

A directionally solidified Ni-base eutectic alloy reinforced by a mixed hafnium-zirconium monocarbide

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The nickel-base eutectic alloy (Ni-10Cr-5Al-5Cr-8.3Hf-1.1Zr-0.7C, NASA HAFNIC-10) was directionally solidified to produce aligned refractory monocarbides in a nickel-rich matrix. The aligned carbides, (Hf, Zr) C, were present as rod- and ribbon-types, with a volume loading of about 8%. A blocky type of Ni₃Al (γ') precipitate, about 45% volume loading, was produced in the nickel-base matrix. The growth direction of both aligned carbide and matrix was parallel to $\langle 100 \rangle$. The effect of thermal cycling between 425 and 1100° C using a 2.5 min cycle time was examined. No microstructural degradation of the aligned carbide fibres occurred after 2000 cycles.

1. Introduction

There has been considerable interest in applications of directionally solidified eutectic (DSE) alloys [1], especially for use as advanced high temperature structural components in aircraft gas turbine engine [2]. To achieve high temperature performance exceeding that of conventional superalloys, the reinforcing phases generally desired in DSE alloys are either high melting intermetallic or refractory compounds. The pseudo-binary eutectics of transition metal monocarbides (Group IV, Va and Ni, Co, Fe [3, 4] are particularly interesting. One of the prime attractions in the eutectic systems is their great flexibility in accepting alloy additions to the matrix and the fibres while maintaining coupled oriented growth.

Cobalt-base eutectic alloys reinforced with TaC (COTAC) and Ni-base eutectic alloys reinforced with TaC (NITAC) have received much attention [5]. A potential problem in the use of COTAC alloys is the degradation of

the TaC fibres under thermal cycling [6]. In NITAC alloys, the TaC fibres are stable under thermal cycling [7]. However, alloying of the Ni-matrix of NITAC alloys severely reduces the volume loading of the reinforcing fibres from about 9% to 3% [8]. For effective fibre reinforcement, the volume loading of the fibres must exceed a critical value [5].

Among the refractory monocarbides (TiC, ZrC, HfC, VC, NbC, TaC), hafnium carbide (HfC) is the most stable compound [9]. The structure and thermal cycling stability of HfC [10] and hafnium-zirconium carbide [11] in a Co-base DSE alloy were previously reported. The aligned HfC and (Hf, Zr) C fibres were present as rod- and ribbon-type with a volume loading of about 10%.

An attempt has been made in this work to use a mixed (Hf, Zr) C fibre as the reinforcing phase in a Ni-base alloy. The simple pseudo-binary eutectics of Ni-HfC and Ni-ZrC [12] have melting points of $1330 \pm 20^\circ\text{C}$ and $1290 \pm$

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20° C, and carbide contents of 15.8 wt% (12.8 vol%) and 14.5 wt% (20.3 vol%), respectively. The hafnium-zirconium mixed carbide was used rather than pure HfC in order to reduce the density of the carbide fibres. The Ni-base DSE alloy is very attractive due to the possibility of introducing ordered Ni₃Al(γ') precipitate for additional matrix strengthening. This paper is concerned with the structure, morphology, and thermal cycling stability of a directionally solidified (Hf, Zr)C fibre-reinforced Ni-base eutectic alloy containing additions of Al, Cr and Co.

2. Experimental

2.1. Ingot preparation

The raw materials used in this work were commercial elements of at least 99.5 wt% purity, except for the hafnium sponge which contained 2.35 wt% Zr. The nominal composition of the alloy was Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C in wt%.

Heats of 1.25 kg were melted in a 50 kW, 10 kHz induction furnace using calcia-stabilized zirconia crucibles and commercially pure argon at a pressure of about 0.5 atm. The argon was admitted to the melting chamber evacuated to about 10 μm. The Ni, Co, and C were initially melted followed by addition of Al, Zr and Hf. After holding about 5 min at 1800° C for homogenization, the melt was poured into zirconia shell moulds preheated to 870° C. Each mould assembly produced six bars 11 mm in diameter and 16 cm long.

