Identification of Cu-Co-oxide phases of reactive air brazed Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-\delta}\)-Ag-14CuO joints by EBSD, EPMA and TEM diffraction

L C Ehle\(^1\), S Richter\(^1\), S Herzog\(^2\), C Broeckmann\(^2\) and J Mayer\(^1\)

\(^1\) R.W.T.H. Aachen University, Central Facility for Electron Microscopy, Ahornstrasse 55, 52074 Aachen, Germany
\(^2\) R.W.T.H. Aachen University, Institute for Materials Applications in Mechanical Engineering, Augustinerbach 4, 52062 Aachen, Germany

E-mail: ehle@gfe.rwth-aachen.de

Abstract. The oxygen transport membrane Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-\delta}\) (BSCF) was wetted by the reactive air brazing alloy Ag-14CuO. Triple point phases of different cobalt-copper-oxides are formed in the reaction zone and are origin of micro-cracks and stress concentration. Therefore, their identification is necessary for understanding the microstructure evolution and designing the interface structure advantageously by an adapted brazing process. However, as the cobalt-copper-oxide system can form many different oxides with solubility of Co and Cu respectively, different analytical methods are necessary for identification. TEM diffraction is used for the correct identification of the occurring crystal structures, EBSD is used for analysis of composition, arrangement and orientation of the triple point phases and EPMA is used to confirm the crystal structures identified by EBSD and to determine the elemental concentrations. As the triple point phases consist of small grains with unpredictable forms and especially, Cu-K\(\alpha\) can excite Co-K\(\alpha\) by characteristic secondary fluorescence, different evaluation procedures for EPMA are performed on FIB lamellae: 1) Approach based on standard lamellae, where FIB lamellae from standards are used to determine the k-factor in dependence of the mass thickness t/\(\lambda\), and 2) Monte Carlo simulation approach, where an iterative procedure is used to calculate the k-ratios, based on bulk standards. The use of FIB lamellae allows excluding the fluorescence effect and incorrect Monte Carlo simulations due to incorrect assumptions of the microstructure below the surface, which is within the excitation volume.

1. Introduction

Ceramic oxygen transport membranes (OTM) allow oxygen separation from air via oxygen ion diffusion during the exposure to an oxygen partial pressure gradient at temperatures above 750 °C [1]. Amongst OTM materials, Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-\delta}\) (BSCF) exhibits superior oxygen permeation rates [2] and is therefore object of investigation in many lab-scale and pilot scale membrane modules [3]. For integration into a metallic module environment, the membranes must be joined gastight to metal components. Perovskite-type OTM like BSCF tend to chemically decompose under typical vacuum brazing conditions, i.e., the BSCF crystal structure loose oxygen and therefore its functional properties. The relatively new method reactive air brazing (RAB) operates at ambient conditions and is the
exclusive brazing option. Typically, the RAB alloy consists of a precious metal filler (for instance Ag) and a reactive component (for instance Cu). The silver acts as basis of the brazing alloy, because it is stable at high temperatures, does not react and is a ductile metal. However, pure silver as brazing alloy, results in poor joint strengths since the only bonding mechanism is adhesion. The addition of Cu to the silver braze leads to the formation of CuO during heating up. The CuO can subsequently wet both oxide joining partners, the ceramic and the passivation layer of the metal component under formation of reaction phases. In this study, Ag-14CuO (14 at% CuO in silver) was used as brazing alloy on BSCF at 1,000 °C (see Fig. 1). The resulting reaction zone at the BSCF-braze interface exhibits new phases at the grain triple points, which are origin of micro-cracks and stress concentration [4, 5]. Identification of these phases allows firstly to understand the microstructure evolution and secondly, to design the interface structure advantageously by an adapted brazing process. The triple point phases consist of different copper-cobalt-oxides with solubility for Co and Cu respectively.

Figure 1. Light microscopic image of the cross-section. Within the BSCF matrix are many small pores, within the BSCF reaction zone are pores and triple point phases.

