OXIDE FIBRES PRODUCED BY INTERNAL CRYSTALLIZATION METHOD AND THEIR USAGE IN COMPOSITE TECHNOLOGY

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SUMMARY: A way of fabrication of oxide fibres based on the internal crystallisation method and their mechanical properties are described. Among the fibres which are fabricated and analysed are such as alumina and alumina based eutectics Al_2O_3-$Al_5Y_3O_{12}$, Al_2O_3-$ZrO_2(Y_2O_3)$, Al_2O_3-Gd_2O_3, etc. The fibres have clearly a potential as reinforcement for a variety of metal, intermetallic, and ceramic matrices since a balance between their mechanical properties and energy input into the fabrication process seem to be favourable for such applications.

KEYWORDS: oxide fibre, sapphire, eutectics, internal crystallization, oxide-fibre/nickel-aluminide-matrix composites, oxide-fibre/oxide-matrix composites, fibre coating

INTRODUCTION

Oxide fibres produced by the internal crystallization method (ICM) [1,2] those being single-crystalline alumina and alumina based eutectics, such as Al_2O_3-$Al_5Y_3O_{12}$, Al_2O_3-$ZrO_2(Y_2O_3)$, Al_2O_3-Gd_2O_3, etc., can now be used as reinforcement for a variety of metal, intermetallic and ceramic matrices since they are sufficiently strong and not so expensive, in terms of the energy input to fabrication process, as well-known fibres produced by the Stepanov's or EFG method [3,4]

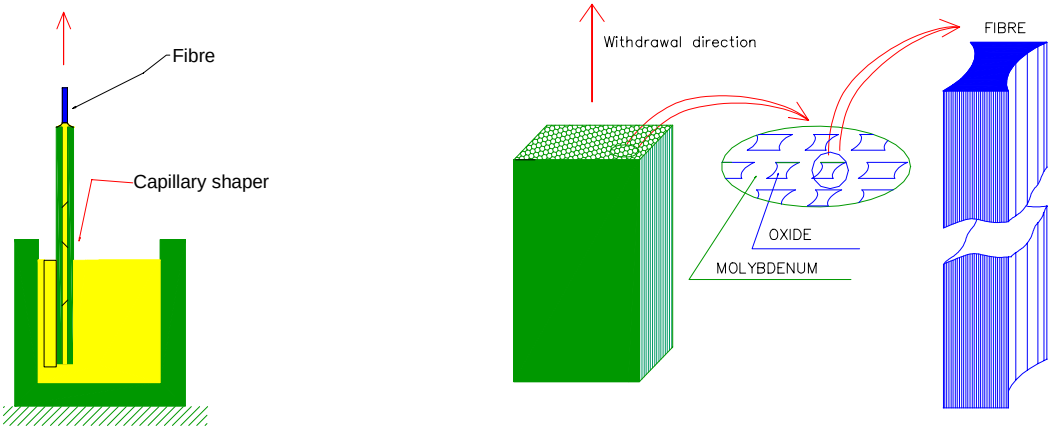
In the present paper, first, EFG and ICM methods of making fibres are compared, then properties of some ICM-fibres are analysed, and finally, fibre usage in various composite systems are briefly discussed.

OXIDE FIBRES OF *ICM* AND *EFG* TYPES

A schematic of EFG and ICM methods of crystallising fibres illustrated in Fig. 1 shows rather clearly both advantages and disadvantages of the methods (see also Table 1). In the internal crystallisation method, a molybdenum carcass with continuous channels is infiltrated with an

oxide melt and then the melt is crystallised to form the fibres of a cross-section shown in Fig. 1 and Fig. 2 that is shaped by molybdenum foil/wire assemblage forming the carcass. The productivity rate of the process which includes crystallising a very large number of the fibres at the same time can be very high that determines the main advantage of the process, namely a low energy input per a unit mass of the fibre. Another important advantage of the ICM-process is an easy possibility to crystallise various oxides in a shape of the fibre without any special adjustments of either method or apparatus. This provides a possibility to crystallise a variety of the fibres including complex oxides containing rare-earth elements as well as eutectics composed of alumina and complex oxides. For example, in addition to sapphire fibres, those of mullite, alumina-YAG eutectic, Al_2O_3-$ZrO_2(Y_2O_3)$-eutectic, Al_2O_3-$Y_3Al_5O_{12}$-eutectic, Al_2O_3-$GdAlO_3$-eutectic were recently obtained and tested being extracted from the molybdenum matrix. Earlier, $SmAlO_3$, $LaTaO_4$, $La_2Ti_2O_7$, $Y_2Ti_2O_7$, and $YAlO_3$ were crystallised in the molybdenum matrix and tested at high temperatures together with the matrix [1].

