

Influence of Firing Temperature and Time on the Quantitative Phase Formation and Recrystallization Behaviour of High Temperature Glass Fibres (AES) and Refractory Ceramic Fibres (RCF)

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Introduction

Commercially available fibre materials are in use for several industrial high temperature applications. In recent times high temperature glass fibres (HTGF) on the base of alkaline earth silicates are produced to substitute refractory ceramic fibres (RCF).

Differential thermal analyses show that recrystallization of RCF starts at 980°C with exothermal reactions and mullite formation. The crystal size varies between 0.02 µm for low alumina contents (30 wt.-%) and 0.1 µm for higher alumina contents. The devitrification causes an enrichment of the residual melt with SiO₂, above 1050°C starts the precipitation of cristobalite [1]. The fibre materials of the system CaO-MgO-SiO₂ show a different crystallization behaviour which has not been objected in particular.

Literature data differs between various types of cristobalite. Theoretically the precipitated cristobalite type is supposed to be of the α-modification, studies show that the high-temperature β-modification occurs as well at room-temperature which is distorted by impurity ions and stacking disorders [2]. The crystallization velocity of fibre materials is dependant on temperature, atmosphere, duration of the thermal treatment and the amount of the impurities.

Due to the devitrification the fibre surface becomes more roughly which is mainly caused by the formation of cristobalite crystals [3]. Small crystal sizes after heat treatment lead to a better thermal resistance of the fibres. Following crystal growth up to dimensions of the fibre diameter and long exposure times cause the destruction of the fibre structure and material failure occurs [4].

Properties like shrinkage and resilience behaviour of HTGF which are important for the industrial application show higher increases nearby their classification temperature due to their higher biopersistence adjusted chemical composition than conventional RCF products [5]. Thus even small thermal overload in the event of malfunctions of the furnace may lead in use of HTGF to failure of the fibre lining [6].

Cristobalite formation is detected after operating temperatures above 900°C but differs in quantity due to the chemical composition of the fibre.

These studies have focused on the phases present when RCF and AES have been heat treated at temperature and time coordinates within the ranges of 1050 to 1250°C and 24 h to 500 h exposure times.

Materials

Different commercially fibre wool samples were chosen for these studies. The material AES 1 and MS represent the HTGF / AES wools based on the system CaO-MgO-SiO₂ and MgO-SiO₂. The RCF group is given by the used fibre materials RCF 1260, RCF 1400 and RCF 1430 Z which have their main components in silica and alumina. The chemical composition of the materials in as-received state is given in

table 1. Fig. 1 and 2 show the phase diagrams CaO-SiO₂-MgO and MgO-SiO₂-Al₂O₃, the compositions of the samples AES 1 and MS are marked.

Experimental

To determine the devitrification behaviour of fibres with different raw material compositions differential scanning calorimetry (DSC) measurements have been performed where 20 mg powder of as-received fibres were compacted in a platinum crucible and heated up with a rate of 10 K/min. The used fibre types for these measurements are AES 1, MS and RCF 1260.

In addition fibre samples with a size of 100 mm x 100 mm x thickness of the blanket were then exposed at selected temperature and time coordinates within the range 1050 to 1250°C and 24 h to 500 h in an electric heated chamber furnace. Due to their higher classification temperature the fibre samples RCF 1400 and RCF 1430 Z were just exposed to the temperatures of 1250°C in time steps between 24 and 500 h.

After the thermal treatment XRD-analysis were performed to determine and identify the development of phases. Further quantitative phase analysis concerning the formation of cristobalite have been performed using an internal standard method with a calibrated cristobalite standard where a reference material has to be added in the same proportion to every sample.

Finally SEM analysis of every heat treated fibre sample have been made to regard the temperature and time dependant crystal growth on the fibre surface.

Table 1: Chemical analysis of the used fibre materials

Material	AES 1	MS	RCF 1260	RCF 1400	RCF 1430 Z
[wt.-%]					
Al ₂ O ₃	0,51	1,59	45,32	53,75	29,12
SiO ₂	64,29	76,48	54,05	46,02	52,89
Fe ₂ O ₃	0,39	0,37	0,04	0,03	0,07
TiO ₂	0,27	0,04	0,02	0,04	0,06
CaO	28,54	0,31	0,03	0,08	0,03
MgO	5,74	20,84	0,25	< 0,01	< 0,01
K ₂ O	0,08	0,23	0,01	< 0,01	< 0,01
Na ₂ O	0,01	0,05	0,10	< 0,01	< 0,01
ZrO ₂	-	-	-	-	17,20

