Analysis by Microscopy Techniques of Metal-Ceramic Dental Restorations with CoCr Support

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Co-Cr classic alloys have been used in dentistry for the first time in 1929 and have since been widely applied as a metallic layer in the prosthetic restorations. The popularity of the metal-ceramic metallic restorations increased due to the higher predictability and positive clinical results validated by scientific evidence on the long term, along with ease procedures for casting metal parts as well as rare reported cases of adverse reactions. The structural integrity and the accuracy of the manufacturing procedures of the Co-Cr metal-ceramic restorations was assessed by metallographic procedures and optical and electronic microscopic examinations.

Keywords: SEM, optical microscopy, Co-Cr alloy, fixed prosthetic restorations, ceramics

The metal-ceramic restorations were the early 60's *gold standard* in dental prosthetics, due to mechanical, aesthetic satisfactory results, clinical acceptability and due to the marginal and internal adaptation quality [1-7].

The popularity of the metal-ceramic restorations has increased due to the higher predictability and positive clinical results validated by scientific evidence on the long term, along with ease procedures for casting metal parts as well as rare reported cases of adverse reactions [8].

The metallic layer substrate and the opaque porcelain layer used for hiding the metal, limit the aesthetic result through the lack of translucency. In fact, the these restorations either absorb or reflect the light, while the dental tissues present a translucid degree [9].

Co-Cr classic alloys have been used in dentistry for the first time in 1929 and have since been widely applied as a metallic layer in the prosthetic restorations [10].

Applying a metallic biomaterial in the oral cavity creates active interfaces, thorough which the body affects the material and the material affects the body. In addition to a number of physical, chemical and mechanical conditions, the biomaterials from the prosthetic restorations must be compatible. Another category of factors that influence the properties of biomaterials used in the fix prosthetic is the correctness of the technological phases [11-14].

Non-noble cobalt chrome alloys have a high mechanical strength due to the presence of sodium silicate in their content and melting temperature range of more than 1400°C. Cobalt-chromium alloys are biocompatible and prosthetic pieces made of them have particular precision regarding dimensions and shape. The chemical composition of these alloys include also in lower proportions other elements such as silicon, nickel, molybdenum, magnesium, titanium, tungsten.

This paper aims to show how structural integrity and the accuracy of the manufacturing procedures of the metal-ceramic restorations can be assessed by metallographic procedures examinations using optical and scanning electron microscopes.

Experimental part

Optical metallography studies on the materials used in the metal-ceramic reconstructions were performed on samples in molded state and after the three thermal cycles with the following parameters: $V_{heating}$ = 50°C/min - keeping for 5min. at approx. 1000°C and cooling with a rate of max.70°C/ min (in the range of 1000°C- 600°C) and then with about 100°C /min.

The metallographic samples were prepared from casted CoCr sheets (1 cm^2 diameter) provided from Bego and Heraeus Company.

Optical microscope (Olympus BX5) and SEM microscope (Philips ESEM XL 30 TMP equipment) provided with backscattered electron signal (BSE) and EDS (energy dispersive X-ray) spectrometer were used for examination the samples.

Results and discussions

Figure 1 shows the corresponding optical micrographs of a Co-Cr alloy sample in the state as-cast and after three thermal cycles. Its microstructure was highlighted by a metallographic reagent solution prepared from: 1g KOH, 4g $KMnO_4$ and 95mL distilled water. One can observe a strong targeted dendritic structure and chemical segregated. Due to the large solidification interval, the dendrite morphology is one arranged in packets in which the dendrites are almost perfectly aligned in the direction of solidification. A microrefinish material section is not observed, although this alloy is susceptible to it, due to the large solidification and high coefficient of thermal contraction. There are also observed some randomly arranged chemical inhomogeneities in material microvolum, being evidenced the microsurfaces where the continuity dendritic structures present a hiatus.

