Bull. Mater. Sci. (2019) 42:154
https://doi.org/10.1007/s12034-019-1839-8

Reaction of $YBa_2Cu_3O_{7-x}$ (YBCO) and fused silica in YBCO glass fibres

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MS received 16 November 2018; accepted 27 December 2018; published online 13 May 2019

Abstract. This work introduces the first reported experiments on drawing $YBa_2Cu_3O_{7-x}$ (YBCO) into fibres with a fused silica cladding using a fibre draw tower to manufacture YBCO glass fibres. These fibre draw experiments allowed manufacturing fibre sections with core diameters between 50 and 200 μm and a length of around 1.2 m. However, reactions between the fused silica cladding and the YBCO core were revealed by the fibre drawing process. Therefore, this study focusses on investigating these reactions (in as-drawn fibres as well as after additional heat-treatments) using energy dispersive spectroscopy analyses on an environmental scanning electron microscope as well as using X-ray photoelectron spectroscopy analyses and a cross-polarized light study. The results showed the formation of silica precipitations inside the as-drawn YBCO core, forming an interface layer between the core and the cladding regions, as well as the presence of a high silicon content inside the core with a possible silicate formation. Additional heat-treatments have shown the formation of silica and copper oxide co-precipitations at 900°C. In addition, heat-treatments at higher temperatures have shown the occurrence of further reactions, which led to a degradation of the core and the formation of new phases.

Keywords. $YBa_2Cu_3O_{7-x}$; YBCO core glass fibres; YBCO–silica reaction phases; superconductor wires.

1. Introduction

Owing to the growing need for higher efficiency in electrical applications, various research efforts have focussed on proposing new superconductive materials that can achieve such efficiency goals. To this end, a promising material that has been proposed in the literature is the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ (YBCO) [1]. YBCO introduces various advantages to many industrial applications. Possessing a critical temperature at around $T_c = 93\,K$ [1], YBCO can be cooled with liquid nitrogen, as opposed to the more expensive liquid helium which complicates the application of superconductors.

In many industrial applications, such as power transmission lines, it is highly advantageous to manufacture superconductors in a wire/tape design. This has led to the introduction of the so-called second generation high-temperature superconductor wires, which are based on a complex tape structure using a YBCO superconductive material or other rare earth cuprate superconductors [2,3]. However, this complexity introduces efficiency challenges in the manufacturing process which restricts utilizing such tape structures for mass production and highlights the need for new and more efficient YBCO wire/tape designs.

To this end, we investigate the possibility of manufacturing long-scale glass fibres with a superconductive YBCO core inside a fused silica cladding, using a fibre draw tower. Owing to its manufacturing efficiency and resulting in large scale fibre lengths, such a design would introduce various advantages in terms of mass production and applicability to various industrial domains.

Previous work by our group [4–7] showed that it is possible to draw superconductive YBCO, bismuth–strontium–calcium copper oxide and tin powders as well as a lead wire into glass fibres using a glass working lathe. These studies proved the possibility of manufacturing glass fibres with a superconductive core. However, the drawn fibre lengths were restricted to a short scale due to the limited working distance of the glass working lathe as detailed in ref. [4]. Therefore, due to the lack of scalability, fibre manufacturing using the glass working lathe can only be used as a preliminary method of assessing the feasibility of the proposed drawing process.

Hence, in this paper, we propose drawing long-scale commercially applicable YBCO fibres using a fibre draw tower. In this respect, the drawn fibres consist of a fused silica cladding with a YBCO core. This drawing method introduces a number of advantages in terms of enabling economically efficient long-scale manufacturing of YBCO glass fibres.

However, drawing YBCO fibres at the draw tower also introduces a set of new challenges. In this regard, during the drawing process at the draw tower, the YBCO powder inside the fused silica preform is exposed to high temperatures over a longer period of time, as compared to the glass working lathe. A longer dwelling time at high temperatures is generally

necessary to soften and draw the thicker fused silica preform into a fibre on the draw tower. Subsequently, the occurrence of reactions between YBCO and silica can lead to difficulties during the drawing process. Reactions between YBCO and silica powders [8–12] and YBCO films on silica substrates, were reported in the literature [13–18], considering temperatures of up to 1000°C. However, no existing work in the literature has studied the reactions within YBCO glass fibres. In addition, to the best of our knowledge, no studies are reported to this point, in which YBCO and silica are exposed to temperatures above 1000°C. Our studies include results from temperatures as high as 2000°C, to which the YBCO glass fibre is exposed during the fibre drawing process.

Hence, this work is the first to provide an in-depth investigation and characterization of the reaction phases of YBCO and silica within a YBCO fibre structure, as well as the first study to consider YBCO and silica reactions at these elevated temperatures. In this respect, the main goal of this paper is to characterize and study the reactions which occur between YBCO and silica in a YBCO fibre at elevated temperatures. This understanding is indispensable in reducing or controlling such reactions, which will, as a result, potentially enable the successful manufacturing of large-scale superconductive YBCO fibres. In fact, first attempts to measure the resistance on the obtained fibre sections were not successful, which indicates the existence of an insulation character of the fibre core. In this regard, an in-depth analysis of the YBCO and silica reaction were performed on as-drawn YBCO fibres and on as-drawn YBCO fibres with additional heat-treatments at different temperatures using energy dispersive spectroscopy (EDS) on an environmental scanning electron microscope (ESEM) and X-ray photoelectron spectroscopy (XPS) analyses. Further analyses on the heat-treated fibre cross-sections were also performed under cross-polarized light using an optical microscope. The performed analyses show the existence of pure silica precipitations inside the core, leading to the formation of an interface layer between the as-drawn YBCO core and the cladding region, as well as a high silicon content inside the core region with possible silicate formation. The additional heat-treatments also show the formation of silica and copper (I)-oxide co-precipitations inside the core, following a 900°C heat-treatment, as well as the occurrence of additional reactions, leading to the degradation of the core and the formation of yttrium–barium-rich and barium–copper-rich phases, following heat-treatments at 1000 to 1200°C.