The microstructure of ICM fibres are clearly far from a perfect one unlike that of EFG fibres which are characterised by nearly ideal microstructure and, hence, they are suitable for the usage in optical devices.



Stepanov's (EFG) method

Internal crystallisation method

Fig. 1. A schematic of EFG and ICM methods

Table 1: Comparison of EFG and ICM types of oxide fibres**.**

	Mechanical properties	Optical properties	Fibre form	Availability	Energy input per a unit mass	Cost
EFG	+	+	Continuos	Commercial	–	–
ICM	+	–	Bundle (can be bound into a carcass)	Develop-mental	+	+

FIBRE STRENGTH

A rather unusual shape of the ICM-fibre cross-section shown in Fig. 2 calls for a special procedure to evaluate the tensile fibre strength by using experimental data on the bending strength. Strength characteristics of fibres occur to be comparable with those normally obtained for EFG-fibres, provided a base for the comparison is effective fibre strength in a composite.

Fibre testing and interpreting the results

A fibre is bent over a rigid steel cylinder of a sufficiently large radius, *R*. A number of the fibre breaks is counted. If the number of breaks is small enough, that means that the ratio of an average distance between neighbouring breaks to a characteristic size of the fibre cross-section is larger than 10 which ensures a possibility to neglect end effects, then the fibre is bent over the cylinder of smaller radius. A new total number of the breaks is counted. The process is repeating until the average distance between the breaks becomes less than about 10.

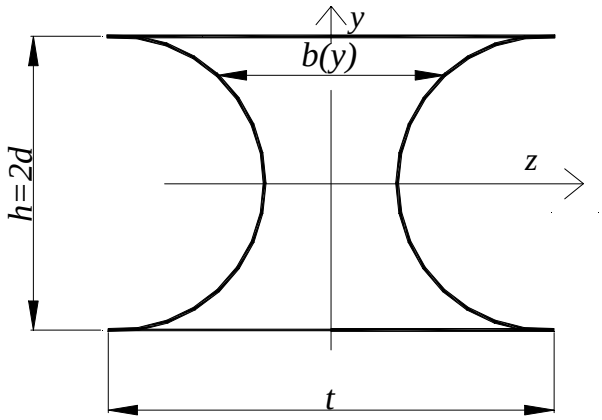


Fig. 2. A fibre cross-section.

The maximum fibre stress corresponding to the rigid cylinder radius is calculated according to

$$\sigma = E\frac{d}{2R}$$

where *E* is the Young's modulus of the fibre material, *d* is the fibre height or the molybdenum wire diameter. To a first approximation, we assume σ to be the fibre bending strength at a length equal to the average distance between the fibre breaks.

The calculation of the fibres strength characteristics calls for use either *volume* or *surface* as a geometrical parameter in the Weibull distribution to describe statistical characteristics of the defect distribution. Let us start with the volume hypothesis. Taking the Weibull distribution in the form

$$P(\sigma,V)=1-\exp\left(-\frac{1}{V_o}\int_V\left(\frac{\sigma(\bar{r})}{\sigma_o}\right)^{\beta}\right)\mathrm{d}V \qquad (1)$$

we obtain a scale dependence for the fibre strength as

$$\sigma^{*}=\sigma_o\left(\frac{V}{V_o}\right)^{-1/\beta} \qquad (2)$$

where σ^* and σ_o are the mean strength values for volumes V and V_o, respectively. It is convenient to introduce a constant characteristic fibre length, l_o, and choose V_o as

$$V_o = l_o A_{av} \tag{3}$$

where A_{av} is the average cross-sectional area in a fibre batch under testing. Our goal is to determine value of β via the strength scatter of fibres of a constant volume, V_o, and then, footing on a known mean value of the strength for that volume to obtain a scale dependence of the mean fibre strength. To determine β, we use well-known approximation $\beta=1.2/\kappa$, κ being the variation coefficient of the fibre strength.

