RESEARCH ARTICLE

FIB/SEM and SEM/EDS microstructural analysis of metal-ceramic and zirconia-ceramic interfaces

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Abstract
Recently introduced FIB/SEM analysis in microscopy seems to provide a high-resolution characterization of the samples by 3D (FIB) cross-sectioning and (SEM) high resolution imaging. The aim of this study was to apply the FIB/SEM and SEM/EDS analysis to the interfaces of a metal-ceramic vs. two zirconia-ceramic systems. Plate samples of three different prosthetic systems were prepared in the dental lab following the manufacturers' instructions, where metal-ceramic was the result of a ceramic veneering (porcelain-fused-to-metal) and the two zirconia- ceramic systems were produced by the dedicated CAD-CAM procedures of the zirconia cores (both with final sintering) and then veneered by layered or heat pressed ceramics. In a FIB/SEM equipment (also called DualBeam), a thin layer of platinum (1µm) was deposited on samples surface crossing the interfaces, in order to protect them during milling. Then, increasingly deeper trenches were milled by a focused ion beam, first using a relatively higher and later using a lower ion current (from 9 nA to 0.28 nA, 30KV). Finally, FEG-SEM (5KV) micrographs (1000–50,000X) were acquired. In a SEM the analysis of the morphology and internal microstructure was performed by 13KV secondary and backscattered electrons signals (in all the samples). The compositional maps were then performed by EDS probe only in the metal-ceramic system (20kV). Despite the presence of many voids in all the ceramic layers, it was possible to identify: (1) the grain structures of the metallic and zirconia substrates, (2) the thin oxide layer at the metal-ceramic interface and its interactions with the first ceramic layer (wash technique), (3) the roughness of the two different zirconia cores and their interactions with the ceramic interface, where the presence of zirconia grains in the ceramic layer was reported in two system possibly due to sandblasting before ceramic firing.

Résumé
L'analyse FIB/SEM récemment introduit en microscopie paraisse offrir une caractérisation plus détaillée des échantillons par sectionnement transversale 3D (FIB) et l'imagerie à haute résolution (SEM). Le but de cette étude était d'appliquer l'analyse FIB/SEM et SEM/EDS à les interfaces d'un métaux-céramique et de deux systèmes zircone-céramique. Des échantillons des trois différents systèmes de prothèses ont été préparées dans le laboratoire dentaire suivant les instructions du fabricant, où la métaux-céramique a été le résultat d'un application de la céramique par la "wash" technique et les deux systèmes en zircone-céramique ont été produites par le CAD-CAM procédures dédiés et ensuite par stratification or par céramique pressée. Dans le système FIB/SEM, une fine couche de platine (1µm) a été déposée sur la surface des échantillons traversant les interfaces, afin de les protéger lors de la mouture. Puis, les excavations, toujours plus profondes, ont été broyées par un faisceau d'ions focalisés, utilisant d'abord un nombre relativement plus élevé et plus tard un courant plus faible d'ions (de 9 à 0,28 nA, 30KV). Enfin, les FEG-SEM (5KV) micrographies (1000-50,000 X) ont été acquises. L'analyse de la morphologie et la microstructure interne a été réalisée dans une SEM par

signaux électrons secondaires et rétrodiffusés (13KV, dans tous les échantillons). Les cartes de composition ont ensuite été effectuées par la sonde EDS seulement dans le système métal-céramique (20kV). Malgré la présence de nombreux vides dans toutes les céramiques, il a été possible d'identifier: (1) les structures des grains du substrats métalliques et de la zircone, (2) la couche d'oxyde à l'interface métaux-céramique et ses interactions avec la première couche de céramique, (3) la rugosité des deux différents zircones et leurs interactions avec l'interface céramique. La présence de grains de zircone dans la couche de céramique a été signalée dans deux systèmes; cela peut être due au sablage avant la cuisson de la céramique.

Key-words
dental materials, FIB/SEM, SEM/EDS, zirconia, ceramic, metal-ceramic, dental lab