2. Experimental

For this study, different-sized fused silica tubes from Technical Glass Products Inc. were used to manufacture the fused silica preforms. The fused silica tubes were overclad with successively larger tubes to produce a thick-walled glass preform by using a glass working lathe, Litton Model HSJ143. Several preforms were prepared and tested; the final preforms' outer diameter varying from 10 to 25 mm and the inner diameter (ID) varying between 1 and 3 mm. Furthermore, different tapering techniques were used to reduce the ID, so that only a small quantity of YBCO powder is exposed to the high temperatures in the hot-zone of the furnace, while softening the preform. Afterwards, the obtained fused silica preforms were filled with commercially available superconductive orthorhombic YBCO (Y-123) powder with a particle size of 2–6 μm, which was purchased from SSC Inc.

After the filling process, the YBCO preform was subsequently drawn into YBCO core glass fibres [19,20] on the fibre draw tower, which was equipped with a graphite furnace. The furnace was steadily heated up to temperatures of around 2000°C to soften the fused silica. This softening process required a time period of around 30 min, during which the YBCO powder that is closest to the hot-zone was exposed to the highest temperatures.

Following the drawing process, cross-sections of the as-drawn fibre samples were polished with successively finer diamond lapping films down to 0.1 μm and characterized with an ESEM, FEI Quanta 600 FEG. EDS for chemical composition point analysis and mapping was performed with an attached Bruker QUANTAX 400 energy dispersive X-ray spectrometer with a high speed silicon drift detector at an accelerating voltage of 20 kV. XPS, PHI Quantera SXM, was performed on an as-drawn fibre cross-section. Furthermore, additional heat-treatments were performed on a set of selected YBCO fibre sections in air at 800–1200°C with heating and cooling rates of 5°C min^{-1} and a dwelling time of 10 min using a standard tube furnace, MTI Corporation Model GSL-1100X, and a muffle furnace, Barnstead Type 1500, for the 1200°C heat-treatment. The additional heat-treatments were performed to further analyse the reactions between the YBCO core and the silica cladding. The heat-treated fibre cross-sections were also studied using an ESEM and under cross-polarized light using an optical microscope, Olympus BX51.

3. Results and discussion

3.1 *Results on as-drawn fibres*

Using the described drawing method in section 2, continuous round-shaped and dense YBCO core fibre sections were successfully drawn, as can be seen in the backscattered-electron (BSE)-image in figure 1 with a length of up to 1.2 m.

The length of the fibre sections is limited by a number of challenges encountered during the drawing process, due to primarily reactions occurring between YBCO and silica. In this respect, in-depth analyses on the drawn fibres were performed to characterize and further understand these reactions.

EDS analyses were performed to primarily study the YBCO core. The obtained EDS data, for the centre of the core, are shown in table 1.

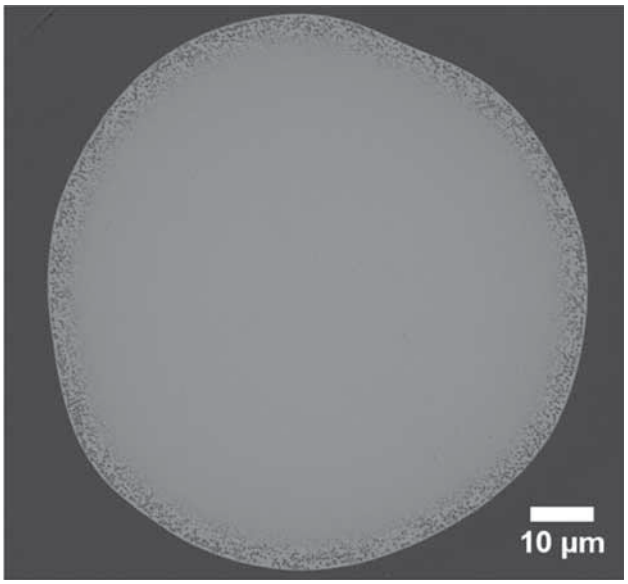

Figure 1. BSE-image of the YBCO core (light grey) of an as-drawn fibre cross-section surrounded by the silica cladding (dark grey).

Table 1. EDS point analysis on the centre of the YBCO core shown in atomic percentage.

Element	Y	Ba	Cu	O	Si
At.%	3.26	5.52	9.34	62.73	19.16

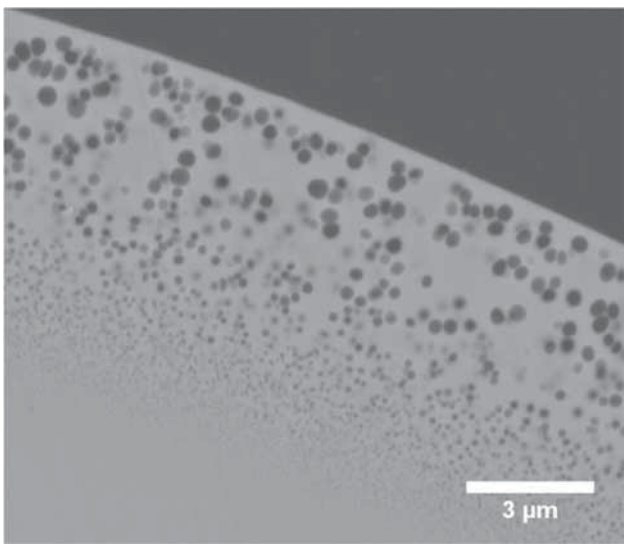

Figure 2. BSE-image of the interface layer between the YBCO core (light grey) and the silica cladding (dark grey) of an as-drawn YBCO fibre cross-section.

