Effects of AlloYing on the Wettability of Copper to Carbon Fibers

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Various dilute binary copper alloys were coated onto the surface of carbon fibers. The wetting behavior of these alloys was examined by scanning electron microscope after heating the coated fibers at 1403 K. Tensile strength of the coated fibers was measured prior to and after the heat treatment. The measured results of the tensile strength were then analyzed by Weibull distribution theory. Alloying additions of Mo, Cr, V, Fe, and Co at one atomic fraction were found to be effective on the improvement of the wettability of copper to carbon fibers. Wetting mechanism was then discussed to conclude that such transition metals can be expected to cause wetting: those forming miscibility gaps in liquid state and having rather small solid solubility in the binary system, and those being able to cause interface reactions. Interface reactions can be controlled by the rather small alloying additions so that the least degradation in the strength of carbon fibers could be resulted.

KEY WORDS: wettability; surface and interface tension; segregation; surface adsorption; miscibility gap; Weibull distribution.

1. Introduction

During the development of fiber reinforced metals (FRM), much attention has been paid to the interface problems especially between metal matrices and carbon fibers because of, in many cases, the poor wettability between them.\textsuperscript{1-4) }Unlike aluminum, at the interface of C/Cu composites copper was reported to be chemically inert against carbon fibers.\textsuperscript{5) }Such an interface, on the one hand, can meet the physico-chemical stability requirements for it in a composite, but on the other hand, because of the poor wettability of copper to carbon fibers, such an interface is not so strong as to transfer the applied load between copper matrix and carbon fibers. Effects of alloying additions to copper on wetting of bulk graphite have been investigated\textsuperscript{6) }by using a sessile drop experiment. The results showed that among twenty different alloying elements, vanadium and chromium additions can cause copper to wet bulk graphite. In another investigation, to strengthen the interface between copper and carbon fibers, some kinds of metal powders such as those of Zr, V, W, Cr and Mo, which are strong carbide formers, were added to and mixed with oxygen free copper powder. The mixed powder and the carbon fibers coated with pure copper were fabricated into C/Cu composite with a hot press method.\textsuperscript{7)

Alloying addition as an approach to improving the wettability of metal matrices to carbon fibers has been highly appreciated. Excessive alloying addition, however, would reduce both the electric and thermal conductivity of C/Cu composite working as an electronic or electric material and would also damage carbon fibers.

Hence, in most cases electroless plating and electroplating process have been generally used to prepare the pure copper coated carbon fibers prior to the fabrication of C/Cu composite. But with these processes it is difficult to coat copper alloys on the surface of carbon fibers.

In the present investigation, various copper alloy was coated on to the surface of carbon fibers and their wetting behavior on the surface of carbon fibers was studied after heat treatment above their melting points. Some binary copper alloys were suggested to be the candidates as coating materials for carbon fibers in C/Cu composite. Tensile strength of the coated fibers was measured before and after heat treatment and the results showed that there was little loss in tensile strength when the alloying additions were rather small and the tendency towards forming their carbides was thermodynamically moderate.

2. Experimental Procedure

Binary copper alloys were prepared by arc melting oxygen free copper and alloying elements with purity ranging between 99.9-99.99 % under argon atmosphere.

General appearance of the phase diagrams of the prepared binary copper alloys tells that these alloys can be classified into three categories, as listed in Table 1. The alloys in the first category are characterized by the existence of miscibility gaps, those in the second one by the formation of continuous series
of solid solutions, and those in the third one by the occurrence of eutectic reactions in their phase diagrams, as shown in Fig. 1. Accordingly, here for convenience sake, we may call them as M-group, C-group and E-group alloys, respectively.

Poly-acrylo-nitrile (PAN) based carbon fibers were used in the present experiment. Before being used they were heated under evacuation at 623 K for 2 h to remove sizing layers. Some of their properties are listed in Table 2.