After the three thermal cycling, microsegregation at secondary axes of the dendrites practically disappears completely, resulting in dendrites that are little, rough but uniform. Significant dendritic segregation and the secondary axes of the dendrites are developed stronger, their length ratio relative to the main axis being about 3: 1.

Dendrite length is reduced and the proportion of solidified alloy with planar front is also reduced. These can be due to the presence of Mn (2%) which is totally soluble into α-Co (according to phase diagram ASM) and considerably reduces the temperature range of solidification. In interdendrite spaces, there is also an intermetallic compound precipitated (dark gray) Mo_4Mn_5 intermetallic

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All authors have equal contribution to the study and the publication

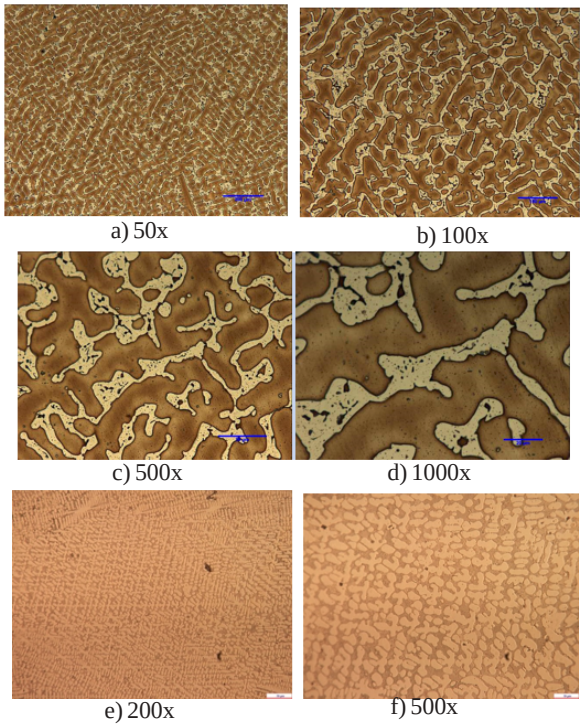

Fig. 1. Optical micrographs of samples taken from the Co-Cr alloy in the several states: (a-d) – as-molded; (e,f) – after three thermal cycles. Attack: 1gKOH, 4g $KMnO_4$, 95mL distilled water

compound. After three thermal cycles at about 1000^0C, both Mn and Mo_4Mn_5 almost disappear reaching a structure with submicron size of interdendritic space (looking for as *salt and pepper* mixture in interdendritic space, fig. 1f).

When examining the interface between metal and ceramics the optical micrographs for cross-section shown that after two thermal cycles a random pores structure is observed for opaque/ metal interface. However, after the third cycle, is observed almost undetectable presence of microcracks, which are formed in the micropores zone at the interface. These microcracks have a systematically a certain inclination angle towards interface.

After the application of the opaque layer, the apparition of few micro pores placed in opaque is observed. By applying the dentine, the pores from opaque disappear and metal-ceramic interface remains virtually the same as it was at the previous cycle. For all ceramic deposition is can be observed that at the end of the cycles the ceramic material, in any form is submitted, show an advanced homogeneity, which means that thermal cycle's parameters and deposition technologies were correct chosen and were properly followed.

The issues above researches are completed with metalographic compositional and morphological examinations by scanning electron microscopy. Table 1 shows the elemental composition of Co-Cr, which is different from standard composition.

Examination by scanning electron microscopy was also performed for the as-cast Co-Cr samples in the state as cast, after the thermal cycling of the samples after and the deposit of the ceramic layer.

