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The strength of carbon fibre-reinforced nickel composites produced by electro-deposition and hot-pressing

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Carbon fibre–nickel composites were made by electro-deposition and hot-pressing. The composites with low volume fraction of carbon fibres had a higher strength than the value obtained by the law of mixtures using the strength of annealed nickel. The current density became lower when the deposited nickel became thicker. The effects of annealing on deposited nickel were also observed and were related to the current density. Nickel deposited at low current density was hard to anneal.

1. Introduction

Nickel- and cobalt-based alloys are the most used materials for high-temperature applications. However, there is a slight solid solubility of carbon in nickel that could provide a mechanism for achieving good fibre–matrix bonding. The carbon diffusion could cause microstructural instability. Work on nickel–carbon system has been carried out in several laboratories, e.g. [1]. Most of them were fabricated by electro-deposition and hot-pressing. Carbon fibre-reinforced nickel composites with uniformly dispersed and well-aligned fibres can be obtained in a wide range of volume fractions by this method. However, there are no data which give a higher strength of the composites than the value calculated by the law of mixtures.

In this paper it is shown that composites produced by this method have a higher strength than the value which is predicted by the law of mixtures from the individual strengths of carbon fibres and annealed nickel. The reason for the deviation from the ordinary law of mixtures is also discussed.

2. Experimental details

A PAN-based high-strength carbon yarn which consisted of 2000 monofilaments (tensile strength $250\,\mathrm{kg\,mm^{-2}}$, modulus $24\,\mathrm{ton\,mm^{-2}}$ (average of monofilaments), diameter $8\,\mu$m) was used as the reinforcement. High purity nickel (99.99% up) was used as an anode.

Nickel was electro-deposited uniformly and compactly onto all the monofilaments in the yarn [2, 3], in order to form a matrix for the fibres after hot-pressing. A hard nickel bath ($NiSO_4$ 150 g/l, NH_4Cl 15 g/l, H_3BO_3 15 g/l) was used for the electrolysis. Electro-deposition was carried out at room temperature and at $0.3\,\mathrm{A\,dm^{-2}}$ initial current density. Current, not current density, was kept constant to plate nickel uniformly during the electro-deposition. The volume fraction of carbon fibre in the subsequent hot-pressed composites was controlled by varying the deposition time and, therefore, the thickness of the deposited nickel layer.

A graphite die was used for hot-pressing. The die was open at both ends so that carbon fibres could be carefully aligned by slightly pulling both ends of the nickel-coated yarn. A massive composite, which was 110 mm long, 3 mm width and 1 mm thick, was obtained by hot-pressing.

Tabs 17.5 mm long and 3 mm wide were fixed on each of the test pieces of 55 mm in length for tensile tests which were carried out at strain-rate of $1\%\,\mathrm{min^{-1}}$.

To investigate the effect of this variation in current density, nickel was deposited on a flat copper plate at constant current density from approximately 0.07 to 1 A dm^{-2}. The copper plate was removed by 50 vol % nitric acid aq. The strengths of the as-deposited nickel were also compared after annealing at 600° C for 60 min. The size of the obtained specimen was 50 mm long, 10 mm wide and 0.2 mm thick. Tabs 10 mm long and 10 mm wide were fixed on each of the test pieces for tensile tests at a strain-rate of 1% min^{-1}.

Crystal structures on the deposited surfaces were examined by back-scattered X-ray diffraction. Cu$K\alpha$ was used for the source. The relative intensities of (1 1 1) and (2 0 0) profiles were observed for the specimens. Grain sizes were also determined from the broadening of the profiles of (1 1 1) and (2 0 0). Spherical annealed nickel powder of 320 mesh was used for a standard in X-ray profiles.

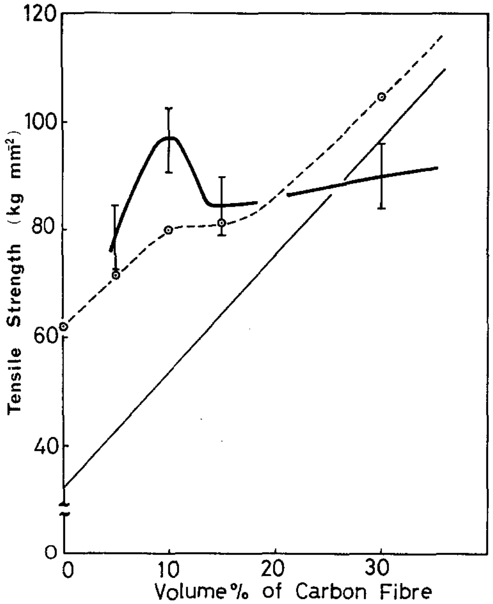

Figure 1 The strength of the carbon–nickel composites. Thick line: observed strength. Thin line: ordinary law of mixtures. Broken line: modified law of mixtures.

