EFFECT OF RECASTING ON THE USEFUL PROPERTIES CoCrMoW ALLOY

Recasting of the previously cast metal can change the chemical composition of the newly formed material, which ultimately could affect the properties of a dental alloy. The research used a dental alloy CoCrMoW trade name Remanium 2001. Three groups of dental alloy were prepared by mixing 50% fresh alloy to alloy remnants from previous castings. The specimens in the first casting group used 100% fresh alloy and served as control (R1). The second group consisted of equal amounts of fresh alloy and alloy remnants cast only once (R2). The third group contained 50% fresh alloy and alloy cast twice (R3). Microstructural analysis was performed and the chemical composition, XRD studies, hardness, and tribological test and the metal–ceramic bond strength was investigated according to ISO9693 standard. New material should be used in casting, and if previously casted material is used, it should be mixed with new material. The use of the recasting procedure can lower the costs of CoCrMoW castings and can be safely in dentistry.

Keywords: cobalt alloys, durability of prosthetic devices, recasting.

In the opinion of Bauer et al. [4] the scrap produced in dentistry is extremely pure due to the fact that this metal is melted in controlled conditions without necessity to apply any chemical process used in industrial conditions. Dental alloys reuse seems promising in case of Ni–Cr [12] and Co–Cr alloys [1] as well as gold based alloys [17].

From references [4, 12, 13] it appears that the properties of recast-ed alloy may differ from the properties of a new alloy purchased from the manufacturer. The differences may be associated with its chemical composition [13], castability [12], as well as with mechanical properties [4]. However the opinions concerning mechanical properties are extremely divided. Some authors [1, 4] think that these properties can increase or decrease [11, 20] but the research carried out by Palaskar et al. [12] demonstrate that there is no statistically significant castability change as a result of alloys recasting. There are experimental studies described in literature [13] and reflecting changed chemical composition of final products under the influence of successive recasting processes and development of new phases determining the changes in alloy properties. The deterioration in the scope of corrosion properties [6] or even cytotoxicity [2] is also possible due to changed chemical composition in case of recasting.
The process associated with remelted materials use may change the composition of metal oxide surface layer which may be of critical importance for metal ceramic bond [24].

Sufficient bond strength between porcelain and metal structure of applied biomaterial [19, 21] is an important factor determining the durability of metal ceramic apparatuses. The use of recycled alloys is not recommended by Ucar et al. [19] to avoid potential reduction of bond strength between porcelain and metal.

Therefore the purpose of the present study was to evaluate the effect of addition of remelted materials on some mechanical properties of CoCrMoW alloy i.e. hardness, tribological wear, metal ceramic bond strength as well as evaluation of microstructure and chemical composition of newly produced castings.

2. Material and methods

Remanium 2001 dental alloy (Dentaurum, Germany) with cobalt matrix and nominal Remanium 2001 (w/w) consisting of 63% Co, 23% Cr, 7.3% Mo, 4.3% W, 1.6% Si and Mn<1% and N<1% [27] has been used in tests. This alloy is used for casting of denture elements (among others crowns and bridges) with permanent ceramic veneers. The microstructure of tested materials and their surface after tribological tests have been analysed by means of Phenom G2 pro desk electron microscope (Veeco Instruments). The wear tests were carried out by means of “ball-on-disc” tribotester manufactured by CSM Instruments, at temperature of 37°C and artificial saliva environment (pH=5.3). The composition of artificial saliva has been prepared on the basis of PN-EN ISO 10271:2012 standard [26]. The balls with diameter of 6 mm and hardness of 2000HV (manufactured by CSM Instruments) have been used as counterpart (ball). The tests were carried out under the load of 10N with linear speed of 1.88 cm/s on the radius of 3 mm. The total travel used to record friction coefficient variation was equal to 100 m. The reduction of specimen material volume occurred in the form of wear trace as a result of specimen - counterpart mating was equal to the wear measure. Therefore Dektak 150 profile contact tester manufactured by Veeco Instruments has been used to measure the surface area of specimen wear profile along specimen circumference (in 12 locations). Tip radius of measuring needle was equal to 2 µm. The volumetric wear has been determined as the average value of specimen wear surface area multiplied by the circumference of the circle of wear trace produced in the ball-on-disc test.