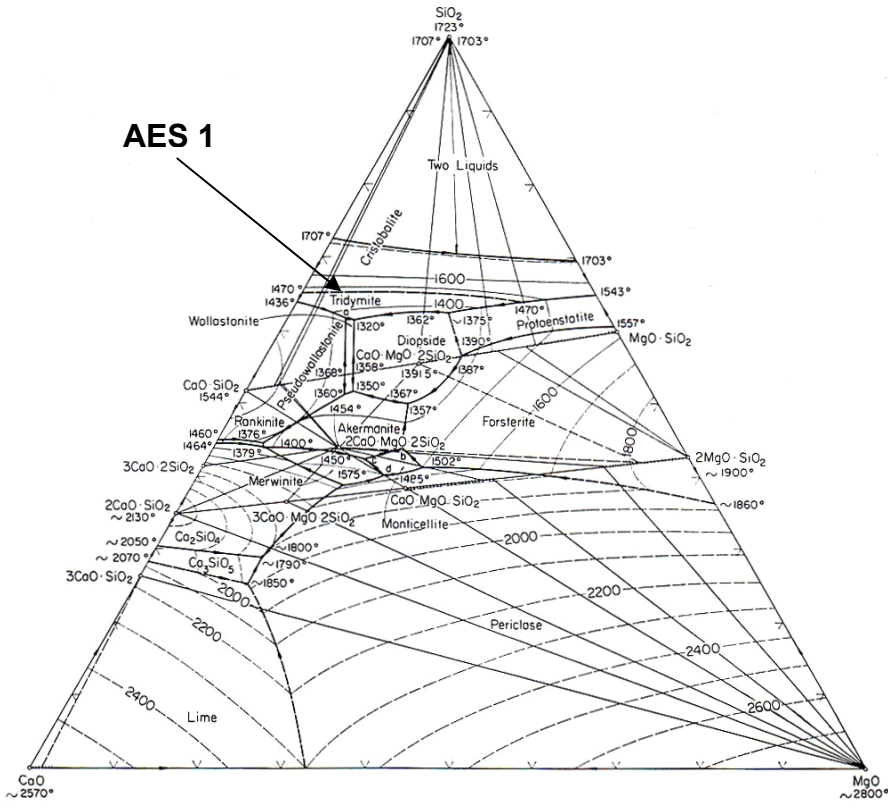


Fig. 1: Phase diagram CaO-SiO₂-MgO, composition of the sample AES 1 is marked

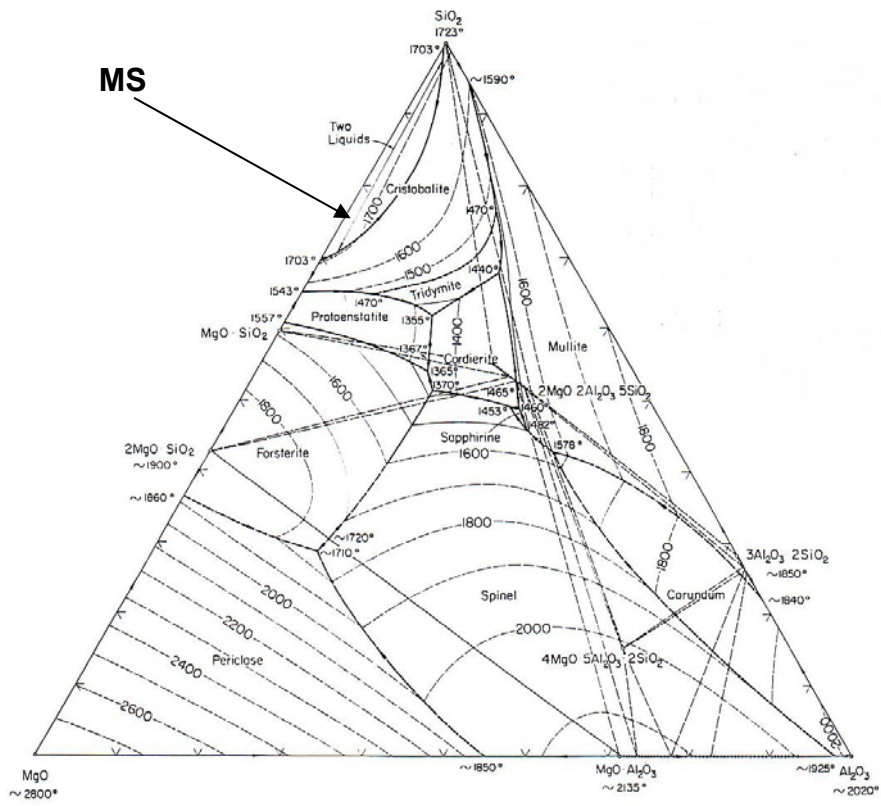


Fig. 2: Phase diagram MgO-SiO₂-Al₂O₃, composition of the sample MS is marked

Results

Differential scanning calorimetry (DSC)

The results for the DSC measurements of the fibre samples AES 1, MS and RCF 1260 are given in fig. 3. Regarding the onset of crystallization leads to the result that the MS type shows the earliest devitrification with a maximum peak at 894.7°C. MS fibres reveal the greatest peak area of all tested materials which means that the temperature range of crystallization is 43 K. The AES 1 material starts to devitrify at 890°C and has its maximum at 921.8°C. The material representing the refractory fibres, RCF 1260, starts its crystallization in these studies at 985°C which is in agreement with results of earlier DTA studies. The peak maximum of the RCF 1260 sample was measured at 999.3°C. The small temperature range for the crystal phase formation of the RCF 1260 was determined to 15 K.