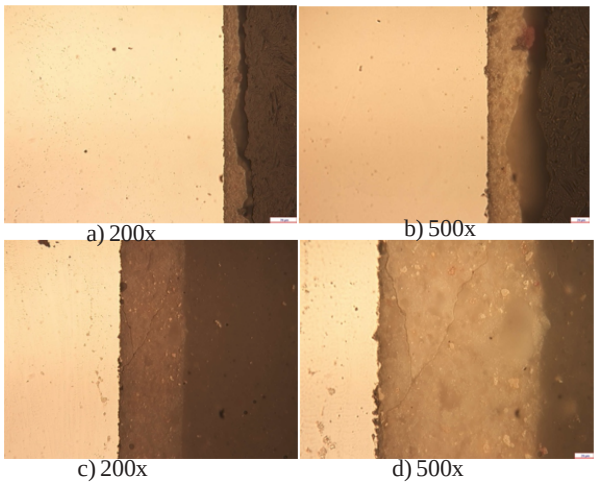

Fig.2 The optical micrographs of the metal-opaque interface (a, b), the opaque-dentin-metal interface (c, d) - non-etched samples of Co-Cr alloy

In the Co-Cr alloy case studied, morphological and compositional image analysis (fig. 3) provide additional information which not legally complete the results from metallographic analysis. The figures 3-a,b,c present SEM images of surface. Onto micro-area analyzed to determine the chemical composition, were recorded as a the percentages of chemical elements (fig. 3-d) show slight deviation of from the composition of the standard, due to the powerful significant microsegregation manufacturer of the material. Figure 3-f shows an interruption of the contact made by ceramic made contact, which left the area and the existence of microcracks therein.

Backscattering electron image shown in figure 3-c indicates clearly the existence in the interdendritic space

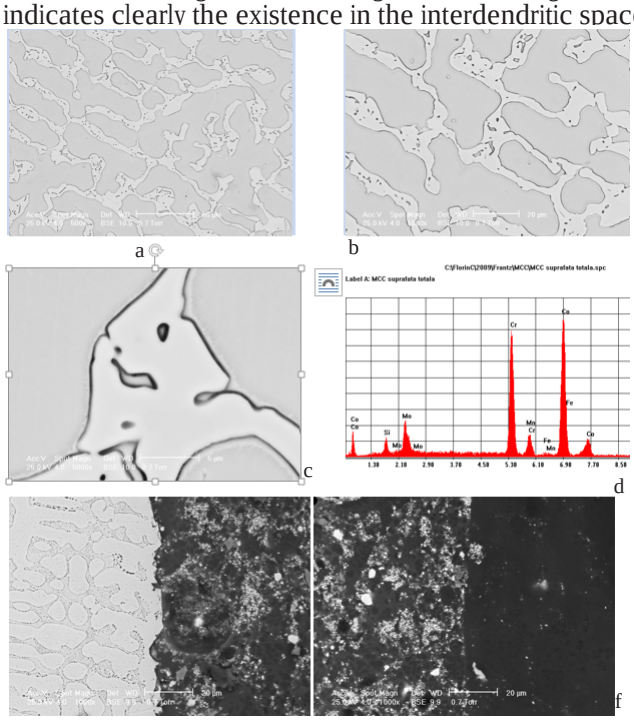

Fig. 3. Results of the analysis by scanning electron microscopy on samples taken from Co-Cr alloy

Table 1

CHEMICAL COMPOSITION of Co-Cr AS RECEIVED SAMPLE DETERRMINED BY XRD ELEMENTAL ANALYSIS DETERMINED BY EDS ON ALLOY SAMPLE

Alloy	Chemical composition [At. %]						
	Co	Cr	Mo	Si	Mn	Fe	Total
Co-Cr	51.7	32.1	6.8	6.8	2.2	0.4	100

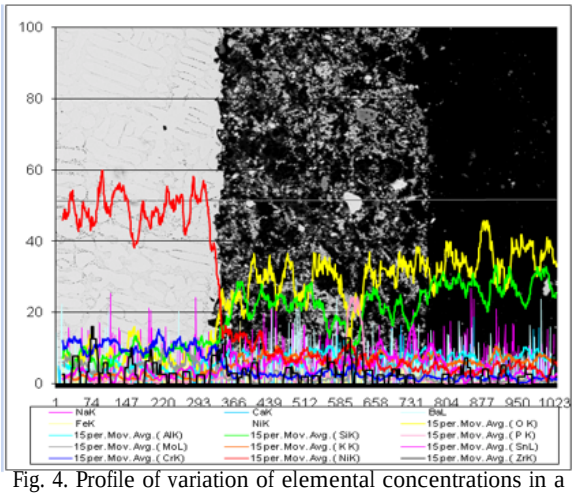

Fig. 4. Profile of variation of elemental concentrations in a preselected direction

