OXIDE FIBRES FOR HEAT RESISTANT COMPOSITES

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ABSTRACT

The internal crystallisation method provides a possibility to produce a family of single crystalline and eutectic oxide fibres suitable to be used as reinforcement for composites aimed at the use at elevated and high temperatures. Each particular composite sets particular requirements to the fibre. For example, metal-matrix composites to be sufficiently creep resistant need fibres strongly bonded to the matrix and, therefore, they are supposed to be strong at small lengths; oxide-matrix composites to be sufficiently crack resistant need fibres, which should be suitable to organise a "weak" fibre/matrix interface and, therefore, they are supposed to be sufficiently strong at much larger lengths.

Recent study that are described in the present paper has shown a possibility to control microstructure and to enhance mechanical properties of fibres of such complex oxides as mullite and yttrium-aluminium garnet as well as a number of oxide eutectics, which have excellent creep properties at temperatures up to about 1600^{o}C. The results can be generalised with an expectation of controlling fibre properties according to requirements of optimising a microstructure of a particular type of the composites.

1. INTRODUCTION

An increasing demand in new materials for elevated and high temperatures does not leave a much choice: there should be developed fibrous composites of various types. Oxide fibres have been always considered as possible reinforcements for metal- and ceramic-based composites. Polycrystalline fibres can be used at temperatures up to about 1200^{o}C. A further increase in the use temperature of ceramic-matrix composites becomes possible with the development of single-crystalline and eutectic fibres. The internal crystallisation method (ICM), which is based on crystallisation of an oxide melt in continuous channels of a molybdenum carcass, while realised in a corresponding fabrication technology allows producing such fibre at a sufficiently low cost to use them in structural applications [1]. At the same time it has been shown that ICM-fibres can be an effective reinforcement for a variety of composites including those with metal [2] and intermetallic [1,3] matrix composites. Each particular composite sets particular requirements to the fibre. For example, metal-matrix composites to be sufficiently creep resistant need fibres strongly bonded to the matrix and, therefore, they are supposed to be strong at rather small lengths; oxide-matrix composites to be sufficiently crack resistant need fibres, which should be suitable to organise a "weak" fibre/matrix interface and, therefore, they are supposed to be sufficiently strong at much larger lengths.

Recent study that are described in the present paper has shown a possibility to control microstructure and to enhance mechanical properties of fibres of such complex oxides as mullite and yttrium-aluminium garnet as well as a number of oxide eutectics, which

have excellent creep properties at temperatures up to about 1600^{o}C. The results can be generalised with an expectation of controlling fibre properties according to requirements of optimising a microstructure of a particular type of the composites.

2. SINGLE CRYSTALLINE MULLITE FIBRES

Obtaining single crystalline mullite in a fibrous form has always been a goal of many research works since it has been considered as the most creep resistant material [4]. Perhaps, the ICM is now the only way to reach the goal [5]. However, obtaining single-phased fibres is still a problem to be solved [6]. Nevertheless, a state of the art of the problem described below allows obtaining high quality fibres that show very high creep resistance.

2.1 Microstructure

Mullite being crystallised from the melt is known to form crystals of the nAl_2O_3:SiO_2 composition with n = 2. To study crystallisation mechanisms of mullite fibres under conditions of ICM, the melts of an initial compositions corresponding to n = 1.5, 1.8 and 2.05 were used [6]. Here we consider a regular microstructure of the fibres produced from the melt corresponding to n = 2.05 (Figure 1).

