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Heat durability of carbon fiber reinforced nickel composites

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Abstract

Carbon fiber is a highly heat resistive material in an oxygen free atmosphere. Nickel is also a heat resistive metal and an important element for a superalloy. We can expect an excellent heat durable composite when they are combined. Nickel was electroplated on a carbon yarn to form a monofilament composite. When the high strength fiber was tested, the composite started to lose its strength at 600°C. The deterioration was caused by graphitization of the carbon in the fiber. This is caused by the difference of the graphitization degree between crystallites in a fiber. A high modulus carbon fiber has little difference of the graphitization degree in a fiber. The high modulus fiber did not react when tested and the fiber strength was maintained after heat treatment at 1100°C for 9 h. From the results, the high modulus carbon fiber composite is promising to be durable at a high temperature.

Keywords: carbon fiber; composite; interfacial reaction; nickel.

1. Introduction

A high specific strength and high specific modulus material with high heat durability is required for the aerospace field or the energy conversion field. Superalloys are generally used in the fields though they have high density. Light materials cannot be used in the fields because they have low strength and low heat resistance. A ceramic is a candidate for a heat resistant material, but it has low toughness.

Carbon fiber maintains high specific strength at the temperature over than 2000°C in an oxygen free atmosphere. Carbon fiber reinforced carbon composites (C/C) are often used for the aerospace field, but the elongation to fracture is less than 2%.

A carbon fiber reinforced metal (MMC) is heat resistant because of the resistance to fracture, even though the heat resistance is much lower than C/C. The heat resistance of a composite generally depends on the heat resistance of the matrix. Light metals are not suitable for the matrix because of their low heat resistance.

Nickel is a heat resistive metal and an important element for a superalloy though it has high density. The density can be decreased by containing light reinforcements. When nickel is combined with carbon fiber, an excellent heat durable composite should be formed.

In this experiment, carbon fiber reinforced nickel composites (C/Ni) were prepared and their heat durability was examined.

2. Experimental procedure

Two kinds of carbon fibers were used. One is a PAN based high strength carbon fiber (T300, Toray, Japan, hereafter, HS-fiber), which is provided as a form of yarn with 2000 monofilaments. The other is a pitch-based high modulus graphite fiber (M40, Toray, Japan, hereafter, HM-fiber), which is also provided as a form of yarn with 3000 monofilaments. A pyrolitic graphite plate (hereafter, PG-plate) was also used to simulate the interfacial reaction between carbon and nickel. The PG-plate has the same distance of (002) plane as the HS-fiber.

The yarn was spread and fixed on a frame with conductive glue. Each fiber was electroplated with nickel to form monofilament composites. The PG-plate was also plated with Ni. The solution of nickel sulfate ($NiSO_4 \cdot 5H_2O$) 15 g/1, ammonium chloride (NH_4Cl) 15 g/l and boric acid (B_2O_3) 15 g/l was used as the electrolyte, because it can be used at relatively low cathode current density (30–40 A/m^2), and the plating can be performed at the room temperature.

The volume fraction of the fiber was controlled by the thickness of the plated nickel. The thickness of the plated nickel was up to 7 μm on the fiber, and was up to 1 μm on the PG-plate.

The Ni plated HS- and HM-fibers or PG-plate were consequently heat treated at the temperature range between 600°C and 1100°C for up to 10 h in a vacuum of $\sim 10^{-3}$ Pa.

The plated nickel on the monofilament composites was removed by nitric acid. The strength of the fibers after nitric acid treatment was also determined to confirm the effect of the acid on the strength.

The morphologies of the surfaces and the cross sections of the fibers were precisely observed by scanning electron microscope (SEM). Compositional distribution at the cross section of the heat treated fiber was examined by EDX or EPMA. The crystal structure was determined by X-ray diffraction using Cu Kα.

Some of nickel plated HS-fibers were packed in a carbon die and were hot-pressed at 600°C for 15–30 min under the pressure of 30 MPa in a vacuum of $\sim 10^{-3}$ Pa to form a block composite. The strength and morphology at the cross section of the block composites were also examined before and after heat treatment.

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3. Results and discussion

3.1. Deterioration process of the C/Ni composite

The diffraction angle 2*θ* of (002) peak for HS-fiber was 25.7° and the half height width was approximately 2° by X-ray diffraction. Similarly, the diffraction angle 2*θ* was 26.4° and the half height width was less than 1° for HM-fiber.

All the filaments in a yarn were uniformly plated with nickel to form monofilament composites. Some of the HS-fibers were formed to a block composite by hot-pressing. The behavior of the block composite by heat treatment was similar to the monofilament composites. Then monofilament composites were mainly examined in this experiment.