2.2. Directional solidification

Each bar was remelted and directionally solidified under a flowing argon atmosphere in a modified Bridgman furnace, as shown in Fig. 1. The power was supplied by a 7.5 kW radio frequency generator operating at 400 kHz. The charge was contained in a recrystallized alumina crucible which was heated by radiation from a graphite susceptor positioned inside an induction coil and lowered at a controlled rate through a water spray ring.

A key requirement in producing aligned eutectics is to maintain a flat liquid-solid interface. The criterion for the planar liquid-solid interface has been expressed [13] as $G/R \geq \Delta T/D$. G is the thermal gradient at the interface, R is the rate of growth, ΔT is the freezing

range, and D is the diffusion coefficient of solute in the liquid. The critical value of the parameter (G/R) for a planar interface of a given composition is constant. Experimentally, a flat interface was achieved by adjusting the heat input to the melt and the thickness of the insulator, shown in Fig. 1. The thermal gradient was estimated to be 250° C cm⁻¹ at the liquid-solid interface. In this work, an aligned eutectic structure was produced at growth rates up to 1 cm h⁻¹.

2.3. Metallography

Microstructures of directionally solidified samples were studied by optical, scanning and transmission electron microscopy. The volume loading of the aligned carbide was determined from scanning electron micrographs (SEM) of transverse sections using quantitative scanning television microscopy [14]. An etching solution of 33HCl, 33HNO₃, 33H₂O, and 1HF was used to reveal Ni₃Al(γ') precipitates in the nickel-base matrix. To reveal the aligned carbide fibre morphology, the matrix was etched electrolytically in a solution of 30HCL,

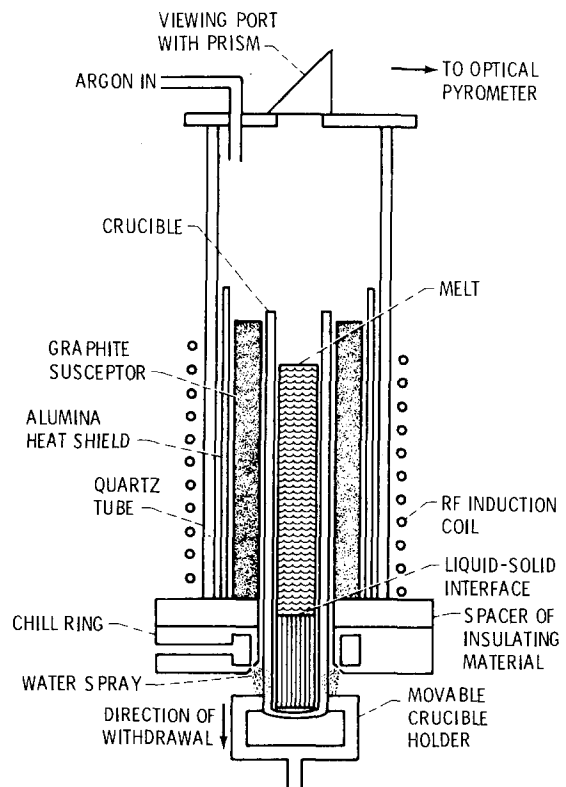


Figure 1 Directional solidification apparatus.

7.5HNO₃, 7.5CH₃COOH, and 55H₂O. The etched samples were coated with a thin layer of a gold–palladium alloy for SEM evaluations.

Thin foils were prepared to obtain diffraction patterns and images of phases by TEM. Slices about 400 μm thick perpendicular to the growth direction were made by an electron discharge machine. From these slices discs about 3 mm in diameter were cut, abraded mechanically to about 150 μm thickness, and then thinned by electrolytic polishing in a solution of 40 ml methyl alcohol, 40 ml ethylene glycol, and 12 ml perchloric acid at -60 °C, 100 V and 45 mA.