Different analytical methods are used for identification. Transmission electron microscopy (TEM) diffraction allows determination of crystal structures provided the grains are either large enough (> 1 µm diameter, for easy tilting) to position the grains in different zone axes for selected area diffraction (SAED) of single grains or the grains are small enough (< ~200 nm) to generate ring patterns with clearly distinguishable lattice plane distances. With electron backscatter diffraction (EBSD) the investigation of larger areas is possible with a spatial resolution of about 45 nm (longitudinal resolution for Cu at 10 kV and 1 nA [6]). It provides crystallographic information based on a reference database. To avoid any ambiguity energy-dispersive X-ray spectrometry (EDS) is used as a support for correct indexing of phases with the same crystal structure like BSCF, Co₃O₄ and CoO, which all have a face centred cubic (fcc) crystal structure. Electron probe microanalysis (EPMA) provides accurate quantification of elemental concentrations. Several different phases with solubility for Cu and Co exist in the Co-Cu-oxide system as was investigated by Zabdyr et al. [7]. The spatial resolution of EPMA, described by the information volume, depends on the chosen acceleration voltage, chemical
composition, density and chosen X-ray line of the analysed phases. It can be well-adjusted to resolve phases with dimensions down to sub-micrometre scale [8]. EPMA corrections are well adapted to handling fluorescence effects within a bulk homogeneous material. But routine EPMA matrix corrections cannot deal with secondary fluorescence from neighbouring materials about which the presence is unknown. There are well established material corrections for thin films, accounting for fluorescence from other layers or for material couples with a simple known geometry [9]. In [10], correction procedures were developed for vertical grain boundaries for instance between pure Co and Cu. However, in the case of an unknown 3D microstructure there exists no fluorescence correction procedure yet. To overcome this problem thin lamellae were cut from each region of interest and EPMA was applied which prevents any influence of neighbouring phases. Disregarding smaller accelerating voltages, using FIB lamellae with thicknesses of less than 150 nm for EPMA is an additional way to reduce the excitation volume, which is then almost limited by the beam diameter [11].

In this work different methods and techniques are used to analyse the phases at the triple points of the reaction zone of BSCF with Ag-14CuO reactive air brazing alloy. Their advantages and disadvantages and their analytical limitations are discussed. In addition, EPMA measurements on Co-Cu-oxide FIB lamellae are performed and evaluated by two different procedures: 1) Approach based on standard lamellae, where FIB lamellae from standards are used to determine calibration factors assuming linear relation between measured X-ray intensities and element concentrations. The dependence on the mass thickness \( t/\lambda \), which is the lamella thickness divided through the mean free path of the electrons [12] is also considered. 2) Quantification by Monte Carlo simulation, where an iterative procedure is used to get the best fit between calculated and experimental \( k \)-ratios, i.e., X-ray intensities calibrated by bulk standards (\( k \)-ratio = background corrected sample intensity / background corrected standard intensity).

2. Experimental

2.1. Sample production
Granulated BSCF-powder (Treibacher) was uniaxially pressed at 180 MPa into a \( d = 20 \) mm pellet and subsequently sintered at 1,100 °C for 5 h. Silver and copper powder (Thermo Fisher Scientific) were mixed in the appropriate amounts to achieve the desired molar ratio of 14 mol% CuO in silver and were uniaxially pressed at 200 MPa into braze pellets of \( d = 6 \) mm. The wetting of the braze pellet on the BSCF pellet was conducted at 1,000 °C for 6 min under air atmosphere, cooling was performed with 300 K/h. A more detailed description can be obtained from [13]. For manufacturing the reference samples CuO, \( \text{Co}_2\text{O}_4 \) and CoO, the starting powders CuO and \( \text{Co}_2\text{O}_4 \) (ThermoFisher Scientific) were manually mixed with a gel binder (B2-gel, Innobraze) and pressed at 200 MPa into pellets with \( d = 20 \) mm. The CuO and the \( \text{Co}_2\text{O}_4 \) pellets were sintered at 760 °C and 850 °C, each for 2 h. To convert the initial powder \( \text{Co}_2\text{O}_4 \) to the high temperature modification CoO [14], a second \( \text{Co}_2\text{O}_4 \) pellet was sintered at 1,080 °C for 48 h, annealed at 950 °C for 24 h and finally quenched in water.