The strength change of the mono-filament composites of the HS-fiber by the heat treatment is shown in Figure 1. The strength was suddenly lost (within 1 h) at temperatures over 600°C [1].

Many pits with the diameter of approximately 5 μm were observed on the surface of the fiber after the heat treatment, as shown in Figure 2. It is inferred that the deterioration of the fiber was caused by the stress concentration at the pits. The reason for the pits forming has to be clarified to improve the heat durability.

A white ring was observed in the heat treated fiber, and the ring moved to the center with the increasing temperature and time as shown in Figure 3.

XRD revealed that the turbostratic structure of the carbon in HS-fiber was changed to graphite by the heat treatment. The decrease of strength of the fiber corresponds to the graphitization [1].

The phenomena were analyzed as follows; the HS-fiber consisted of many crystallites. Some of them had highly graphitized structure and some of them had turbostratic structure, which was inferred from the X-ray profile. The carbon atoms in the turbostratic structure had higher internal energy and then dissolved into nickel more easily than the graphitized one. Consequently, the concentration gradient of carbon atoms in the nickel was caused between the graphitized part and the turbostratic part. The carbon atoms diffused from the turbostratic part to the graphitized part through Ni, and deposited on the graphitized crystallites to form a projection as shown in Figure 3A.

When the projection became a certain height, carbon atoms deposited on the side of the projection more easily than on the top of the projection. Then the top of the projection grew to the circumference direction (Figure 3B), and the projections connect with each other (Figure 3C and D). Consequently, nickel was cut apart to form islands (Figure 3D). The nickel islands connect with each other, and the series of the islands form a solid ring as shown in Figure 3E. Hence the white ring structure was formed and the carbon atoms diffused continuously from inside to outside through the nickel ring. The ring was pushed to the center of the fiber and finally the migrating nickel ring concentrated at the center of the fiber as shown in Figure 3F.

In this case, newly formed crystallites had a less oriented structure and the strength of the fiber decreased. X-ray diffraction and EPMA analysis confirmed that the white ring and the white zone at the center of the fiber were not nickel carbide but pure nickel.

The intensity change of the (002) peaks of turbostratic carbon and graphitized carbon indicated that the carbon inside the inner ring (newly formed ring) had a turbostratic structure, and the carbon between two rings (electrodeposited Ni and new ring) had a more graphitized structure.

The migration of the white ring was simulated by using a Ni plated flat PG-plate. The thickness of the plated Ni was less than 1 μm because a thicker Ni layer tended to come off during heat treatment. Migration of a white zone in the plate was confirmed as shown in Figure 4. The phenomena were similar to the case of the HS-fiber. Migration rate was observed by changing the heat treatment temperature and holding time. From these results, the activation energy of the migration of the white ring was determined and the value was 166 kJ/mol which agreed well with the activation energy of carbon atoms in nickel in the former report [2]. This value and the phenomena described above indicate the migration of

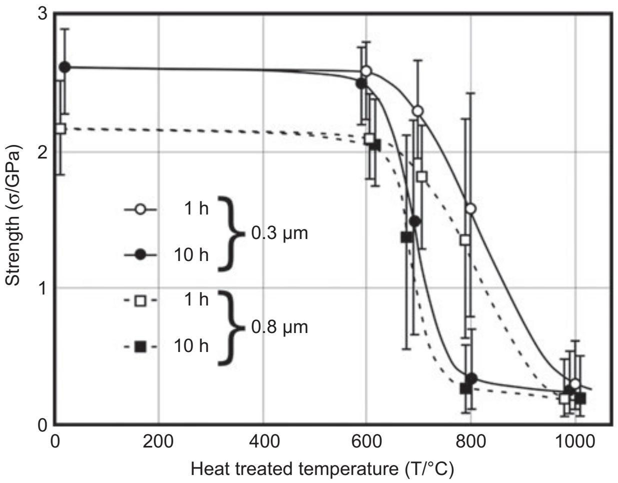

Figure 1 Strength change with heat treated temperature and time.

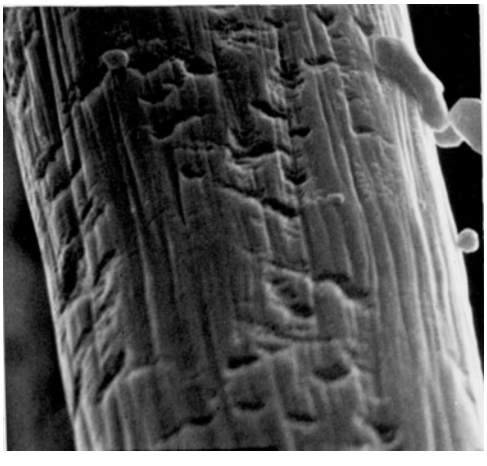

Figure 2 Scanning electron microscope photograph of pits on HS-fiber after heat treatment.