Since we have experimental points as a set of (V, σ^*) values, we need to use a step-by-step approximation method. Chose, as a first approximation, a typical value of β, say $\beta = 3$. Then use Eq (2) to calculate the strength values at V_o. A set of the strength values obtained yields a value of the standard deviation and, consequently, value of κ. The value of κ yields a new value of β. Then the procedure is to be repeated. Normally, three or five iterations are sufficient provided the first approximation for the value of β has been chosen properly. A set of the Weibull parameters, that is $[\beta, \sigma_o, V_o]$ is obtained as a result of the calculations. It is convenient to replace a notation σ_o with σ_o^b to stress relation of it to bending. Hence, we obtain actually parameter set $\lfloor \beta, \sigma_o^b, V_o \rfloor$ and wish now to calculate $\lfloor \beta, \sigma_o^t, V_o \rfloor$ where σ_o^t relates the statistical characteristics to the tensile strength of fibres.

A model that connects the bending, σ_o^b, and tensile, σ_o^t, characteristic stresses for a brittle material is presented elsewhere [5]. A general relationship is

$$\sigma_o^t = MV(\beta)\sigma_o^b \tag{4}$$

where $MV(\beta)$ is determined by comparison of the probabilities for tension and pure bending, namely

$$P(\sigma, l) = 1 - \exp\left(-\frac{l}{l_o}\left(\frac{\sigma}{\sigma_o}\right)^{\beta} \right) \tag{5}$$

and

$$P(\sigma, V) = 1 - \exp\left(-\frac{h}{l_o F_o}\left(\frac{\sigma}{\sigma_o}\right)^{\beta} \int_0^l \mathrm{d}x \int_0^1 \xi^{\beta} b(\xi)\mathrm{d}\xi \right), \tag{6}$$

respectively. For a fibre cross-section shown in Fig. 2 we have

$$b = d\left(\alpha - \sqrt{1-\xi^2}\right),\ F_o = \frac{d^2}{2}\left(\alpha - \frac{\pi}{4}\right), \text{ and } \xi = y/h$$

where $\alpha = t/d$ and d is the wire diameter. Hence, following the procedure outlined in Ref. [5] we obtain

$$M = MV_{ICM} = \left(\alpha - \frac{\pi}{4}\right)^{-1/\beta} \left[\int_0^1 \xi^{\beta} \left(\alpha - \sqrt{1-\xi^2}\right) \mathrm{d}\xi \right]^{1/\beta}. \tag{7}$$

Strictly speaking, the relationship, we are going to use, is effected by a shape of the fibre given by ratio *t/d*. So the procedure can be considered as an approximate since the values of *t* and *d* vary even within one fibre batch.

If we assume that characteristic defects are located on the fibre surface or at the vicinity of it then the iteration procedure to obtain a set of the strength characteristics, that is $\left[\beta, \sigma_o^b, S_o\right]$, remains as described above for the *volume* hypothesis, just Eq. (3) is replaced with

$$S_o = l_o P_{av}$$

where P_{av} is an average value of the cross-section perimeter.

To obtain σ_o^t we use corresponding relationship derived in Ref. [5] that is

$$M = MS_{ICM} = \left(\frac{\beta+1}{4}\frac{P}{h}\right)^{-1/\beta} = \left(\frac{(\beta+1)(\pi+2\alpha)}{2}\right)^{-1/\beta} \tag{8}$$

Experimental data

Original experimental data for a number of the batches of sapphire and one batch of Al_2O_3-$Y_3Al_5O_{12}$-eutectic fibres are presented in Fig. 3. The following features of the strength behaviour of the fibres are important. First, the strength scatter is large, obviously, blocks V054 and K164 contain sets of the somehow different fibres. Second, thin fibre coating enhances the fibre strength essentially certainly because an essential portion of a defect population that determines the fibre strength characteristics is located on the fibre surface.