BSCF crystallises in a perovskite structure (\( \text{ABO}_3 \)) with \( A = \text{Ba}_{0.5}\text{Sr}_{0.5} \) and \( B = \text{Co}_{0.8}\text{Fe}_{0.2} \). Wetting the BSCF with alloy Ag-14CuO results in a reaction zone enriched with new phases at grain triple points (see Fig. 2). The triple point phases consist of different copper-cobalt-oxides as well as elemental silver. As reference materials powder-sintered \( \text{CuO} \), \( \text{Co}_2\text{O}_4 \) and CoO samples were taken and their stoichiometric composition was confirmed by XRD and TEM diffraction. In order to exclude any kind of influence of neighbouring grains, FIB lamellae were cut from single grains of copper oxide and cobalt oxide as well as a FIB lamella containing several different grains of the triple point phases. The FIB preparation was performed on a Strata 400 by FEI.

2.2. XRD analysis
To confirm the crystal structure of the manufactured reference samples and to exclude the existence of any other phases X-ray interferences were registered on a Seifert XRD 3003 PTS with a step size of
Figure 2. SE image of reaction zone with triple point phases, micro-cracks and pores. Triple point phases consist of different cobalt-copper-oxides.

0.05° and a counting time of 12 s each. Cr-Kα was used while Cr-Kβ was suppressed by means of a vanadium filter. The standard JCPDS-cards #00-043-1003 (Co$_3$O$_4$), #01-089-2803 (CoO) and #01-080-1916 (CuO) were taken to confirm the phase purity.

2.3. TEM analysis
The selected area diffraction patterns were acquired by a Veleta camera installed at a FEI TEM Tecnai F20. The reference data for identification of the crystal structures are from the online ICSD database with CollCode109462 for BSCF, CollCode16025 for CuO, CollCode36256 for Co$_3$O$_4$, and CollCode9865 for CoO [15]. For the acquisition of thickness maps a Gatan GIF camera was used.

2.4. EBSD measurement
For the EBSD measurements, a JEOL JSM7000F scanning electron microscope and a Hikari EBSD camera were used. The data collection and the analysis were performed with a combined EDS/ EBSD system from EDAX-TSL consisting of an Octane Plus SSD EDS detector and a “Hikari” EBSD camera. For the measurements, the system was operated at an acceleration voltage of 20 kV and a probe current of approximately 20 nA. The measured areas have been scanned with a step size of 100 nm each. The software used for measurement and data evaluation was OIM DATA COLLECTION and OIM ANALYSIS by EDAX-TSL, both in version 8.0.

2.5. Electron probe microanalysis (EPMA)
All measurements were performed by field emission JEOL JXA-8530F microprobe equipped with five wavelength-dispersive X-ray spectrometers. The operating conditions were 15 kV for the acceleration voltage and 40 nA for the beam current. Kα-line X-ray intensities were calibrated by using bulk standards of pure Cu, Co and Fe$_2$O$_3$ (for oxygen). For bulk analysis, the wetted sample was embedded in epoxy resin and a polished cross-section was prepared. For conductivity, a copper tape was fixed on the epoxy surface – no carbon coating was used. For EPMA analysis on FIB lamellae, the sample holder in Fig. 3 was used. In order to exclude any kind of influence of neighbouring grains, FIB lamellae were cut from single grains of copper oxide and cobalt oxide. In addition, a lamella containing several different grains of the triple point phases was made for comparison. For validation of quantification algorithms (for the Monte Carlo approach on lamellae) and for determination of $k$-factors for the approach based on standard lamellae, FIB-lamellae were also cut from reference samples CuO and Co$_3$O$_4$. 


Figure 3. For the EPMA measurements on FIB lamellae, a t-EBSD (transmission-EBSD) holder of the company Micro to Nano was used together with a self-made holder, which fits to the EPMA stage. All components of the holder are made of steel and aluminium to prevent X-rays occurring from the sample holder (the original brass screws and copper plates were replaced by molybdenum plates and steel screws). The grids for the FIB lamellae are made of molybdenum.