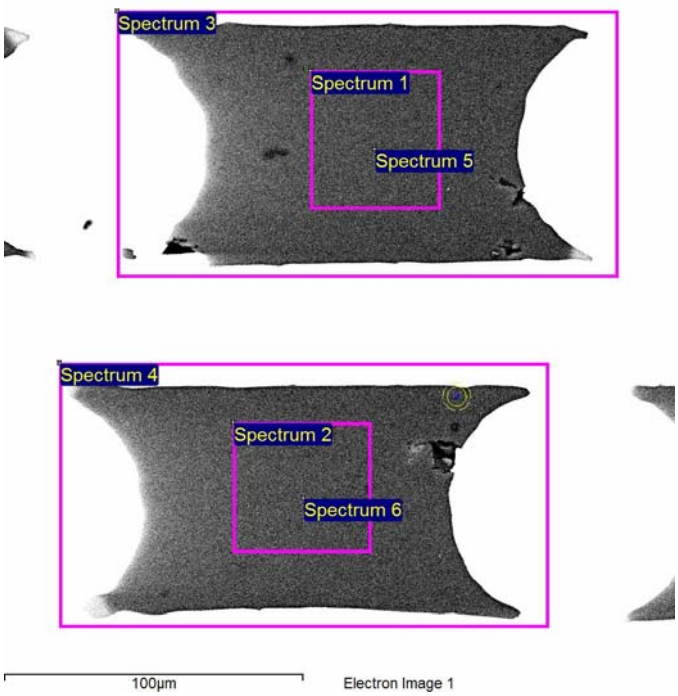


Figure 1. A mullite fibre with a single crystalline body and small glassy phase inclusions at the sharp corners of the cross-section.

X-ray microanalysis shows that the black phase in SEM-pictures has atomic ratio Al/Si slightly higher than that in the initial melt, the value of n is between 2.06 and 2.20. A systematic deviation from the exact molar ratio, 2:1, does not contradict to various phase diagrams published with a rather broad field of the existence of mullite. However, it is not clear what reasons cause this phenomenon. At the same time the fibres contain a “white” phase in the sharp corners of fibre cross sections, which is composed of silica mainly and occurs certainly as a result of radial temperature gradient in a fibre during

crystallisation. A decrease in the value of *n* in the initial melt composition yields obviously an increase in the size of the "white" phase inclusions.

2.2 Creep resistance

The initial composition of the melt affects the creep resistance of the fibres, which was measured by testing mullite-fibre/molybdenum-matrix composite specimens according to a procedure outlined in Ref. [7]. The results are presented in Figure 2. One can see that the creep resistance of single crystalline mullite fibres reaches really high values at a temperature of 1400°C despite the fibres contain silica-based inclusions. These inclusions lower the creep resistance at a temperature of 1500°C. However, it remains sufficiently high.

3. SINGLE CRYSTALLINE YAG ($Y_3AL_5O_{12}$) FIBRES

The Al_2O_3-$Y_3Al_5O_{12}$ system has been studied rather thoroughly [8,9] and now it is well known that an overheating of a melt composed of alumina and silica in the ratio corresponding to $Y_3Al_5O_{12}$ yields formation of perovskite $YAlO_3$ and Al_2O_3. As the authors of Ref. [9] state, formation of solid nuclei of $Y_3Al_5O_{12}$ containing 8 formula units and, correspondingly, 160 atoms is thermodynamically more difficult than that of $YAlO_3$ containing 4 formula units and 20 atoms only. Special features of the ICM described in Ref. [1] make difficult avoiding an overheating of the melt, and this creates a problem in making homogeneous YAG fibres.