Pure copper and its binary alloys were coated onto the surface of carbon fibers, respectively, in a high vacuum electron beam evaporation apparatus, ULVAC DRP-40E. Carbon fibers in tow were raveled and wound on the surface of a drum frame as uniform as possible. The drum frame was then installed to a spindle in the evaporation chamber. During coating the frame was driven at a rate of 30 rpm so that uniform coating layers could be obtained. The thickness of the coating layers could be controlled to be within 0.2 μm by controlling suitable operating parameters such as electron emission power and coating time accordingly. The coated carbon fibers were then subjected to a heat treatment at 1403 K for 30 min in evacuated quartz tubes, followed by a water quench.

Tensile strength of the coated fibers, both before and after heat treatment, was measured by a mini-Instron-type testing machine. Weibull distribution theory was employed to analyze the results of the tensile strength test. As the failure probability is relevant to the gauge length of the test specimen, in the present case the dimensions of the specimen were taken as shown in Fig. 2.

The wetting behavior of copper and its binary alloys on the surface of carbon fibers was observed under a JEOL JSM-15 scanning electron microscope (SEM).

3. Results

3.1. Observation of Wetting Behavior

The surface morphologies of the carbon fibers as-received and coated with copper are shown in Fig. 3. From Figs. 3(b) and 3(c) it can be seen that some copper droplets, which must have formed in liquid state when heated up to over the melting point of copper and remained their shapes by the water quench, exist on the surfaces of carbon fibers. This proves the poor wettability of copper to carbon fibers.

Fig. 4 shows the surface morphologies of the carbon fibers coated with the binary copper alloys. From Figs. 4(a) to 4(j) are the carbon fibers coated with the alloys in the M-group. There were three types of wetting behavior for the alloys in the M-group. One of them was shown by the alloys of Cu–1at%Pb, Cu–1at%Ta, and Cu–1at%Nb. These alloys formed many droplets smaller than those formed by pure copper, as shown in Figs. 4(a) to 4(c). The second type was demonstrated by the alloys of Cu–0.4at%Cr, Cu–1at%Cr, Cu–0.3at%V, Cu–1at%V and Cu–1at%Mo. It is seen from Figs. 4(d) to 4(h) that comparing with pure copper these alloys showed improved wettability; and that with the increase in concentration of the

| M-group | Element | Concentrations (at%) | Pb | Nb | Ta | Cr | V | Mo | Fe | Co |
|---------|---------|---------------------|----|----|----|----|---|----|----|----|
|         |         |                     | 1  | 1  | 1  | 0.4 | 0.3 | 1  | 1  | 1  |
| C-group | Element | Concentrations (at%) | Mn | Pd | Ni |     |     |    |    |    |
|         |         |                     | 1  | 1  | 1  | 1, 5, 10 |     |    |    |    |
| E-group | Element | Concentrations (at%) | Si | Sn | In | Ti | Mg |     |    |    |
|         |         |                     | 1  | 1  | 1  | 1  | 1  |     |    |    |

Fig. 1. Representative phase diagrams of (a) M-group alloys, (b) C-group alloys and (c) E-group alloys.
Table 2. Nominal properties of the carbon fibers as received.

| Property                              | Value         |
|---------------------------------------|---------------|
| Weight (gm⁻¹)                         | 0.38          |
| Single fiber diameter (µm)            | 0.65          |
| Tensile strength (MPa)                | 2.43 x 10⁶    |
| Elasticity modulus (MPa)              | 3.43 x 10⁶    |
| Density (g cm⁻³)                      | 1.8           |
| Thermal conductivity (kcal mol⁻¹ h⁻¹ K⁻¹) | 100           |
| Specific heat (cal g⁻¹ K⁻¹)           | 0.17          |
| Tensile elongation (%)                | 0.6           |
| Linear thermal expansion coefficient  | -0.5          |
| Specific resistivity (Ω cm)           | 9.4 x 10⁴     |

alloying elements from 0.4 to 1 at% for Cr and from 0.3 to 1 at% for V in Cu the contact angles decreased to less than 90°, as shown in Fig. 5. The alloys of Cu–1at%Co and Cu–1at%Fe exhibited another type of wetting behavior, as is shown in Figs. 4(i) and 4(j). It is seen that the carbon fibers coated with these two alloys showed smooth surfaces. The photographs of the transverse sections of these fibers (Figs. 6(e) and 6(f)) reveal that the coating layers of these alloys do evenly exist on the surfaces of the carbon fibers, indicating excellent wettability of these alloys to carbon fibers.