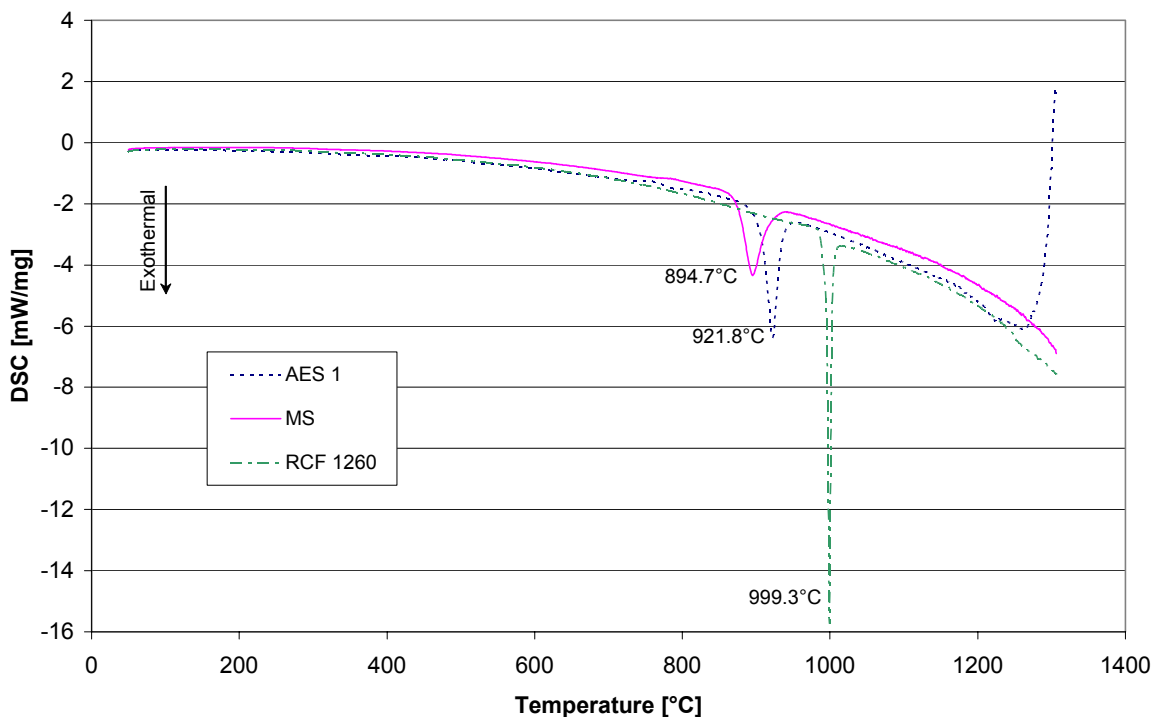


Fig. 3: DSC measurements of the fibre types AES 1, MS and RCF 1260

Phase formation and quantitative cristobalite formation

Exposed to high temperatures the used fibres reveal an assemblage of mixed, complex crystalline phases.

The qualitative phase formation after 24 h heat treatment shows that the devitrification of the AES 1 fibre types commences much below 1000°C. At 1000°C a strong intensity for an amorphous phase is regarded as well as for wollastonite [CaSiO₃]. Diopside [CaMg(SiO₃)₂] was measured in a weak concentration. At higher temperatures (1200°C) the wollastonite peak lowers in intensity and a strong intensity of cristobalite can be recognized. This phase assemblage with weak intensities for diopside and wollastonite and a strong intensity for cristobalite was found up to 1300°C. The amorphous phase disappeared at 1200°C.

The influence of the variation of the time and temperature coordinates on the quantitative crystal phase formation of cristobalite for the fibres type AES 1 is given in fig. 4. In general the cristobalite formation is time dependant for the experiments at

different temperatures between 1050 and 1250°C. The tendency of the qualitative XRD measurements of higher cristobalite amounts after exposure to higher temperatures can be seen as well. The biggest steps can be recognized between 1050 and 1100°C where the cristobalite amount increases from 1.5% up to 12.5% and between 1100 and 1250°C with increasing values up to 20% after 250 h. The time coordinates show that the establishment of the crystal phase has mainly taken place after 100 h since the values show small deviation up to 500 h.