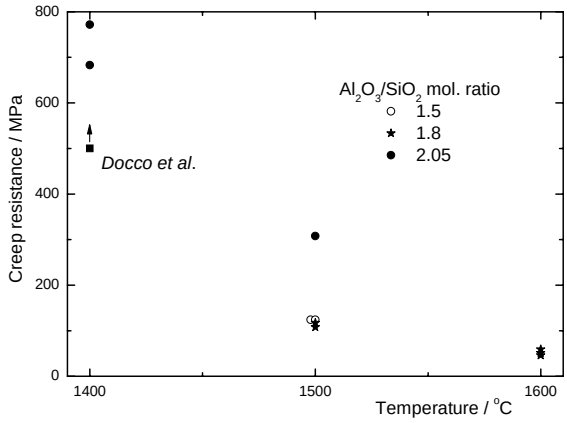
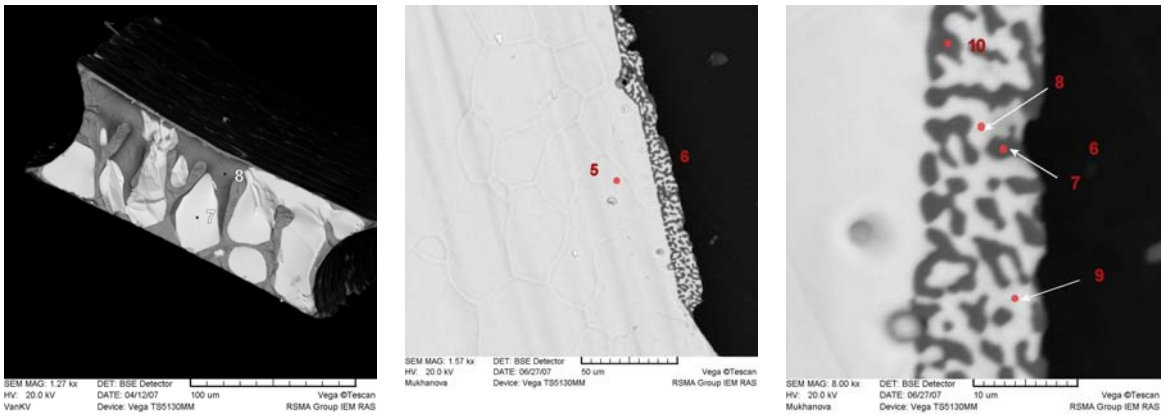


Figure 2. Creep resistance (a stress to cause 1% of creep deformation for 100 h) of mullite fibres with different Al_2O_3/SiO_2 ratio in the initial melt composition versus test temperature. A single point is after Docco et al [4], obtained by testing a bulk crystal.

3.1 Microstructure

The only way to decrease the overheating is to approach the melting by increasing the power supplied to the heaters as slowly as possible and start to pull the oxide/molybdenum block to a cold zone of the furnace as soon as the channels in the block have been infiltrated with the melt. This procedure can be described only qualitatively. Hence, we present the microstructures obtained at regimes **Q** (quick), **S** (slow) and **VS** (very slow). Regime **Q** was realised without any precautions about the overheating, the **S** was carried out with precautions (a slow electric power increasing) and the **VS** was realised in a most accurate way. Characteristic microstructures of the fibres obtained in regimes **Q** and **S** are presented in Figure 3. They are non-

homogeneous; the compositions of the inclusions are given in Table 1. A fibre obtained in the **VS**-regime is composed entirely of garnet, and this proves a possibility to produce pure single crystalline YAG fibres by using the internal crystallisation method.



Q- regime. **S**- regime.

Figure 3. SEM micrographs of fibres obtained in two regimes.

Table 1. Ratios of aluminium to yttrium (atomic %) obtained by the X-ray microanalysis of the fibres in the points shown in Figure 3.

Points	**Q**-regime		**S**-regime			
	7	8	5	8	7	9
Al:Y	1.00	4.13	1.67	2.31	8.81	2.05

The data presented in Table 1 show that fibres obtained in the **Q**-regime are composed of very large perovskite ($AlYO_3$) inclusions ("white" phase, Al:Y = 1) and Al_2O_3-$Y_3Al_5O_{12}$-eutectic matrix. The Al:Y ratio in "grey" phase corresponds to a eutectic point in published phase diagrams [8].

A fibre obtained in the **S**-regime is composed mainly of garnet; two-phased inclusions are pushed out to the coldest areas of the fibre cross-section during crystallisation, which are located at the corners surrounded by molybdenum. The composition of these inclusions is possibly that of the Al_2O_3- $Y_3Al_5O_{12}$ eutectic one, see Table 1, despite the accuracy of the measurements of chemical composition in points 8 and 9 is non-sufficient due to a small characteristic size of the microstructure as compared to the characteristic size of the excitation band of a characteristic X-ray radiation.