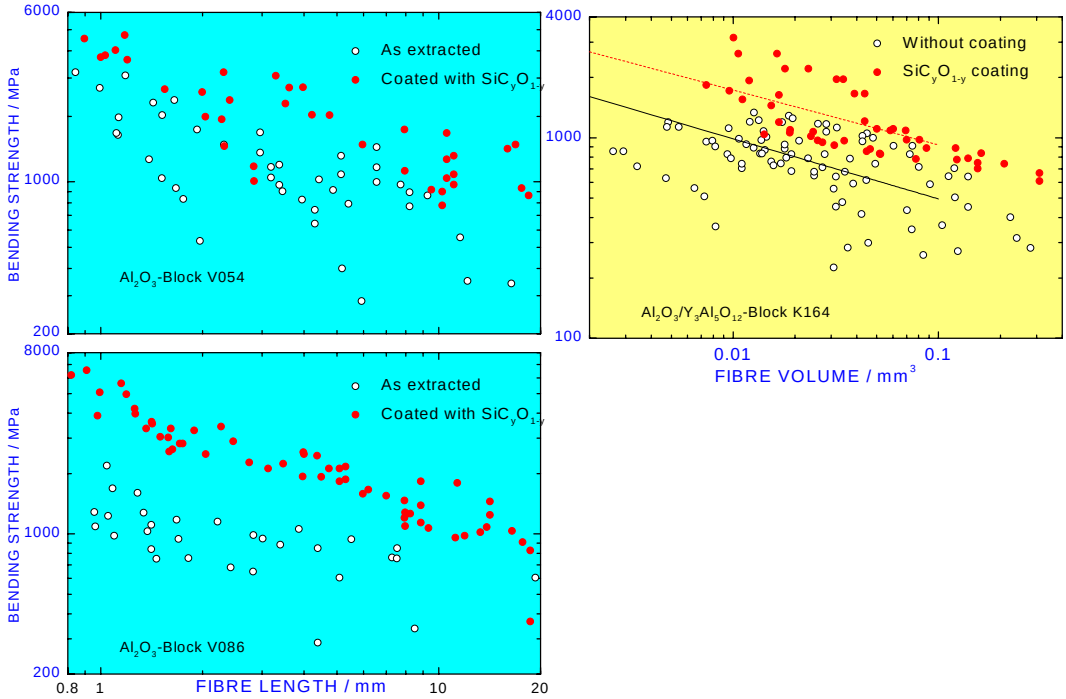


Fig. 3. Original experimental data for two batches of sapphire and one batch of Al_2O_3-$Y_3Al_5O_{12}$-eutectic fibres. Thickness of the coating is about 1 μm [6,7].

To reveal a reason for the large strength scatter let us consider behavior of separate fibres in the batches tested. This is important as fibres in a batch can differ from each other, at least by cross-sectional sizes. Accepting the same procedure as outlined in the previous section

(although the procedure can be different in this case) and introducing characteristic fibre diameter *D*, such as $\pi D^2 = F$ where *F* is the cross-section area, yields results presented in Fig. 4 and Fig. 5. The dependencies of the tensile fibre strength on characterisic fibre diameter calculated are plotted for various fibre volumes. For all the volumes used and all the diameters tested the fibre strength increases with the diameter increasing. This is an unexpected result. Perhaps, peculiarities of the surface defects in ICM fibres are responsible for such a behaviour. In more details, this finding will be described elsewhere [8].

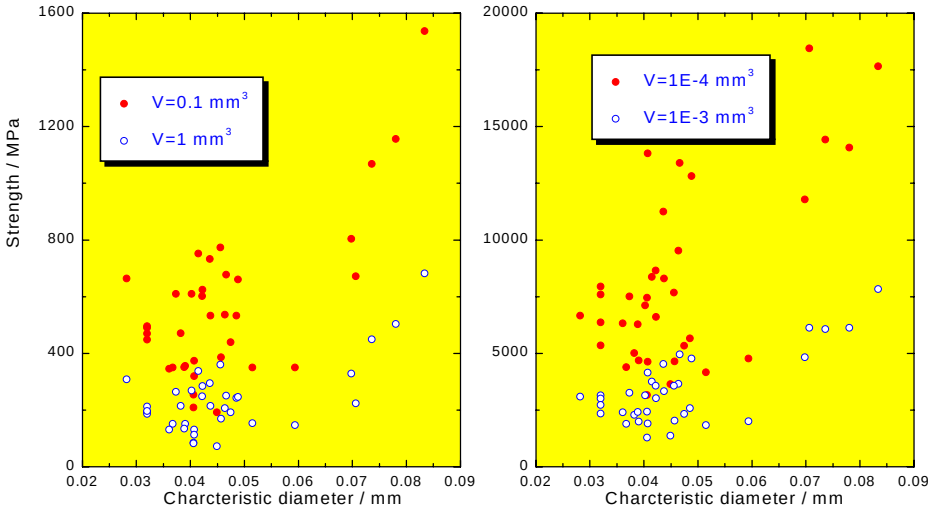


Fig. 4. Calculated tensile strength at four fibre volumes shown in the field of three batches of sapphire fibres (blocks V118, V145, and V205) versus characteristic fibre diameter. Note that each point corresponds to one fibre.

