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A comparison of various imaging modes in scanning electron microscopy during evaluation of selected Si/refractory sessile drop couples after wettability tests at ultra-high temperature

Adelajda Polkowska[1], Małgorzata Warmuzek[1], Julia Kalarus[2], Wojciech Polkowski[1], Natalia Sobczak[1,3]

[1]Foundry Research Institute, ul. Zakopiańska 73, 30-418 Krakow, Poland
[2]AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30 Av., 30-059 Krakow, Poland
[3]Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warsaw, Poland

E-mail: adelajda.polkowska@iod.krakow.pl

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Abstract

In this work, FEI Scios™ field emission gun scanning electron microscope (FEG SEM) equipped with a unique combination of analytical and imaging detectors was utilized to examine structure and chemistry of selected Si/refractory couples. The couples were obtained in wettability tests performed by the sessile drop method coupled with contact heating of a refractory substrate (h-BN, SiC) at ultra-high temperature (up to 1750°C). The SEM observations were carried out on top-views of the couples, in order to evaluate surface and interfacial phenomena in Si/h-BN and Si/SiC systems. A full range of available detectors (e.g. classical Everhart-Thornley detector (ETD) or advanced in-lens detectors) working under various operation modes (secondary electrons (SE), backscattered electrons (BSE), a mixed mode), were used upon analyses in order to reveal specific features of obtained structures.

Keywords: *scanning electron microscopy, sessile drop method, silicon, refractories, in-lens detectors*

1. Introduction

Wettability, reactivity and infiltration phenomena in metal/metal or metal/ceramic systems play a key role in many important liquid-assisted technological processes [1]. A special attention should be paid on the high temperature interaction between involved liquid/solid phases upon joining of dissimilar materials, a fabrication of metal matrix composites (where a good wetting/infiltration is needed) or during a selection of refractories for a melting and casting processing (where wetting/infiltration should be absolutely avoided) [2]. It should be noted that the extent of aforementioned phenomena is strongly determined by (I) the type of selected metal/metal or metal/ceramic couples; (II) applied working (processing) conditions – i.e. temperature and pressure values affecting phase stability of the system.

Very recently, [3,4] silicon and silicon based alloys have been proposed in the AMADEUS Project as very promising phase change materials (PCMs) intended for ultrahigh temperature latent heat thermal energy storage (LHTES) and conversion applications. In such devices, the latent heat from melting/solidification of the PCM is utilized to storage any kind of energy (e.g. coming from concentrated solar power systems) and then to convert it to the electricity (by using advanced thermoionic converters). However, one of the biggest challenge that has to be faced in order to successfully accomplish the goals of AMADEUS Project [4], is to select proper refractory materials that are able to withstand a long-term contact heating/cooling with molten silicon (or silicon based alloys). The Si is characterized by an extremely high latent heat value that should allow overcoming energy density limitations of actually existed salt-based systems. On the other hand, its high chemical affinity to oxygen, nitrogen and carbon makes it very reactive and easily wettable with almost all of existed ceramics [5]. Thus, the high temperature behavior of Si/refractories couples needs to be very carefully examined. In this regard, the commonly accepted experimental approach includes testing of the wettability by a sessile drop method (i.e. *in-situ* measurements of contact angle values and spreading rates) followed by an investigation of reactivity by using microscopic methods (light microscopy, scanning electron microscopy or transmission electron microscopy) to evaluate involved surface and interfacial phenomena.

The main purpose of this paper is to demonstrate the results of our experiments on the reactivity of selected Si/refractory systems by using advanced field emission gun scanning electron microscopy (FEG SEM). A wide spectrum of available detectors and observation modes was applied in order to reveal morphology of specific structural constituents, as well as to just present their visual beauty.

2. Methods and results

Ultra high purity polycrystalline silicon (7N) and commercially available refractories: (I) sintered hexagonal boron nitride (99.5% h-BN) (Henze HeBoSint® D100) and (II) polycrystalline sintered silicon carbide (98% SiC) (FRIALIT® 198D), were used upon wettability tests. The Si/h-BN and Si/SiC couples were selected to compare two strikingly different behaviors. The former couple has been previously recognized as the only one exception showing the non-wetting and low-reactivity with Si at temperatures up to 1500°C [6], while the latter is well-known to be a strongly reactive and wettable by molten Si [7].