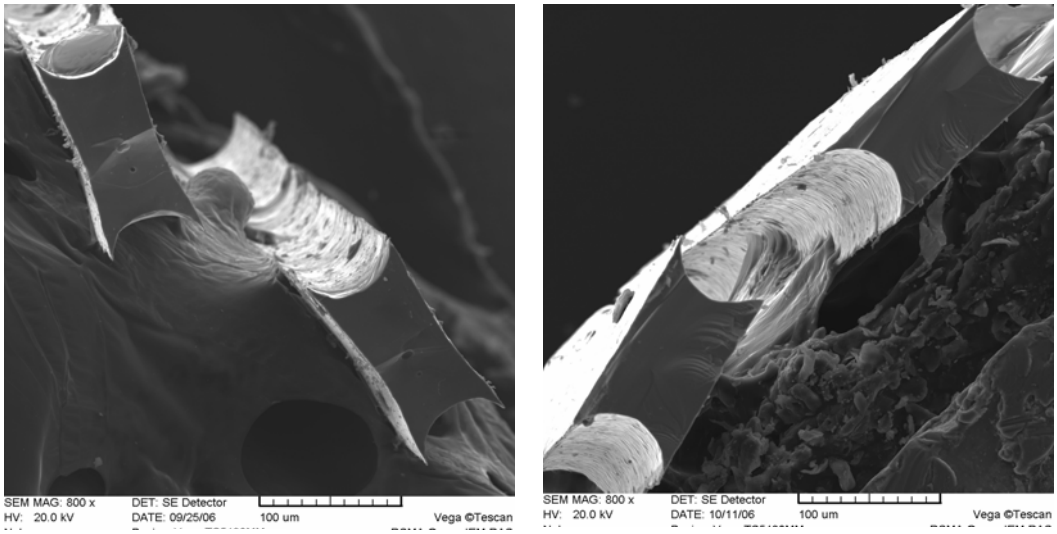
3.2 Strength and creep resistance

Fibres obtained by the internal crystallisation method have non-circular cross-section; hence, it is convenient to measure the fibres strength by bending a fibre over a series of rigid cylinders of decreasing diameters and counting an average distance between fibre breaks on each step of the experiment [10].

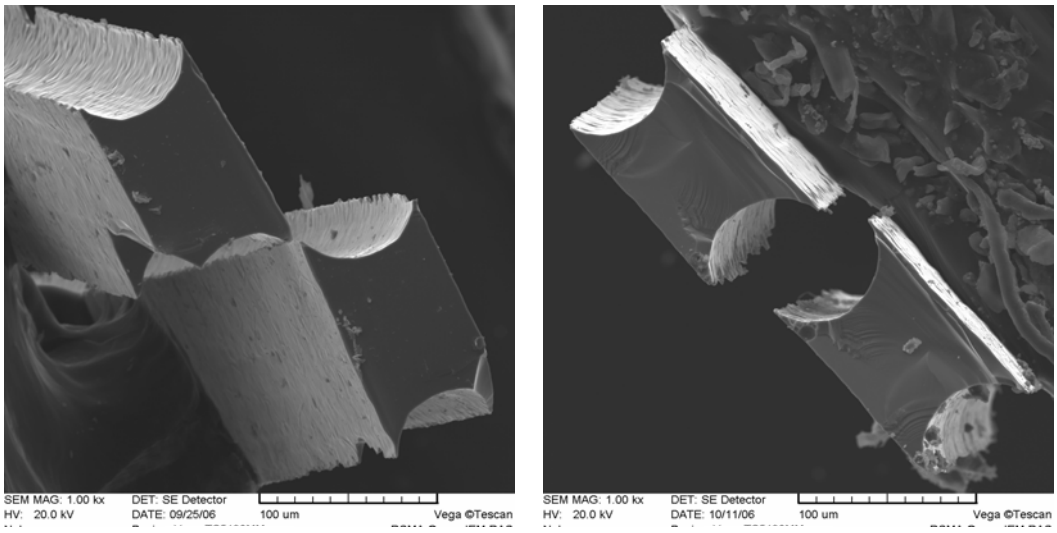
Low values of fibre strength σ_f^*, from about 300 MPa at a length of 10 mm to about 1000 at a length of 1 mm, measured previously [11] means that the fibres contain rather large defects. If an average value of critical stress intensity factor K^* for single