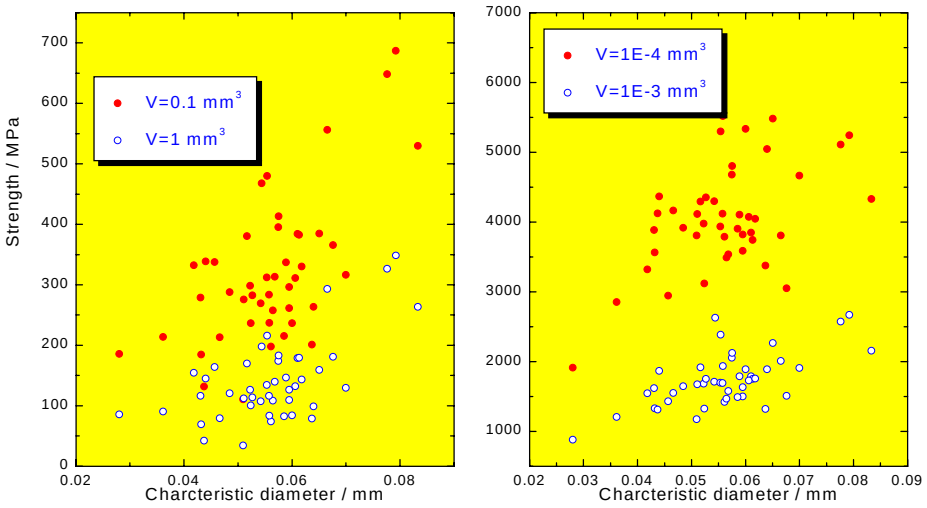


Fig. 5. Calculated tensile strength at four fibre volumes shown in the field of two batches of Al_2O_3-$Y_3Al_5O_{12}$-eutectic fibres (blocks K164 and S146) versus characteristic fibre diameter. Note that each pointcorresponds to one fibre.

Strength of ICM and Stepanov's (EFG) fibres

There is no reason to compare the strength of as-received EFG and ICM fibres: obviously, the microstructure of the former fibres is nearly perfect, their strength is high, the strength scatter is low, and the strength/fibre-length dependence is weak (see, e.g., corresponding data provided by Saphikon and cited in Ref. [9]. However, an interaction of perfect sapphire fibres of an EFG type with a molten Ni-based matrix during composite fabrication process yields occrring surface defects that cause a drastic decrease in the average fibre strength as well as in the strength scatter which leads to a strong dependence of the strength on fibre length. A comparison of the scale dependence of EFG-fibres extracted from a NI-based matrix [10] and those for sapphire fibres produced by ICM and extracted from milybdenum matrix is pesented in Fig. 6.

A question arises what is a behaviour of both types of the fibres as reinforcement of a composite? The answer depends on both a type of the composite and its structure.

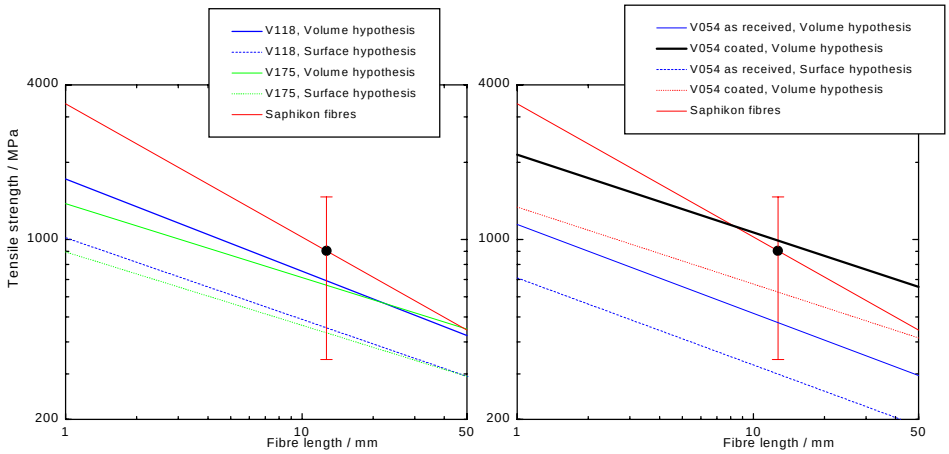


Fig. 6. Tensile strength versus fibre length of Saphikon sapphire fibre extracted from a NI-based matrix and a number of batches of ICM-sapphire-fibres extracted from molybdenum matrix. The data for ICM fibres are obtained in a way which is clear from the above considerations. Those for Saphikon fibres are obtained by using the data presented in Ref.[9]. Note that the strength scatter of the Saphikon fibres yields value of Weibull parameter $\beta < 2$.