From Figs. 4(k) to 4(o) are the carbon fibers coated with Cu–1at%Mn, Cu–1at%Pd, Cu–1at%Ni, Cu–5at%Ni and Cu–10at%Ni alloys, which are classified into the C-group in Table 1. It is seen that these alloys at one atomic fraction of alloying elements could not well wet carbon fibers. But with the increase in concentration of the alloying elements, as in the cases of Cu–5at%Ni and Cu–10at%Ni, the coating layers tend to spread over and adhere to the surfaces of carbon fibers, as shown in Figs. 6(c) and 6(d).

Carbon fibers coated with Cu–1at%Si, Cu–1at%Sn, Cu–1at%In, Cu–1at%Ti and Cu–1at%Mg are shown in Figs. 4(p) to 4(t). These alloys belong to the E-group in Table 1. There are many small droplets formed on the surfaces of some of these fibers. Among these alloys only Cu–1at%Mg contacts carbon fibers at an angle less than 90°. Some of them appear to have sound surfaces, but in the photographs of the transverse sections of these fibers there is no obvious evidence to show the coating layers remaining on the fiber surfaces.
3.2. Tensile Strength of the Carbon Fibers Coated with Copper Alloys

Tensile strength of the carbon fibers, with and without coating, before and after heat treatment, were analyzed with Weibull distribution theory. Weibull distribution function can be expressed as

\[ F(x) = 1 - \exp \left[ -\left( \frac{x}{\beta} \right)^{\gamma} \right]. \]

This function can be rewritten as the following form;

\[ \ln \left[ -\ln \left( 1 - F(x) \right) \right] = \frac{1}{\alpha} \ln x - \frac{1}{\alpha} \ln \beta, \]

where, \( F(x) \): the probability of failure of a fiber when the applied load is equal to or
less than \(x\)

\[\alpha, \beta: \text{the parameters to be derived by plotting ln } x \text{ against the failure probability, respectively.}\]

\[P_n, \text{ which is defined as } P_n = m/(n + 1), \text{ } (3)\]

where, \(m, n: \text{the sample order and size, respectively.}\)

Let \(x=\hat{\beta}\), then Eq. (2) becomes

\[\ln [-\ln (1 - F(\hat{\beta}))] = 0, \text{ } (4)\]

\[F(\hat{\beta}) = 1 - 1/e = 0.632, \text{ } (5)\]

It becomes obvious that \(\hat{\beta}\) denotes the load when the applied load is equal to or less than which the failure probability \(P(x=\hat{\beta})\) of a carbon fiber is 0.632. \(\alpha\) is the parameter concerning the distribution shape.\(^5\)

The obtained parameters of \(\alpha, \beta, \hat{\alpha}, \text{ and } S_\beta, \text{ are tabulated in Table 3.}\)

4. Discussion

4.1. Adsorption of Alloying Elements on the Surfaces of Copper Alloys

The modification of the properties in the surface of copper, especially the interface between copper and carbon fiber, is considerably important to the improvement of the wettability. And the surface adsorption plays an important role in this respect. For a two component system, by using the dilute approximation, Gibbs adsorption equation\(^9\) can be written as

\[\Gamma_4 = -\frac{1}{RT} \frac{d\gamma}{d \ln x}, \text{ } (6)\]

Table 3. Statistics parameters \(\alpha, \hat{\beta}, \hat{\alpha}, \text{ and } S_\beta\) in Weibull distribution for the tested carbon fibers.