3. Results and discussion

3.1. Strength of the composites

To conduct mechanical tests on fibre-reinforced composites, it is essential to have sound samples, which means a well-controlled fibre fraction, no deterioration of the fibres [4], a uniform dispersion of the fibres in the matrix, no voids, and, in the case of unidirectional composites, a good alignment of fibres [5–8]. The specimens in this experiment were observed microscopically and were found to exhibit all these qualities. However, when the volume fraction of carbon fibre was lower, the sample had a tendency to have a higher void fraction up to several % for the specimen with 5 vol % carbon fibre.

Tensile tests for each volume fraction of fibres were carried out. The relationship between volume fraction of fibres and measured composite strength is shown as a thick line in Fig. 1. As shown, the strength of the composites was 70 kg mm^{-2} over most of the tested range of volume fractions, although the curve has a small peak at 10 vol % carbon fibres. The thin line of Fig. 1 shows the composite strengths predicted by the law of mixtures using the individual strengths of carbon fibres and annealed nickel (32.7 kg mm^{-2}). Comparing the observed and predicted lines, the observed value at 30 vol % carbon fibres agrees with the strength by the law of mixtures. However, the observed value at 10 vol % carbon fibres is about twice as high as the theoretical one. The deviation becomes larger if the composite strength is calculated from the law of mixtures using the matrix strength at the fracture strain (σ_m^*) instead of the ultimate tensile strength of the annealed nickel (σ_m).

Fractographs are shown as Fig. 2a and b. The holes after the fibres were pulled out are constricted in Fig. 2a while the holes are larger in Fig. 2b. The boundaries of the electro-deposited nickels are observed in Fig. 2a, although these specimens were hot-pressed at a temperature high enough [9] for grain growth of nickel and the boundaries could not be seen microscopically in the polished sample as predicted above. This phenomenon will be discussed later.

It is well known that the strength and hardness of electro-deposited nickel are affected by current density, bath temperature, bath components and pH of the electrolyte [10]. In this experiment, all the conditions except current density were kept constant electric current was maintained during deposition, the current density decreased as the thickness of the nickel layer increasing. This was because the surface area of the round fibres increased as their diameters increased. When the initial current density was 0.3 A dm^{-2} the final current density became 0.21 A dm^{-2} for 50 vol %, 0.16 A dm^{-2} for 30 vol %, 0.11 A dm^{-2} for 15 vol %, 0.09 A dm^{-2} for 10 vol %, and 0.07 A dm^{-2} for 5 vol % fibres.

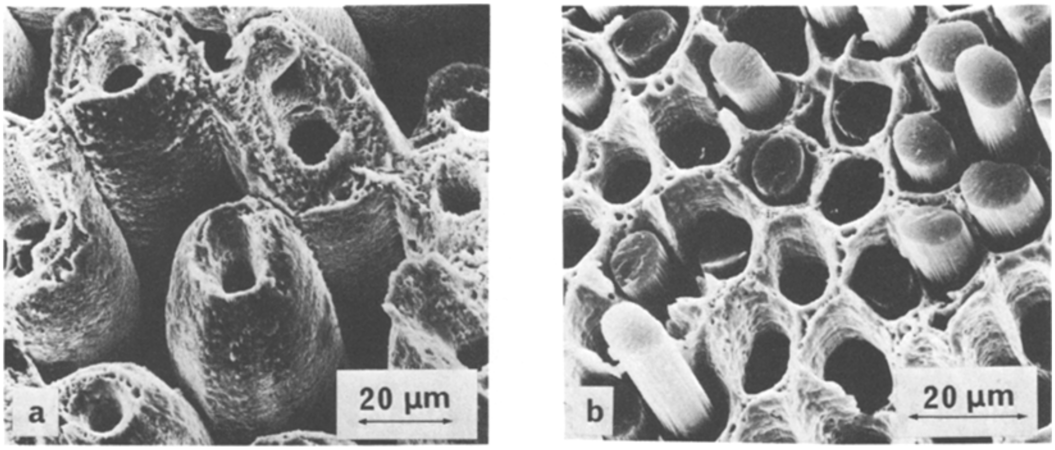

Figure 2 Fractographs of the carbon–nickel composites. (a) 10 vol % carbon fibres. (b) 30 vol % carbon fibres.