crystalline YAG is assumed to be 2 MPa·m$^{-1/2}$ [12] then an order of the magnitudes of size c, $c \approx \left(\frac{K^*}{\sigma_f^*} \right)^2$, of a crack-like defect should be microns.

Traces of such kind of defects can be seen on failure surfaces of a fibre broken at four sites at different fracture stresses, Figure 4. A site with the lowest fracture stress, 40 MPa, has the trace of a pore on the failure surface, which has certainly arisen during crystallisation of the fibre. Despite it locates at the centre of the cross section of the fibre tested in bending, it could affect the fracture being just a nuclei of a larger crack arose during cooling. The value of the fracture stress yields an estimation of a characteristic size of the crack of about the size of the fibre cross-section.



$\sigma_f^* \approx 40$ MPa $\sigma_f^* \approx 260$ MPa



$\sigma_f^* \approx 210$ MPa $\sigma_f^* \approx 730$ MPa

Figure 4. Four failure surfaces of a fibre of block V0800. Both sides of each failure site are shown. Also the fracture stresses are indicated.

A relief of the failure surface of site with the fracture stress 260 MPa reveals a feature along a plane external surface of the fibre extended for about 10 μm, which can be

considered as a defect. The next failure site, $\sigma_f^* \approx 210$ MPa, reveals an inclined plane at a corner of the failure surface, which can be a boundary of a eutectic inclusion similar to that shown in Figure 3 (the fibre obtained in the **S**-regime). A similar sharp stress concentrator can be seen just outside of the failure site. Such sites can be assumed to nest the eutectic inclusions. Finally, the strongest site, $\sigma_f^* \approx 730$ MPa, uncovers similar defects.

The stress concentrations arisen at the vicinity of the defects can be amplified by permanent stresses in a fibre that built up during cooling as a result of a radial temperature gradient. Therefore, annealing fibres in homogeneous temperature field should increase the fibre strength. The annealing effect occurs to be quite pronounced as can be seen in Figure 5: annealing the fibres at 1950°C for 1 h followed by slow cooling yields an essential increase in the average fibre strength at lengths between 10 and 100 mm. At lower lengths, about 1 mm, the increase in the fibre strength is much less.

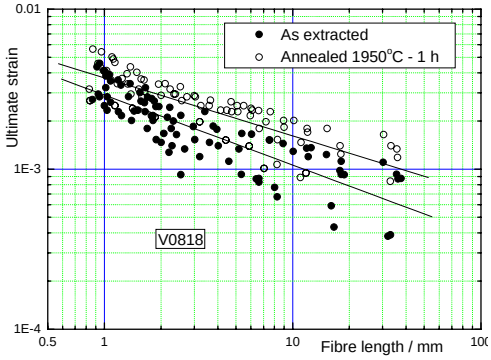


Figure 5. Ultimate strain versus fibre length for as extracted and annealed YAG fibres.

Creep resistance of fibres with orientation of the fibre axis along the <100> crystal direction presented in Figure 6 is slightly lower than that of mullite fibres (Figure 2).

