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Direct observation by high resolution autoradiography of interfacial diffusion in a Ni, Cr-TaC composite

D. REBOUT, J. F. STOHR
ONERA, Direction OM, 29 Avenue de la Division Lederc, 92320 Chatillon, France
M. AUCOUTURIER
Laboratoire de Métallurgie, Bâtiment 413, Université Paris Sud, 91405 Orsay, France

Interfacial diffusion has been evidenced in a eutectic-like Ni, Cr–TaC composite, using high resolution autoradiographic techniques. The structure of the fibre–matrix interface has been determined by using high voltage electron microscopy. The fibre–matrix interface has been shown to be a diffusion short circuit in the temperature range 700° C to 900° C.

1. Introduction

Refractory composite materials comprising a nickel or cobalt base superalloy matrix reinforced by transition metal monocarbide fibres, generally tantalum carbide or niobium carbide, exhibit a combination of mechanical properties that places them above the best available superalloys [1]. The particularly high mechanical strengths of these composites are essentially due to reinforcement by perfect monocrystalline carbide fibres.

The thermal stability of the carbide fibres is critical for extended use of the materials at high temperatures, in the neighbourhood of 1100° C. Moreover, the severe thermal conditions in aircraft engines may lead to a morphological degradation of the reinforcement, such as "fibre coarsening" or "fibre pinching" [2, 3]. The kinetics of the fibre coarsening or pinching are controlled either by bulk diffusion or by diffusion along the fibre–matrix interface.

A knowledge of the different diffusion parameters, i.e., the diffusion coefficient in the bulk or along the interfaces, is essential to predict the degradation rate of the fibres. Moreover, a knowledge of these coefficients would enable one to determine the exact role played by the fibre–matrix interface in fibre degeneration observed at high temperatures.

The diffusion study undertaken with the Ni, Cr–TaC composites has two purposes:

(a) to determine if preferential interface diffusion really exists in the metal–carbide fibre eutectic-like composites; and

(b) if this diffusion along the fibre–matrix interfaces does exist, to use the diffusion parameters as a means of characterization of the different interfaces.

2. The Ni, Cr–TaC composite

2.1. Structure and crystallography

The Ni, Cr–TaC composite is directionally cast from a nickel-base alloy whose nominal weight composition is: Ni, 10% Cr, 17.7% Ta, 0.4% C. This composite includes two phases, the matrix, a Ni–Cr–Ta solid solution, and the tantalum carbide monocrystalline fibres (Fig. 1). The composite has a columnar polycrystalline structure and the elongated grains are parallel to the $\langle 100 \rangle$ growth direction. Inside each grain, the matrix and the fibres are epitaxial with the relation $\langle 100 \rangle_{TaC}$ parallel to $\langle 100 \rangle_M$, where the subscript M refers to the matrix [4]. The fibre cross-section (Fig. 2), has a truncated square form. The fibre faces are the $\{110\}$ planes while the truncatures are the $\{100\}$ planes. Therefore the two phases are not

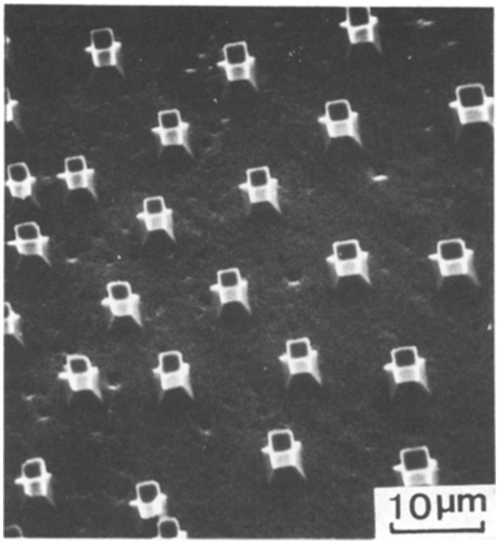

Figure 1 Ni, Cr–TaC composite. SEM micrograph revealing TaC fibres after selective etching of the matrix.

coherent since their lattice parameters differ by more than 25%.