ICM FIBRES IN INTERMETALLIC MATRICES

If a composite with a ductile matrix, e.g. an intermetallic matrix at high temperature, is appropriately designed that is the composite fails under loading with fibre break accumulation, then a real contribution to the composite strength is made by short fibre fragments between neibouring breaks. In this case composite strength is determined by the fibre strength on short lengths as well as by the fibre/matrix interface strength. Fabrication, microstructure and strength/failure behaviour of ICM-oxide fibres in Ni_3Al-based matrix are discussed in a paper submitted to ICCM-12 [10].

Experimental data obtained at present show clearly that (i) ICM-oxide-fibres can be introduced to a matrix generated via a liquid-phase route and sufficiently homogeneous fibre distribution can be achieved; (ii) strength characteristics of composites with EFG and ICM fibres should be nealy the same provided a necessary value of the interface strength is achieved.

POSSIBILITIES TO USE ICM FIBRES IN CERAMIC MATRIX

Similar problems arise while ICM-fibres are to be incorporated into a ceramic matrix, those being homogeneous fibre distribution and an appropriate interface microstructure. Obviously, oxide fibres are best suited for oxide matrices. It is known that sufficiently weak interface in oxide/oxide composites can be either of refractory metals [11] or oxides of MXO_4 types (M=La, Y, Nd, X=V, Nb, Ta, P) [12] or mika-like oxides [13]. No principal obstacles are seen to coat ICM fibres with such metals and compounds, although some technical problems encountered. Nevetherless, preliminary experiments performed in the author's group with both molybdenum and $AlPO_4$ show a possibility to use coated ICM fibres in oxide matrices.

An advantage of the molybdenum coating is that it can be used in liquid-phase route of generating the matrix that hopefully will produce the matrix with high mechanical properties. An example of an alumina-based eutectic as a matrix and sapphire-fibre composite produced in such a way is presented in Fig. 7. On the contrary, the oxide coating has advantages of being more resistant to gas corrosion and to be used in a more simple powder-metallurgy route of matrix generating.

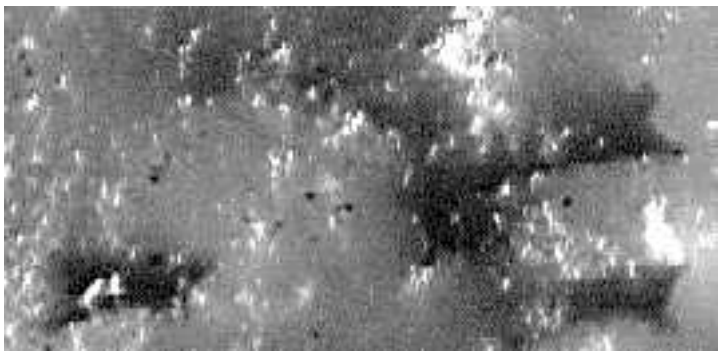


Fig. 7. ICM-sapphire fibres coated with Mo in Al_2O_3-$Al_5Y_3O_{12}$ matrix produced by casting the matrix.

Concerning the strength characteristics of ICM-fibres, they can be considered as satisfactory since design of ceramic-based composites calls for the usage of fibres with defect allowing to trigger a toughening mechanism based on the fibre pull-out [1].

Finally, it should be noted the internal cystallisation can be applied directly to form a fibre system in an oxide matrix containing the channels [14]. However, coating the internal surface with an appropriate material is a problem which remains to be solved.

CONLUSIONS

A variety of oxide fibres can be produced by using the interanl crystallisation method, that is crystallisation of the fibres within pre-made channels in an auxilliary matrix.

The effective strength characteristics of the fibres can be suffiently high to use them in metal, intermetallic, and ceramic matrices.

ACKNOWLEGEMENTS

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