The specimens for ceramic bond strength tests have been prepared in accordance with requirements included in PN-EN ISO 9693 [25] standard in the form of rectangular plates with dimensions of 25×3×0.5 mm. IPS d.SIGN dental porcelain (IvoclarVivadent, Schaan, Liechtenstein) with dimensions of 8×3×1 mm has been applied centrally onto the metal plates. The whole process associated with dental porcelain fusion to metal was carried out in conditions existing in professional prosthetic dental laboratory. Nine (9) specimens from each test group have been used for test. Three point bending test has been carried out by means of Zwick Z100 universal testing machine equipped with 500N measuring head. The distance between the supports was equal to 20 mm and the diameter of specimen supporting rollers was equal to 2 mm. The testing speed (traverse beam feed) was equal to 1.5 mm/min. The loss of bond strength was indicated by the value of force at which a load disturbance (reduction) was observed in deflection curve. Then the bond strength \( t_b \) has been determined using the following formula [25]:

\[
t_b = k \cdot F_{\text{fail}}
\]

where: \( k \) – the factor depending on thickness of base metal and Young module, \( F_{\text{fail}} \) – the force causing the loss of metal-ceramic bond strength.

The microstructure of tested materials and their surface after tribological tests has been analysed by means of Phenom G2 pro desk top scanning microscope.

3. Tests results and discussion

The microstructure of tested cast alloys is characterized by typical coarse grained dendritic structure (Fig. 1). The microstructure of castings containing remelted material is similar to microstructure of brand new castings. There were no inclusions which could originate from charge contamination in the form of investment material. Furthermore diversified carbides shapes have been revealed in course of SEM analysis. The carbides phases are characterized by dual structure i.e. occurring in the form of blocky precipitations as well as lamellar precipitations (“pearlitic type”). In the opinion of some authors [15],
the lamellar structure of carbides is caused by cooling rate variation between 8 and 16 °C/min; 35 °C/min [16] is the maximum cooling rate for the creation of eutectoid phase. Carbides precipitations may have decisive impact on increased reinforcement of an alloy and its reduced plasticity [20].

The average hardness achieved by a brand new alloy and recycled materials reaches a value similar to that declared by the manufacturer of 336HV10 (Fig. 2). There are no significant differences between R1 and R2 groups (p=0.942) demonstrated by non-parametric test for independent test by U Mann-Whitney (for α=0.05) carried out by means of STATISTICA program. However the difference found between R1 and R3 group (p<0.05) as well as between R2 and R3 group (p<0.05) was significant.

Hardness results have been additionally analysed by means of Kruskal-Wallis test at assumed significance level α=0.05. However no significant difference has been found between R1 and R2 groups but the difference found between R1 and R3 group (p<0.05) as well as between R2 and R3 group (p<0.05) was significant. Detected hardness differences are closely associated with changed chemical composition of remelted materials and particularly with percentage of carbon content contributing to the formation of hard carbides. The changes of chemical composition in tested materials are presented in table 2.

It should emphasized that there is information about elements concentrations under 1% indicated in manufacturer’s data. The carbon content for R1 and R2 groups is similar and average hardness values are identical in the both groups (334HV10). However a change in carbon concentration has been denoted in remelted materials from R3 group which could be the explanation for hardness increase. However, the determining factor in the increase in the hardness of the alloy R3 is a large percentage of the hard carbide Cr₃C₂ (Fig. 3) as compared

![Fig. 1. SEM microstructure of castings: (a) control sample R1, (b) recasting R2, (c) recasting R3](image1)

![Fig. 2. The comparison of Vickers hardness of tested alloys groups](image2)

| Table 2. Chemical composition of alloys under test [wt. %] |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Groups          | C         | Si        | Mn        | P         | S         | Cr        | Mo        | Ni        |
| R1              | 0.059     | 1.136     | 0.152     | 0.0014    | <0.00020  | 22.86     | 8.426     | 0.058     |
| Sd.             | 0.0076    | 0.013     | 0.0020    | 0.0020    | 0.125     | 0.085     | 0.025     |
| R2              | 0.060     | 1.221     | 0.153     | 0.0014    | 0.0029    | 22.84     | 8.570     | 0.052     |
| Sd.             | 0.0038    | 0.028     | 0.0022    | 0.0011    | 0.403     | 0.221     | 0.0026    |
| R3              | 0.073     | 1.199     | 0.146     | 0.0014    | 0.0039    | 22.05     | 8.435     | 0.193     |
| Sd.             | 0.017     | 0.047     | 0.014     | 0.0022    | 1.230     | 0.085     | 0.0029    |