To investigate the characteristics of nickel deposited at each current density, nickel was electro-deposited onto a flat plate at constant current density. The strengths of all the as-deposited specimens were 70 to 90 kg mm^{-2}, independent of current density as shown in Fig. 3. On the other hand, nickel specimens deposited at a current density higher than 0.3 A dm^{-2} were easily annealed with the strength decreasing to less than 30 kg mm^{-2}, whereas nickel deposited at a comparatively lower current density could not be annealed so easily. The nickel which was deposited at less than 0.11 A dm^{-2}, maintained a strength of more than 60 kg mm^{-2} after the annealing treatment. Nickel, deposited at a higher current density and which then could be easily annealed, was the major part of the nickel matrix for the composites with a higher volume fraction of fibres. On the other hand, nickel, which was hard to anneal, was the major part of the composites with a lower volume fraction of carbon fibres (Fig. 4). The strength of the nickel in a composite thus became stronger, as the volume fraction of fibres decreased. From these results, the average strength of matrix nickel for each carbon-fibre volume fraction was calculated by the following equation and as shown also in Fig. 4:

$$\sigma'_{\mathrm{m}} = \frac{\int_a^b x\sigma_x \mathrm{d}x}{\int_a^b x \mathrm{d}x}$$

where σ'_{m} is the average strength of the matrix, σ_x the strength of nickel of each part, a the radius of the carbon fibre, b the outer radius of deposited nickel.

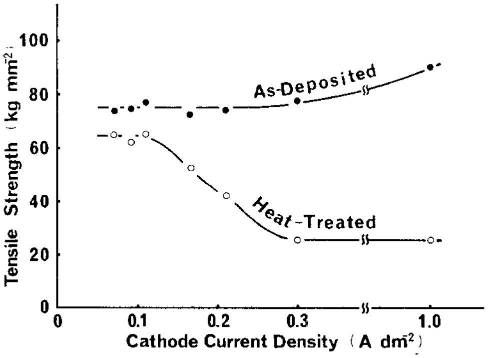

Figure 3 The variation with cathode current density of the deposited nickel strength.

From the results described above, it can be shown that the strength of the composite cannot be calculated from a single strength of the matrix using the well-known law of mixtures. Therefore, the law of mixtures must be modified and the strength (σ'_{m}) of the matrix nickel corresponding to the volume fraction of carbon fibre, as in Fig. 4, should be used to apply the law of mixtures. The strength of 61.2 kg mm^{-2} for the matrix of 5 vol % carbon fibre composites must, therefore, be used to apply the law of mixtures, and 60.4 kg mm^{-2} for 10 vol %, 51.6 kg mm^{-2} for 15 vol %, etc. The calculated values are also shown in Fig. 1, and they are connected by a broken line. This curve implies the peak of the observed strength at the correct volume fraction, although the peak value at

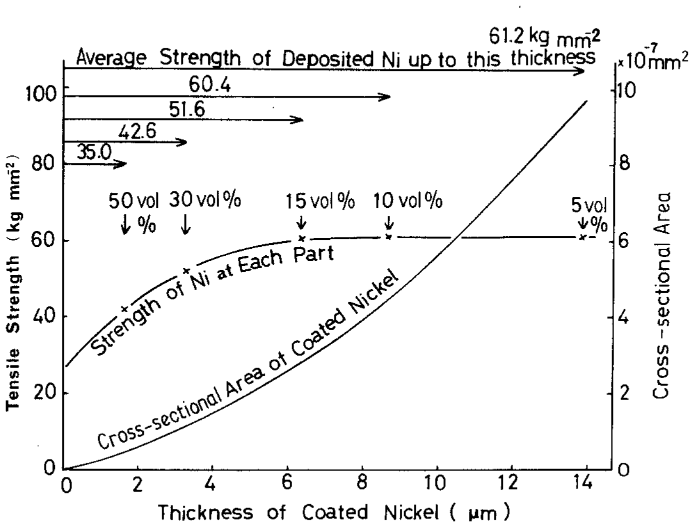

Figure 4 The average strength and the strength of each part of the deposited nickel on a carbon fibre.

10 vol% carbon fibre is still lower than the observed value.

3.2. Crystal structure of electro-deposited nickel

It is well known that electro-deposited metal has a tendency to have a certain preferred orientations of crystals [10]. It is also well known that grain size is affected by current density [10], and the strength depends on the grain size [11–13].

To investigate the relationships between them, the intensities and broadening of (1 1 1) and (2 0 0) profiles were carefully examined by X-ray diffraction [14]. The other profiles showed no obvious difference.

The results of relative intensity are shown in Fig. 5. When the nickel was deposited at 0.09 A dm^{-2}, the relative intensity was rather similar to that of annealed nickel powder. This implies that the crystals had a random orientation. When annealed, the intensity of (2 0 0) became slightly stronger. However, in the case of a higher current, the crystals became highly oriented and the intensity of (2 0 0) became much stronger. This means that the orientation of nickel crystals, which were deposited at a relatively high current density, was increased more easily than that of nickel which was deposited at a relatively low current density. Moreover the intensities of (2 0 0) profiles of the specimens at current densities higher than 0.16 A dm^{-2} became much stronger after annealing treatment.