| Coating materials       | \(\alpha\) | \(\hat{\beta}\) (MPa) | \(\hat{\alpha}\) (MPa) | \(S_\beta\) (MPa) |
|-------------------------|-----------|-----------------------|-----------------------|------------------|
| As-received, NH*        | -0.285    | 2.32                  | 2.85                  | 793              |
| Cu, NH                  | -0.351    | 1.67                  | 2.35                  | 817              |
| Cu-1at%Cr, NH           | -0.244    | 1.83                  | 2.81                  | 824              |
| Cu-1at%Co, NH           | -0.298    | 1.63                  | 2.65                  | 834              |
| Cu-1at%Fe, NH           | -0.322    | 1.51                  | 2.48                  | 810              |
| Cu, H**                 | -0.369    | 5.69                  | 9.51                  | 271              |
| Cu-1at%Cr, H**          | -0.45     | 6.52                  | 1.15                  | 456              |
| Cu-1at%Co, H            | -0.319    | 1.51                  | 2.56                  | 845              |
| Cu-1at%Fe, H            | -0.272    | 1.56                  | 2.45                  | 644              |

* No heat treatment
** Heat treatment

where, \(\gamma\): the surface tension

\[\Gamma_4: \text{the quantity of surface adsorption of the solute.}\]

One of the factors which the surface adsorption is dependent on is the surface tension of an alloying element. The alloying element with a low value of surface tension tends to segregate to the surface to reduce the surface tension of the alloy. According to the present paper such sort of elements is in the E-group in Table 1. The second factor affecting the surface adsorption is the heat of mixing of an alloy. A large value of the heat of mixing makes a positive contribution to the surface adsorption. Such kind of elements appears in the M-group.

The SEM observation of carbon fiber surfaces showed that the alloying additions of Mo, Cr, V, Fe, and Co exhibited favorable effects on the improvement of the wettability of copper to carbon fibers.
As shown in Fig. 1(a), for the alloy in the M-group in Table 1 the existence of miscibility gaps in liquid state is a characteristic of their phase diagrams. Furthermore, the alloying elements in these alloys exhibit rather small solid solubility. These characteristics correspond to positive values of heat of mixing of their copper alloys, which provide the motive force for the segregation of alloying elements to the surface. But all these alloying elements except Pb in the alloys of the M-group have large values of surface tension which are unfavorable to the surface adsorption. On the other hand, most of the alloying elements in the M-group alloys are comparatively easy to form carbides with carbon, which promote the alloying elements to segregate to the interface to reduce the interface tension.

The experiment results showed that none of the alloys at one atomic fraction of alloying additions in the G-group in Table 1 could well wet carbon fibers. This can be explained as that because of the existence of the continuous series of solid solutions (Fig. 1(b)) and the high values of the surface tension of these alloying elements, the segregation of the alloying elements to the surface is not likely to occur in coating layers. The facts that with the increase in concentration of Ni in copper the coating layers become visible under SEM can be explained as that the increase in concentration of Ni in Cu could cause more adsorptions of Ni atoms on the surface and the interface.

For the alloys in the E-group in Table 1, on the one hand, the alloying elements have high solubility and can form intermetallic compounds with copper (Fig. 1(c)), which is unfavorable to the surface adh- sorption, but on the other hand, most of these alloying elements have small values of surface tension, which promotes the surface adsorption. However, later it will be known that much reduction in surface tension of an alloy would lower its adhesion strength to carbon fiber, even though the reduction in surface tension may benefit wetting. From Fig. 4(a) it is seen that among these alloys only Cu-Mg alloy can spread over the surface of carbon fibers, which may be attributed to its rather low surface tension (0.583 N m⁻¹).

4.2. Wettability Evaluation Based on Surface and Interface Tension

In a physico-chemical sense an workable interface in a composite should possess adequate adhesive property. The adhesion work, \( W_{s-d} \), is defined as the work required to pull apart a solid-liquid joint

\[
W_{s-d} = \gamma^s + \gamma^l - \gamma^{s-l}, \quad \text{................. (7)}
\]

here, \( \gamma^s \), \( \gamma^l \), \( \gamma^{s-l} \): the surface tension of a liquid metal, that of the solid carbon substrate, and the interface tension between them, respectively.