The EDS data in table 1 show that in addition to yttrium, barium, copper and oxygen, silicon is also present in the core with a relatively high atomic percentage. To further investigate the presence of silicon in the core, the cladding and core regions were studied using higher magnification BSE-imaging as shown in figure 2.

In this regard, figure 2 shows the presence of an interface layer between the cladding and the core regions. This interface layer is shown in figure 2 and contains round precipitations which decrease in size towards the centre of the core and indicate the occurrence of a diffusion process during the fibre drawing process. To investigate the nature of these precipitations, EDS point analyses were performed, which demonstrate that the precipitations are rich in silicon and oxygen with a 1:2 ratio as seen in table 2.

Table 2 also shows low percentages of yttrium, barium and copper. However, this is due to the large excitation volume of X-rays. Hence, the EDS point analysis results shown in table 2 indicate the presence of pure silica precipitations in the formed interface layer. In addition, further EDS analyses showed that the silicon content decreases towards the centre

Table 2. EDS point analysis on a dark precipitation at the interface layer shown in atomic percentage.

Element	Y	Ba	Cu	O	Si
At.%	1.07	2.23	3.55	61.82	30.79

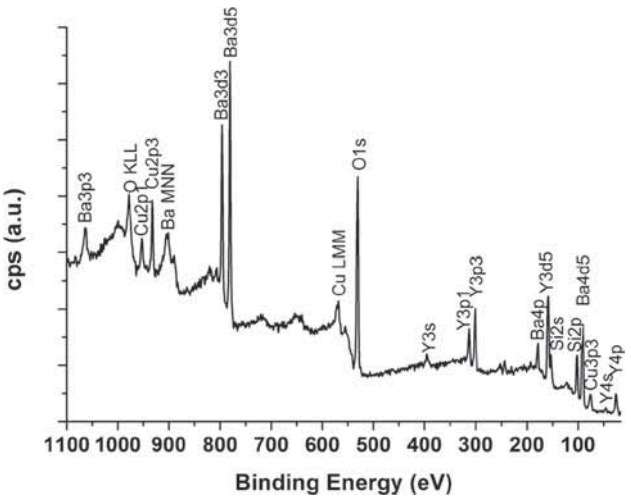

Figure 3. XPS overview spectrum of a sputtered as-drawn YBCO core surface.

Table 3. XPS analysis on the centre of the as-drawn YBCO core shown in atomic percentage.

Element	Y	Ba	Cu	O	Si
At.%	10.1	5.6	5.3	59.8	19.3

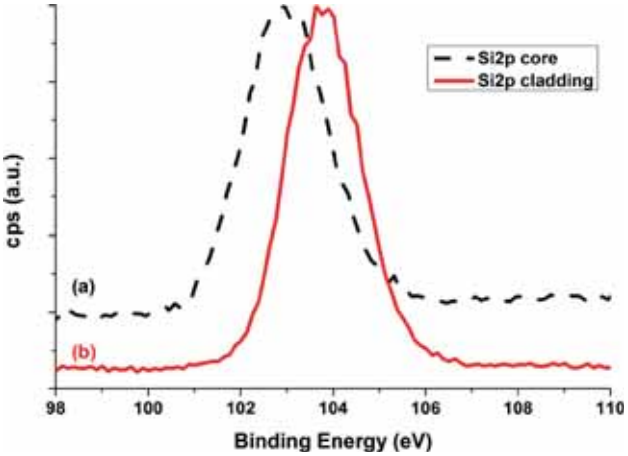

Figure 4. Normalized XPS Si2p peak of the high resolution scan on the non-sputtered surface of (**a**) the YBCO core (black dashed line) and (**b**) the silica cladding (red solid line).

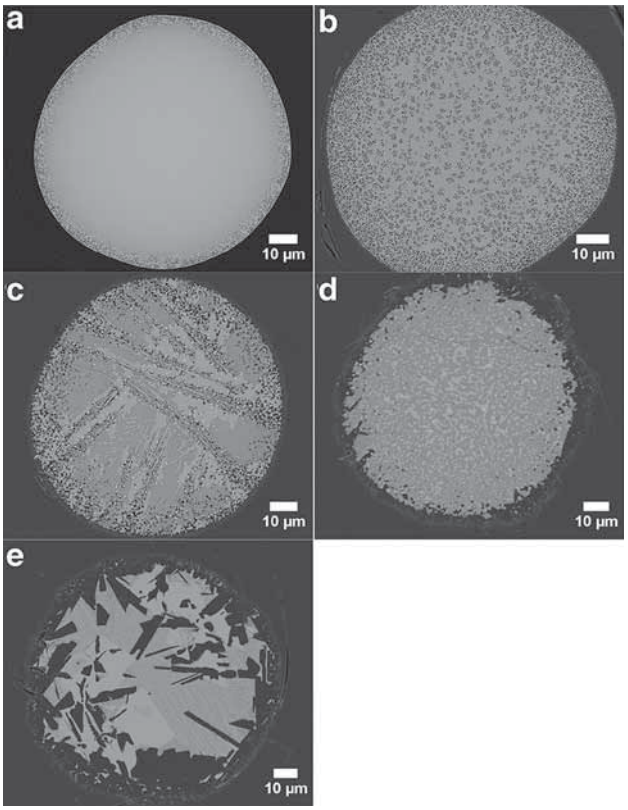

Figure 5. BSE-images of YBCO fibre cross-sections heat-treated at (**a**) 800, (**b**) 900, (**c**) 1000, (**d**) 1100 and (**e**) 1200°C for a dwelling time of 10 min in air.