2.5.1.1. Approach based on standard lamellae - EPMA on FIB lamellae. Lamellae cut from CuO and Co$_3$O$_4$ standards were thinned stepwise to gain areas of different lamella thicknesses. Wavelength-dispersive X-ray spectrometry (WDS) measurements with EPMA were performed on different thicknesses and the background corrected intensities ($I$) of Cu-Kα and O-Kα for CuO and accordingly Co-Kα and O-Kα for Co$_3$O$_4$ were used to determine the $k$-factors (see Eq. 1) for the known concentrations:

$$\frac{c_{Cu}}{c_{O}} = k_{CuO} \left( \frac{t_{Cu}}{t_{O}} \right) \frac{I_{Cu}}{I_{O}}$$ (1)

The same equation was applied for the intensities and concentrations of Co$_3$O$_4$.

2.5.1.2. Approach based on standard lamellae - Thickness determination of FIB lamellae with TEM. The Gatan Imaging Filter (GIF) camera in the TEM contains a magnetic prism that allows the selection of electrons with different energies after passing the FIB lamella. According to Eq. 2, where $t$ is the thickness of the lamella, $\lambda$ is the average mean free path for low-energy loss electrons, $I_e$ is the total intensity of electrons with energy between 0 and 50 eV (electrons which suffer an energy loss by passing through the FIB lamella due to plasmon interaction and ionisation) and $I_0$ is the zero loss peak intensity (electrons which pass through the FIB lamella without energy loss), $t/\lambda$ can be used as equivalent for the thickness of the lamella provided the mean atomic number of the sample remains similar (since $\lambda$ also depends on the average atomic number [12]).

$$\frac{t}{\lambda} = \ln \frac{I_e}{I_0}$$ (2)

If the $k$-factor is known for different $t/\lambda$ for the standard lamellae, then the $k$-factor can be determined for known $t/\lambda$ for the sample lamellae and with the measured corrected intensities the concentrations can be calculated. The $k$-factor depends on the lamella thickness, which is usually inhomogeneous within a lamella and different between standard and sample lamella. The standard lamellae were cut with different steps of lamella thicknesses to gain a relationship between $k$-factor and $t/\lambda$. If standard lamellae and sample lamellae have similar mean atomic number, the $k$-factors determined on the standard lamellae can be used to determine the compositions of the sample lamellae.
2.5.2. Monte Carlo approach. Based on the quantification technique described in [16] a new procedure was developed to quantify thin lamellae under EPMA conditions. Simulations were performed using PYMONTECARLO, a common programming interface written in Python to run different Monte Carlo codes [8]. We used PYMONTECARLO to run WINCASINO 2.5.1.0. We are not using the GUI version because we have direct access to the code, which offers a self-supporting thin film as specimen geometry. Simulations were run for both standards and unknown concentrations to calculate simulated $k$-ratios of Co-K$\alpha$, Cu-K$\alpha$ and O-K$\alpha$ (bulk standards: Co, Cu and Fe$_2$O$_3$) and were compared with the experimental ones. The best fit between experimental and calculated $k$-ratios was chosen to determine the elemental concentrations.

3. Results
In Fig. 3 is a secondary electron (SE) image of the cross-section of the reaction zone between BSCF matrix and Ag-14CuO brazing alloy. Micro-cracks are formed in the reaction zone close to the soldering point starting at the triple point phases. In order to investigate the distribution of the elements present in the triple point phases X-ray intensity maps were acquired by EPMA (Fig. 4). These triple point phases mainly consist of cobalt-copper-oxides and sometimes of silver. According to [7] different combinations of oxides can occur in the Co-Cu-O system like CoO, Co$_3$O$_4$, CuO, Cu$_2$O, and Cu$_2$CoO$_3$ with different solubility of Cu and Co. TEM diffraction is used to identify the occurring crystal structures because EBSD can only identify known crystal structures. That means: EBSD does not determine the occurring phases, it only fits the measured Kikuchi patterns to the – from the operator suggested – reference phases. If incorrect phases are chosen or the reference data of occurring phases are missing, the indexing will be wrong. Additionally, the EPMA maps in Fig. 4 reveal that there are also mixed Cu-Co-oxides existing. Especially for small grains, the Kikuchi patterns will be bad (due to overlapping information of neighbour grains) and the EBSD software could fit any phases to these patterns. Furthermore, even if all correct phases were chosen, EBSD is unable to differentiate between different phases with the same crystal structure (for instance: CoO, Co$_3$O$_4$ and BSCF are all fcc) unless the EDS signal is acquired during the EBSD measurement as well.