2.2. Interface morphology [5]

The fibre–matrix interfaces are, as a first approximation, the {110} and {100} planes. In fact, a more accurate examination of these interfaces reveals that when one of the {110} or {100} planes is parallel to the electron beam, the fibre–matrix interface appears as a broken line (Fig. 3), with each portion of the broken line being parallel either to the [220] or $[2\bar{2}0]$ direction. Moreover, when observed in a high voltage electron microscope (HVEM), sets of linear defects are visible in the interfaces (Fig. 4). The broken line appearance of the interface, observed in some tilt conditions, as well as the two sets of linear defects which appeared when the composite is observed in a HVEM, can be explained if the real habit planes between the fibres and the matrix are assumed to be the {111} planes. Fig. 5 clearly shows that the {111} plane intersections with the {110} plane lead to a network consisting of a set of parallel lines normal to the fibre axis (Fig. 5b), while the {111} plane intersections with the {100} plane give rise to two sets of parallel lines, normal one to the other, and inclined at 45° to the fibre axis (Fig. 5b).

Thus, the real habits planes between the matrix and the fibre are the {111} planes, while the rough surfaces, limiting the fibres on a smaller scale, appear to be the {110} and {100} planes.

3. Interfacial diffusion

3.1. Experimental

Diffusion along the fibre–matrix interfaces was determined by radiotracer and autoradiographic techniques [6–8]. The diffusion study was confined to the element Ni. The ^{63}Ni radiotracer was chosen for the following two reasons: (a) nickel is the major constituent of the alloy, and (b) ^{63}Ni is a low energy β emitter. This second point is very important for high resolution autoradiographic techniques, since the limit of resolution decreases with increasing energy of the tracer. With the ^{63}Ni radiotracer, the limit of resolution is 7000 Å in the case of bulk specimens of the Ni, Cr–TaC composite. Then discrimination between bulk diffusion in the fibres and diffusion along the fibre–matrix interface is only possible if the fibre diameter is larger than 1.5 μm, and the fibre spacing larger than 5 μm.

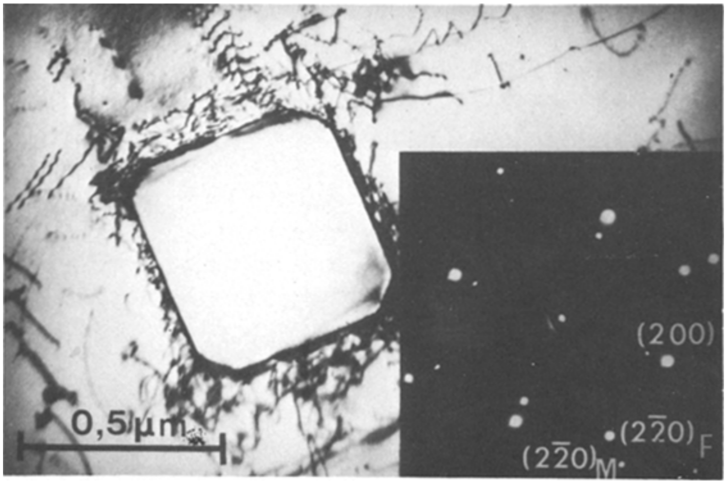

Figure 2 TEM micrograph of Ni, Cr–TaC. Foil normal to the growth axis of the composite.