2.4 X-ray pole figure

An X-ray pole figure technique was used to determine the crystallographic orientation of the fibres and matrix in the aligned sample. A disc sample was taken perpendicular to the growth direction and the surface of the transverse section polished through 600 grit. A Norelco X-ray generator with Siemens pole figure device having a copper target operated at 35 kW and 25 mA was used to determine the pole density of reflection planes. The pole densities of the selected crystallographic planes were plotted as contour lines on a polar stereo net by selecting appropriate intensity levels.

2.5. Thermal cycling

The directionally solidified alloy in the form of 12.5 mm diameter by 75 mm length specimens was subjected to thermal cycling in a Mach 0.3 gas velocity burner rig simulating the environment of a jet engine [15]. The specimens were heated to 1100 °C in the combustion gases resulting from

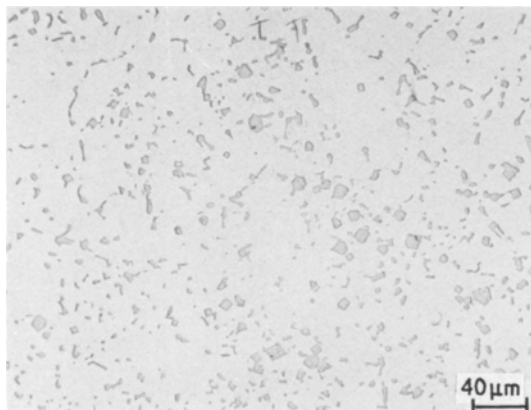


Figure 2 Optical micrograph of conventionally cast Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C.

the burning of a mixture of Jet A grade fuel and air, while being rotated in a sample holder at 450 r.p.m. to ensure uniform temperature. Specimens were held at temperature for 1 min, then cooled to 425 °C with a Mach 0.7 blast of room temperature air. The elapsed time for each cycle was 2.5 min.

3. Results and discussion

3.1. Alloying elements

A simple binary eutectic of Ni-(Hf, Zr)C was modified by additions of Al, Cr and Co. The addition of Al was made primarily to introduce coherent ordered Ni₃Al (γ') precipitates into the matrix, which would offer matrix strengthening. The Cr was added to enhance oxidation and sulfidation resistance. The Co was added to raise the eutectic isothermal temperature. The mixed

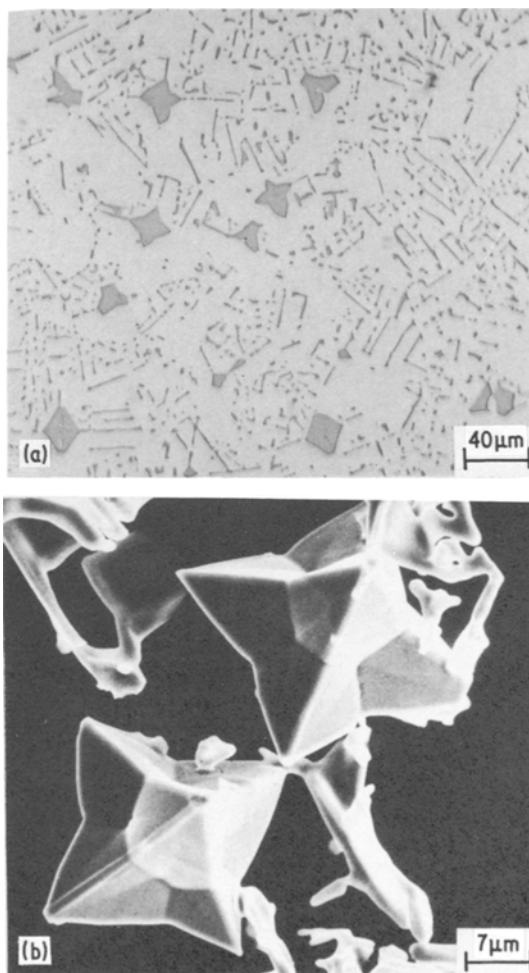


Figure 3 Morphology of bottom of directionally solidified Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C. (a) Excess carbide sort-out zone. (b) SEM of primary carbides.

carbide ($\text{Hf}_{0.8}\text{Zr}_{0.2}\text{C}$) in at. % was selected for the reinforcing phase. A nominal composition (in wt %) of Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C (NASA-HAFNIC-10) was used in this work. The microstructure of the conventionally cast HAFNIC-10 alloy is shown in Fig. 2. The dark polygonal phase is the $(\text{Hf}, \text{Zr})\text{C}$, and the matrix is the Ni-rich solid solution. Differential thermal analysis showed that the alloy has a freezing range of 20°C with a solidus temperature of 1320°C and a liquidus temperature of 1340°C .