The grain sizes of crystals in the deposited nickel were also determined from the broadening of the profiles of (1 1 1) and (2 0 0). As the broadening of a profile is caused not only by small grain sizes but also by internal strain, there is some query about the determined grain sizes of as-deposited specimens. However, the internal strain should be released by the annealing conditions (600° C, 1 h) [9]. The results are shown in Fig. 6. All the grains from the (1 1 1) and (2 0 0) profiles in as-deposited specimens had very small sizes of less than about 1000 Å which are shown by an oblong region in Fig. 6. When the specimen deposited at 0.09 A dm^{-2} was annealed, the profiles of (1 1 1) and (2 0 0) were still broad, although broadening by strain cannot be expected. Therefore, the grain sizes of (1 1 1) and (2 0 0) profiles of both specimens, as-deposited or annealed, should be small. On the other hand, grain

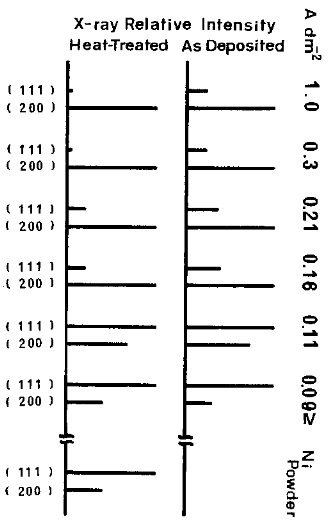

Figure 5 The variation with cathode current density of the relative intensity of (1 1 1) and (2 0 0) profiles.

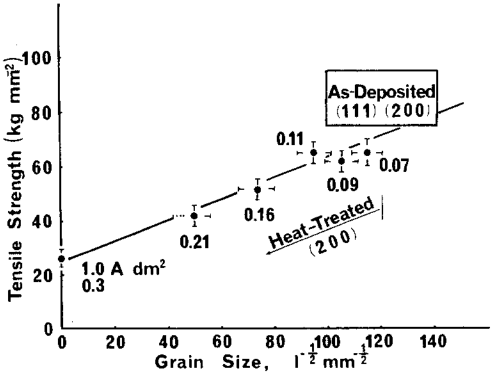

Figure 6 The variation of the tensile strength with grain size of electrodeposited nickel. The grain sizes of (1 1 1) and (2 0 0) in as-deposited nickel and their strengths are in the rectangle. The grain sizes of the heat-treated specimens are of (2 0 0).

growth, especially of (2 0 0), was remarkable when the current density was comparatively high, although the crystal sizes in the specimens at current densities over 0.21 A dm^{-2} are suspicious. The growth of (2 0 0) in the deposited nickel resembles the growth of (2 0 0) which is a usual preferential plane in secondary recrystallization of rolled f c c metals [15]. From these results on crystal growth, it is obvious that random crystals do not grow as easily as highly oriented ones. The fractograph shown in Fig. 1a, implies that diffusion at the boundaries between electro-deposited nickels was not sufficient to bind them to each other under these experimental conditions. This should support the fact that nickel, which was electro-deposited at a relatively low current density, could not grow easily as shown in Fig. 6. The relationship between grain size and strength agrees well with the well-known Hall–Petch relation [11–13]. The oblong region is slightly higher than the Hall–Petch relation. This must be caused by the internal strain, as the specimens in this region were not annealed.

However, in Fig. 2, the observed strengths for 5 and 10 vol% fibres are still higher than the newly calculated values. This must be for the following reasons: (1) An annealed nickel matrix with fibres has higher strengths than the nickel with no fibres, as the fibres may interrupt the movement of dislocations during annealing and tensile testing [16, 17]. (2) Carbon fibres in the nickel matrix have a higher strength than without the matrix, as notch effects on the carbon fibres are lessened by the nickel. (3) The strength of the nickel may be estimated as being still lower, as the nickel may be deteriorated by acid during removal. (4) The fibres in the matrix may be subjected to a higher force than those without the matrix, as the fibres in the composite are compressed by the force from the difference of the thermal expansion coefficients between the fibre and nickel during cooling down from the hot-pressing temperature [18–20].

4. Conclusions

Nickel–carbon fibre composites produced by electro-deposition and hot-pressing have a higher strength than that predicted by the ordinary law of mixtures when the carbon fibre volume fraction is low. The nickel matrix of such composites was deposited at a low current density as the current was kept constant, and had random orientation of crystals. The grain sizes of as-deposited samples were less than 1000 Å, and were independent of current density, but the nickel which had random orientation of crystals was difficult to anneal. Nickel, which was hard to anneal, formed the major part of composites with a lower volume fraction of carbon fibres, so the strength of annealed nickel cannot be used for the law of mixtures, even though the composites are made at a high temperature.

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