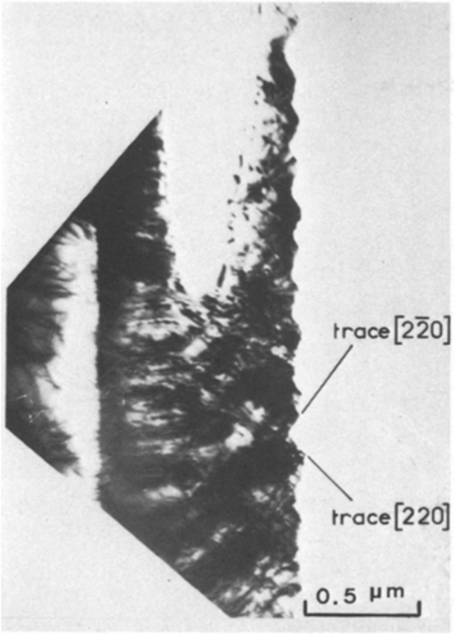

Figure 3 TEM micrograph of a TaC fibre revealing the broken line aspect of the fibre–matrix interface. The interface is parallel to the electron beam.

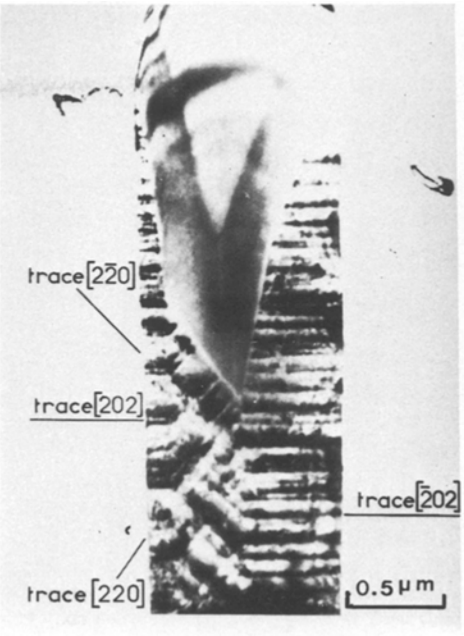

Figure 4 High voltage electron micrograph of Ni, Cr–TaC composite showing the interface structure.

A Ni, Cr–TaC composite which satisfies these conditions has to be produced at solidification rates lower than 0.4 cm h^{-1}.

Diffusion treatments were carried out in quartz containers in a purified argon atmosphere. The diffusion parameters, the time and the temperature were estimated from Ni–Cr diffusion data [9]. Both the temperature and the time were chosen so as to limit the penetration of Ni by bulk diffusion to a few micrometres.

The activity versus penetration depth curves were obtained by the residual acitivity technique [10], which is justified by the low energy of the ^{63}Ni tracer.

3.2. Results and discussion

Autoradiographs (Fig. 6) clearly show a discontinuous diffusion phenomenon related to the fibres in the temperature range 700° C to 900° C. Beyond 1000° C, this discontinuous diffusion phenomenon

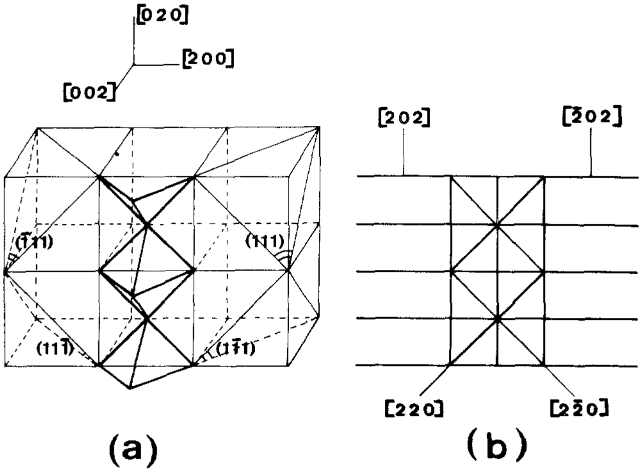

Figure 5 Schematic diagram of the interface structure (a) and linear defect network (b).

