanotubes will fill the pores, thus raising the compactness; on the other hand, the carbon nanotubes will impede the fusion of the composites during pressing and sintering, thus reducing the compactness. These two factors function simultaneously. When the volume fraction of the carbon nanotubes is low, they can be effectively dispersed by the copper particles and do not aggregate very often, therefore the filling effect is predominate. With increasing the content of carbon nanotubes, the impeding effect enhances obviously, which leads to the reduction of the compactness.

The variation of the Vicker's hardness is caused by the fiber strengthening effect and the deformation strengthening effect and the change of the compactness with increasing volume fraction of the carbon nanotubes. When φ_f is larger than 9%, with φ_f increasing, the compactness begins to decrease and there occur adhesions

Fig.3 Dependence of Vicker's hardness (HV) and compactness (d_r) of carbon nanotubes-reinforced Cu-based composites on content of carbon nanotubes

(a) —HV vs φ_f; (b) —d_r vs φ_f

between the carbon nanotubes, which leads to the slower increase of the Vicker's hardness, so φ_f = 9 % is the point of inflection of the variation of the strength. When φ_f is larger than 12 %, the reduction effect of the compactness exceeds the fiber strengthening effect, while there occur severe adhesion between the carbon nanotubes, therefore the Vicker's hardness decreases rapidly. When φ_f goes beyond 15 %, the severe adhesion between the nanotubes will reduce the ratio of slenderness and damage the continuity of the copper matrix. And the aggregated carbon nanotubes will form stress concentrations during the pressing process and act as crack sources. Thus fractures easily occur in the following rolling process. In conclusion, the volume fraction of the carbon nanotubes should exceed 15 %.

The optimum volume fraction of the carbon nanotubes-reinforced Cu-based composites is 12 %, while that of the common carbon fibers is about 30 %. This is due to the fact that the carbon nanotubes are very small, therefore more copper powder is needed to disperse the carbon nanotubes under the same conditions.

3.3 Rolling properties of composites

When φ_f = 15 %, the largest deformations in straight rolling and Cu-sheathed rolling are 45 % and 60 % ~ 70 % respectively, and the Cu-sheathed rolling remains a ratio of rolling reduction about 40 % after annealing. The effect of the ratio of rolling reduction on the Vicker's hardness and the compactness of the composites in straight rolling are shown in Fig.4. With increasing ratio of rolling reduction, the Vicker's hardness and the compactness increase, and after the peak values are reached, they begin to decrease. For the composites with φ_f = 15 %, when the ratio of rolling reduction is smaller than 35 %, the Vicker's hardness and the compactness increase obviously with increasing ratio of rolling reduction. This is because before rolling the compactness is relatively low, the rolling reduces the porosity, thus enhancing the Vicker's hardness. When the ratio of rolling reduction goes beyond 35 %, the compactness does not increase obviously, because the compactness is close to the theoretic value. Especially when the ratio of rolling reduction is 40 % ~ 45 %, the compactness almost does not change, and at this moment, the powders are deformed severely, the deformation strengthening enhances and the Vicker's hardness continues to increase, and 30 % is a point of inflection. When the ratio rolling reduction exceeds 45 %, the Vicker's hardness and the compactness begin to reduce, and the reduction of the former is very obvious, there occur macrocracks in some specimens when the rolling reduction is about 40 % for the Cu-based composite rein forced by 15 % of carbon nanotubes. The

Fig.4 Dependence of Vicker's hardness (HV) and compactness (d_r) of carbon nanotubes-reinforced Cu-based composites on ratio of rolling reduction (η)
(a) —HV vs η; (b) —d_r vs η

variations of the Vicker's hardness and the compactness with the ratio of rolling reduction of the Cu - based composite reinforced by 8 %of carbon nanotubes are similar to those of the Cu-based composites reinforced by 15 % of carbon nanotubes, but less obvious. The optimum ratio of rolling reduction is 50 % ~ 60 %, which is relatively higher than that of the Cu-based composite reinforced by 15 % carbon nanotubes.

Different contents of the carbon nanotubes affect the Vicker's hardness and the compactness of the composites to some different extents, and the corresponding optimum ratios of rolling reduction are slso different. Compared with Cu-based composite reinforced by 8 % carbon nanotubes, the Cu-based composite reinforced by 15 % carbon nanotubes has lower compactness and stronger deformation strengthening effect, as a result, the porosity reduces relatively faster. In addition, larger content of carbon nanotubes produces stronger strengthening effect, which leads to the faster increase of the Vicker's hardness and the compactness and also makes the strengthening limit reached earlier, consequently the optimum ratio of rolling reduction is lower.

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