3.2. Metallographic study

Metallographic examination of the directionally solidified structure was conducted for specimens grown at 1 cm h^{-1} , which was the maximum growth rate used to produce the aligned structure. Three different morphological zones were observed in directionally solidified samples. At the early stage of solidification, an excess carbide zone was formed, an aligned carbide fibre region

was produced in the next stage, and the last stage was a carbide depleted dendritic zone. These morphological structures were also found in directionally solidified eutectics of TaC-Ni, Co, and Fe [16]. The microstructure of the excess carbide zone is shown in Fig. 3a. The formation of the excess carbide zone is due to hypereutectic composition which is rich in carbide, so that primary particles of $(\text{Hf}, \text{Zr})\text{C}$ form at the liquidus of 1340°C , and grow in the liquid until they are large enough to sink to the bottom of the melt. As solidification proceeds, the carbide content of the melt continuously decreases until it reaches the compositional equilibrium of the eutectic. In the excess carbide region (carbide sort-out zone), formed as a result of the adjustment of the eutectic composition, the primary carbide crystals in the melt assume faces that are slow-growing, because fast-growing planes tend to grow themselves out of existence. Extracted primary carbide particles in the sort-out zone, shown in Fig. 3b, have the shape of pseudo-octahedra, whose faces comprise three facet planes slightly inclined to the $\{111\}$ plane.

The microstructure of a longitudinal section of the directionally solidified sample (Fig. 4a) shows the carbide fibres aligned parallel to the growth direction. Fig. 4b shows a transverse section of the directionally solidified alloy. Some of the fibres are interconnected to form ribbons. In Fig. 5, the matrix has been partially etched away to reveal the fibre morphology. The fibres are present as rod- and ribbon-types, with surfaces which are round or polygonal. The morphology of the fibres may be related to the shape of the

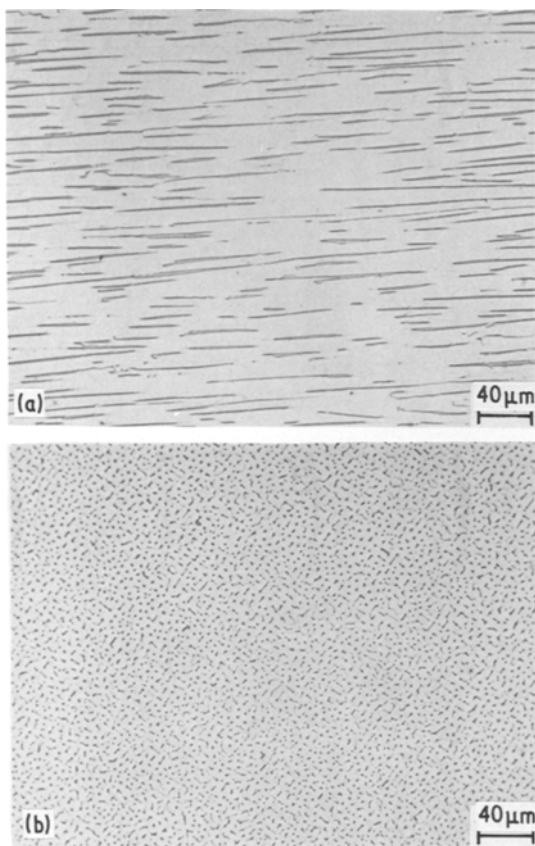


Figure 4 Optical micrograph of aligned $(\text{Hf}, \text{Zr})\text{C}$ fibres in Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy. (a) Longitudinal. (b) Transverse.