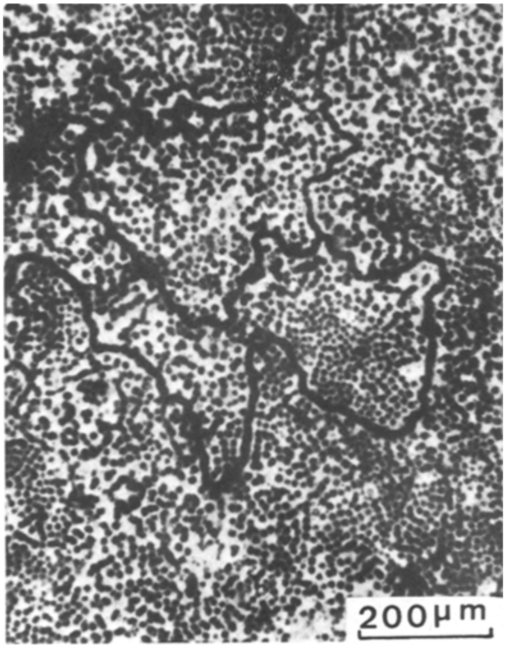

Figure 6 Autoradiography revealing discontinuous diffusion related to the TaC fibres. Diffusion treatment conditions; 800° C, 100 h. (Silver grains appear as dark areas on the optical micrograph).

is no longer observed. High resolution autoradiography, and autoradiography performed on the same specimen, are quite similar (Fig. 7). However, high resolution autoradiography clearly shows that the discontinuous diffusion phenomenon is due to preferential diffusion along the fibre–matrix interface, between 700° C and 900° C. Both the lack of bulk diffusion of nickel in the fibre marked by the absence of light areas on the fibre itself, and diffusion around the fibre shown by light areas due to the agglomeration of silver grains are shown in Fig. 8. These two observations prove that the diffusion of nickel occurs first along the fibre–matrix interface and then in the matrix from the interface. Diffusion along the fibre–matrix interface is further confirmed by the fact that the diameter of the disc limiting the diffusion zone around the fibre increases with the temperature. This last point is simply due to the fact that the penetration distance by bulk diffusion is larger at 900° C than at 800° C, for example (Fig. 8). The total absence of nickel diffusion in the fibre has been confirmed by high resolution autoradiography performed on thin foils. The resolution limit depends only upon the foil thickness, and is about 1300 Å. The complete absence of Ni radiotracer in the fibre, and the presence of Ni tracer around the fibre and along the interface are evident in Fig. 9. The dark silver grain visible in front of the fibre (A) is within 1300 Å from the interface.

All these observations confirm the existence of a preferential diffusion of nickel along the fibre–matrix interface in the temperature range 700° C to 900° C.

The activity versus penetration depth curves clearly show the three regions (Fig. 10). The first region is that of bulk diffusion, the second that of interfacial diffusion and the third corresponding to the grain-boundary diffusion, as can be seen on autoradiographs performed in each region. The activity drop observed in the grain-boundary diffusion region at least at some temperatures is not understood, but the phenomenon seems to be reproducible.

Fisher [11] or Suzuoka [12] grain-boundary diffusion models do not allow the calculation of an interfacial diffusion coefficient $Di\,\delta$, where δ is the interface thickness, since these models are only

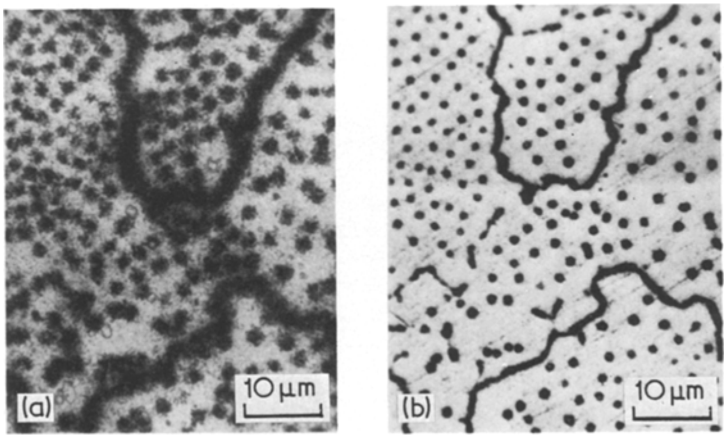

Figure 7 Comparison between (a) autoradiography and (b) high resolution autoradiography. Diffusion treatment conditions 800° C, 100 h.