The Si/h-BN and Si/SiC couples were subjected to the wettability tests by a sessile drop method combined with contact heating procedure, by using the experimental complex described elsewhere [8]. The tests were performed under a static argon atmosphere (pressure of 850−900 mbar) at ultrahigh temperatures up to 1750°C. The experiment was performed in accordance to the temperature profile containing five intervals (steps) at: 1450°C/5 min, 1550°C/5 min, 1650°C/5 min, 1700°C/5 min and 1750°C/5 min. After the end of experiments, the solidified couples were removed from the high temperature chamber and then subjected to microscopic observations. The observations were performed on top-views of the couples.

The FEI Scios™ DualBeam™ used in this work, is an ultra-high-resolution analytical FEG SEM that is equipped with in-lens FEI Trinity™ detection technology. This technology allows collecting all signals (i.e. secondary and backscattered electrons – SE and BSE) simultaneously giving distinctly different contrast to reveal specific topographic and chemical features of the observed microregions, especially at low applied voltage. Additionally, retractable concentric backscatter detector enhances efficiency, enabling an ease separation of materials and topographic contrast.

The following detectors and operating modes were used upon presently shown SEM evaluations:

1. **Everhart–Thornley detector** (ETD) – a classical, conventional "in-chamber" detector that may operates in both SE and BSE modes.

2. **T1 in-lens detector** – located inside the column. The T1 detector is dedicated mostly to capture BSE images. However, by taking the fact that, the active area of this detector is divided on two parts (A and B), it might works in four different imaging modes:

   a) the Z-contrast (A + B);

   b) a pseudo-topographic contrast (A-B): in this mode the Z-contrast is minimized;

   c) separated signals from A or B segments.

3. **T2 in-lens detector** – located inside the column. The T2 detector allows receiving almost "pure" SE signal (as compared to the ETD) due to its in-column position that strongly limits detrimental effects of BSE interaction with either the sample itself (SE_2) or surrounding materials (SE_3), including the objective lens pole piece, microscope chamber walls, or the detector housing [9].

Additionally, the performance of both in-lens detectors (T1 and T2) might be adjusted by controlling the potential of A-Tube electrode. The arrangement of detectors in the SEM working space is schematically shown in Figure 1 [10].

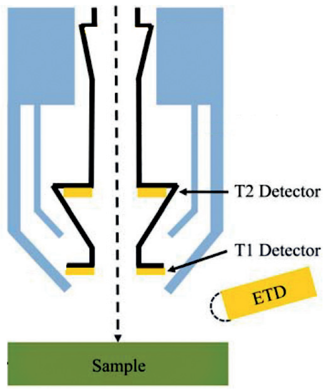

Fig. 1. A schematic presentation of the FEI SCIOS SEM setup – the positions of the ETD, T1 and T2 detectors are indicated (based on [10])

3. Discussion of results

3.1. The Si/SiC couple

A macroscopic view showing a comparison the Si/SiC couple before and after the ultrahigh temperature wettability test, is shown in Figure 2. Furthermore, se-