Figure 4. EPMA intensity maps of Sr-L$\alpha$, O-K$\alpha$, Co-K$\alpha$ and Cu-K$\alpha$. 
3.1. XRD measurements
Figure 5 presents the diffraction pattern of the pressed and sintered reference samples. All peaks were identified according to the JCPDS reference data and belong to the desired phase. There are no major peaks from competing phases, for instance Cu$_2$O in CuO, Co$_3$O$_4$ in CoO and CoO in Co$_3$O$_4$ which confirms the phase purity of the reference samples.

![XRD pattern of reference samples](image)

Figure 5. XRD of the reference samples. The markers show the position of the peaks of JCPDS reference data.

3.2. TEM diffraction
A FIB lamella was cut from the triple point phase and selected area diffraction (SAED) was performed on single grains oriented in different zone axes. In Fig. 6, selected diffraction patterns of three different grains of the brightfield image (BF) of the FIB lamella are shown. The determined lattice plane distances as well as the reference lattice plane distances and the dedicated hkl’s are listed in the tables below the diffraction patterns. The grains are identified as monoclinic CuO, fcc CoO and fcc Co$_3$O$_4$. CoO and Co$_3$O$_4$ differ by their lattice parameter, which is 4.263 Å for CoO and 8.072 Å for Co$_3$O$_4$.

3.3. EBSD bulk measurements
In Fig. 7, the image quality (IQ) and the EDS maps of the EBSD measurement are depicted. As the expected phases BSCF, CoO and Co$_3$O$_4$ are all fcc, the EDS signal is necessary for the automated identification and indexing procedure. However, the EDS signal for Co, Cu and O does not change significantly for CoO and Co$_3$O$_4$ respectively. Thus, the more sensitive EPMA maps are used. In Fig. 4 three different phases can be clearly identified in the triple point phase: 1) A copper-oxide phase (identified as CuO), which contains almost no cobalt, 2) a cobalt-oxide phase, which contains almost no copper (identified as Co$_3$O$_4$) and 3) a cobalt-oxide phase, which contains some copper (identified as CoO). Within one triple point, the phases CoO and Co$_3$O$_4$ have similar orientations. As the lattice parameter of Co$_3$O$_4$ is almost twice as big as that of CoO, more bands appear in the Kikuchi patterns as demonstrated in Fig. 8. The different number of counting bands can be used to distinguish between CoO and Co$_3$O$_4$ in the EBSD measurement.
Figure 6. TEM results; selected area diffraction of single grains in zone axis. The identified phases are monoclinic CuO, fcc CoO and fcc Co$_3$O$_4$.

Figure 7. EBSD Image Quality (IQ) with overlaid phase and inverse pole figure (zIPF) map. EDS maps of strontium, cobalt, copper and oxygen. The EBSD map was acquired on the same position as the EPMA maps in Fig. 4.

Figure 8. Kikuchi-Pattern for CoO and Co$_3$O$_4$ and corresponding oriented unit cell.
3.4. EPMA measurements

In Fig. 9, k-ratio profiles of Co-Kα, Cu-Kα and O-Kα across the triple point phases of the bulk samples are labelled according to TEM and EBSD results. As can be seen, within the cobalt-oxide phase (Co₃O₄) a small amount of copper X-rays is measured and within the copper-oxide phase (CuO) cobalt X-rays are measured. There appears to be a phase containing a relative high amount of cobalt and copper (labelled CoO?); however, this could be the result of a poor spatial resolution. Different phases are present in the excitation volume.