Introduction
Recently introduced FIB/SEM analysis in microscopy seems to provide a high resolution characterization of the samples by 3D (FIB) cross-sectioning and (SEM) high resolution imaging[1-6; 24-27]; in fact, a previous study of some of the authors pointed out that there is the scientific need for more detailed FIB-based studies in comparative analysis concerning dental materials and systems, particularly in zirconia-ceramic structures, where further FIB/SEM based studies are still required for improving the understanding of the actual clinical failure modes[5]. The same could be reported about SEM/EDS analysis, that is well known in basic material science as well in the field of dental materials[7-17], and was recently used in the characterization of porcelain-fused-to-metal techniques[17, 18] as far as in the zirconia-ceramic systems[19, 20]. Both the analysis systems were used together in the literature only in one study, but it was related to the dental structure without the use of some kind of restorative material[21]. So, we thought that metal-ceramic and zirconia-ceramic systems need a FIB/SEM and SEM/EDS characterization because the zirconia-ceramic structures are available on the market for the production of prosthetic devices by the means of CAD-CAM un-direct (in the dental laboratory; there are no devices for the dental office) procedures where the zirconia-based frameworks can be produced by hard-machining or soft-machining, and the latter necessarily with a final sintering[19, 20]. Then, the ceramic veneering can be produced by wash layering or heat-pressed technique, where the latter need the dedicated devices that are available only for the dental lab[19, 20]. Even if metal-ceramic systems can be produced by CAD-CAM, they are widely used by the loss-wax technique with melting of the alloys to produce the framework and with an oxidation firing of the alloys surface before the ceramic layering[17, 18]. Since several clinical failures were reported in the literature, mainly at the zirconia-ceramic interface, in the form of ceramic chipping[19, 20], we thought about the laboratory procedures as the moment where the problem begin as far as was reported in our previous studies on mechanical properties[22, 23]. The aim of this in vitro study was to apply by FIB/SEM and SEM/EDS analysis to the interfaces of a metal-ceramic and two zirconia-ceramic systems following a dental laboratory manufacturing of the samples, in order to investigate their microstructural evolution due to processing, and to find a predictive information on the mechanical behavior of the systems

Materials and methods
Plate samples (4 mm × 4 mm × 3 mm) of the three different prosthetic systems (Table 1) were prepared in the dental lab following

Alloy VE® - 8853 S.p.A. (Pero, MI, Italy) High nobel content (ISO 9693, 22674): Au 15, Pd 52.1, Ag 21.6, In 5.9, Sn 4.2, Ru and Ga (traces)	Ceramic Avanté® Pentron Ceramics Inc. (Somerset, NJ, USA)
Will-Ceram® ZTM Zirconia 'K' Blocks - Provident Dental Products (Somerset, NJ, USA)	Ceramic Avanté® ZTM Pentron Ceramics Inc. (Somerset, NJ, USA)
IPS e.max® ZirCAD Ivoclar-Vivadent AG (Schaan, Liechtenstein)	Ceramic IPS e.max® ZirPress Ivoclar-Vivadent AG (Schaan, Liechtenstein)

Table 1: composition of the three different prosthetic systems: the frameworks materials used (left column) and the dedicated aesthetic ceramics (right column).

the manufacturers' instructions, where metal-ceramic was the result of a ceramic veneering (porcelain-fused-to-metal) and the two zirconia-ceramic systems were produced by the dedicated CAD-CAM procedures of the zirconia cores (both with final sintering) and then veneered by layered or heat pressed ceramics. After conductive resin based embedding, the specimens were lapped and polished by no-particles-release diamond sheets for brittle ceramics and/or porous materials. After the use of 30 and 15 (µ-particle size) sheets, the subsequent steps were performed by diamond solutions (6, 3, 1 µ-particle size) up to the finished mirror-like surface. After each step, samples were washed with pure ethanol (99.9%). Since part of the materials (zirconia based and ceramic layers) are no conductive, a gold sputter coating (10-20 nm thick) was applied. Thus does not significantly affect the surface morphology of the sample, while it may lead to an artifact in the compositional analysis (quantitative), EDS, in the case that a test material contains a certain amount of gold. The tablets, after being stuck by a silver-based conductive glue on a sample holder stub, were ready for SEM and FIB dual beam analysis. In a FEI Helios NanoLabTM 600 (FEI CompanyTM, Eindhoven, Netherlands), a thin layer of platinum (1µm) was deposited on samples surface crossing the interfaces after a tilting of the column (52°). Then, the cross-sections were milled by a focused ion beam, by using a decreasing sequence of the ion currents (from 9 nA to 0.28 nA, 30KV). The sections were used to acquire high-resolution FEG-SEM (5KV) micrographs (1000–50,000X) using both the electron and the ion guns for imaging. In a scanning electron microscopy (SEM, FEI XL30 model, LaB6) the analysis of the morphology and internal microstructure was performed by 13KV secondary and backscattered electrons signals (in all the samples). The compositional maps were then performed by EDS probe only in the metal-ceramic system (20kV).

