

ICM-OXIDE-FIBRE/Ni₃Al-BASED-MATRIX COMPOSITES: FABRICATION, MICROSTRUCTURE AND SOME MECHANICAL PROPERTIES

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SUMMARY: Sapphire and alumina-YAG-eutectic fibres produced by the internal crystallisation method are used as reinforcement in a Ni₃Al-intermetallic-based matrix. Because of rather unusual form of the reinforcement, special procedures were developed to deal with the fibres including coating and introducing them into the matrix by using pressure infiltration technique. A possibility to improve matrix properties by uni-directional crystallisation of it was also checked. Tensile testing of the composites at a temperature of 1200°C shows that oxide fibres produced by the internal crystallisation method (ICM-fibres) have a potentiality to be reinforcement for heat resistant composites. Sapphire fibres with a great scale dependence of the strength introduced into a Ni-based alloy not modified specially to serve as a matrix for the composite cannot contribute their potential strength to the composite strength because of a weak fibre/matrix interface. Occurring a rare-earth-metal oxide as a fibre component yields certainly an increase in the fibre/matrix strength, which determines an essential increase in the composite strength. All the experiments described were conducted on a background of a corresponding theory of composite strength.

KEYWORDS: heat-resistant materials, intermetallic matrix composites, oxide fibre, fabrication methods, pressure infiltration, strength, creep rupture, fibre coating.

INTRODUCTION

Oxide-fibre/intermetallic-matrix composites are potential candidates for heat resistant materials. Usage of single crystalline or eutectic fibres reinforcing a nickel-aluminide-based matrix opens a possibility to enhance a service temperature of metal-type materials up to 1200°C [1]. Oxide fibres produced by the internal crystallization method (ICM) [1,2,3] are characterised by the mechanical properties that yield necessary mechanical properties of the composites provided they are properly introduced in an appropriate

matrix. Usage of nickel-aluminide-based alloys as matrices for heat resistant composites calls for the development of a fabrication technology to organise a microstructure of the materials that allows to realise a high strength of the oxide fibres. This is a really composite problem that includes a large number of particular problems. The present paper reviews only (i) requirements to the composite microstructure; (ii) methods to enhance the fibre/matrix interface by using fibre coating; (iii) a method to improve the matrix characteristics by uni-directional crystallization of the matrix, (iv) first results of high-temperature testing of the oxide/intermetallic composites.

REQUIREMENTS TO COMPOSITE MICROSTRUCTURE

The strength model for a brittle-fibre/ductile-matrix composite [3] is used here to evaluate dependencies of strength of oxide-fibre/Ni₃Al-based-matrix composites on fibre volume fraction, homogeneity of fibre packing, fibre characteristics, matrix characteristics, and fibre/matrix interface strength. The evaluation yields, in particular, requirements to the above-mentioned parameters, a part of which should be satisfied by an appropriate composite processing. Therefore, the development of processing methods is based on a solid foundation, but not on the errors-and-trials approach.

Fig. 1 illustrates the usage of the above-mentioned strength model in the present context. Immediate results following from the consideration are

1. The stronger fibre/matrix interface, the larger is the rate of composite strength increase with increasing fibre volume fractions v_f at low v_f .
2. Improving homogeneity of fibre packing in a composite makes longer the interval of v_f in which the strength increase takes place.
3. To make that interval wider, which should be wanted as can yield an increase in the specific composite characteristic, we need to improve the fibre packing with increasing the interface strength.

COMPOSITE FABRICATION BY PRESSURE INFILTRATION

The whole process of making composites in a work described in the present paper includes the following stages:

1. Preparing molybdenum carcass.
2. Obtaining an oxide/molybdenum block.
3. Extracting fibre bundle from the molybdenum matrix.
4. Inserting fibres into a casting mould.
5. Pressure casting to obtain oxide-fibre/Ni₃Al-based-matrix composite.
6. Making a tensile specimen.

The first two stages are described elsewhere [1,2]. The 3rd and 4th ones are now under patenting. Stages 5 and 6 shall be briefly described here together with characterisation of the fibre and matrix material.