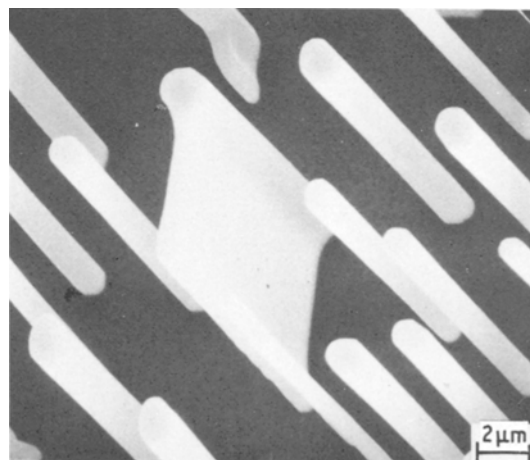


Figure 5 Scanning electron micrograph of $(\text{Hf}, \text{Zr})\text{C}$ fibres in Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy.

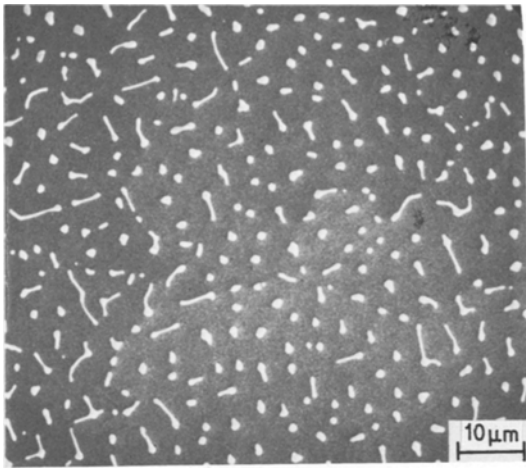


Figure 6 Scanning electron micrograph of transverse section for the measurement of volume fraction of aligned fibres in Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy.

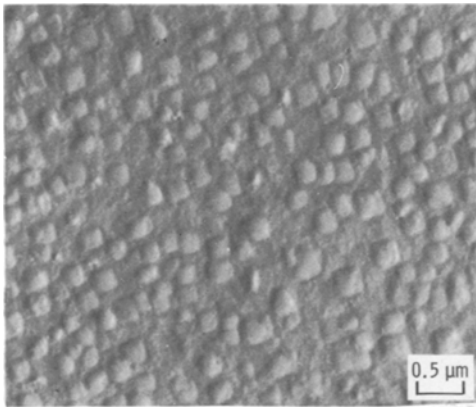


Figure 7 Transmission electron micrograph replica of the matrix of Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy.

primary carbide particles, shown in Fig. 3b. The multiple facet planes of the pseudo-octahedral particles provide more than one direction of rapid growth. A direction of the most rapid growth during directional solidification will form the axis of the aligned fibre. The ribbon-type fibres may be produced by the growth of other planes oriented sideways to the fibre axis. Walter and Cline [16] also observed the ribbon-type TaC fibres in COTAC alloys from the pseudo-octahedral primary particles. On the other hand, they observed only rod-type TaC fibres in NITAC alloys from the regular octahedral carbide particles.

The volume fraction of aligned carbide was measured on transverse sections as shown in Fig. 6. The fibre volume loading in HAFNIC-10 was

about 8%, which is considerably higher than that of TaC fibres in a NITAC type alloy (about 3 to 4% [8]). The high volume loading of the carbide fibres is very attractive in terms of the fibre reinforcement of the alloy, especially at temperatures above about 1040°C. Current conventional superalloys cannot maintain a high temperature strength above about 1040°C due to the dissolution of the major strengthening γ' precipitates into the matrix.