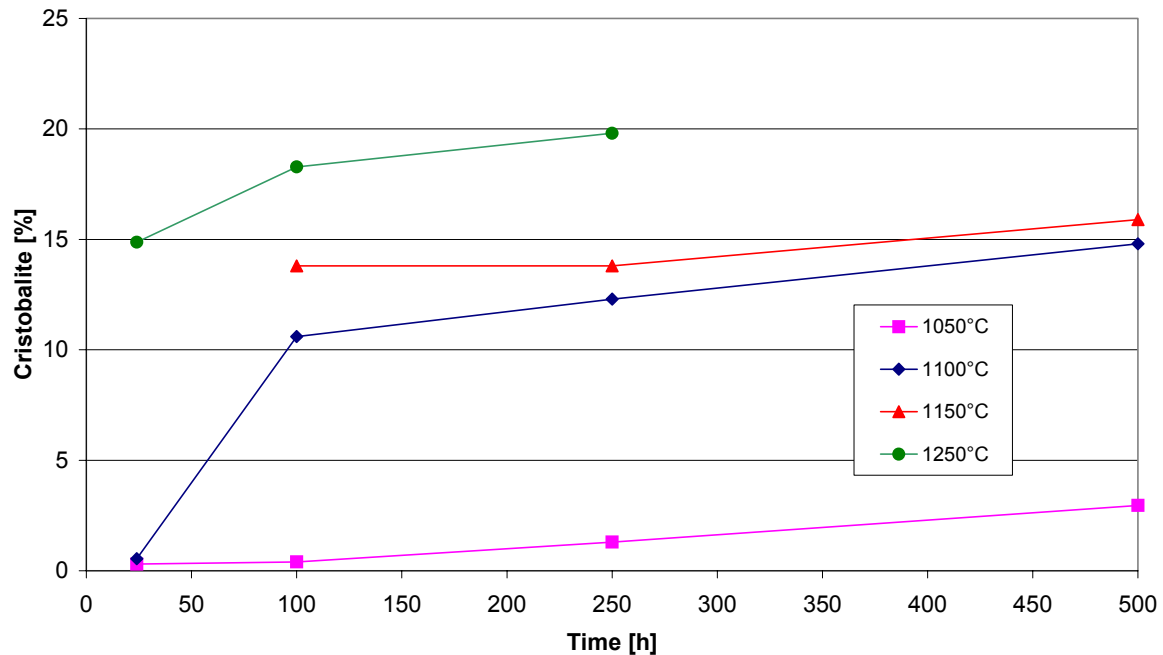


Fig. 4: Time and temperature dependant amount of cristobalite formation of AES 1

The XRD measurements after 24 h exposure time for the fibres of MS type reveal a strong intensity for clino-enstatite [MgSiO_3] next to a very high amount of amorphous phase. The devitrification for the fibre of MS type occurs very rapidly since at 1100°C a strong intensity of crystal silica in form of cristobalite is measured. Disappearance of the amorphous phase and a decreasing amount of clino-enstatite can be regarded. The stable phases up to a temperature of 1400°C are cristobalite (strong intensity) and newly formed proto-enstatite [MgSiO_3] (middle intensity).

The results of the quantitative XRD measurements are in very close correlation to the qualitative 24 h experiments. For the MS fibre type the cristobalite values show a very little scatter due to variation of time and temperature (Fig. 5). At 1050°C an amount of 25% cristobalite has been measured after 100 h. Higher temperatures cause an increase in cristobalite formation up to values of 27.5% (1100°C) and 32.5% (1250°C) after 24 h. The relative fast kinetic for the cristobalite formation for this fibre type can be seen at the steep increase of cristobalite formation between 24 and 100 h exposure time at 1050°C.

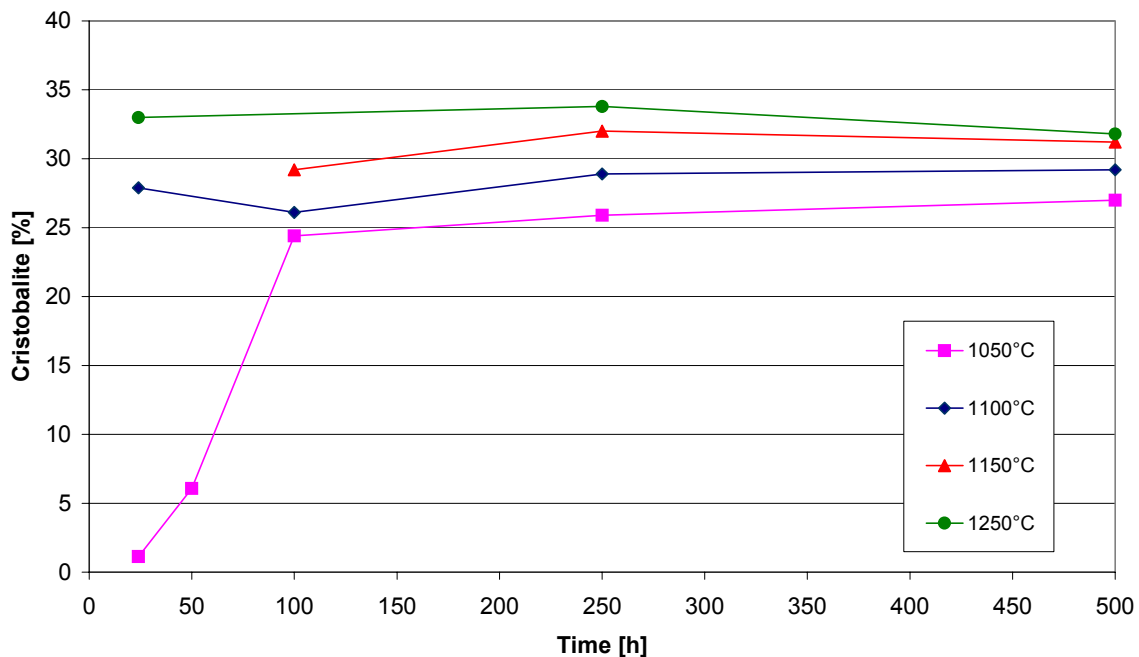


Fig. 5: Time and temperature dependant amount of cristobalite formation of MS

The formation of crystal phases in strong intensities starts for the fibres of RCF 1260 type at 1200°C with the formation of mullite $[3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2]$. This phase shows very strong intensities up 1350°C. At this temperature cristobalite formation has occurred and a strong intensity can be measured. Nevertheless a very high amount of amorphous phase can be found up to a temperature of 1300°C.