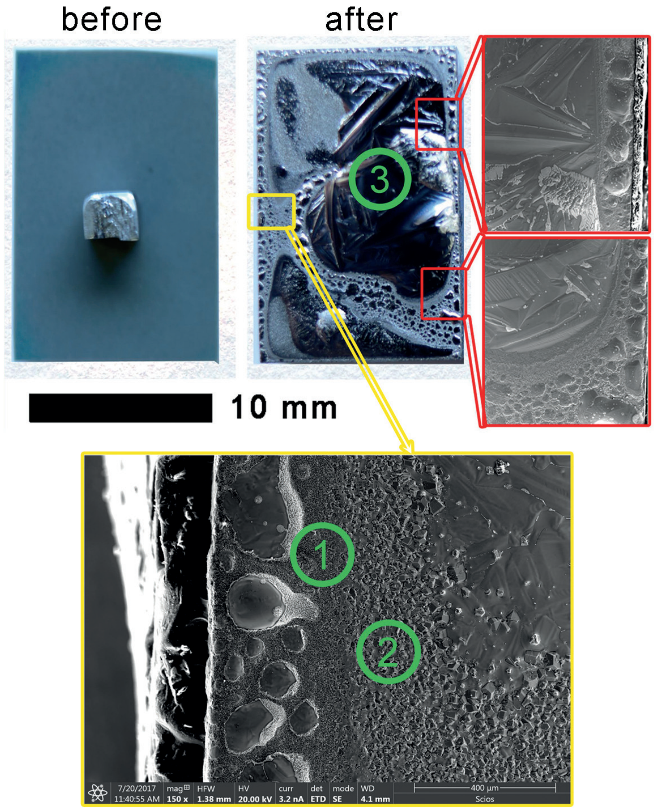

Fig. 2. A macroscopic top-view of the Si/SiC couple before and after the ultrahigh temperature wettability test. The sites of more detailed SEM study are also indicated by 1–3 digits

lected sites for more detailed SEM evaluations are also indicated.

Even a very brief overview of the solidified Si/SiC couple reveals that an extensive reaction took place during the wettability test at temperature up to 1750°C. After melting, the Si piece was completely spread on the SiC surface leading also to the formation of numerous separated features. The results of a more detailed SEM study carried out by using various imaging modes and taken in different sites indicated in Figure 2, are presented in Figures 3–5.

By comparing results presented in Figure 3a–c, it is found that the in-lens detectors (T1 and T2, Fig. 3c and Fig. 3b, respectively) allows extracting "pure" BSE and SE information, while that recorded by the ETD (Fig. 3a) seems to be mixed of these signals (although it was pre-assumed to be a "pure" SE).

Thus, prominent differences between results obtained by using different detectors should be concluded from the above presented SEM evaluations. Although the presented analysis is strictly qualitative in nature, it is found that the in-lens detectors (the T1 and the T2) give a more unambiguous contrast than that of the conventional ETD detector, both in the BSE and the SE modes (please compare Fig. 4a with Fig. 4c, and Fig. 4b with Fig. 4d, respectively). Furthermore, by comparing the Figure 4a and Figure 4c, it is clearly documented that the in-lens location of the T1 detector increases its detection area (as compared to the "in-chamber" ETD). It should be noted that due to the side position of the ETD detector (Fig. 1) some part of the observed structural constituent is not available for the electron beam (it maintains within "the shadow zone").

It is also shown that a very high sensitivity of the T2 detector working in SE mode (Fig. 4d) allows revealing even discrete surface contamination. This feature coming from the high "purity" of obtained SE signal may be treated both as the advantage and disadvantage of this detector. It gives the opportunity to receive very detailed information on the surface morphology, but on the other hand it also enhances adverse effects originating from the contaminations introduced upon the surface preparation or sample handling.

3.2. The Si/h-BN couple

A macroscopic view showing a comparison the Si/h-BN couple before and after the ultrahigh temperature wettability test, is shown in Figure 6. Furthermore, selected sites for more detailed SEM evaluations are also indicated.

As opposite to the Si/SiC system described in the previous section, the Si/h-BN couple showed a poor wettability and a relatively low reactivity. The visual inspections revealed the color changeover of the h-BN substrate from initially white to yellowish after the test.