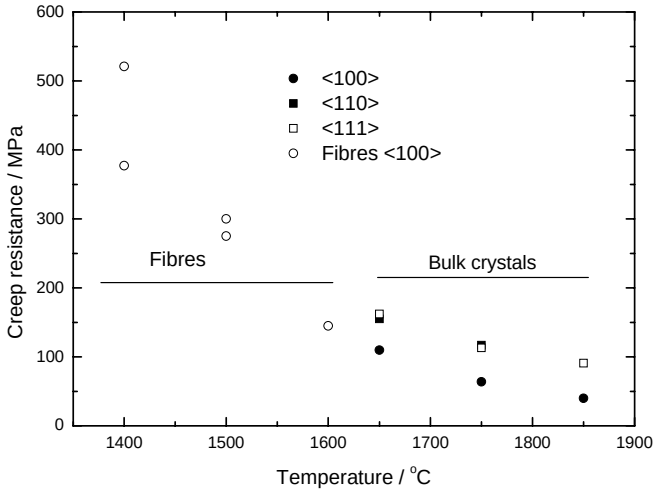


Figure 6. Temperature dependence of the tensile creep resistance of ICM-YAG-fibres in comparison with that of bulk crystals [13].

4. EUTECTIC FIBRES

Eutectic fibres (Al_2O_3-$Re_3Al_5O_{12}$ and Al_2O_3-$MeAlO_3$ (here Re and Me stand for Y or lanthanouid elements), which have been obtained by using ICM, are characterised by lower strength scatter than those of homogeneous oxides, compare for example Figure 7 and Figure 5 [14]. The figures just mentioned illustrate higher strength of garnets as compared to perovskite.

Obviously, a characteristic size of the eutectic microstructure decreases with increasing the crystallisation rate (see Figure 8). There have been not obtained systematic data on an affect of the crystallisation rate on the fibre strength; however, preliminary data presented in Figure 9 give a hope to optimise the fabrication technology to reach maximum strength characteristics.

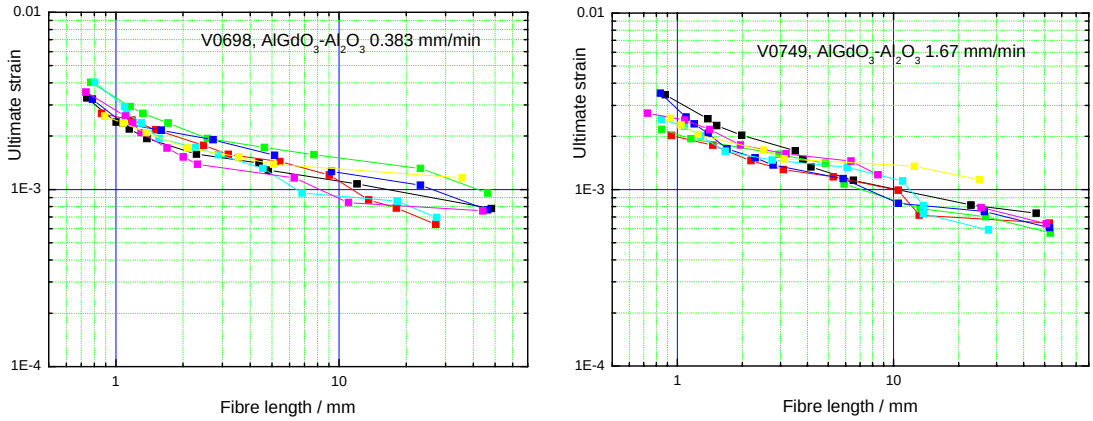
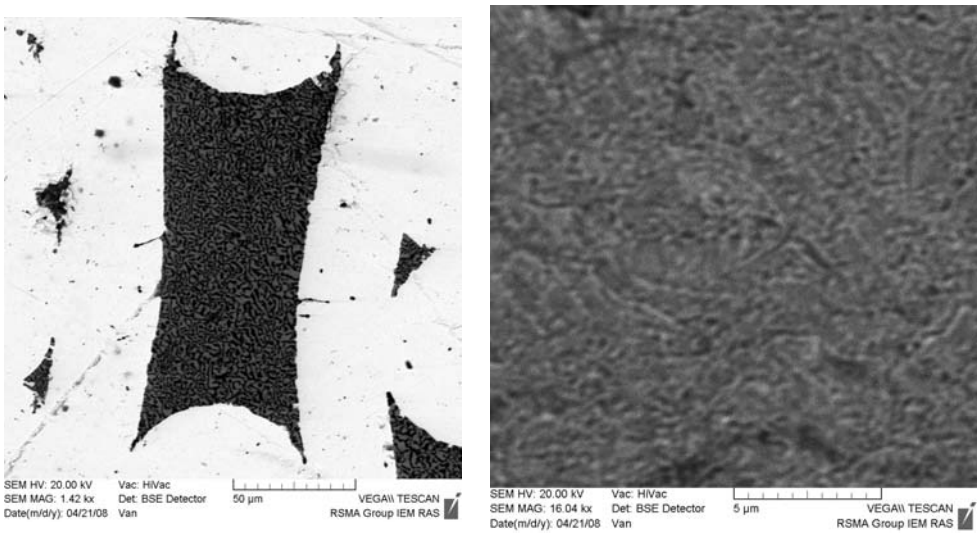