Fig. 6 shows the quantitative results of the phase formation of cristobalite for RCF 1260. In agreement to the qualitative XRD measurements RCF 1260 fibres show no devitrification and crystallization to cristobalite below 1100°C. At 1100 and 1150°C no cristobalite has been precipitated after 100 h exposure times of the samples. After 500 h cristobalite has been measured in quantities of 2.5 and 2.7% at 1100 and 1150°C. Between 1150 and 1250°C an increase of crystallization takes place which leads to cristobalite values of 11% after 250 h and 12.5% after 500 h at 1250°C.

The RCF 1400 fibre type with a higher amount of alumina reveals a similar crystallization behaviour after the 24 h experiments shifted to different temperature ranges. The mullite formation occurs for the RCF 1400 fibre below 1000°C. Cristobalite reaches middle intensities in maximum at 1350°C. The amorphous phase nearly disappears at this temperature.

The RCF 1400 fibre type with a higher alumina content reveals lower cristobalite values after heat treatment at 1250°C. The value increases from non detection after 24 h up to 2.5% after 250 h (Fig. 7).

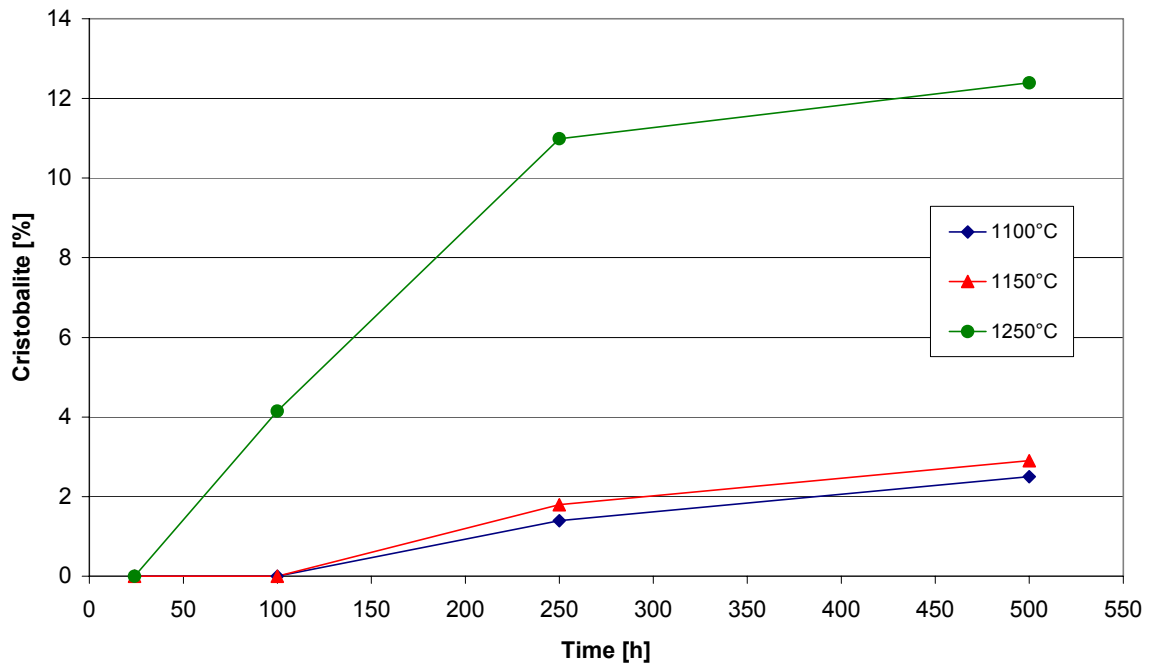


Fig. 6: Time and temperature dependant amount of cristobalite formation of RCF 1260