Matrix strengthening of the HAFNIC-10 was accomplished by the introduction of γ' precipitates through the addition of Al. The morphology of the γ' precipitates is shown in the electron micrograph shown in Fig. 7. The precipitates are

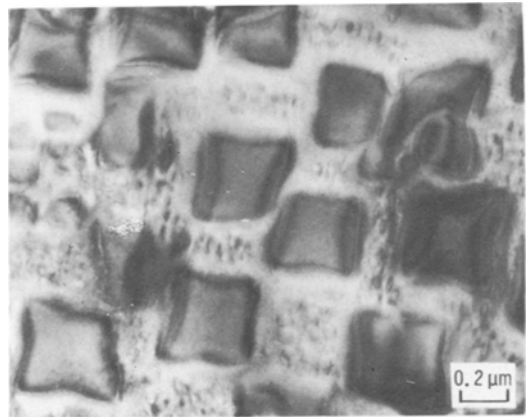


Figure 8 Transmission electron micrograph of thin foil of matrix of Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy.

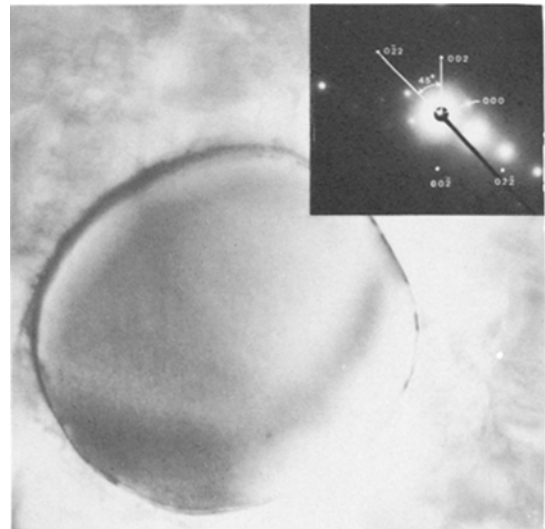


Figure 9 Transmission electron micrograph of bright field image and diffraction pattern of carbide in Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy.

of the typical blocky type with an average size of about $0.2\ \mu\text{m}$. The volume loading of the γ' in the matrix was estimated to be 45%. Morphology of the γ' precipitates is also shown in the transmission electron micrograph of a thin foil (Fig. 8). The bright field image of the thin foil again shows the blocky type precipitates.

The crystallographic orientation of the aligned fibres was determined by the selected area diffraction of a fibre. Fig. 9 shows the bright field image of the fibre with the electron diffraction pattern. The analysis of the pattern showed that the fibre axis is parallel to $\langle 100 \rangle$.

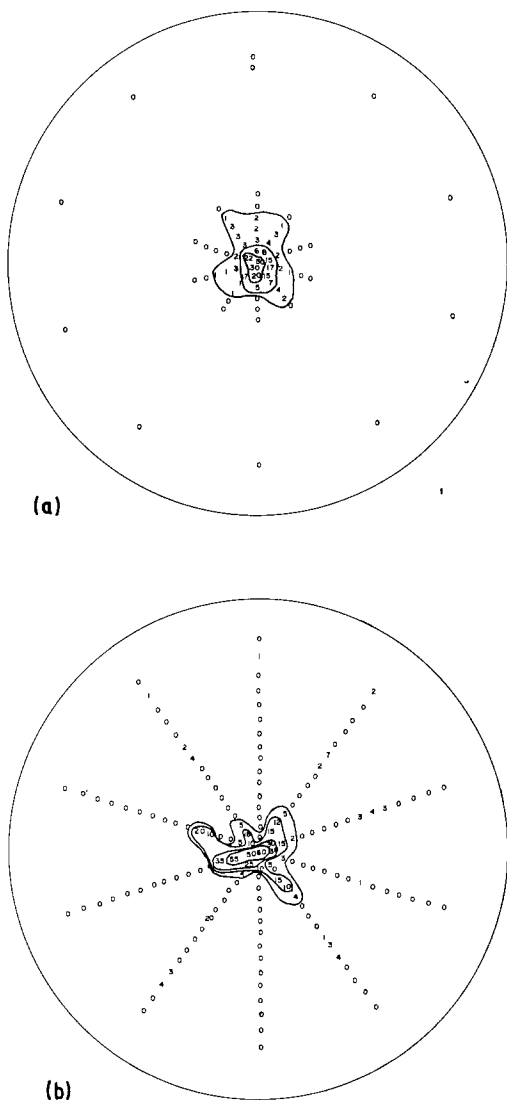


Figure 10 Pole figure of $\{200\}$ reflection plane in Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy. Section perpendicular to growth direction, preferred orientations show $\langle 100 \rangle$ direction. (a) (Hf, Zr)C fibres. (b) Ni alloy matrix.