Results:

In all the samples, the FIB/SEM analysis showed the presence of a lot of voids in the ceramic layers at the interface, but it was possible to observe in the frameworks: (1) the grain structures of the metallic and zirconia substrates, (2) the thin oxide layer at the metal-ceramic interface and its interactions with the first ceramic layer (wash technique), (3) the roughness of the two different zirconia cores and their interactions with the ceramic interface. The presence of zirconia grains in the ceramic layer was reported in two systems possibly due to sandblasting before ceramic firing or to an increased presence of defects during mechanical processing of the Zirconia (Fig. 1-9). The microstructural analysis by SEM-EDS showed no interfaces phenomena in zirconia-ceramic systems, but significant changes in microstructure of the metal alloy at the interface of metal-ceramic system. In

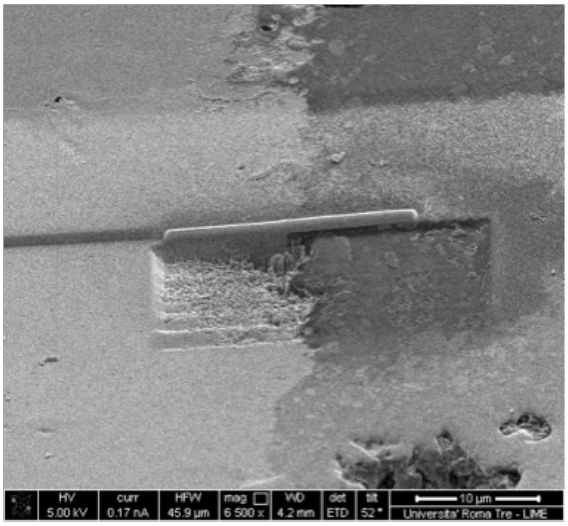


Fig. 1: FIB/SEM analysis of the interface between Alloy VE® (left) and Ceramic Avanté® (right) at 5000X. After a deposition of a thin layer (1µm) of Platinum (upper side of the milling), it was possible to start the ion beam sample preparation.

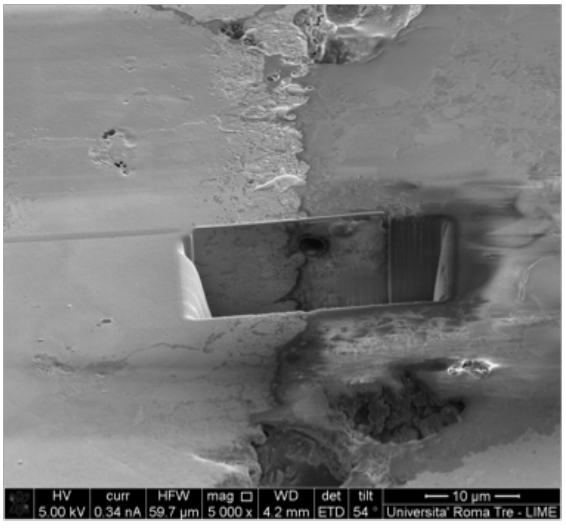


Fig. 2: FIB/SEM analysis of the interface between Alloy VE® (left) and Ceramic Avanté® (right) at 6500X. Milling stop due to the presence of a void.

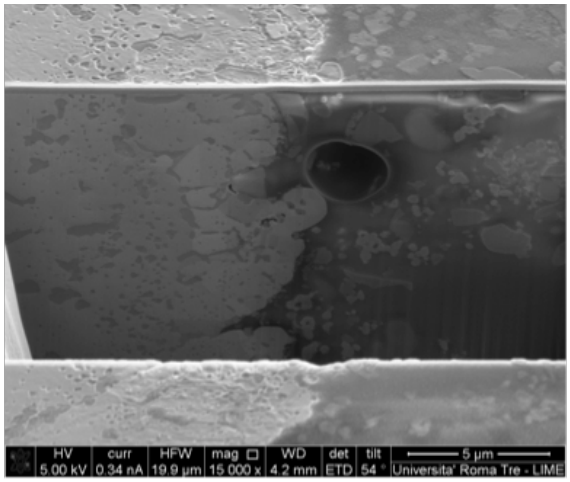


Fig. 3: FIB/SEM analysis of the interface between Alloy VE® (left) and Ceramic Avanté® (right) at 15000X. At higher magnification it is possible to observe the thin alloy oxide layer (about 10 µm).