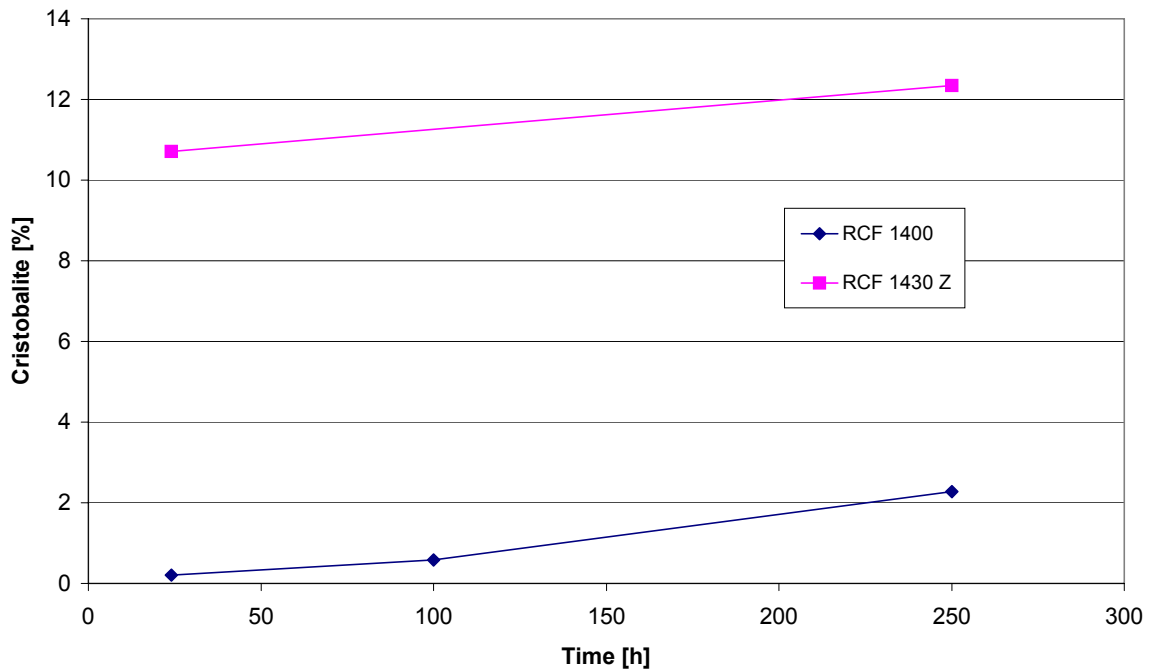


Fig. 7: Time dependant amount of cristobalite formation of RCF 1400 and 1430 Z at 1250°C

The addition of $ZrSiO_4$ to the mullite composition of the fibre type 1430 Z leads to a different crystal phase formation. The amorphous phase shows lower intensities after 1100°C since mullite, zirconia and cristobalite are precipitated in comparable amounts. At 1200°C the RCF 1430 Z fibre reveals a XRD pattern with middle

intensities of cristobalite, mullite and zirconia [ZrO₂] with no variations up to a temperature of 1500°C.

Fig. 7 demonstrates that the establishment of crystal phases in particular cristobalite for the fibre RCF 1430 Z shows a fast kinetic since after 24 h a stable amount of 11% was found after a temperature of 1250°C. Longer exposure times up to 250 h cause no changes in the quantities of phase formation.

Determining devitrification by SEM

The examination of the fibre materials by SEM reveals for the AES 1 fibre type both: Micro structural changes due to time and temperature. At 1050°C the fibre surface becomes more rough which is more obvious after an exposure time of 100 h. A temperature increase of 50 K up to 1100°C leads to significant round crystals of 2 µm diameter on the fibre surface (Fig. 8). Longer exposure times at this temperature strengthen the effect of the temperature since the fibres become more brittle. These changes in the microstructure are recorded for small as well as for large fibre diameters. Effects of first sintering could be regarded after an exposure of 100 h at 1150°C leading to a decreasing elasticity of this fibre type (fig. 9).