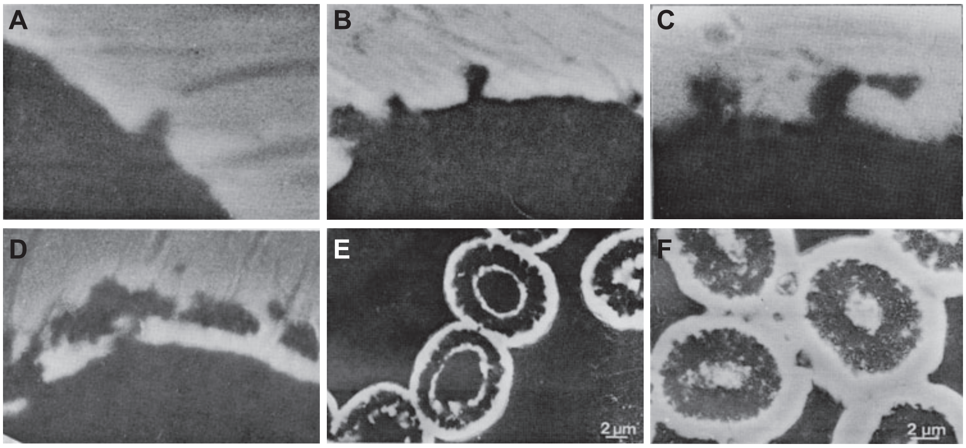

Figure 3 Scanning electron micrographs of the incubation stage and the migration of the nickel ring. Deterioration of the carbon fiber corresponds to the graphitization by the Ni ring.
(A) Projection appears from carbon to nickel. (B) The top of the projection grows to the circumference direction to form a bulge. (C) The bulge grows further. (D) The edges of bulges connect with each other to form nickel islands. The series of the islands forms a ring. (E) A white ring is observed in each fiber. The ring migrates to the center with heating time. (F) The white ring concentrates at the center of the fiber.

the white ring in the fiber or white zone in the PG-plate was caused not by diffusion of nickel in carbon but by diffusion of carbon in nickel.

3.2. Candidate of heat durable composite

From above results, it is expected that a carbon fiber with highly graphitized structure and without defects is not reactive. It was already confirmed that a HM-fiber was less reactive than a HS-one in the former study [3], but the detail was not known yet. A HM-fiber is heat resistant because it has highly oriented structure and the variation of the graphitization degree in a fiber is minimal, which is inferred from the X-ray profile. The interlayer distance of the used HM-fiber was 0.3378 nm and the half height width of its (002) peak was less than 1° as described above.

When the HM-fiber was used, the fiber did not react even after heat treatment at 1100°C for 9 h. The strength of the HM-fiber was not lost so much as shown in Figure 5. The data to the left in Figure 5 are for original HM-fiber and nitric acid treated fiber. The acid treatment was performed to confirm the effect on the strength of the fiber during removal of nickel. As is shown, the deterioration was not caused by the acid. Others were the HM-fibers which were extracted from monofilament composites after heat treatment at the temperature denoted below.

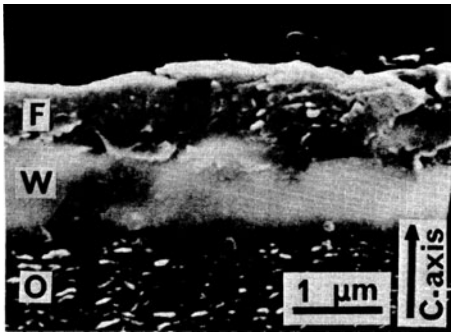

Figure 4 A white zone (W) was observed in the pyrolytic graphite. F, newly formed graphite; O, original pyrolitic graphite.

The morphology change of the monofilament composite of HM-fiber by heat treatment is shown in Figure 6. Figure 6A shows the uniformly plated Ni. Remarkable grain growth of the plated Ni was observed in Figure 6B. The plated Ni formed grains on the HM-fiber by surface tension as shown in Figure 6C. Facet surfaces were observed on each grain. A typical surface of the HM-fiber after heat treatment is shown in Figure 6D. No pits or no reaction were observed on it. There were very few areas which reacted to the heat treatment and therefore they were difficult to observe. However, when these areas were examined, they were wide and had little depth (Figure 6E). In contrast to the deep pits, these areas did not cause stress concentration.