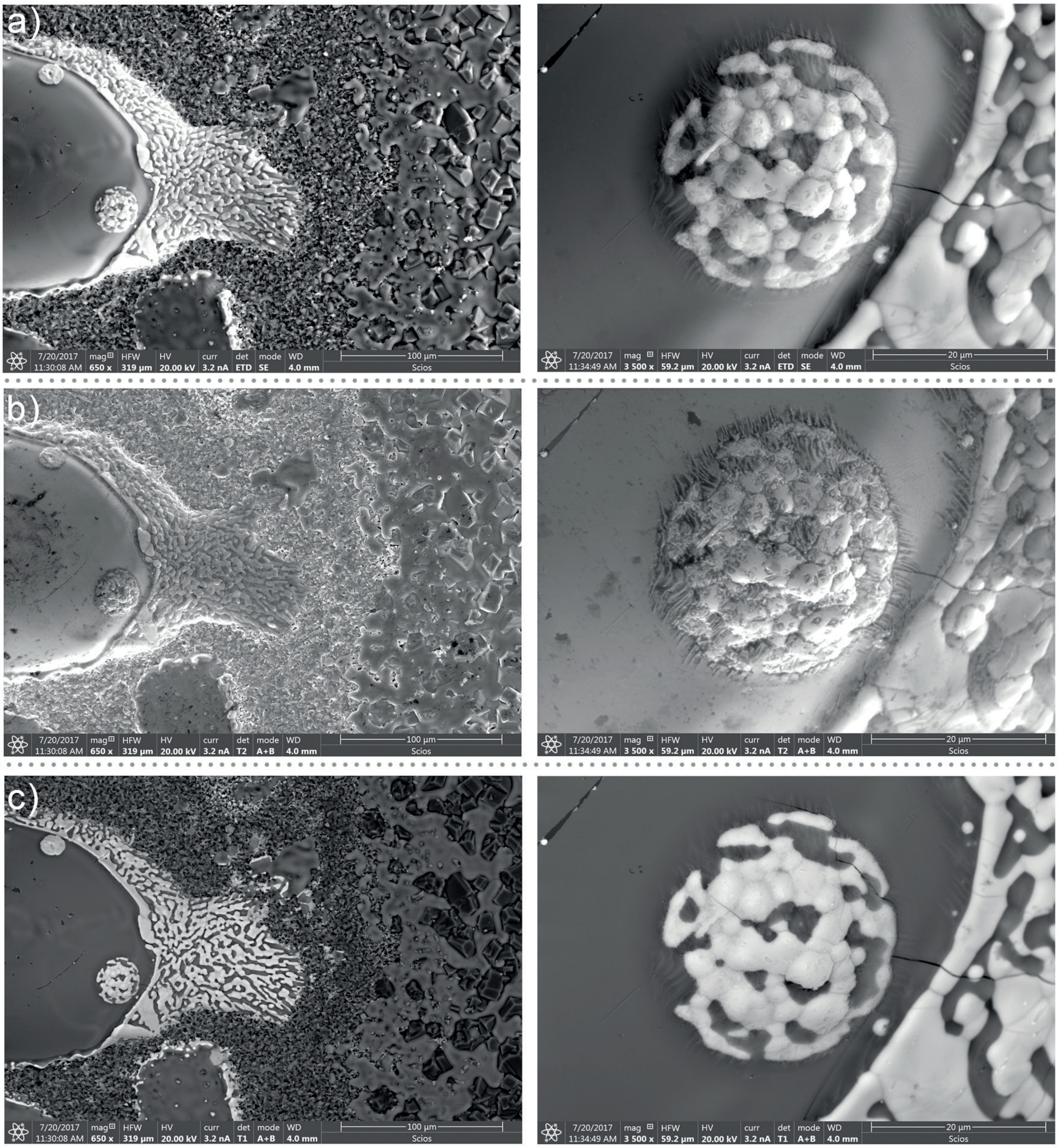

Fig. 3. High magnification SEM images taken in location #1 the Si/SiC couple (Fig. 2) by using: a) the ETD detector working in SE mode, b) the T2 detector working in topographic mode (SE), c) the T1 detector working in A + B mode (Z-contrast = BSE)