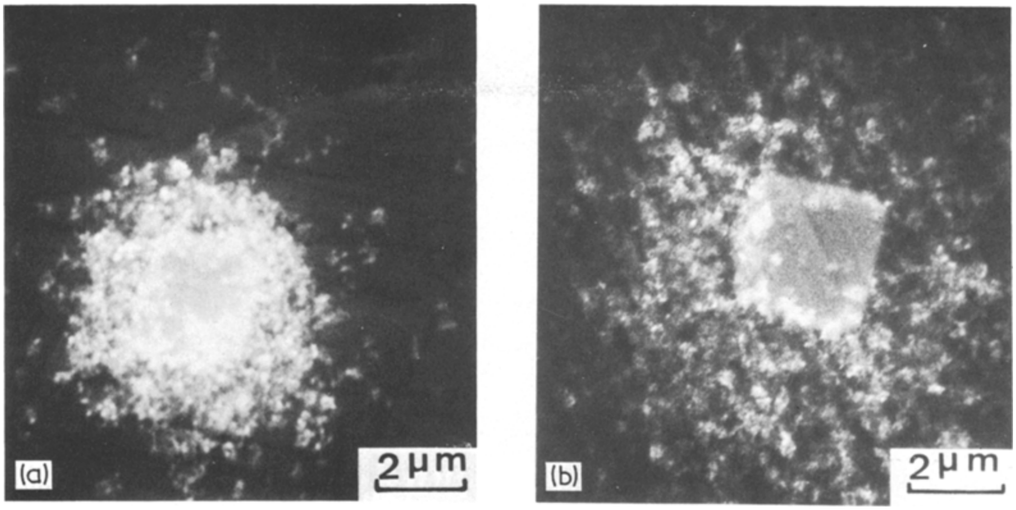

Figure 8 Two aspects of diffusion at (a) 800° C and (b) 900° C showing the extent of bulk diffusion around the fibres. (Silver grains appear light on the SEM micrograph).

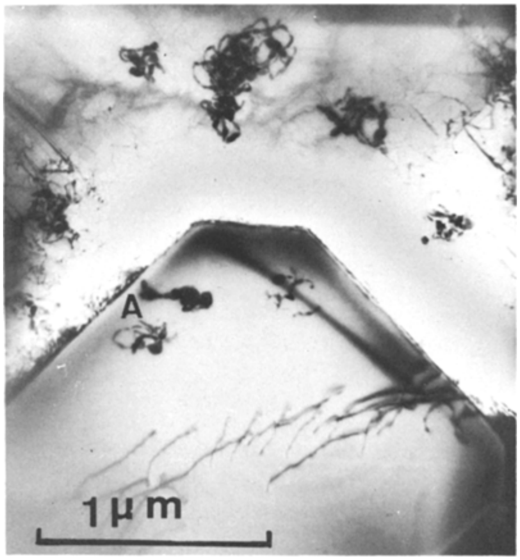

Figure 9 High resolution autoradiography on a thin foil; HVEM micrograph. Diffusion treatment conditions; 800° C, 100 h. (Silver grains appear dark on the TEM micrograph).

valid in the case of diffusion in one direction only. In the case of diffusion along the fibres, the diffusion is bi-dimensional with a cylindrical geometry. In order to calculate an interfacial diffusion coefficient $Di\ \delta$, a mathematical model with a cylindrical geometry has to be developed [13]. Nevertheless, even an approximate quantitative analysis of the activity versus penetration depth curves allows the determination of a set of parameters which enables the interfaces to be characterized. These are shown in Table I as: (a) the maximum penetration distance along the interface as a function of temperature, and time, and (b) a comparison between the penetration depth due to bulk diffusion x_B (the length measured from the specimen surface to a point beyond which bulk diffusion is no longer observed by the autoradiographic technique) and diffusion along the interface x_I (defined in the same way as x_B).

