### References

- 1. W. A. KRIVSKY and R. SCHUHMANN, Trans. Met. Soc. AIME 221 (1961) 898.
- 2. G. ERIKSSON, Acta Chem. Scand. 25 (1971) 2651.
- 3. E. R. STULL and H. PROPHET, "JANAF Thermochemical Tables", 2nd Ed., NSROS-NBS 37 (1971).
- 4. A. HENDRY, in "Nitrogen Ceramics", Edited by F. L. Riley, (NATO Advanced Institute Series, Noordhoff, Leydon, 1977) p. 183.
- L. J. GAUCKLER, H. L. LUKAS and G. PETZOW, 5. J. Amer. Ceram. Soc. 58 (1975) 346.
- 6. R. O. WILLIAMS, Met. Trans. A 8A (1977) 1008.

## Received 29 September and accepted 13 October 1978

L. GAUCKLER\* E. HUCKE<sup>†</sup> H. L. LUKAS G. PETZOW Max-Planck-Instut für Metallforschung, Institut für Werkstoffwissenschaften, Heisenbergstrasse 5. D-7000 Stuttgart-80, Germany

\*Now with Swiss Aluminium Ltd. Research and Development, CH-8212 Neuhausen, Switzerland. <sup>†</sup>University of Michigan, Materials and Metallurgical Engineering, Ann Arbor, Mich 48109, USA.

# High-temperature compatibility of pyrolytic carbon with nickel-copper alloys

Compatibilities of carbon fibres and pyrolytic carbon with pure nickel at elevated temperatures were discussed in detail in our previous papers [1-3]. A migrating nickel layer was observed in each sample of carbon. Graphitization was caused by the catalytic reaction of the nickel layer. Degradation of carbon fibres by the graphitization was observed. The rate determining step of the graphitization was the diffusion of carbon atoms in nickel. A carbon fibre-nickel composite material with higher stability at elevated temperatures could be obtained if the diffusion could be prevented.

In the present work, the effect of adding copper to nickel on the migration rate of the metal layer was examined. As carbon does not diffuse through solid copper, its solubility in copper must be exceedingly small [4]. Therefore solubility and diffusivity of carbon should be affected and should be decreased by the alloying, when copper is added to nickel.

Pyrolitic carbon ( $c_0 = 6.85$  Å), which was obtained by pyrolysis of methane, was used as a sample. Copper was electro-plated on the polished surface of the pyrolytic carbon and afterward nickel was electro-plated. An ordinary copper bath based on copper sulphate and an ordinary hard nickel bath based on nickel sulphate were used for the electro-platings. Both the electro-platings were 1518

carried out at room temperature with a current density of 0.2 A dm<sup>-2</sup>. The total thickness of the double electro-plated layer was 0.8 µm for all samples. The plated thickness of each metal was controlled by varying the electroplating time according to the required copper concentration (5, 10, 20 at %, respectively) in the alloy.

The double plated carbon samples were kept at  $450^{\circ}$  C for 1 h in a vacuum of  $2 \times 10^{-5}$  mm Hg to allow tight adherance at the carbon-copper and copper-nickel interfaces. No reaction or interdiffusion was observed at either of the interfaces during heat treatment.

A heat treatment temperature of 1000° C was found to be appropriate for observing the



Figure 1 X-ray intensities of nickel and copper by EPMA. The carbon with Ni-Cu(10 at %) was held by 1000° C for 16 h. S: surface of the pyrolytic carbon; F: flakey area; W: white layer, i.e. alloy layer; O: original pyrolytic carbon.



Figure 2 Migration depth of the alloy layer with holding time at  $1000^{\circ}$  C.

migration behaviour, as from the previous results [3]. It was estimated from diffusion data [5] that copper and nickel would interdiffuse to form a homogeneous alloy with 1 min at 1000° C. Then, if the holding time at elevated temperature is long enough for the alloying time to be discounted almost all of the holding time would be spend on the alloy reacting with carbon. Therefore the double plated samples were kept at 1000° C for between 2 h and 36 h in a vacuum of  $2 \times 10^{-5}$  mm Hg.

The inward migrating layer in the pyrolytic carbon was examined by scanning electron microscopy and by electron probe microanalysis. The morphological features of the carbon and the alloy layer were exactly the same as those in the case of pure nickel, as shown in the previous paper [3]. Fig. 1 indicates the results of electron probe microanalysis. Only copper and nickel intensities are presented. The migrating layer was confirmed as an alloy by analysis similar to that used in previous work [2, 3]. Migration depths of the layers at each holding time are shown in Fig. 2. Migration behaviours of pure nickel and pure copper are also shown in the same figure. From Figs. 1 and 2, it is assumed that the migration mechanism of the alloy layer is the same as in the case of pure nickel.

The initial gradient of each curve in Fig. 2 signified the migration rate of the layer. The relative migration rates, i.e. relative reaction rates, are shown as a function of copper concentration in Fig. 3. The migration rate for the 5% copper alloy decreased slightly from the rate for pure nickel.



Figure 3 Relative migration rate versus copper concentration in Ni-Cu alloy.

However the migration rate decreased for higher concentrations of copper. This effect was considerably more pronounced when the copper concentration exceeded 10%.

As no diffusion data for carbon in coppernickel alloy are available, further analysis is difficult. However, it is obvious from these results that alloying copper in nickel is very effective in reducing the reactivity between carbon and nickel. These results should be of use in preventing reactions, not only between carbon and nickel, but also between the other combinations of reinforcements and matrices when a composite material is required for high temperature use.

### References

- 1. I. SHIOTA and O. WATANABE, J. Japan Inst. Met. 38 (1974) 794.
- 2. Idem, ibid. 39 (1975) 122.
- 3. Idem. J. Mater. Sci. 14 (1979) 699.
- 4. Hansen, "Constitution of Binary Alloys," 2nd edition, (McGraw-Hill, New York, 1958) p. 353.
- 5. Diffusion Data, 1 (1967) 13, 2 (1968) 121, Diffusion Information Centre, Ohio, USA.

### Received 10 October, and accepted 17 November 1978

ICHIRO SHIOTA OSAMU WATANABE National Research Institute for Metals, 3-12, 2-chome, Nakameguro, Meguroku, Tokyo 153, Japan