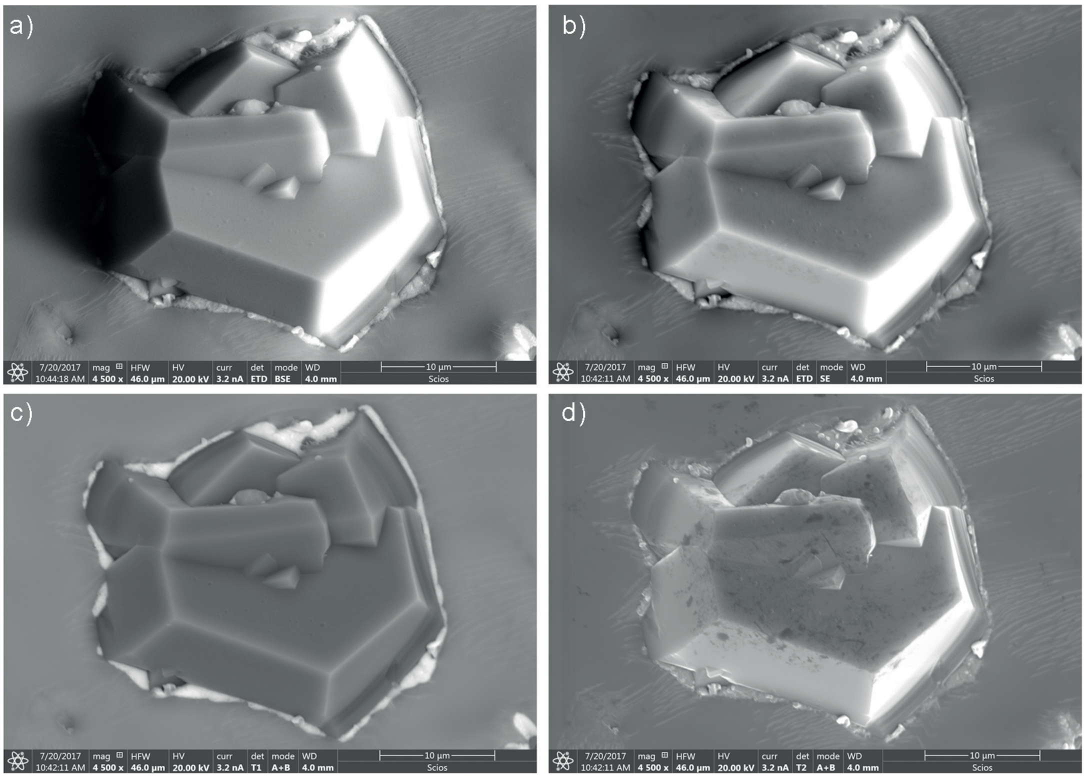

Fig. 4. High magnification SEM images taken in location #2 the Si/SiC couple (Fig. 2) by using: a) the ETD detector working in BSE mode, b) the ETD detector working in SE mode, c) the T1 detector working in A + B mode (Z-contrast = BSE), d) the T2 detector working in topographic mode (SE)