Fibres

Sapphire fibres, Fig. 2, used in this study were made by using the internal crystallization method as described in [1,2,3]. Crystallization rate of the fibres was 1.3 mm/min; the fibre axis was oriented along the *c*-axis of sapphire. Room temperature strength of the fibers was also analysed in the above references following the procedure outlined in [4]. Geometrical parameters and statistical strength characteristics of the fibres are as

presented in Table 1. $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$ -eutectic fibres were produced in the same manner, details of the procedure as well as fibre microstructure and properties are described in Ref. [5]. All the fibres have an average cross-sectional size about 0.08 mm.

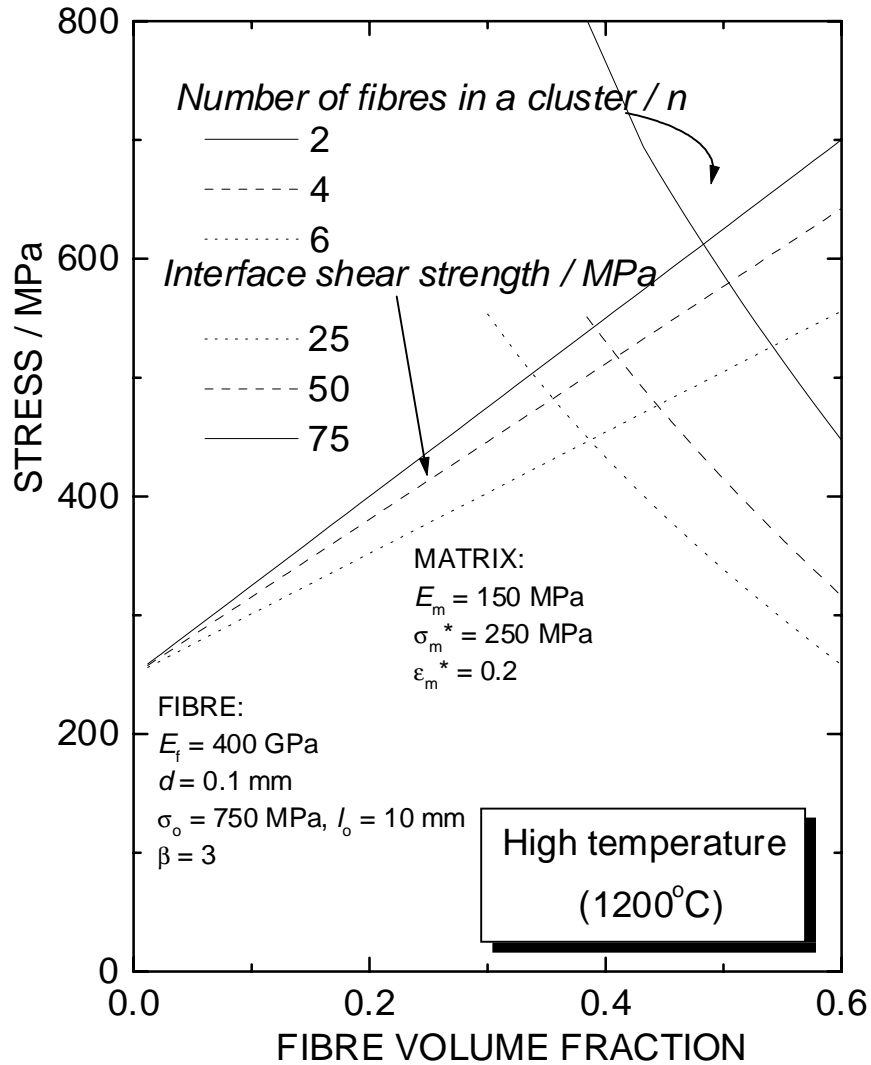


Fig. 1. The calculated high-temperature-strength/fibre-volume-fraction dependencies of oxide-fibre/ Ni_3Al -based-matrix composites assuming components parameters showed in the field.

Matrix

Chemical composition of the alloy, VKNA-4Uⁱ, [6] chosen as the matrix is presented in Table 2. The alloy consists normally of a solid solution based on Ni_3Al , γ' -phase (about 80%), a solid solution based on Ni, γ -phase (about 9%), and a eutectic γ' -phase (about 11%). In addition, there exist, in small quantities, β' -phase (of a Ni_2Al type) and various metal carbides (α -phase). It should be noted that the alloy microstructure is effected

ⁱ Russian Trade Name.

essentially by crystallisation process and subsequent heat treatment. Typical mechanical properties of the intermetallic-based alloy are shown in Table 3.