In Eq. (7) the surface tension of carbon fiber, \( \gamma^f \), is a constant. Therefore the larger the value of \( \gamma^f \) and the smaller the value of \( \gamma^{s-l} \), the higher the value of \( W_{s-d} \). The values of \( \gamma^s \) and \( \gamma^{s-l} \) of the copper alloys concerned in the present paper have been calculated in a theoretical work on the evaluation of the wettability of copper alloys to carbon fiber by the present authors. The results showed that the interface tension \( \gamma^{s-l} \) plays a more important role than the surface tension \( \gamma^s \) in determining the value of \( W_{s-d} \). For the alloying elements in the M-group except Pb in Table 1, the existence of miscibility gaps in liquid state and their rather small solid solubility in copper make the same contribution to the surface and interface adsorptions, but the comparatively strong interface reactions between these alloying elements and carbon fiber make their adsorptions at the interface much easier than those at the surface. The interface reactions result in much reduction in interface tension.

It is seen from Fig. 4 that the binary copper alloys of these elements at one atomic fraction adhere to the surfaces of carbon fibers at contact angles less than 90° even after heat treatment at above their melting points. It is because the interaction between Pb and carbon in a sense of carbide forming tendency is too weak to reduce the interface tension although a positive interface adsorption is possible due to its rather low surface tension (0.400 N m⁻¹). In cases of tantalum and niobium, their copper alloys should have wet carbon fiber well, but in the present experiment their results were not so good as predicted. This may be because the difficulty in preparing their binary copper alloys by arc melting as stated by Hansen.

For the elements in the G-group alloys, although they are also relatively easy to form carbides, because of the existence of the continuous series of solid solutions only one atomic fraction of alloying additions is not high enough to cause the enrichment of the alloying elements in the interface.

4.3. Chemical Reactions in the Interfaces

The investigation by D. A. Mortimer and Nicholas showed that the wetting on the interface between copper and carbon occurred only when alloying elements formed adherent reaction products with carbon. The reaction products, i.e., carbides, form most often with the elements in fourth period of the periodic table. With the formation of carbides on the interfaces the interface tension between copper and carbon fibers can be reduced. On the other hand, it is not true that the easier the alloying elements form carbides, the better candidates they would be as alloying elements of coating alloys. It is clear that if the interface reactions are too strong they will reduce the intrinsic strength of carbon fibers because of both the reduction in effective fiber cross section and the formation of the brittle surface layer. In order to control the interface reactions the concentrations of alloying elements in copper alloys should not be too high and the reactions should be thermodynamically moderate. Fig. 7 shows the standard free energies of formation \( \Delta G_f \) for some carbides.

4.4. Strength of Carbon Fibers Coated with Copper Alloys

Fig. 8 shows Weibull distribution of the tensile
strength of the carbon fibers with and without some kinds of coatings, before and after heat treatment at 1403 K. From Fig. 8 and Table 3 it can be seen that the value of average failure strength $\delta$ and the standard deviation of strength, $S_\delta$, for the Cu-1at%Co alloy and Cu-1at%Fe alloy are little influenced by the heat treatment. This signifies that the interface reactions between Fe and Co and carbon fibers are not so strong as to significantly degrade the strength of carbon fibers. But the tensile strength of the carbon fibers coated with Cu-1at%Cr alloy is degraded to a certain extent. Referring to Fig. 7 we may give the reason for this as that Cr is a stronger carbide former than Fe and Co.

5. Conclusion

In summarizing the words described above, the following conclusions can be drawn:

(1) Alloying addition to copper is an effective approach to the improvement of the wettability of copper to carbon fibers.

(2) Transition metals which binary alloys form miscibility gaps in liquid state and which have rather small solubility in solid state in copper are the possible candidates for this purpose. The wettability of cop-
per to carbon fibers can be improved by alloying a small quantity of Mo, Cr, V, Fe, or Co to copper.

(3) The improvement of the wettability can be mainly attributed to the interface adsorption of alloying elements and the interface reactions between alloying elements and carbon fibers which lead to the reductions in interface tension.

(4) The little degradation in tensile strength of the coated carbon fibers can be attributed to the rather small quantity of alloying additions and the moderate tendency towards forming carbides.

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