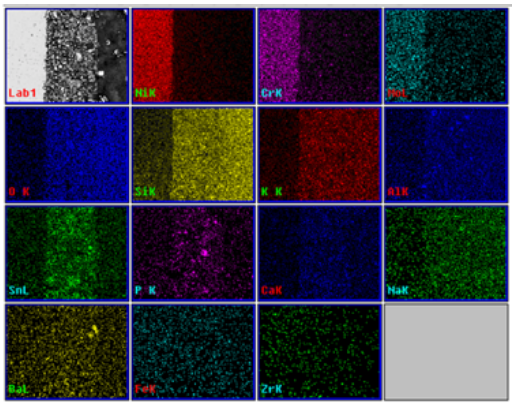

Fig. 5. Distribution of concentration maps item, for various elements within the section of deposit

of Co-Cr type intermetallic compound in a percentage less than 10%, likely based on Co_3Cr stoichiometry (23% Cr). This intermetallic compound is *placed* in the σ phase, which has a higher percentage of Cr (from 50.5 to 63%) compared to the majority phase that is a σCo dendrite structure. Owing to the narrow interdentritic space, the EDS analysis could not identify quantitatively the intermetallic compound and π phase. Therefore, our assessment is based only on qualitative image and correlation diagram of balance. Backscattering electron image shown in figure 3-c combined with chemical microanalysis also confirms the presence of intermetallic compound Mo_4Mn_5 compound (light gray).

Backscattering electron image of the metal-ceramic interface shown in figure 3-f indicates an interruption (discontinuities) of the contact made by ceramics, which left the area, and also the existence of microcracks therein, oriented perpendicular to the surface of the ceramic material deposit. This rift can ascribe to the difference in coefficients of thermal expansion between the ceramics and metallic alloy.

The images showing metal-ceramics and ceramics interface (figs. 3e and 3-f) are representative for continuity and absence of pores, being highlighted the ceramics homogeneity. In determining the degree of homogeneity of the two ceramic layers deposited on the support and determining the accuracy parameters of thermal cycles applied to obtain a good section of deposit, semiquantitative determinations for the representative elements (Ni, Cr, Mo, Al, Si, O, P, K, Zr, Sn) were performed. The results are presented in figures 4 and 5.

As shown in figures 4 and 5, the concentration maps of section of the ceramic material is indicate a quite uniform distribution of elements. However, P and Zr elements show a maximum variation within opaque-dentin interface. The other elements that such as K and Sn have a relatively uniform distribution section. Under the support material, the dendrite structure leaves its mark on the compositional variation of Ni, which is a majority element in the main axis of the dendritic and interdendritic, reaching a nadir the lowest value in the area. Cr axis shows a minimum percentage in dendrites, leading to their increasing them to the edges. Follow the A variation of CrMo content but was also found in interdendritic space.

Conclusions

In the as-cast Co-Cr specimens examined by optical microscopy, chemical inhomogeneities were observed in the material arranged randomly, with a hiatus in the continuity of dendritic structures. When examining samples after three thermal cycling, we have found the presence of a less fine dendritic structure, but a smooth surface. However, the appearance of pores after thermal cycling at the interface between metal and ceramics was observed, leading to an opaque/ metal interface.

The elemental analysis by EDS performed to determine the chemical composition has indicated mild deviations from the standard composition due to a significant segregation of the Co-Cr alloy.

An examination by scanning electron microscopy with backscattering electron signal has found discontinuity of contact between the two materials (ceramics and Co-Cr alloy) and cracks. They are certainly due to the difference in thermal expansion coefficients between ceramic material and metallic alloy.

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