4. Conclusions

Preferential diffusion of nickel along the fibre–matrix interface in the temperature range 700° C to 900° C is shown to exist in the Ni, Cr–TaC composite. It is not yet possible to calculate true interfacial diffusion coefficients, but determination of the penetration depths of nickel along the interfaces constitutes a means of characterization of the fibre matrix interfaces in composite

TABLE I Parameters for characterization of the interface

Diffusion parameters		Penetration depth (µm)	
T(° C)	t(h)	x_B	x_I
750	500	1.5	4.5
800	100	4	11
850	100	6	13
900	50	8	16

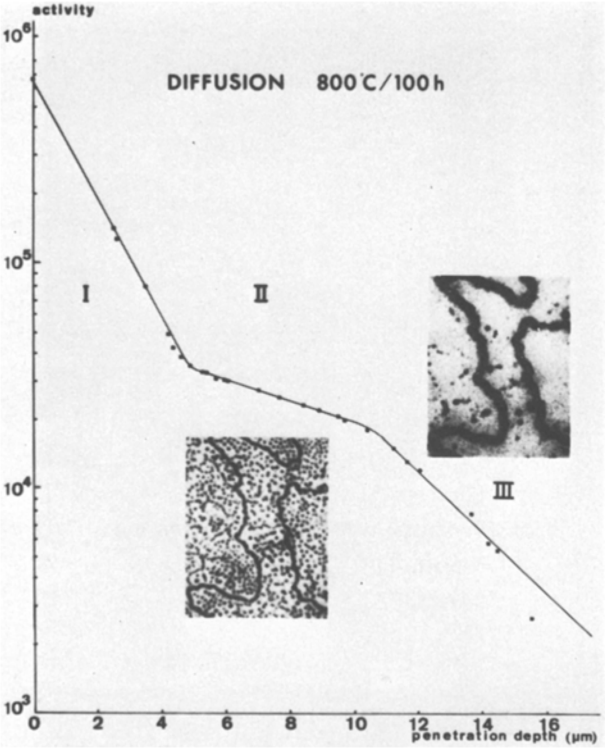

Figure 10 Activity versus penetration distance curve illustrating the three distinct diffusion region: (I) bulk diffusion, (II) diffusion along the interface, (III) grain-boundary diffusion.

materials having a nickel or cobalt base alloy matrix reinforced by transition metal carbide fibres.

References

1. H. BIBRING, T. KHAN, M. RABINOVITCH and J. F. STOHR, 3rd International Symposium on Superalloys, Seven Springs, Pa, USA, (1976).
2. D. R. H. JONES, *Mater. Sci. Eng.* **15** (1974) 203.
3. J. F. STOHR, J. M. HAUSER, T. KHAN, M. RABINOVITCH and H. BIBRING, *Scripta Met.* **10** (1976) 729.
4. H. BIBRING, J. P. TROTTIER, M. RABINOVITCH and G. SEIBEL, *Mem. Sci. Rev. Met.* **68** (1971) 23.
5. J. F. STOHR, to be published.
6. J. P. LAURENT and G. LAPASSET, *Internat. J. Appl. Radiation Isotopes* **124** (1973) 213.
7. A. M. HUNTZ, D. MARCHIVE, M. AUCOUTURIER and P. LACOMBE, *ibid.* **24** (1973) 689.
8. A. M. HUNTZ and P. LACOMBE, *Canad. Met. Q.* **13** (1974) 155.
9. P. MOULIN, to be published.
10. P. L. GRUZIN, *Doklady Akad. Nauk. SSSR* **86** (1952) 289.
11. J. C. FISHER, *J. Appl. Phys.* **22** (1951) 74.
12. T. SUZUOKA, *Trans. Jap. Inst. Met.* **2** (1961) 25.
13. G. MARTIN, Private communication.

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