![Figure 9. k-ratios of Co-Kα, Cu-Kα and O-Kα measured across triple point phases on bulk sample. According to the identified phases by TEM diffraction, the supposed compositions are collated.](image)

As the triple point phases do not have predictable form and size, the influence of excitation volumes including more than one phase (below the surface) and especially, fluorescence effects of Cu-Kα exciting Co atoms by secondary fluorescence X-rays cannot be excluded. That means:

- If the excitation volume includes more than one phase (no matter if it is CoO, Co₃O₄ or CuO) the determined composition will be wrong.
- If the excitation volume includes only CuO, spreading Cu-Kα can excite Co atoms of neighbouring CoO / Co₃O₄ grains resulting in an increased Co content.

Additionally, CoO can solve a wide range of Cu atoms (up to 36 at%). In order to exclude any influence of surrounding grains, FIB lamellae are cut from single phases and – additionally – one lamella that contains several grains (see Fig. 6).

In Table 1 the results of the thin lamella analysis are presented. On the right side, the values were evaluated by using the Monte Carlo simulation programme PYMONTECARLO [8]. For the validation thin lamellae were cut from standards of well-known composition (reference samples), i.e., CuO and Co₃O₄, and measured at the same conditions as the lamellae of the unknown phases of the specimen. It turns out that the measured copper and cobalt concentration is lower than expected. It can be explained with the help of the diagram shown in Fig. 10a. Here the relative deviation of the k-ratios with and without contribution of continuum fluorescence is plotted versus the thickness of the lamellae (calculation was performed by using the programme STRATAGEM [17, 18] assuming a thin film on a hydrogen substrate). For a thickness of 150 nm (density was given) the relative deviation is about 3.3 % for Co-Kα and about 4.5 % for Cu-Kα. Since the k-ratios are the measured X-ray intensities of the lamellae calibrated by bulk standards, continuum fluorescence cannot be neglected for the bulk standards.
Table 1. Mass concentrations for Cu, Co and O determined on FIB lamellae with standard lamella based and Monte Carlo based approach. Crystal structures have been confirmed by selected area diffraction. The values show average and standard deviation of more than 6 measurement points each (except for multigrain lamella).

|                  | stoichiometric | $k$-factor CuO | MC CuO          |
|------------------|----------------|----------------|-----------------|
|                  | CuO            | single         | multi          | single         | multi         |
| Cu mass. %       | 79.9           | 76.12±0.45     | 78.08±0.08     | 76.62±0.45     | 72.16±0.41    | 73.96±0.41    |
| Co mass. %       | 0.0            | 6.61±0.42      | 3.24±0.13      | -              | 6.85±0.06     | 3.62±0.41     |
| O mass. %        | 20.1           | 17.27±0.28     | 18.68±0.08     | -              | -             | -             |

|                  | stoichiometric | $k$-factor CoO | MC CoO          |
|------------------|----------------|----------------|-----------------|
|                  | CoO            | single         | multi          | single         | multi         |
| Cu mass. %       | 0.0            | -              | 15.37±0.08     | -              | 14.40±0.03    |
| Co mass. %       | 78.6           | -              | 62.79±0.22     | -              | 61.67±0.24    |
| O mass. %        | 21.4           | -              | 21.84±0.28     | -              | -             |

|                  | stoichiometric | $k$-factor Co$_3$O$_4$ | MC Co$_3$O$_4$ |
|------------------|----------------|------------------------|---------------|
|                  | Co$_3$O$_4$    | single                 | multi        | single        | multi        |
| Cu mass. %       | 0.0            | 3.13±0.27              | 2.94±0.13    | -             | 2.99±0.28    | 2.71±0.04    |
| Co mass. %       | 73.4           | 69.84±0.90             | 69.81±0.41   | 72.19±0.44    | 68.93±0.76   | 67.81±0.72   |
| O mass. %        | 26.6           | 27.03±0.98             | 27.25±0.38   | -             | -            | -            |

Figure 10. a) relative deviation of the $k$-ratios with and without contribution of continuums fluorescence is plotted versus thickness of the lamella; b) contribution of characteristic and continuum fluorescence for thin lamella consisting of CuO and 7.0 wt% of Co (instead of Cu).