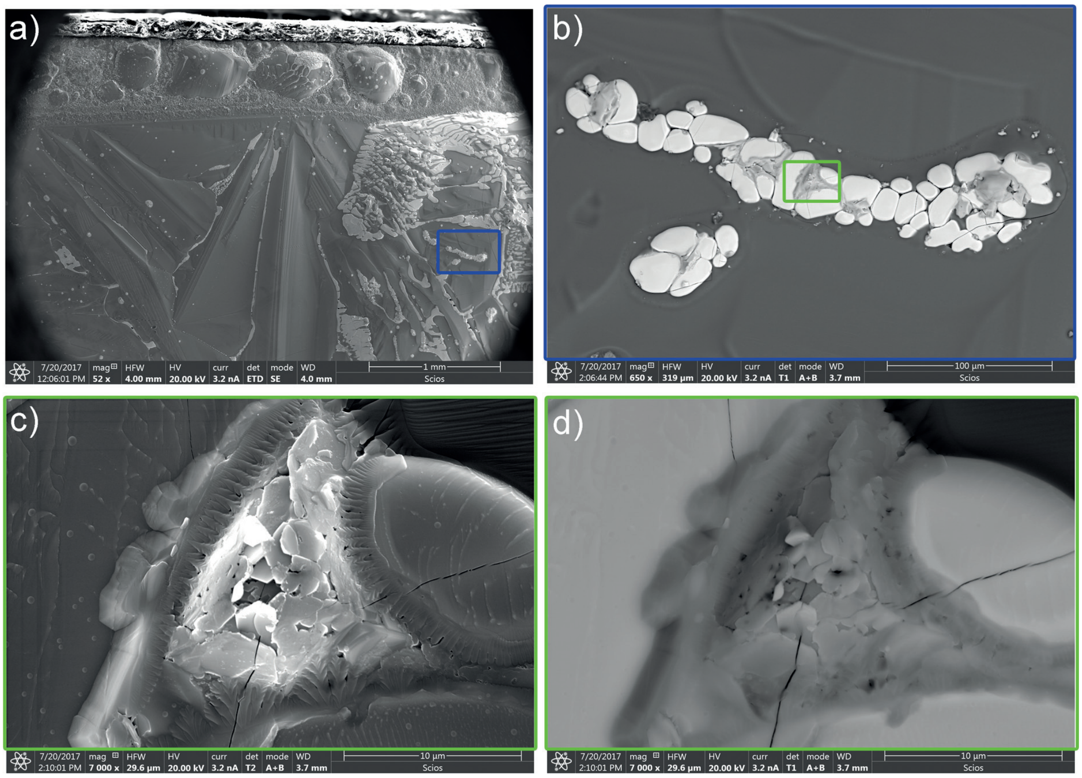

Fig. 5. The SEM images taken in the vicinity of location #3 of the Si/SiC couple (Fig. 2). A low magnification ETD/SE image, b) the enlarged view of the area indicated in Fig. 5a, c,d) the comparison of performance of T2 and T1 detectors

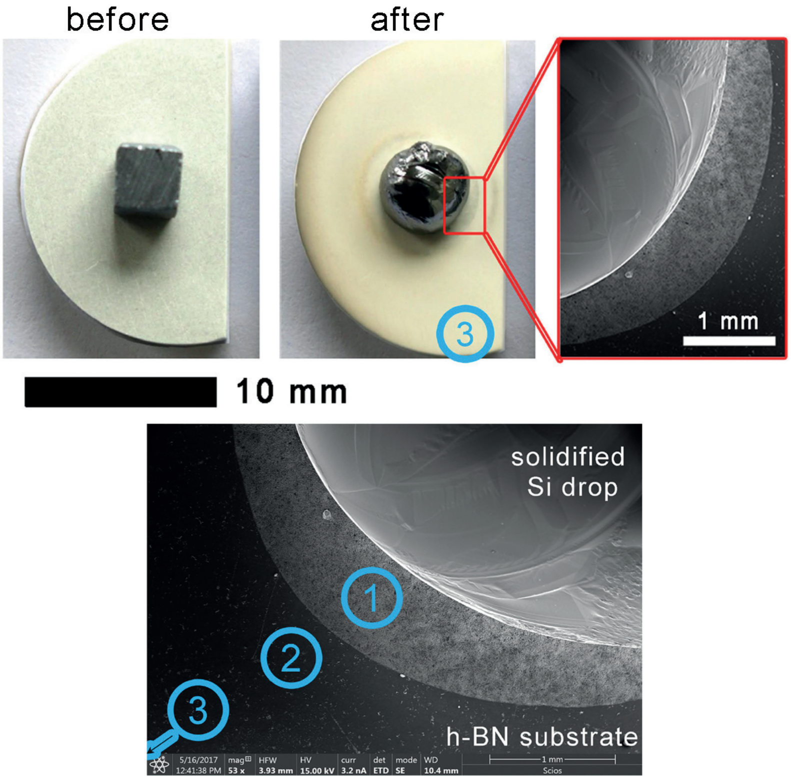

Fig. 6. A macroscopic top-view of the Si/h-BN couple before and after the ultrahigh temperature wettability test. The sites of more detailed SEM study are also indicated by 1−3 digits