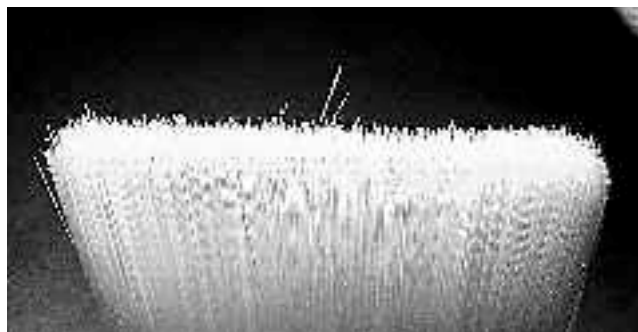


Fig. 2. A top of a sapphire fibre bundle after removing a molybdenum carcass.

Table 1. The geometrical characteristics parameter and Weibull parameters of sapphire fibres.

Fibre block	Average cross-section circumference	Average cross-section area	Volume hypothesis				Surface hypothesis			
			β	σ_o bending	σ_o tension	V_o	β	σ_o bending	σ_o tension	S_o
				MPa	MPa	mm ³		MPa	MPa	mm ²
V086	0.65	0.012	3.1	733	484	0.059	3.1	432	172	17
V118	0.68	0.012	2.8	1480	966	0.059	3.2	594	244	60
V020	0.65	0.010	3.9	790	551	0.051	4.2	553	272	16
V145	0.48	0.005	3.1	967	665	0.025	3.2	598	261	12

Table 2. Chemical composition (w %) of the matrix alloy.

Ni ₃ Al	Cr	W	Mo	Ti	Co	C
Balance	4.8	2.2	4.9	1.15	4.4	0.11

Table 3. Mechanical properties and gas corrosion resistance of VKNA-4U alloy crystallized under various conditions.

	T°C	Equi-axis	Columnar structure	Single crystalline		
				<111>	<001>	<011>
Strength, MPa	20	650	770	1340	600	750
	1200	85	190	170	165	168
Ultimate elongation, %	20	18	26	15	50	30
	1200	18.5	35	37	40	60
Stress rupture at 100 h	1100	50	95	110	100	95
	1200	22	45	50	45	38

Composite processing

Since (i) the fibres are produced in a form of the fibrous block shown in Fig. 2, (ii) the matrix material can be only processed by using a casting technology, and (iii) the fibres are not wetted by the matrix melt, the pressure infiltration seems to be the only choice for the fabrication process. Experiments showed that a most serious technical problem arisen is obtaining a homogeneous fibre distribution in a composite cross-section. A method, which is now under patenting, yields sufficiently homogeneous fibre distribution in cylindrical rods; an example is shown in Fig. 3. The fibre distribution in a specimen with two heads, which is produced by either one-step process or two-steps one, the latter includes making a composite rod and then casting the heads in a corresponding mould with the inserted composite rod, is still to be improved. At the same time, it should be noted that the infiltration method just mentioned allows producing elements of a complicated three-dimensional form. The fabrication process will be described in more details elsewhere [7].

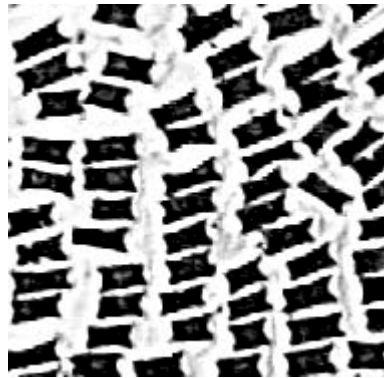


Fig. 3. A part of the cross-section of a composite rod.

Composite Microstructure

At present, the most important feature of the composite microstructure to be essentially improved is the fibre/matrix interface microstructure that determines the interface strength and, consequently, the composite strength (see Fig. 1). This problem has been addressed by many authors (see e.g. Refs. [8,9,10]). It is now clear that formation of some compounds on the interface in oxide/metal systems can yield sufficiently high bond strength. In particular, in Al_2O_3 -fibre/ NiAl -based matrix composites, formation of either Al_2O_3 - Yb_2O_3 complex oxide [9] or Ni-Cr-Al spinel [11] yields an essential increase in the shear strength of the interface. Still, the problem remains to be considered since not all the features of the fibre/matrix bond are clear. Moreover, the fibre effects crystallization process of the matrix material that leads to occurring a sufficiently thick interface zone with chemical composition and mechanical properties different from those of the matrix alloy [12]. This complicates the situation on the fibre/matrix interface even more.