The typical morphology of the cross section of the HM-fiber after heat treatment at 1100°C for 9 h is shown in

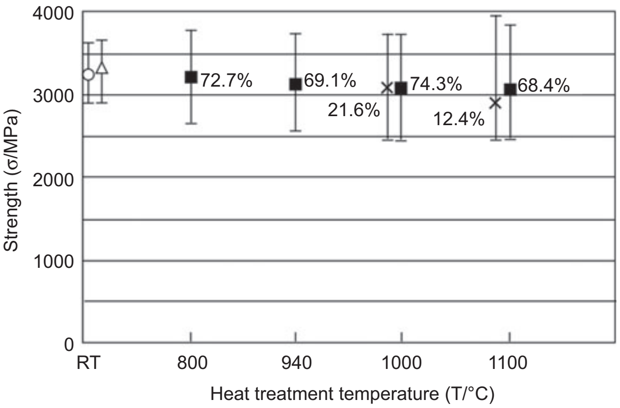

Figure 5 Strength of original fiber (○), HNO_3 treated fiber (Δ), Ni removed fibers (■, ×) after heat treatment. Numbers denote V_f.

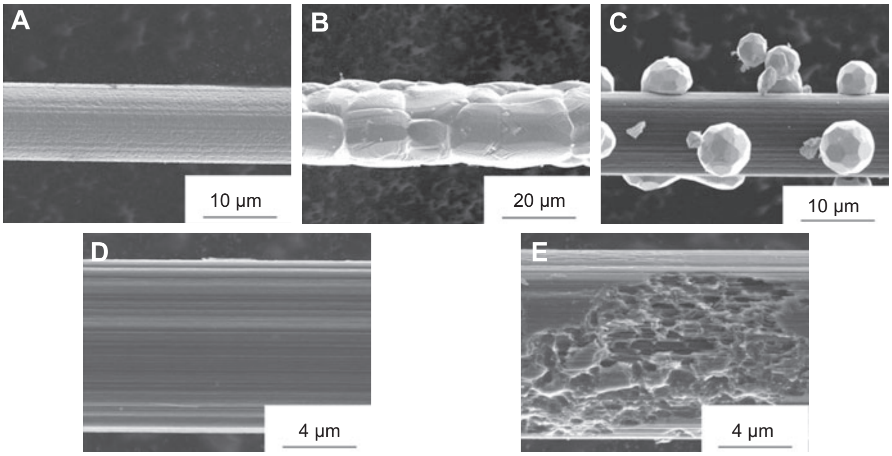

Figure 6 Morphological change of the surface of a monofilament composite.
(A) Ni is uniformly plated on a HM fiber. (B) Grain growth of plated Ni is observed. (C) The plated Ni forms grains by surface tension. (D) Typical surface of HM fiber. Ni was removed after heat treatment at 1100°C for 9 h. Reaction is hardly observed. (E) Reacted parts are rarely observed, but they are not deep pits.

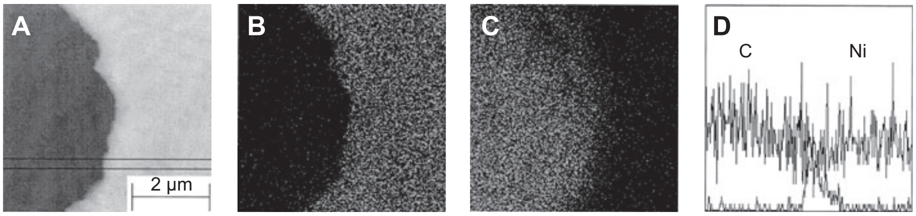

Figure 7 Interface between HM fiber and nickel after heat treatment at 1100°C for 9 h.
(A) SEM image at the interface. (B) Ni distribution by EDX. (C) C distribution by EDX. (D) C and Ni distribution between two lines in the left photo by EDX.

Figure 7A. The results of compositional analysis by EDX are shown in photos (B) and (C). The result of line analysis between two lines in the photo (A) is shown in (D). There is no diffusion between carbon and nickel, though the compositional changes of C and Ni in Figure 7D showed slopes in the range of approximately 1 μm. They were caused by the diameter (approx. 1 μm) of the electron probe of EDX. From these results, no reaction was observed at the interface even though the heat treatment temperature was as high as 1100°C and the time was long as 9 h. Thus the composite with HM fiber is promising to be durable at a high temperature.

4. Concluding remarks

In the case of HS-fiber, the strength was suddenly lost at temperatures over 600°C even though the time was as short as 1 h. The deterioration caused by graphitization was caused by diffusion of carbon atoms in nickel. When the HM-fiber was used, the fiber did not react even after heat treatment at 1100°C for 9 h, and the strength of the HM fiber was not lost. The composite with HM fiber is promising to be durable at a high temperature.

Acknowledgments

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