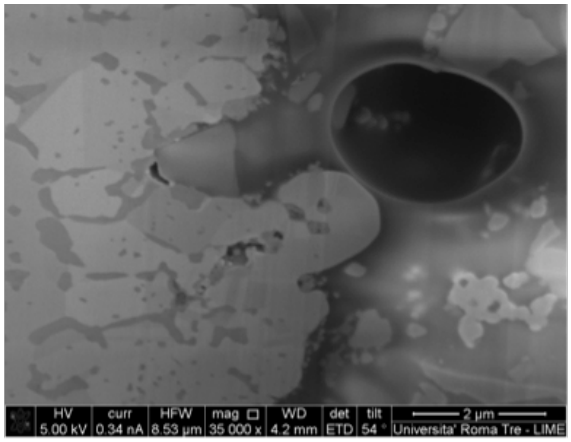


Fig. 4: FIB/SEM analysis of the interface between Alloy VE® (left) and Ceramic Avanté® (right) at 35000X. At higher magnification it is possible to observe the interaction between the low melting oxides of the alloy and an embedded zirconia or alumina grain probably due to the sandblasting laboratory procedures or ceramic firing.

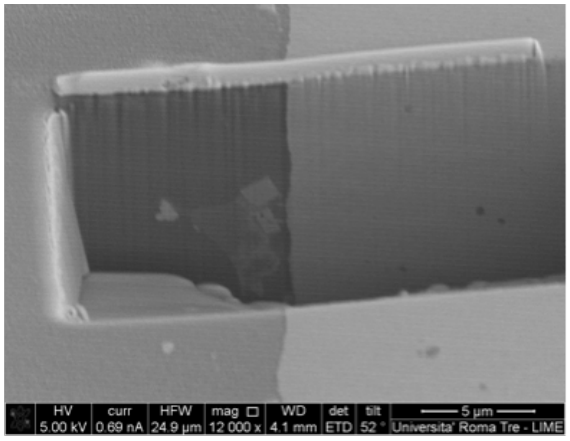


Fig. 5: FIB/SEM analysis of the interface between Will-Ceram® ZTM Zirconia 'K' Blocks (right) and Ceramic Avanté® ZTM (left) at 12000X. Stop of the ion beam milling due to the presence of several zirconia grains in the veneering ceramic.

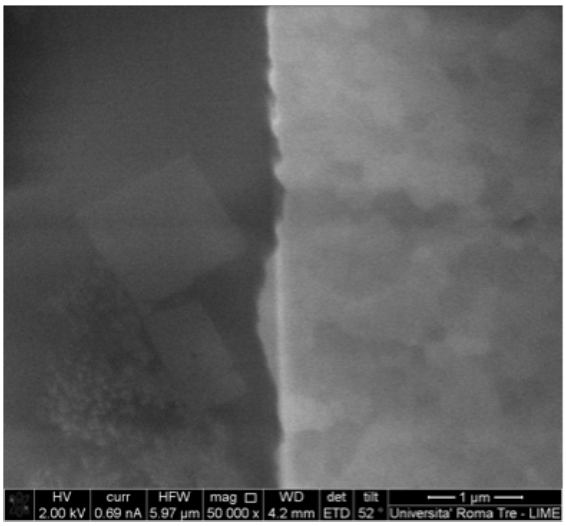


Fig. 6: FIB/SEM analysis of the interface between Will-Ceram® ZTM Zirconia 'K' Blocks (right) and Ceramic Avanté® ZTM (left) at 50000X. At higher magnification it is possible to observe the presence of zirconia grains in the ceramic from the sandblasting of the framework or to an increased presence of defects during mechanical processing of the Zirconia.

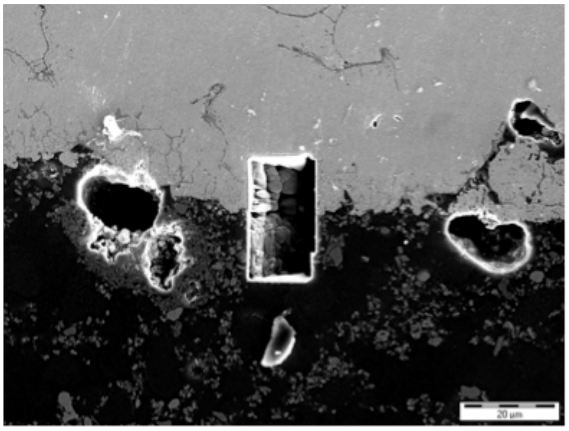


Fig. 7: despite the presence of many voids it was possible to perform the ion beam milling crossing the interface between IPS e.max® ZirCAD (up) and IPS e.max® ZirPress (down) (SEM, BSE, 1000X).