Figure 7. Ultimate-strain/length dependencies for $AlGdO_3$-Al_2O_3 eutectic fibres crystallised with pulling rate of 0.383 and 1.67 5 mm/min.



S0172 2 mm/min S0174 220 mm/min

Figure 8. The microstructure of Al_2O_3-$Y_3Al_5O_{12}$-eutectic fibres crystallised with rates 2 and 220 mm/min.

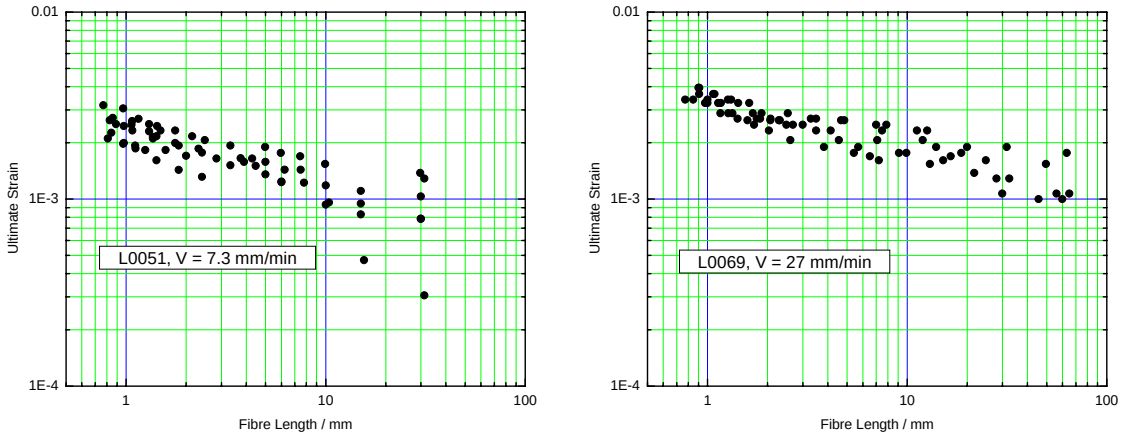


Figure 9. Ultimate-strain/fibre-length dependence for Al_2O_3-$Y_3Al_5O_{12}$-eutectic fibres crystallised with different rates 7.3 and 27 mm/min. Characteristic sizes of the microstructure of the fibres are ~10 and 5 μm, respectively.

5. THE MAIN CONCLUSION

Recent results obtained in studying single crystalline and eutectic fibres produced by using the internal crystallisation method have revealed a high sensitivity of the fibre microstructure and their mechanical properties on fabrication conditions. This means a possibility to control fibre properties adjusting them to particular requirements set by a particular composite.

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