of the YBCO core. This is an indication of the occurrence of silicon diffusion from the cladding inside the core. In fact, previous analyses [14–18] reported the diffusion of silicon from the silica substrate into a YBCO layer on a silica substrate. As

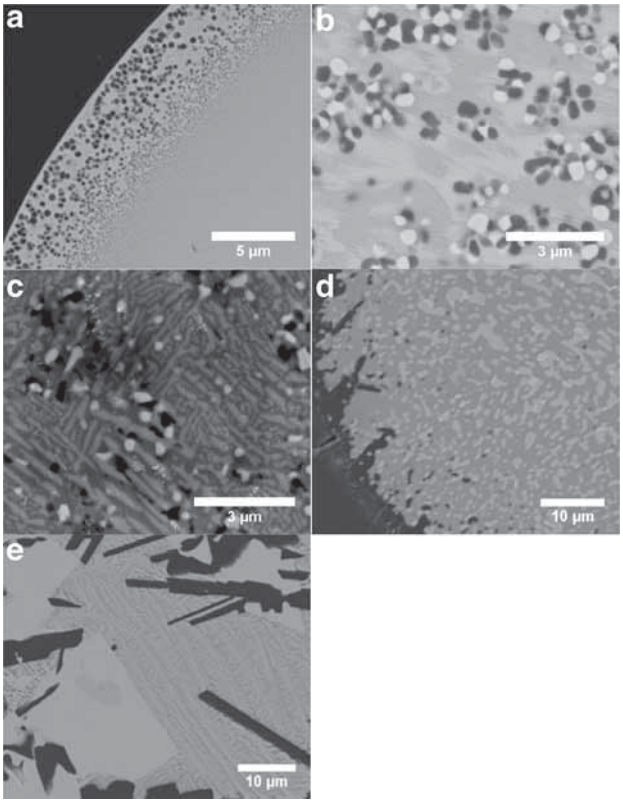

Figure 6. Higher magnification BSE-images of YBCO fibre cross-sections heat-treated at (**a**) 800, (**b**) 900, (**c**) 1000, (**d**) 1100 and (**e**) 1200°C for a dwelling time of 10 min in air.

such, such a diffusion process appears to manifest in YBCO fibres also.

In this respect, the silicon diffusion inside the core indicates that the presence of the pure silica precipitations inside the as-drawn YBCO glass fibre core, shown in figure 2, is not due to a silica diffusion process during the drawing process, but rather due to a reaction between the diffusing silicon and oxygen. In fact, since silicon diffuses inside the core and oxygen can potentially diffuse/dissolve from the silica cladding during the drawing process into the core (and vice versa), this could lead to the formation of the silica precipitations. In this regard, excess of oxygen at the interface layer can thermodynamically favour the formation of silica precipitation. Indeed, the formation of silica precipitations was also suggested in silicon optical fibres (silicon core/silica cladding) [21] during the fibre drawing process.

To further study the silicon content inside the core, XPS analyses were performed on an as-drawn YBCO fibre section. For these XPS studies, overview spectra of the cladding and the core were recorded with a spot size of 50 µm. In addition, the fibre cross-section was sputtered layer by layer (∼100 nm) to remove any surface contaminations. The XPS spectrum of the core after sputtering is shown in figure 3. The result of the XPS analysis shown in table 3 confirms the presence of silicon inside the core (19.3 at.%).

Table 4. EDS point analysis on the lighter and darker co-precipitations in the YBCO core, heat-treated at 900°C for a dwelling time of 10 min under air, shown in atomic percentage.

Element	Y	Ba	Cu	O	Si
Darker (At.%)	1.38	1.47	9.51	58.08	28.86
Lighter (At.%)	1.04	1.45	44.22	41.76	10.56

To investigate the nature of this silicon content, a high resolution scan of the Si2p peak was performed in the cladding and the core regions, as shown in figure 4, to determine whether silicate formation occurred, for which the Si2p peak is broader and shifted as described in ref. [22]. The high resolution scan was performed on the non-sputtered surface so that no bonding information is lost due to the sputtering process. In this regard, figure 4 shows that broadening and shifting of the Si2p peak occurred. The Si2p peak of the cladding region has a binding energy of 103.6 eV, which corresponds to the