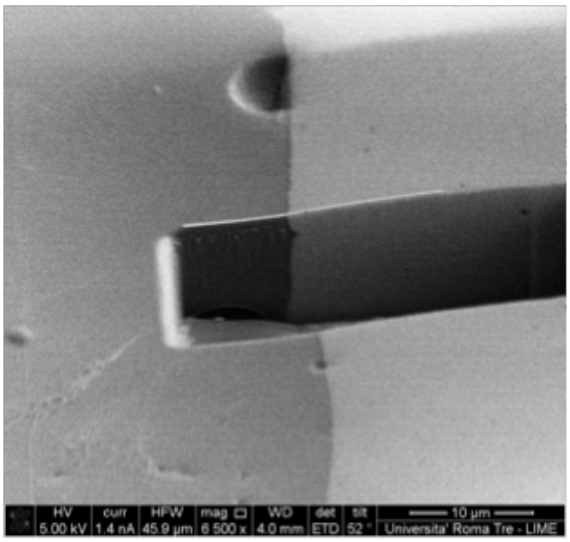


Fig. 8: FIB/SEM analysis of the interface between IPS e.max® ZirCAD (right) and IPS e.max® ZirPress (left) at 6500X. At Higher magnification it is possible to observe the thin Platinum layer (1µm) crossing the interface to protect the sample during the ion beam milling.

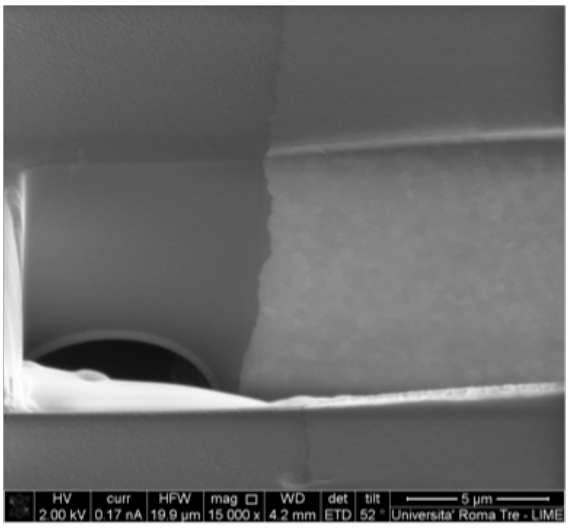
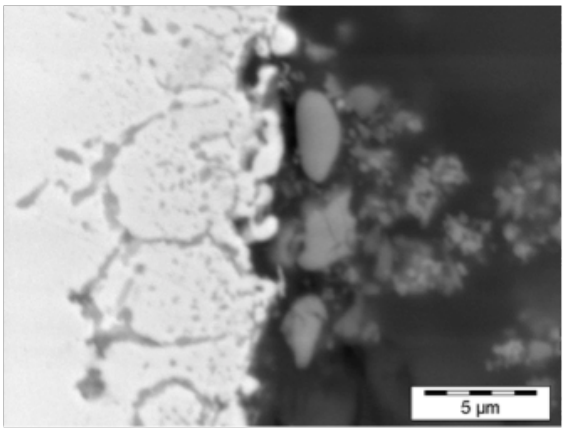


Fig. 9: FIB/SEM analysis of the interface between IPS e.max® ZirCAD (right) and IPS e.max® ZirPress (left) at 15000X. Stop of the ion beam milling due to the presence of a void in the ceramic. It is also possible to observe the zirconia grains structure.

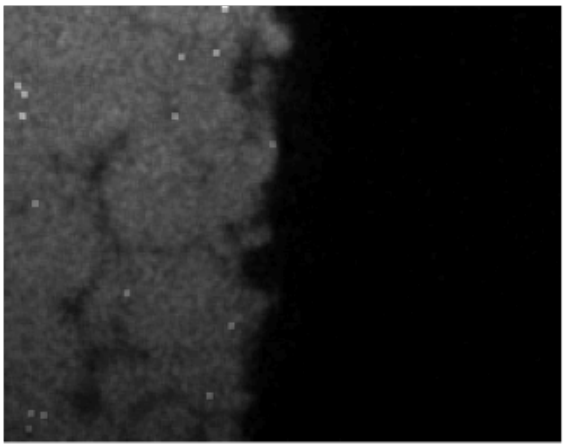
fact, the EDS map showed a high distribution of alloying elements (Sn, In, Ga) and the presence of zirconium-rich particles (probably zirconium oxide) within the layer of matting (Fig. 10).