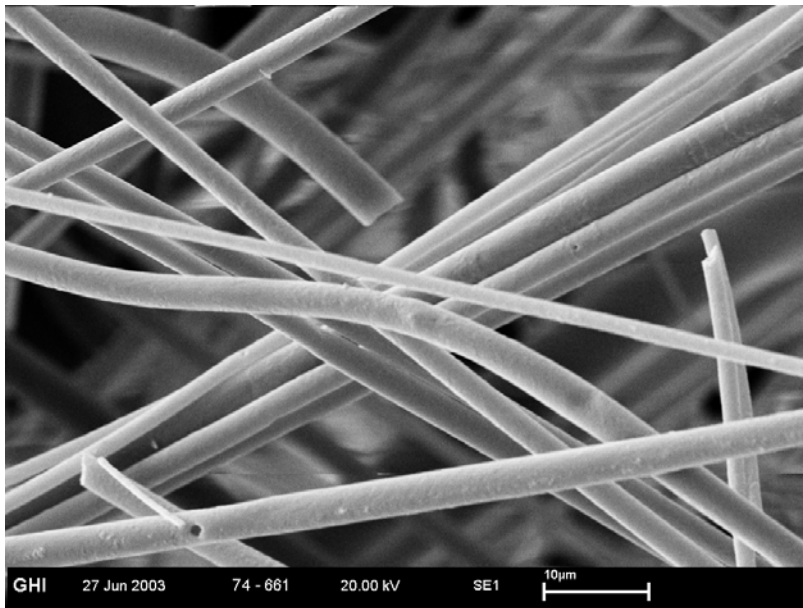


Fig. 8: Fibre type AES 1 after 1100°C / 100 h

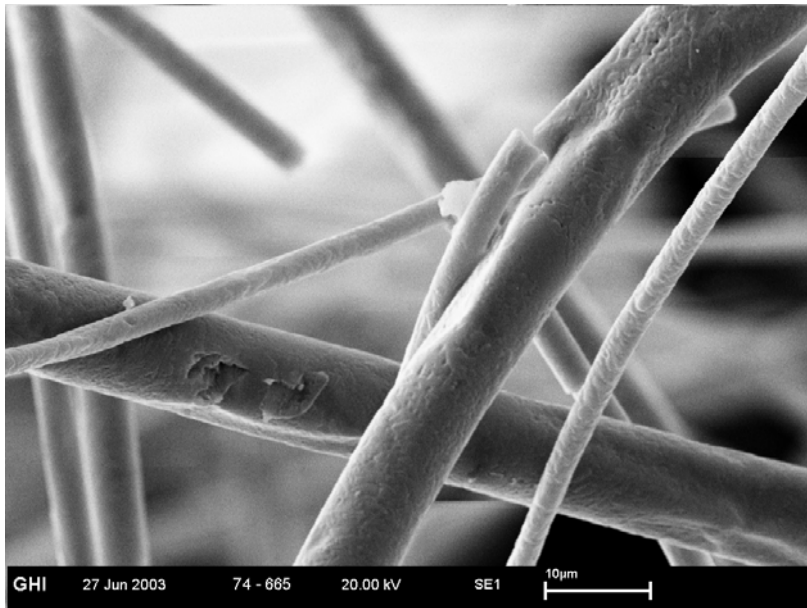


Fig. 9: Fibre type AES 1 after 1150°C / 100 h

First changes in the microstructure of the MS fibre type can be registered at 1050°C where the fibre surface is no longer even, at 1100°C this becomes more significant. Exposure times below 100 h seem to have no influence on the roughness of the fibres since an uneven surface cannot be regarded using shorter periods. Crystal growth occurs for this fibre type at 1150°C starting at the fibres of small diameter after 24 h. After 100 h at 1150°C the whole fibre structure shows crystallization on the surface and in some case bending of fibre parts can be recognized (Fig. 10). Exposure times of 250 h at 1150°C lead to a crystal growth up to 3 μm which means in some case the fibre diameter. A further temperature increase of 100 K up to 1250°C leads to a fully recrystallized fibres with crystal sizes on the fibre surface between 5 and 7 μm independent of the fibre diameter.

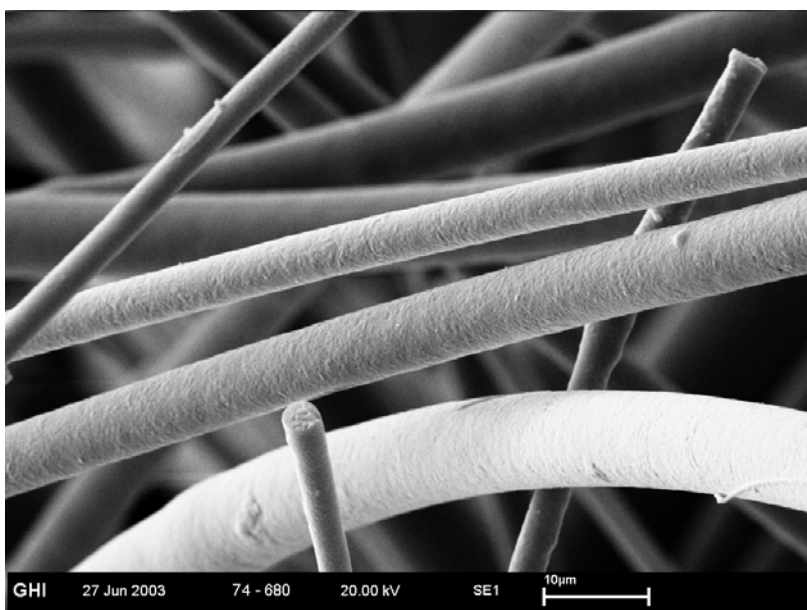


Fig. 10: Fibre type MS after 1150°C / 100 h

At its classification temperature of 1250°C the RCF 1260 material shows no surface roughness, changes in diameter or crystal growth (Fig. 11). Also higher temperatures up to 1550°C reveal no indication for massive crystal growth on the fibre surface. This is independent of the fibre diameter although the brittleness and the shrinkage of RCF 1260 increase at these temperatures leading to a significant loss in the fibre diameter (Fig. 12).