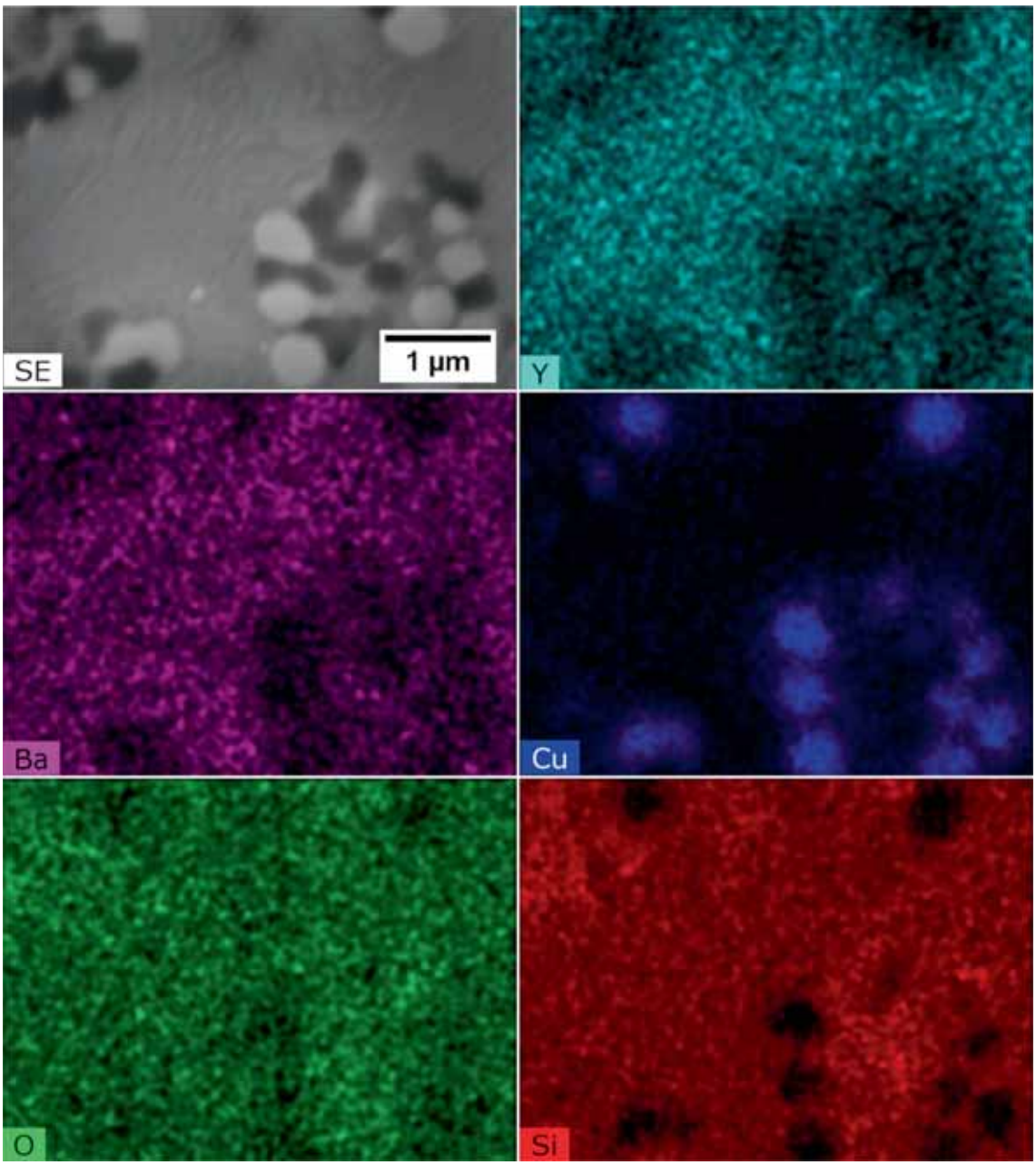

Figure 7. EDS mapping of the co-precipitations inside the YBCO core heat-treated at 900°C for a dwelling time of 10 min in air (scale bar = 1 µm).

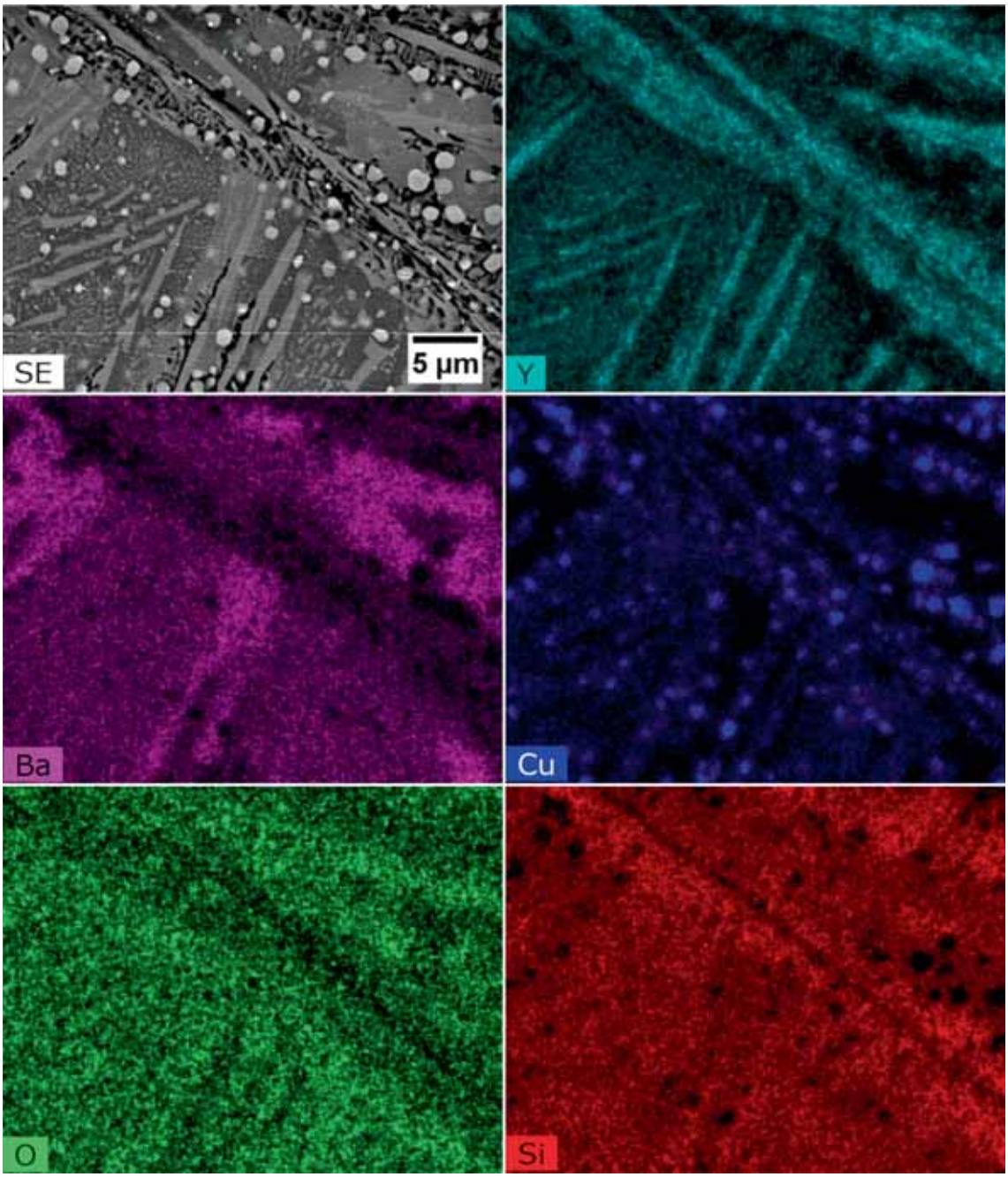

Figure 8. EDS mapping of the YBCO core heat-treated at 1000°C for a dwelling time of 10 min in air (scale bar = 5 µm).