Discussion

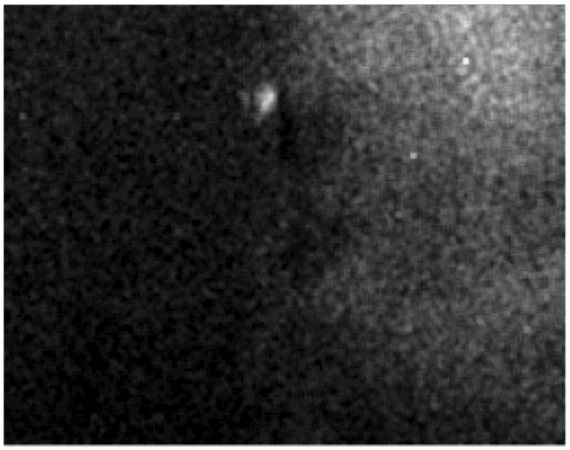
By the limits of this in vitro study, FIB/SEM analysis of metal-ceramic and zirconia-ceramic systems seems to be useful in the mor-



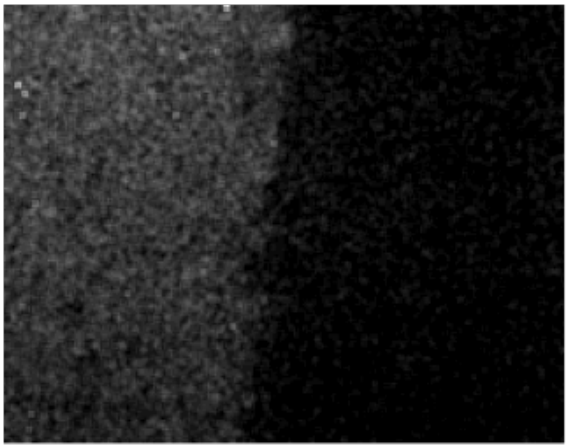
EM-BSE, 25kV, 5000x, 5000 CPS



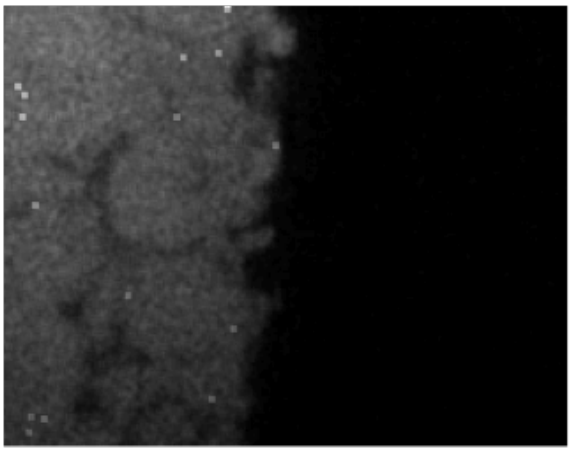
Ag



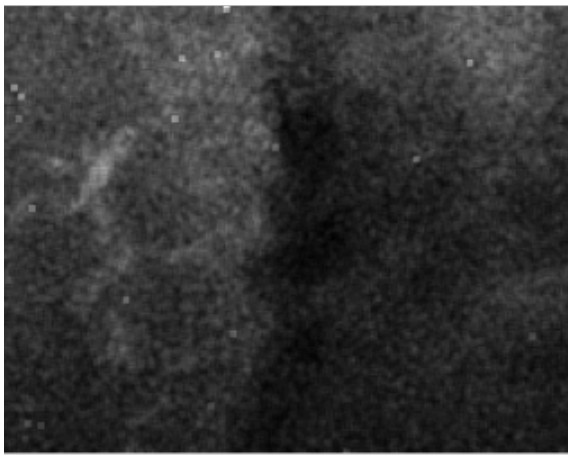
Al



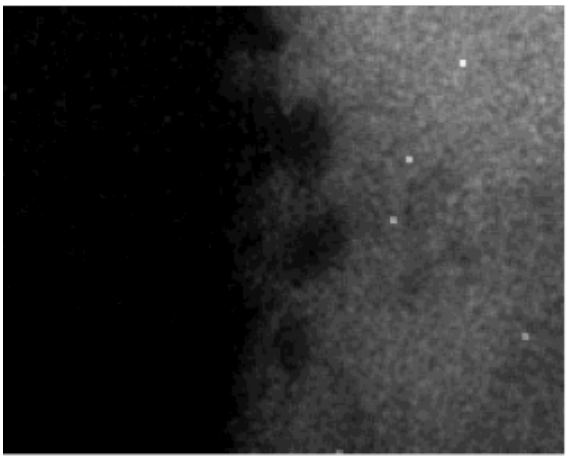