An effect of the weak interface on the composite strength shall be discussed below. Here we just show a scanning electron micrograph, Fig. 4, of a typical site of the failure surface of a sapphire-fibre/ Ni_3Al -based-matrix composite that clearly show delamination at the interface. At the same time, it is now clear that some treatments of the composites can be found that change the appearance of the interface, see e.g. Fig. 5.

Usage of Coated Fibres

There are known two ways of improving wetting and enhancing the fibre/matrix interface strength, namely fibre coating and matrix modification. Metal and compound coating were applied on ICM-oxide fibres and coated fibres were used in composite fabrication experiments. It occurred that both molybdenum and oxy-silicon-carbide coatings required for their usage sufficiently high vacuum and pure argon gas in pressure infiltration machine. Hence, usage of coated oxide fibres needs a rather complicated equipment that enhances the fabrication cost.

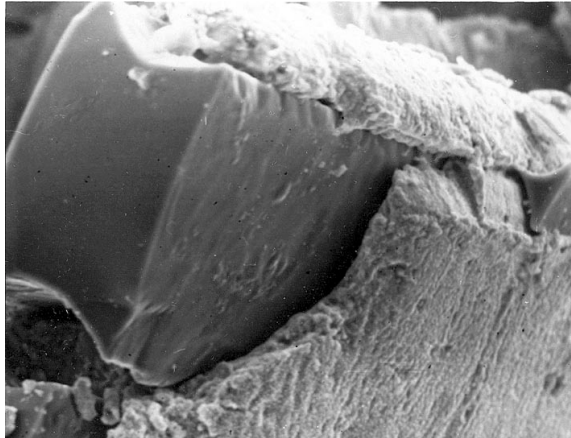


Fig. 4. Scanning electron micrograph of a typical site of the failure surface of a sapphire-fibre/ Ni_3Al -based-matrix composite.

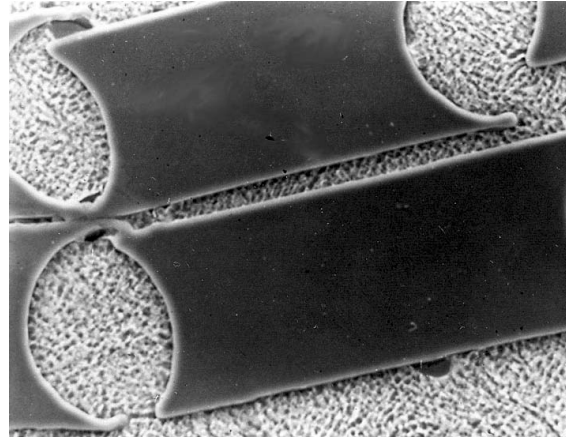


Fig. 5. Scanning electron micrograph of a cross-section of sapphire-fibre/ Ni_3Al -based-matrix composite after a special heat treatment.

Uni-Directional Matrix Crystallization

A composite reinforced with high strength fibres requires a matrix with correspondingly high strength and fracture toughness characteristics. The Ni_3Al -based alloy used as a matrix is very sensitive to its microstructure, see Table 3. While in single crystalline form, its properties are higher than those for isotropic polycrystals and depend strongly on the orientation of the specimen. Hence, a possibility to crystallize the matrix unidirectionally to get an appropriate crystallographic orientation was checked. The possibility occurs to be real, although some work should still be done to preserve the configuration of the fibre system in a composite during the process, Fig. 6.

The uni-directional crystallisation of the matrix yields a change in the microstructure and properties of the matrix in a vicinity of the fibre as shown in Fig. 7 by presenting results of measuring microhardness of the matrix. Certainly, this is a result of an interaction between the fibre and matrix during the crystallisation process which is unknown at present, but should be studied in details to use it to enhance the composite properties.