binding energy of pure silica [22]. On the other hand, the binding energy of the Si2p peak of the core region is shifted to lower binding energies and lies around 102.9 eV. Furthermore, it is visible that the Si2p peak of the core region is broader as compared to the peak of the cladding material. Hence, this shifting and broadening indicate the formation of silicate inside the core, which, as a result, confirms that silicon diffusion occurs.

Here, we note that the difference in atomic percentages of yttrium, barium and copper, measured with EDS and XPS, can be due to different phases inside the core region.

3.2 *Results of heat-treated fibres*

To further study the reactions between the silica cladding and the YBCO core, heat-treatment studies on as-drawn

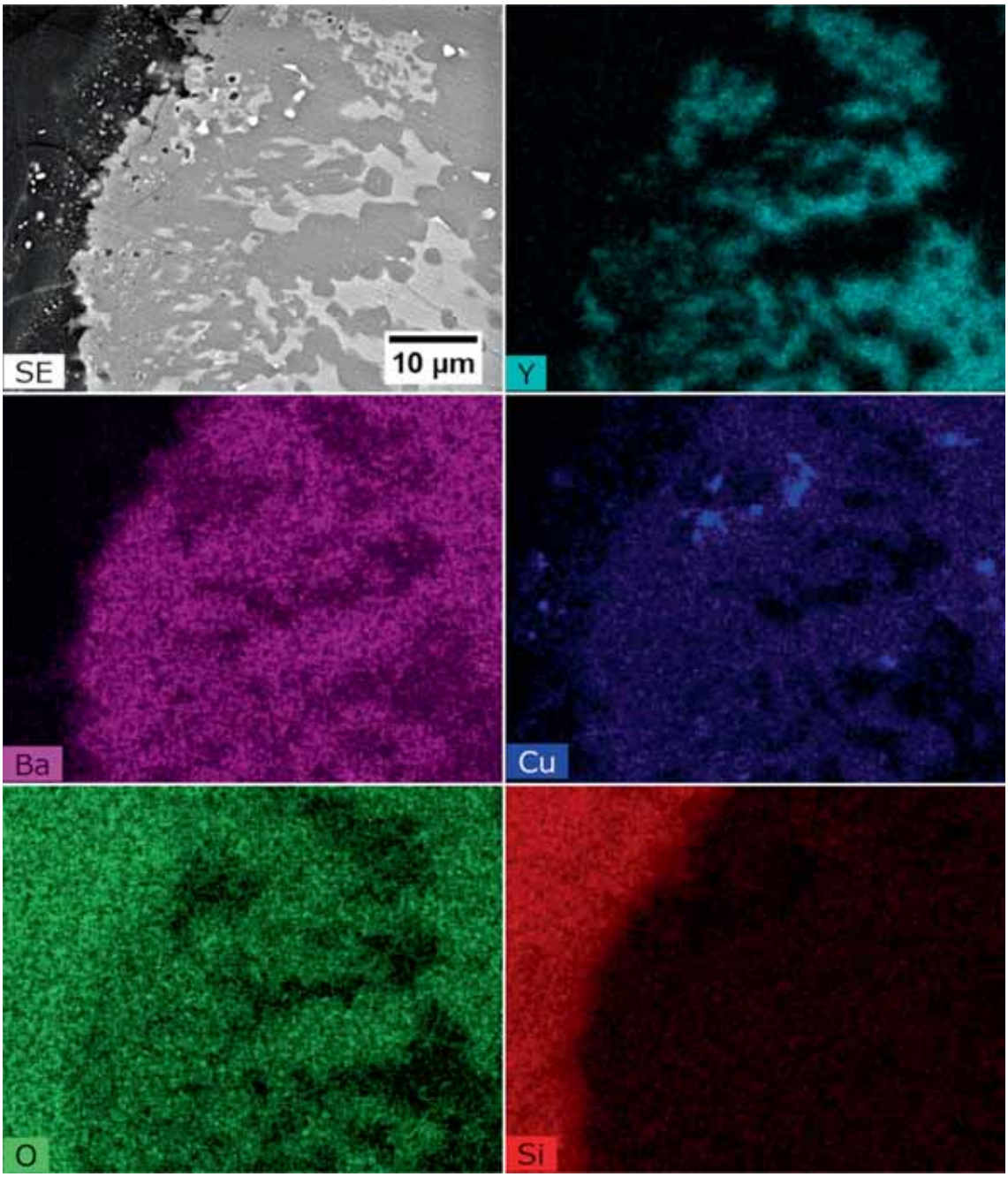

Figure 9. EDS mapping of the YBCO core heat-treated at 1100°C for a dwelling time of 10 min in air (scale bar = 10 µm).

YBCO fibre sections were performed at elevated temperatures. In this regard, BSE-images of the reaction profile of the YBCO core, heat-treated at temperatures between 800 and 1200°C for a dwelling time of 10 min with heating and cooling rates of 5°C min^{-1} in air, are shown in figures 5 and 6.