Au



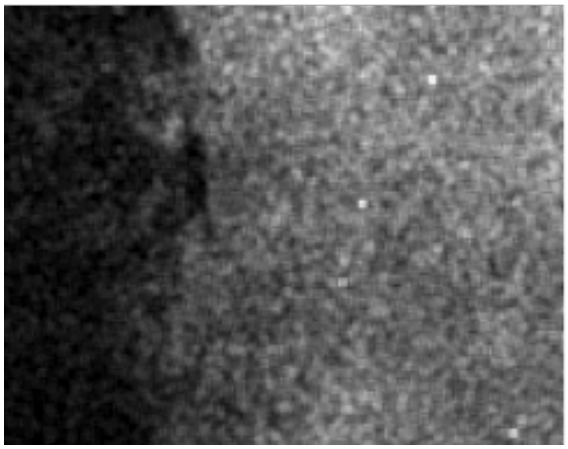
Pd



In



Si



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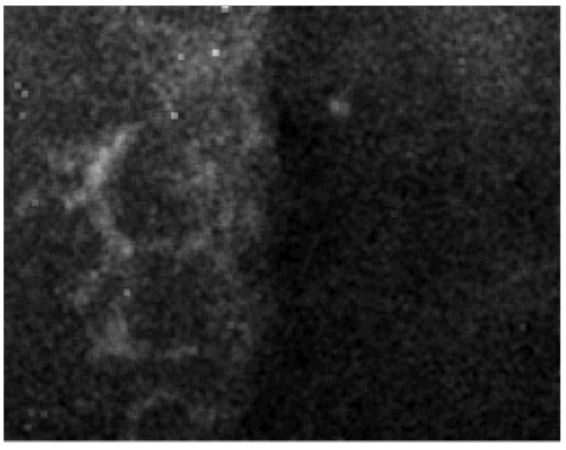
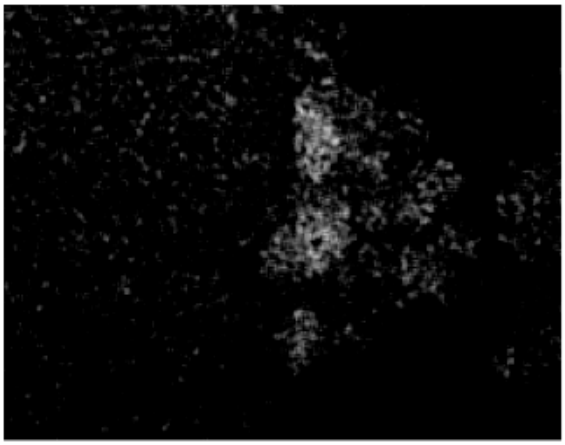
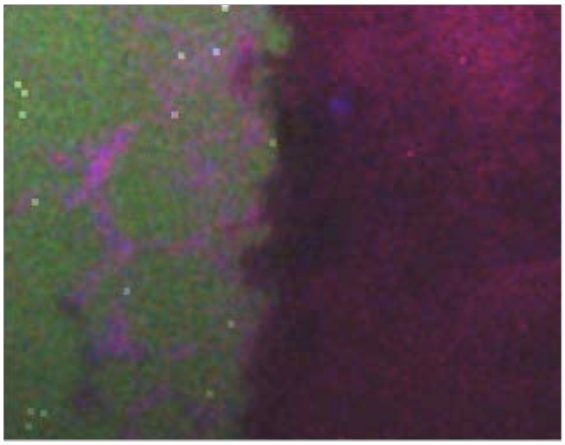


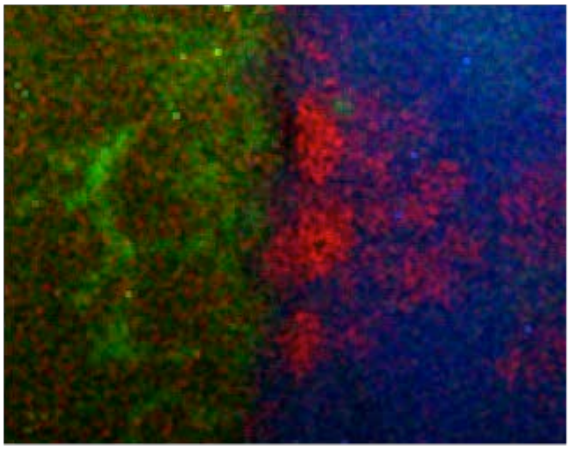
Sn



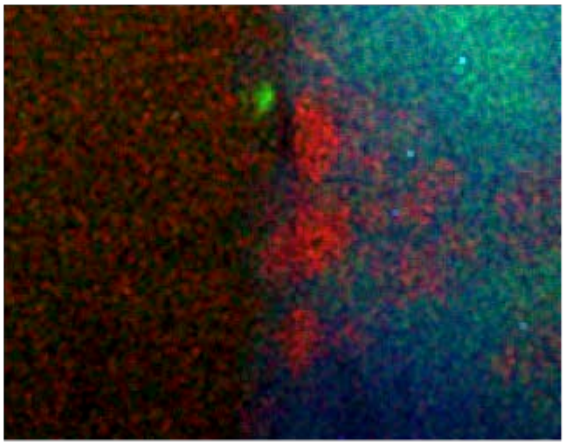
Zr



In, Pd, Sn (RGB)