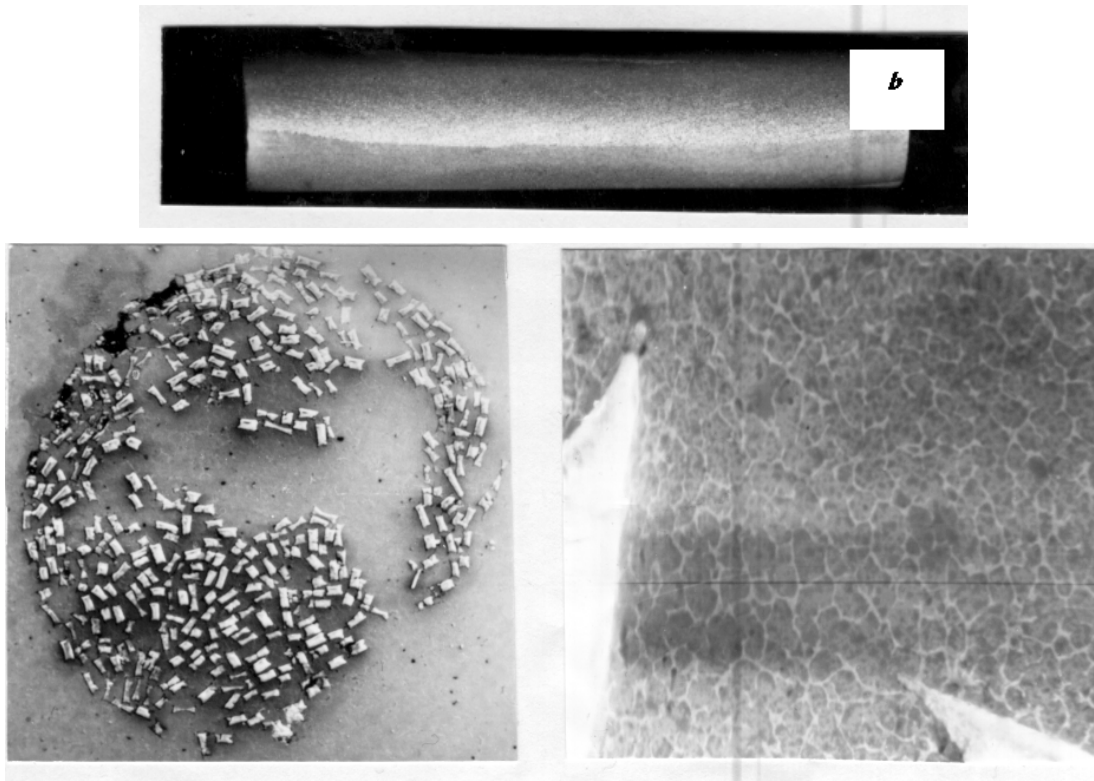


Fig. 6. Macro- and microstructure of the composite after directional solidification of the matrix. At the upper photograph longitudinal matrix grains run along the whole length of the composite rod.

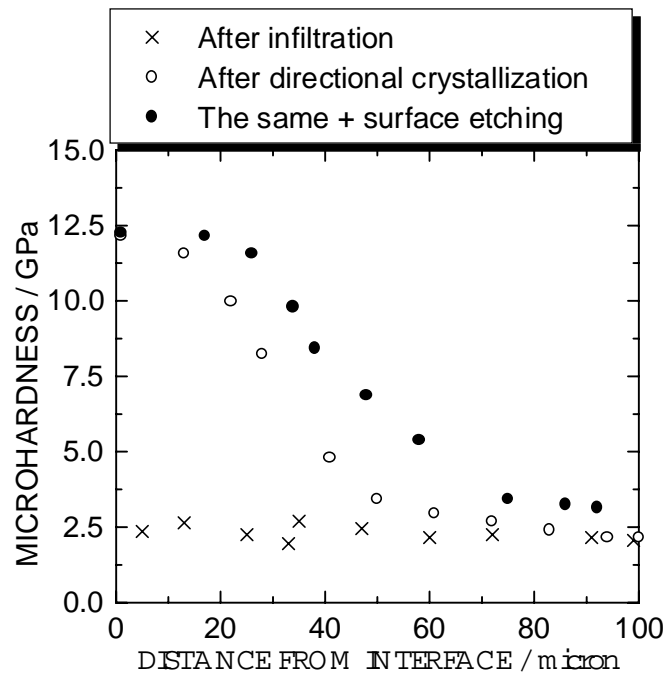


Fig. 7. Microhardness of the matrix in the vicinity of the fibre/matrix interface in an $\text{Al}_2\text{O}_3\text{-Al}_5\text{Y}_3\text{O}_{12}$ -fibre/VKNA-4U-matrix composite.