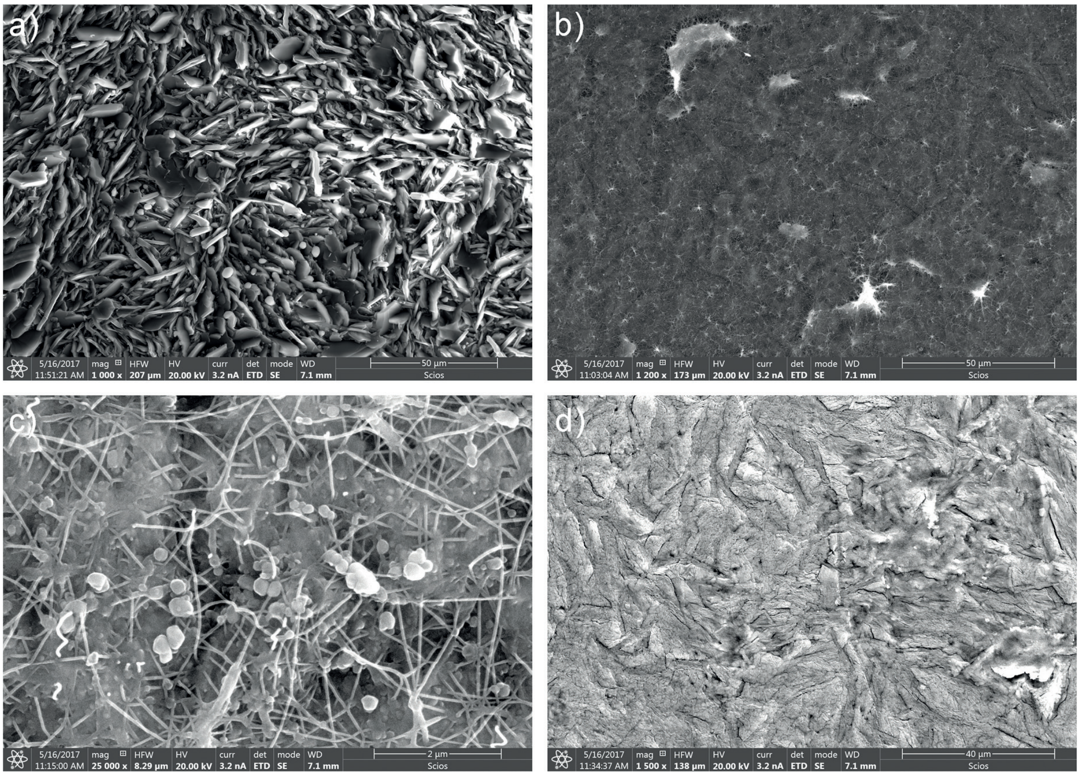

Fig. 7. The SEM images taken in different sites of the Si/h-BN couple (Fig. 6): a) the dewetting zone (area #1), b,c) the spider web like features (most probably boron nitride nanotubes and nanobelts) in area #2, d) the morphology of area #3 (Fig. 6) located far away from the Si drop. All images were taken by using ETD/SE mode

The formation of dewetting zone and a ring around the solidified Si drop was also noticed. The SEM images taken in locations 1−3 (Fig. 6) are shown in Figure 7.

It should be noted that the dewetting zone (area #1 in Fig. 6) is characterized by a platelets like morphology and a presence of small fine droplets (that was more probably left after the movement of Si drop) (Fig. 7a). This area was covered by molten silicon during the high temperature exposition and it was revealed during the cooling and solidification step. Furthermore, a presence of "spider web" like features (Fig. 7c, Fig. 7d) covering almost all remaining h-BN surface, was also noted. Since conducted EDS analyses did not reveal any other elements except boron and nitrogen, these specific objects are most probably boron nitride nanotubes and nanobelts. However, in the view of a high practical importance of the Si/h-BN system in terms of the LHTES applications, we have decided to perform a much more extensive research to clarify the involved interaction mechanism in this system [11]. Therefore, the reactivity of Si/h-BN system will not be further discussed in this paper.

The performance of the ETD and in-lens detectors upon imaging of boron nitride nanotubes is compared in Figure 8. It is clearly observed that the T2 detector gives the following advantages over the ETD: (I) a higher contrast of SE imaging; (II) revealing of much more discrete details; (III) ensuring a higher spatial resolution. The same findings are also drawn from the images showing the dewetting zone presented in Figure 9. It should be noted that once again the nominally pure SE signal