Zr, Sn, Si (RGB)



Zr, Ai, Si (RGB)

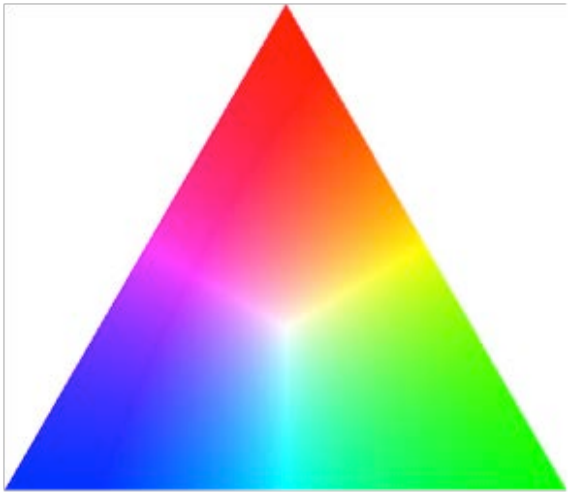


Fig. 10: SEM/EDS mapping of the interface between Alloy VE® (left) and Ceramic Avanté® (right) (25KV, 5000X). The map shows the presence of zirconium-rich particles (probably zirconium oxide) within the layer of matting. However, it seems that zirconium is also present in the alloy: this is actually an artifact due to the fact that the M peak of Gold (present in the alloy) is almost superimposed on the Zr L lines.

phological and microstructural characterization of the interfaces improving the knowledge about the interpretation of failures. In a comparative analysis with the our previous study[5], a lot of voids were reported in all the ceramic layers probably due to the dental laboratory production procedures, even if the operators strictly followed the manufacturer instructions. It is also worth noting the presence of a strong interfacial roughness, resulting from the previous blasting process or to mechanical processing of the Zirconia. In the SEM/EDS analysis, we observed no interfacial interactions in zirconia-ceramic systems, but a thin oxide metal layer in the metal-ceramic system

as a result of the oxidation/diffusion process. In details, we observed a segregation of low-melting point elements and a general change in the microstructure of the alloy compared to the bulk; moreover, the presence of zirconium-rich particles (probably zirconium oxide) within the layer of matting. However, it seems that zirconium is also present in the alloy: this is actually an artifact due to the fact that the M peak of Gold (present in the alloy) is almost superimposed on the Zr L lines. The distribution of elements is due to the low diffusivity of oxygen flux particularly high in high-Pd content alloys. The oxygen diffuses usually in the first 10 µm, also along the grain boundaries, forming oxides with some alloying elements (Sn, In, Ga). This phenomenon occurs during the course of oxidation of the alloy immediately before the preparation and sintering of ceramics. Probably, the oxygen diffusion and precipitation of oxides also occurs along the grain boundaries. It follows a structure similar to an oxide. The crystalline grains are larger than the mesh of the oxide (an average of about 50 µm, while the mesh shown here are approximately 5 µm). The layer of so-called "internal oxides" is therefore the significant change of the interface that occurs mostly prior to completion of ceramics. During the sintering of ceramics there is only a minimal additional precipitation of "internal oxides" in the alloy and passage of oxides from the alloy to ceramic (a few microns). The interface roughness which is known as pre-existing oxidation is achieved by blasting the surface oxide of the alloy. This may also explain the presence of a particle-rich aluminum wedged at the interface. The oxidation has the effect of some oxides that form on the surface only slightly alter the general trend of the roughness obtained with the prior sandblasting. In any case, as we report in previous studies[22, 23], changes of this type at the interface (morphology, microstructure and hardness) should result in an increase of interfacial toughness and then adhesion between the two layers. A further issue that is currently under investigation is the effect of the residual stress due to processing on the mechanical behavior of the two systems. The focused ion beam microscope has been recently proposed as an innovative tool for the high resolution measurement of residual stress at specimen surface[25-27]. Currently ongoing work involves the measurement of residual stress at specimen surface and the correlation with failure modes during scratch and indention testing.

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