The BSE-images, in figures 5 and 6, show no significant change in the silica precipitation layer at 800°C as compared to the as-drawn fibre shown in figure 1. However, at 900°C, it can be observed that co-precipitations are formed in the entire core. Moreover, at 1000°C, these co-precipitations start reacting and forming new phases. At 1100°C, the sharp interface between the cladding and the core disappears. In addition, it is shown in figure 6 that more than one phase is present in the matrix at 900 and 1000°C, which form a lamellar structure.

To analyse the precipitations and phases formed, EDS point analysis was performed on the heat-treated fibres. The EDS point analysis of the co-precipitations, which formed at

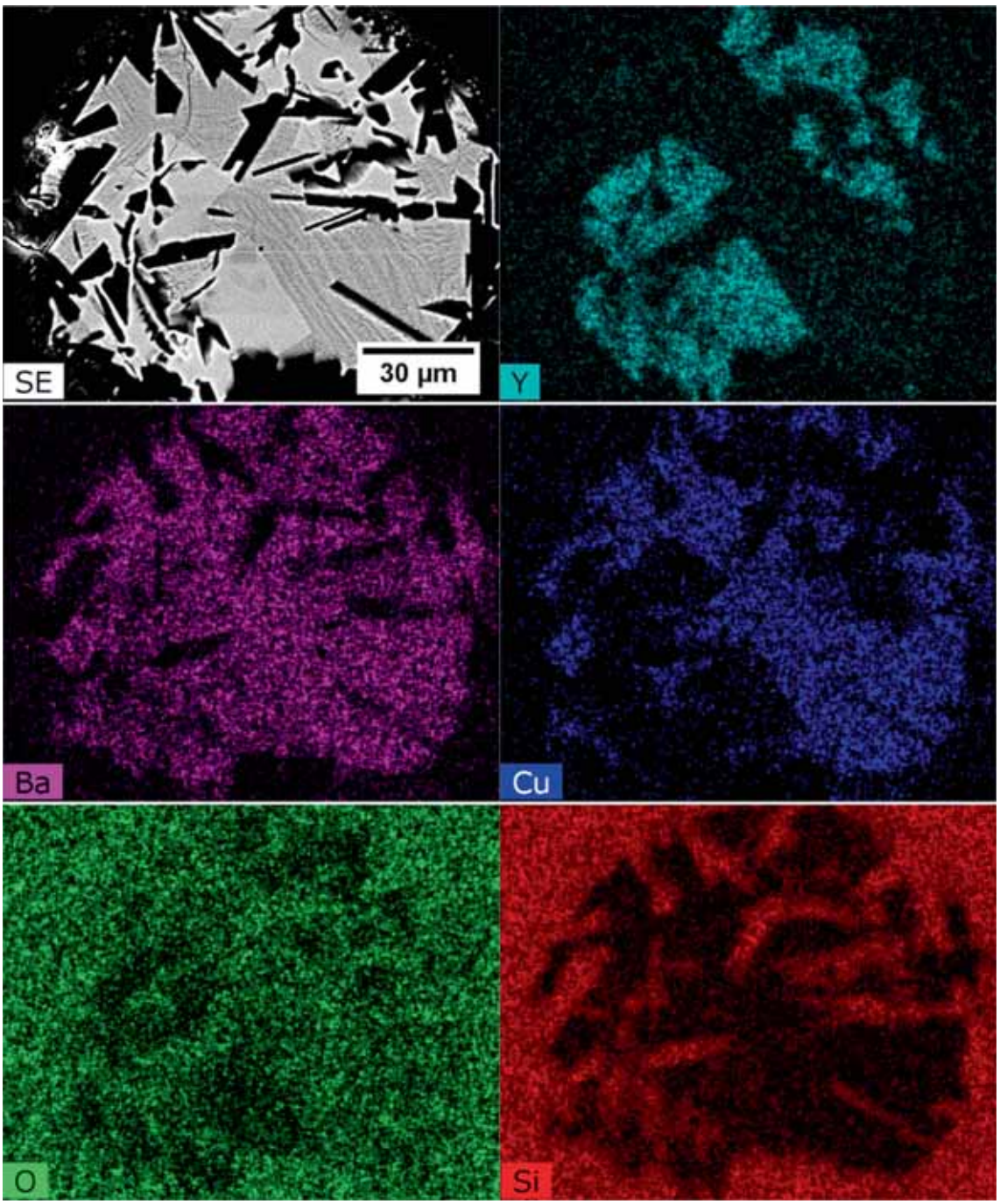

Figure 10. EDS mapping of the YBCO core heat-treated at 1200°C for a dwelling time of 10 min in air (scale bar = 30 µm).

900°C, shows that the darker precipitations are rich in silicon and oxygen with a ratio of 1:2 and the lighter precipitations are rich in copper and oxygen with a ratio of 2:1, as can be seen in table 4 taking the large excitation volume of the X-rays into consideration and accounting for the overlap with the SiO_2 phase. Hence, this indicates the formation of copper (I)-oxide precipitations next to silica precipitations, which form co-precipitations. To further visualize the composition distribution of silicon in the co-precipitations, a high magnification EDS mapping of the co-precipitations was performed and is shown in figure 7.

Figure 7 shows that at the copper-rich precipitations (lighter precipitations), the silicon content is highly reduced, which confirms the formation of copper oxide precipitations inside the core. The EDS mappings of the YBCO core heat-treated at 1000–1200°C are shown in figures 8, 9 and 10.

As shown in figures 8, 9 and 10, and confirmed with additional EDS point analyses, an yttrium–barium-rich phase begins to form at 1000°C. Figures 8, 9 and 10 show that in addition to the yttrium–barium-rich phase, also a barium-rich phase is formed inside the core at 1000°C, which transforms to a barium–copper-rich phase at 1100°C. Figure 10 also shows the presence of the cladding material inside the core at 1200°C.