HIGH TEMPERATURE STRENGTH

High temperature tensile tests of composite specimens were conducted at 1200°C in vacuum. The specimens were cylindrical rods of a diameter of about 5 mm with two heads. The load was applied via its flat surfaces, a distance between which was about 35 mm. No case of shearing the composite rod from the head was observed.

Dependencies of the high temperature composite strength on fibre volume fraction are presented in Fig. 8. The composites behave in a qualitative agreement with a theory outlined in details in Ref. [3] and illustrated in Fig. 1: at low fibre volume fraction the strength, σ^* , increases with fibre volume fraction v_f increasing; however, reaching a critical value of v_f , the strength goes down. The first portion of the dependence corresponds to a failure mechanism based on the fibre breaks accumulation that yields enhancing the effective fibre strength with shortening the fibre. The second portion corresponds to a failure mechanism based on the formation of fibre break clusters, which are really microcracks of a critical size yielding catastrophic crack propagation.

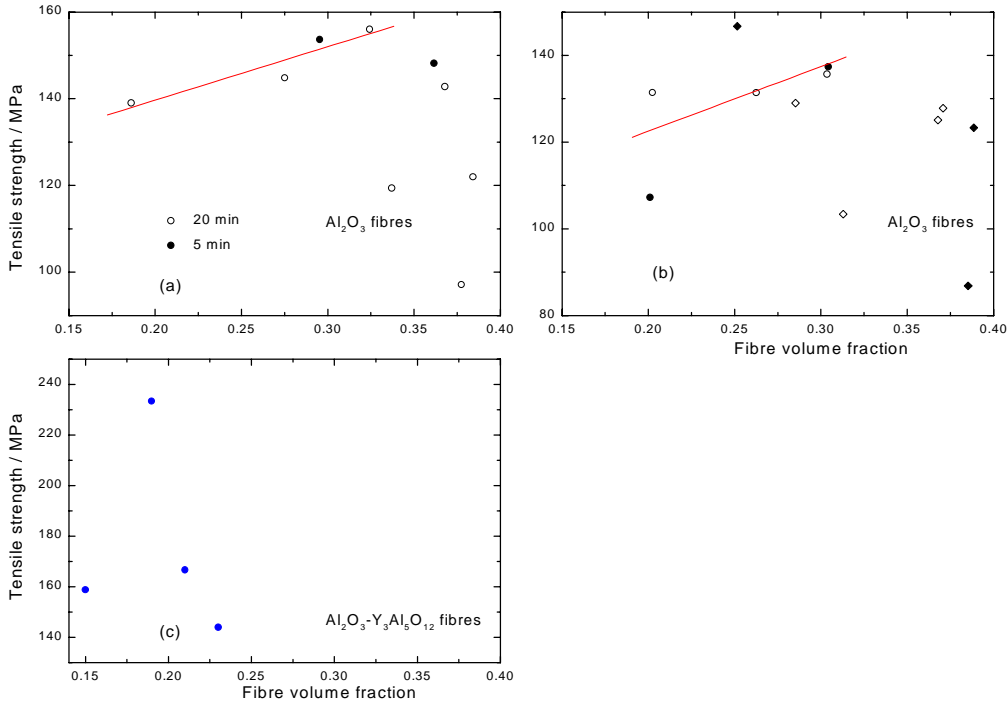


Fig. 8. Tensile strength at 1200°C of oxide-fibre/ Ni_3Al -based-matrix composites produced via one-step (a,c) and two-steps (b) fabrication routes. The infiltration temperature for all the specimens was 1510°C. The total time of the fibre contact with the matrix melt at the highest temperature is shown in the graph field for a-route; for b,c-routes it varies from 5 to 10 min.