The diagram in Fig. 10b shows the situation for the thin lamella consisting of CuO and 7.0 wt% of Co (instead of Cu). The contribution of characteristic fluorescence is evident for the thin lamellae (red spotted and dashed line) and together with the continuum fluorescence contribution of the bulk standard the relative deviation gets smaller to about 2 % for a thickness of 150 nm (see red spotted line). The small deviation of 2 % is visible in the results shown in Table 1. The measured and by MC calculated concentrations for a thin lamella cut from a single grain (i.e., homogeneous composition) reflect the expected concentrations. Expected concentrations mean that the Cu atoms are substituted by the Co atoms during diffusion of Co into CuO. Figure 10b also shows that the characteristic fluorescence of Co decreases with lamella thickness. If the lamella thickness is below 150 nm – which is usually the case for lamella investigated in the TEM – the contribution of Co-K characteristic fluorescence is below 1 %.

For the approach based on standard lamellae, the $k$-factors are determined on the standard lamellae using Eq. 1. The $k$-factors for CuO and Co$_3$O$_4$ are $k_{\text{CuO}} = 1.93 \pm 0.05$ and $k_{\text{Co}_3\text{O}_4} = 1.86 \pm 0.03$, respectively. There is no clear dependence of the $k$-factors on the lamella thickness identifiable considering that steps of different thicknesses were cut for the standard lamellae. One reason is that the $t/\lambda$ value is also influenced by bending contours and the exact position of the EPMA measurements on the FIB lamellae cannot be determined. However, the deviation of the $k$-factors is small (see Fig. 11).

Thus, the average could be used for quantification. The concentrations of Cu, Co and O in the sample lamellae can be calculated using the measured intensities on the sample lamellae, the determined average $k$-factors of the standard lamellae, Eq. 1 and the assumption that the total equals 100. Table 1 compares the stoichiometric concentration of the Co-Cu-oxides and the determined concentrations for the $k$-factor and the Monte Carlo method. The average and the standard deviations for more than 6 measurement points are shown (except for the measurements on the multi grain lamella).

As can be seen the MC method and the method based on standard lamellae ($k$-factors) give quite similar results that lie within the standard deviation except for the Cu concentration in the CuO single grain lamella. The results of the multigrain lamella deviate to the determined values of the single grain lamella, in particular for the CuO lamella, where the Co content of the multigrain lamella is only about half the content of the single grain lamella. As different solubility is possible perhaps a grain of different composition was picked. For the CuO lamellae (standard and single grain lamella), the sum of Cu and Co is significantly higher than the stoichiometric Cu concentration compared to the CoO and Co$_3$O$_4$ lamellae, where the sum of Co and Cu almost meet the stoichiometric Co concentration. The reason for this effect can be explained with Fig. 10a, where the influence of continuum fluorescence in the standard bulk sample is higher for Cu than for Co. For CuO in the multi grain lamella the sum of Cu and Co is less than the stoichiometric Cu content, however, as only one measurement point was available no conclusions or explanations can be given.
4. Discussion

As the results showed, TEM diffraction allows the accurate determination of the occurring crystal structures because the grains are big enough for tilting and SAED of single grains in zone axis. Furthermore, the lattice distances of the occurring phases differ enough for unambiguous identification. For EBSD, the correct identification is much more complicated. As there are three phases with fcc crystal structure (BSCF, CoO and Co$_3$O$_4$), unambiguous identification of the phases without EDS signal is impossible. BSCF can be identified by the Sr-signal, but for CoO and Co$_3$O$_4$ the differences in Co, Cu and O signal of the EDS data is not strong enough for differentiation (see Fig. 7). WDS is much more sensitive and does clearly show the difference of Co, Cu and O content in CoO and Co$_3$O$_4$ (see Fig. 4). However, as the WDS signal is not coupled with the EBSD data it does not help for the automated indexing. As the lattice plane distance of Co$_3$O$_4$ is almost twice as large as that of CoO, the Kikuchi patterns of Co$_3$O$_4$ contain more bands than the ones of CoO (see Fig. 8), which can be used for the counting bands in the Hough transformation. Within one triple point, CoO and Co$_3$O$_4$ have almost the same orientations because the change in crystal structure only depends on small changes in composition.