Furthermore, cross-polarized light microscopy was performed on the heat-treated YBCO glass fibres since it can be used to identify anisotropic grains in an opaque material due to the characteristic correlation between a certain colour and its associated phase [23]. A number of studies in the literature [23–27] describe the use of such a cross-polarized light study to generally determine the presence of YBCO impurity phases and the superconductive Y-123 phase.

The study on cross-polarized light using an optical microscope (figure 11) shows that at 800°C, neither the core nor the cladding show any colour of polarization, which is an indication of an isotropic structure. However, the interface layer is visible in a yellow colour. At a temperature of 900°C, the co-precipitations show a red/orange colour, which intensifies at 1000°C. Moreover, at 1100°C, the red colour is still present in the centre of the core. However, a darker blue layer is present between the core (red) and the cladding region (yellow). At 1200°C, the core is entirely blue and the interface contains an orange/yellow colour.

In this regard, it is stated in ref. [26] that a red colour observed under cross-polarized light is a sign of Cu_2O impurity formation in YBCO. Hence, the cross-polarized imaging results confirm the formation of Cu_2O inside the core, which is also identified in table 4. Even though Cu (II)-oxide typically transforms into Cu (I)-oxide above 1026°C [28], the reason as to why Cu_2O forms at lower temperatures can be attributed to reactions between silica and YBCO, as it has been shown in ref. [18] to occur for a YBCO film on a silica substrate. Moreover, it is reported in ref. [29] that no copper silicates or solid solutions are formed in the $CuO–Cu_2O–SiO_2$ system up to 1072°C. This, as a result, explains the stability of Cu_2O and the formation of silica co-precipitations. Furthermore, the blue colour inside the core at 1100 and 1200°C is an indication of the formation of barium copper silicate [30]. This is, in general, the first study on YBCO and silica, which demonstrates the formation of barium copper silicate.

Here, we note that the superconductive Y-123 phase would be indicated by a golden colour in cross-polarized light [28]. This golden colour was not observed in this study.

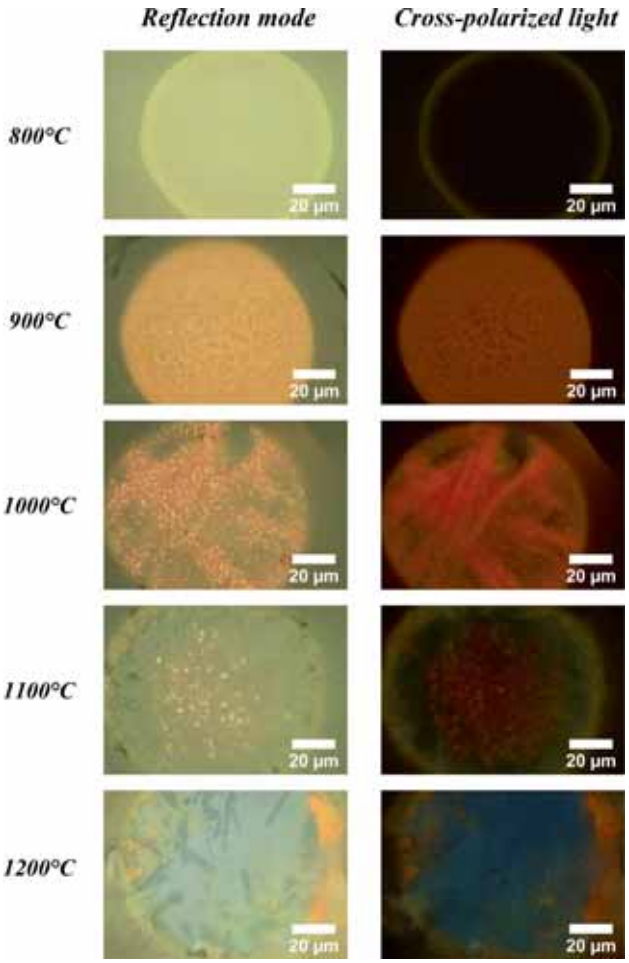

Figure 11. Optical microscopy images, in reflection mode and with cross-polarized light, of YBCO fibre cross-sections heat-treated at temperatures between 800 and 1200°C for a dwelling time of 10 min in air.

4. Conclusion and future work

This is the first work to show the success in drawing YBCO glass fibres using a fibre draw tower. The drawn fibres have shown the occurrence of reactions between the YBCO core and the silica cladding. In this regard, this paper has provided an in-depth analysis of these reactions. It was, indeed, first shown that the as-drawn YBCO glass fibre samples exhibit an interface layer, which contains precipitations that are rich in silicon and oxygen with a ratio of 1:2. In addition, a high silicon content was also detected inside the core using EDS analyses and was further confirmed using XPS analyses which indicates silicon diffusion inside the core with possible silicate formation. Furthermore, heat-treatment studies on the as-drawn YBCO fibre sections were performed and analysed. In this regard, copper oxide (Cu_2O) and silica co-precipitations were shown to form at 900°C, which transform into yttrium–barium-rich and barium–copper-rich phases at higher temperatures. The formation of copper oxide precipitations and the possibility of barium copper silicate formation have also been confirmed using cross-polarized imaging on an optical microscope.

To further characterize these phase formations, next steps will include performing micro-XRD analyses on the as-drawn and heat-treated fibre cores. This analysis will allow determining whether the as-drawn YBCO fibre core exhibits a

crystalline structure or whether the fast cooling process at the draw tower and the silica content inside the core led to an amorphous core. This will, furthermore, allow defining the reaction products of the heat-treated fibre cores and will enable a profound understanding of the phase relations within YBCO glass fibres which is a first step in the direction of a potential future manufacturing of long-scale superconductive YBCO glass fibres.

Acknowledgements

We would like to acknowledge Jay Tuggle for performing the XPS measurements.

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