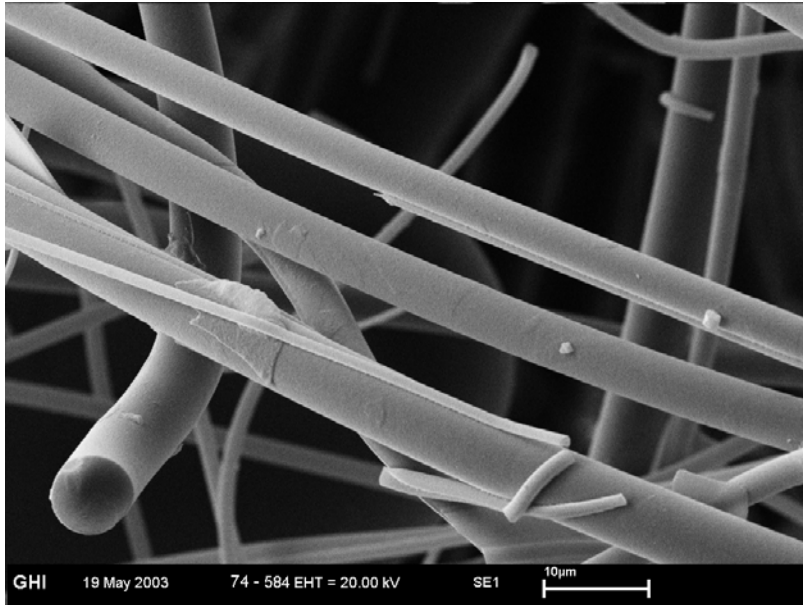


Fig. 11: Fibre type RCF 1260 after 1250°C / 500 h

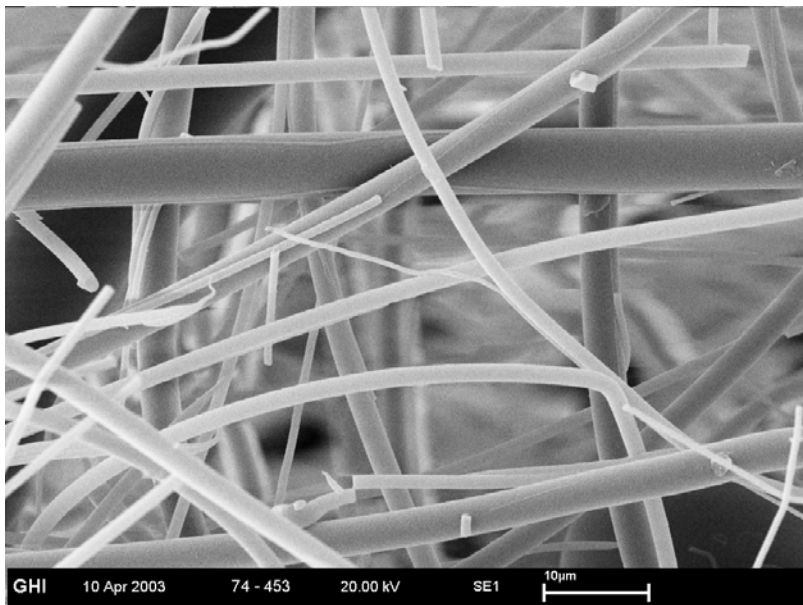


Fig. 12: Fibre type RCF 1260 after 1550°C / 100 h

Discussion and conclusion

The results of the XRD measurements and the SEM experiments show good correspondence in registration of the devitrification of the fibres used for these studies. Since the influence of the recrystallization on the thermo physical and thermo mechanical properties are different the correlations have to be discussed for each fibre type in particular. The classification and maximum use temperature have also to be taken into consideration.

If small temperature ranges or short time periods are needed for the formation of crystal phases the resulting changes in structure and properties lower the performance of the fibre lining. The overload of temperature will then lead to poorer thermal properties or material's failure.

Fibre type AES 1

The temperature range for a recognizable cristobalite formation lies between 1050 and 1100°C for this fibre type which is a high but reasonable temperature range for this material [7]. The formation becomes obvious with a steep increase after 100 h at 1100°C up to 11% (fig. 4). Enhancing the application temperature leads then to higher amounts of cristobalite but since wollastonite is established in fairly high intensities the cristobalite formation is limited (fig. 1). The chemical composition leading to a lower classification temperature can also be seen as a result of the formation of crystals on the fibre surface what becomes very obvious in fig. 8 and at higher temperatures (fig. 4 and 9). The good correspondence of the XRD measurements and SEM experiments can be recognized in the continued crystal phase formation with an enhanced brittleness of the fibres at 1100°C. After 100 h at 1100°C and after 24 h at 1150°C the steep increase in the cristobalite intensity is registered along with more rough fibre surfaces with starting and establishing crystallization.

Fibre type MS

Fig. 5 demonstrates the kinetic aspect of cristobalite formation at elevated temperatures very well. The value rises from 1% after 24 h up to nearly 25% after 100 h at 1050°C. Higher temperatures lead to higher values between 27 and 33% after 24 h. In difference to the AES fibre type the MS material is supposed to formulate high amounts of cristobalite due to its chemical composition and the resulting position in the phase diagram (fig. 2).

The high amount of crystal phase after heat treatment above 1100°C can also be regarded by the SEM observation. The SEM experiments reveal uneven surfaces and a growing brittleness of the fibre structure (fig. 10). The mainly influenced material properties are shrinkage and resiliency. Recrystallization coming along with crystal phase formation at temperatures of 900°C with mainly silica phases and an increased crystal growth (1150-1250°C) lowers these properties as a consequence.

Fibre type RCF 1260

In these studies no important amounts of cristobalite were found at temperatures below 1250°C which is mainly overlapped by the formation of mullite as a consequence of the higher alumina content. Remarkable is the relatively slow kinetic of the cristobalite formation at 1250°C showing a steeper increase in a time range of 250 h (fig. 6). Similar to the appearance of low amount of crystal phases at elevated temperatures by XRD the SEM experiments reveal shrinkage as the main change

within the fibre structure. At the classification temperature (1250°C) the fibre surface still has an even habit, at 1550°C the fibres show mainly shrinkage behaviour without having enormous crystal growth on the surface (fig. 11 and 12).

Fibre types RCF 1400 and RCF 1430 Z

The low cristobalite content of the fibre type RCF 1400 after 250 h at 1250°C has its origin in the chemical composition of the material with an alumina content of 53.75%. The qualitative XRD measurements named mullite the major phase from 900 up to > 1300°C.

The addition of zircon to the Al₂O₃-SiO₂ system leads to crystal phases of cristobalite after 24 h at 1250°C in quantity of 11%. The disintegration of zircon followed by the a formation of cristobalite is a possible mechanism of this appearance.

The shrinkage and resilience behaviour are not influenced in a negative way since fibres type RCF 1400 and RCF 1430 Z showed the best values of RCF materials in other studies [5]. Also the fibre structure has not been changed in its main constitution. The above described mechanisms of crystal growth and the distinct and measurable consequences of devitrification are shifted to higher temperature ranges.

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