3.3. Crystallographic orientation

The crystallographic orientations of both fibre and matrix were also determined by using the X-ray pole figure technique. The results of the pole figure provide an average orientation of the fibres and the matrix. Fig. 10a is the pole figure of $\{200\}$ reflection planes in the fibres, while Fig. 10b is that of $\{200\}$ reflection planes in the Ni-matrix. In both pole figures, the projection planes are perpendicular to the growth axis. For the fibres a strong peak located at the $\langle 100 \rangle$ pole in the projection plane shows that the growth direction of the carbide fibres is parallel to the $\langle 100 \rangle$ direction. The pole figure for the matrix is shown in Fig. 10b. The preferred crystallographic orientation of the matrix is also parallel to the $\langle 100 \rangle$ direction.

The same crystallographic orientations of the growth axis for both fibre and matrix would produce the smooth surface of fibres, as in Fig. 5. When the orientations of the fibre and the matrix are different, one may expect that the aligned fibres become serrated or corrugated in the growth from the melt. Walter and Cline [16] observed corrugated TaC fibres in a NiCr matrix when the orientation between the fibres and the matrix were different.

3.4. Thermal cycling

The microstructure of (Hf, Zr)C fibres in the directionally solidified HAFNIC-10 after 2000 thermal cycles between 425 and 1100°C is shown in Fig. 11. The alloy was cycled 2000 times, using a 2.5 min cycle time. There is no observable

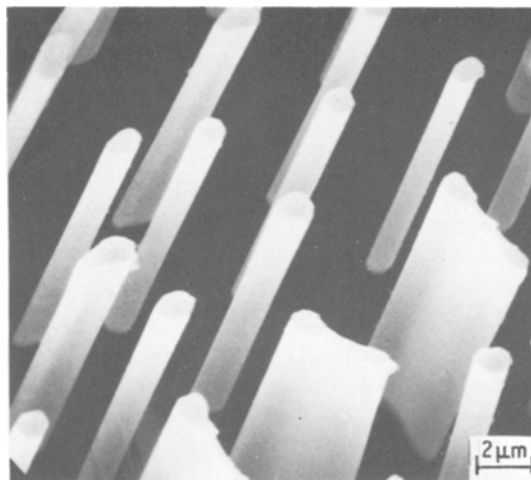


Figure 11 Scanning electron micrograph of Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C DSE alloy thermally cycled between 425 and 1100°C for 2000 cycles.

microstructural degradation of the fibres after cycling. It was previously reported [11] that the (Hf, Zr)C fibres in a Co-base DSE alloy were also stable under thermal cycling, using the same experimental variables. In the evaluation of materials for aircraft gas turbine components, structural stability under thermal cycling is an important parameter. The thermal cycling stability of the (Hf, Zr)C fibres in the Ni-base eutectic alloy shows good potential for using this alloy system for high temperature structural materials.

4. Summary and conclusions

A nominal composition of Ni-10Co-5Cr-5Al-8.3Hf-1.1Zr-0.7C was directionally solidified to produce aligned monocarbide, (Hf, Zr)C in a γ/γ' matrix. The structure, morphology, and thermal cycling stability of the alloy were investigated. The results can be summarized as follows:

(1) The carbide fibres were present as rod- and ribbon-type. The volume loading of the fibres was about 8%.

(2) A blocky type of Ni₃Al (γ') precipitated in the matrix after solidification. The volume loading of Ni₃Al was about 45%.

(3) The grow direction of the fibres and the matrix was parallel to $\langle 100 \rangle$ direction.

(4) No microstructural degradation of the fibres occurred during 2000 thermal cycles between 425 and 1100°C.

Consideration of the volume loading of reinforcing fibres coupled with the thermal cycling stability of γ/γ' matrix suggests the potential for using this alloy system in high temperature structural applications.

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