The strength/fibre-volume-fraction dependence at low fibre volume fractions is described by the following expression

$$\langle \sigma^* \rangle = \alpha \langle \sigma_f^* (l^*) \rangle v_f + \sigma_m^* v_m \quad (1)$$

where $\langle \sigma_f^* (l^*) \rangle$ is the mean fibre strength on length l^* , l^* is the average distance between fibre breaks, σ_m^* is the matrix strength, α is a constant, $\alpha \approx 1$. Approximation of experimental data

presented in Fig. 8, *a* and *b*, by Eq. (1) yields values of the strength parameters given in Table 4. The effective strength of sapphire fibres of about the same characteristic diameter grown in a molybdenum matrix without predetermining the crystallographic orientation is also given in Table 4. One can see that the effective fibre strength in the Ni-based matrix is much lower than that in molybdenum matrix. At least two reasons for that should be considered:

- 1) Very low fibre/matrix interface strength in this composite system.
- 2) Fibre strength degradation as a result of chemical interaction between fibre and matrix materials, presumably during contacting the fibre to the molten matrix.

Table 4. Ni₃Al-based matrix and sapphire fibre characteristics evaluated on the basis of tensile strength characteristics of the composites.

	σ_m^*	$\alpha \langle \sigma_f^* (l^*) \rangle$ in Ni ₃ Al-based matrix	$\alpha \langle \sigma_f^* (l^*) \rangle$ in Mo matrix [3]
	MPa	MPa	MPa
Fig. 8a	115.0	238.2	≈ 600
Fig. 8b	92.8	241.6	≈ 600

These factors can yield a combine effect on the composite strength and revealing a contribution of each of them in a strict manner needs to perform special experiments. The problem is complicated by a difference in the effective strength of the fibre in a matrix and the strength of fibres tested separately [13]. At a present stage of the experimental work, there are only non-systematic data that can be a base for speculations on the relative importance of the factors mentioned. First, failure surfaces of the specimens, Fig. 4 being an example, verify clearly a low strength of the interface. Secondly, preliminary push-out tests at room temperature have shown the interface strength values in sapphire/Ni₃Al composites to be about 100 MPa only. Third, it is interesting to compare strength characteristics of sapphire fibres used in the present work before introducing them into the matrix with those of fibres produced by Saphikon that have been tested by Asthana et al. [14] after etching them out of composites with Ni-based-superalloy matrix produced by pressure casting. It was found in the paper cited that contacting the sapphire fibres with the molten matrix causes an essential change in strength characteristics of the fibres tested separately. The comparison of the strength characteristics of these two types of the fibres performed in Ref. [2] shows that the strength characteristics of the ICM-fibres at room temperature are nearly the same as those of EFG-fibres after contacting to the Ni-based melt.

On the other hand, preliminary tests of composites with Al₂O₃-Y₃Al₅O₁₂-eutectic fibres, Fig. 8c, provide some indication of a higher interface strength than in the case of composites with sapphire fibres which corresponds to higher rate of the composite strength increase at low fibre volume fraction. This correlates to results by Tewari et al. [9] who exploited a known property of complex oxides containing rare-earth elements to adhere to Ni-based alloys better than pure alumina, to increase the interface strength in sapphire-fibre/Ni-based matrix composites by providing conditions for formation of a complex oxide containing Yb on the fibre/matrix interface. On the same time, the data presented in Fig. 8 reveal a decrease in a fibre volume fraction value corresponding to a maximum composite strength with increasing

the effective fibre strength. This is also in a qualitative agreement with the theory illustrated in Fig. 1.

It should be noted that very preliminary results of room temperature tensile tests, just started by testing of two specimens, one with low fibre volume fraction having the strength of 778 MPa and another with a high fibre volume fraction having the strength of 195 MPa are in accordance with both the composite strength theory and a hypothesis of the weak fibre/matrix interface.

These observations yield a conclusion that the main reason for a relatively low strength of sapphire-fibre composites, that means a relatively low effective fibre strength, is a low interface strength. At the same time, they show a way to enhance the interface strength and, hence, the composite strength.

CONCLUSIONS

Main conclusions can be formulated as follows:

1. Oxide fibres produced by the internal crystallisation method (ICM-fibres) have a potentiality to be reinforcement for heat resistant composites.
2. Sapphire fibres with a strong scale dependence of the strength introduced into a Ni-based alloy not modified specially to be a matrix for the composite cannot contribute their potential strength to the composite strength because of a weak fibre/matrix interface.
3. Occurring a rare-earth-metal oxide as a fibre component yields certainly an increase in the fibre/matrix strength, which determines an increase in the composite strength.
4. Unidirectional crystallisation of the matrix in the composites under consideration can yield a further increase in composite properties.

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