The WDS measurements on the FIB lamellae of the sample (single grains) clearly showed that a certain amount of Co/ Cu is within the CuO/ CoO and Co$_3$O$_4$. Influences of different phases of neighbouring grains as well as characteristic secondary fluorescence effects can be excluded. The lower Cu- and Co-concentrations measured in the standard lamellae could be explained with continuum fluorescence effects. Still, the Co content in CuO is too high (see Table 1) according to the quasi-binary Co-Co-oxide phase diagram, where the Co content is limited to $\sim$2.0 mass% at room temperature [7]. Furthermore, no CoO should exist at room temperature, although it is definitely identified by EBSD, TEM diffraction, and EPMA in the triple point phases. As CoO can be formed above 847 °C, which lies above the brazing temperature of 1,000 °C, its crystal structure might be stabilised during cooling due to oxygen deficiency. However, the oxygen partial pressure that is considered in the ternary phase diagram and especially the oxygen solubility kinetics are not known in the real brazing process and can only be estimated in dependence of the cooling rates [19]. Additionally, small amounts of iron can exist within the triple point phases as well and may change the phase stabilities. Therefore, the quasi-binary Co-Co-oxide phase diagram might not be applicable for this material system and needs to be modified.

The two different quantitative EPMA approaches on FIB lamellae show almost the same values within the standard deviation. It can be concluded that the standard lamella-based approach can be applied for standard lamellae with composition close to that of the sample. The thickness of the lamella does not seem to have a significant effect on the quantification at least for $0.9 < t/\lambda < 3.4$. As the Monte Carlo approach gives comparable results, it is much less time-consuming and no standard lamellae are necessary, it is a valuable and easy alternative to get quantitative information about the composition. Together with crystallographic information by TEM diffraction, it also provides unambiguous identification of phases with grain sizes much smaller than the excitation volume in bulk samples.

5. Conclusion

Co-Co-oxide phases have been identified as CuO, CoO and Co$_3$O$_4$ by TEM diffraction, EBSD and EPMA on FIB lamellae. For EPMA on FIB lamellae two different approaches were tested: An approach based on standard FIB lamellae with a composition close to the sample lamella, and an approach based on a modified Monte Carlo simulation. For both approaches, quite similar results are gained. The CuO phase contains $\sim$3.24 - 6.85 mass% Co, the CoO phase contains $\sim$14.40 - 15.37 mass% Cu and the Co$_3$O$_4$ phase contain 2.71 - 3.13 mass% Cu. Thus, for small phases of unpredictable form and size and element combinations causing secondary fluorescence effects, WDS measurements on FIB lamella allow the quantification of these phases. As the standard FIB lamella-based approach requires standard lamellae with similar composition, it is quite time consuming. However, the presented Monte Carlo approach results in comparable values and is based on bulk standards and, therefore, is a time-saving and reliable alternative to bulk EPMA quantification, especially if TEM diffraction is required anyway.
The comparable high amount of 14 mol% CuO in the brazing alloy was selected for the presented investigations to observe trends and effects of the microstructure evolution that cannot be observed when using only 3 mol% CuO in the brazing alloy. For Ag-3CuO the triple point phases are small and almost no micro-cracks are visible [13]. Nevertheless the BSCF/braze interface is the weakest position in BSCF-Ag-3CuO-steel joints in 4-point-bending tests. The present phase identification of the triple point phases is the first step for future simulations that should answer the following questions:
1. Which kinetic has the solidification of the braze and the precipitation of the triple point phases?
2. When are the micro-cracks formed during cooling?

A thermodynamic dataset for the simulation of solidification will be extended in future by CuO, CoO and Co3O4. The subsequent microstructure simulation based on a 2D representative volume element comprising one triple point phase will be added with Young’s modulus and coefficient of thermal expansion of CuO, CoO and Co3O4 as well as the fracture strength of BSCF to model the crack formation. These simulations allow the choice of the optimal chemical composition of the braze alloy and temperature-time profile for the reactive air brazing of BSCF.

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