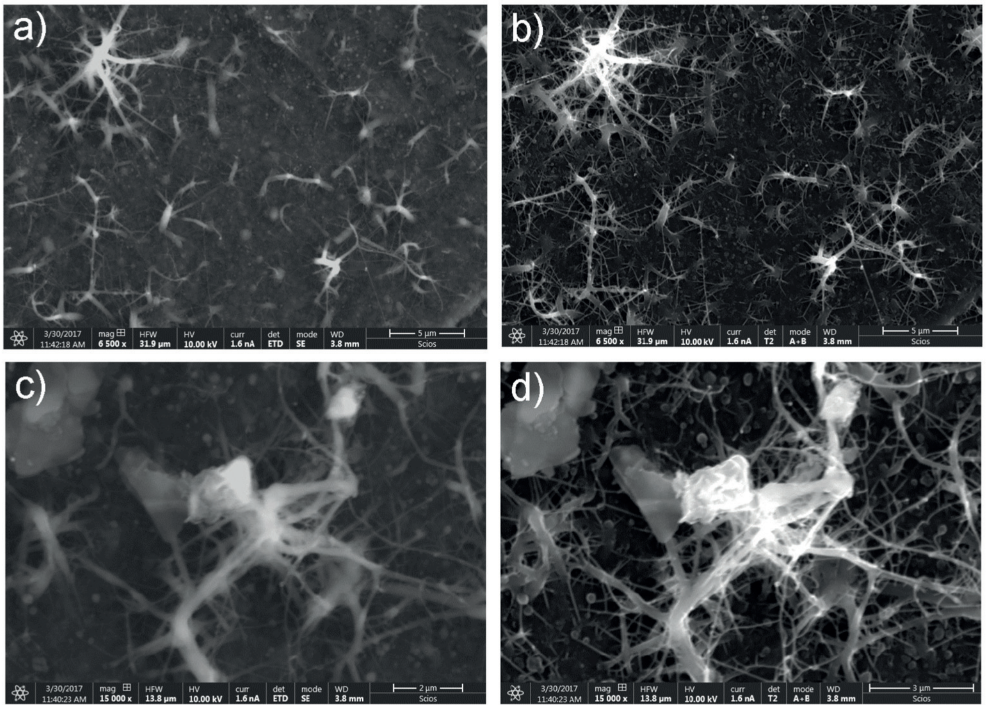

Fig. 8. The comparison of the ETD (a,c) and T2 in-lens detector (b,d) upon imaging of boron nitride nanotubes. Both detectors worked in the SE mode

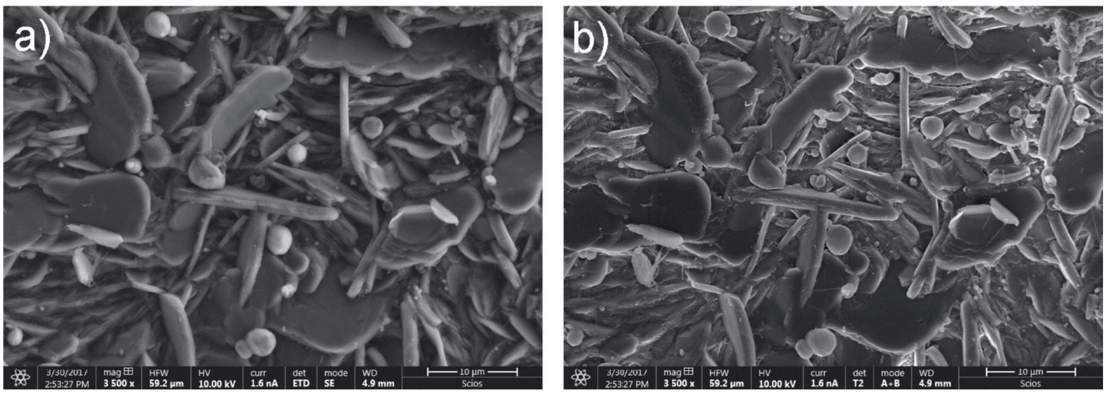

Fig. 9. The comparison of the ETD (a) and T2 in-lens detector (b) upon imaging of the dewetting zone. Both detectors worked in the SE mode

of the ETD detector is "distorted" by the backscattered electrons – Si-enriched droplets (having a higher Z) seems to be brighter than the boron nitride background (Fig. 9a). Furthermore, the T2 detector reveals few very thin tubes that were invisible for the ETD (Fig. 9b).

4. Conclusions

In this work, the FEG SEM working under various operational modes was implemented in order to examine the interfacial phenomena taking place in Si/SiC and Si/h-BN couples during wettability tests at temperatures up to 1750°C. Although the presented analysis was strictly qualitative in nature, it allow concluded that the in-lens detectors (the T1 and the T2) give a more unambiguous contrast than that of the conventional ETD detector, both in the BSE and the SE modes. The in-column position of T1 and T2 detectors increases the "observation" area, as compared to the ETD detector that is positioned on a side of the sample. Furthermore, due to a limitation of undesired interaction of electron beam with the SEM chamber components; and by using various combinations of A and B segments of the in-lens detectors, a "pure" SE or BSE signal might be extracted.

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