| Groups          | W         | Fe        | Al        | Cu        | Nb        | N         | Ti        | Co        |
| R1              | 4.299     | <0.005    | <0.005    | 0.0068    | <0.005    | 0.192     | 0.0048    | 62.77     |
| Sd.             | 0.034     | –         | –         | 0.0003    | –         | 0.052     | 0.0003    | 0.111     |
| R2              | 4.320     | <0.005    | <0.005    | 0.0069    | <0.005    | 0.203     | 0.0051    | 62.52     |
| Sd.             | –         | –         | 0.021     | 0.0001    | –         | 0.071     | 0.0002    | 0.150     |
| R3              | 4.315     | <0.005    | 0.140     | 0.0068    | <0.005    | 0.184     | 0.0047    | 63.23     |
| Sd.             | 0.011     | 0.209     | 0.0002    | 0.057     | 0.0003    | 0.904     |
to the carbides present in the other study groups. The carbon content within 0.059–0.073% indicates that materials under analysis belong to low carbon alloys group.

Figure 3 illustrates XRD pattern for the alloys groups under test indicating only the reflections from carbides without any reflections from matrix. The tests demonstrated the co-existence of carbides i.e. mainly Cr$_7$C$_3$, Cr$_2$C$_3$ and Cr$_3$C$_2$ in the alloys under test. Cr$_7$C$_3$ carbides percentage is the highest in R1 control group; Cr$_2$C$_3$ carbides prevail in R2 group and Cr$_3$C$_2$ in R3 group. Such circumstances are associated with changed chemical composition and carbides transformations occurring in course of alloy recasting processes. Additionally the presence of the following intermetallic phases has been detected in course of tests: Cr$_{0.7}$Mo$_{0.3}$ and Mo$_6$Co$_7$ – not marked on XRD pattern. However the authors of studies [9, 14] found that Cr$_7$C$_3$, Cr$_2$C$_3$ carbides may be produced in alloys with low chromium content but this opinion has been not confirmed in our tests (about 23% Cr). However Karaali et al. [8] emphasize that carbides i.e. MC, M$_7$C$_3$, M$_{23}$C$_6$ and M$_8$C may be produced in cobalt alloys for medical and dental applications but the carbon content occurring in said data is equal to 0.1–0.35%C and CoC ralloys for dental applicationsshould be low carbon alloys.

The results of tribological tests in artificial saliva demonstrated average friction coefficient on the level $\mu$=0.32–0.341 – similar for all materials groups under test (table 3).

<table>
<thead>
<tr>
<th>Groups</th>
<th>Average $\mu$</th>
<th>Standard deviation</th>
</tr>
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<tbody>
<tr>
<td>Never cast (R1)</td>
<td>0.320</td>
<td>0.021</td>
</tr>
<tr>
<td>Cast once (R2)</td>
<td>0.329</td>
<td>0.043</td>
</tr>
<tr>
<td>Cast twice (R3)</td>
<td>0.341</td>
<td>0.019</td>
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Figure 4 illustrates the changes of friction coefficient for mating surfaces CoCrMoW (specimen) – Al$_2$O$_3$ (counterpart) along the distance of 100 m. The top points of roughness profile are sheared off first, therefore the initial values of friction coefficients are higher. As a result of running – in of friction surface, the contact area between mating surfaces increases and the friction coefficient is reduced and stabilized. The stabilization of friction coefficients is practically observed in all cases under test after the distance of 20 m. The higher carbon content in an alloy and consequently increased hardness causes increased friction coefficient observed for R3 alloy.

Hard carbides precipitations constitute a natural barrier for the counterpart material. The analysis of wear profiles (Fig. 5) and surface of paths –SEM pictures (Fig. 6) indicate to abrasive wear mechanism. The microcutting in the form of continuous cracks along wear traces and abrasion wear abrasion wear of relatively soft matrix are prevailing factor in this case. The wear process is intensified as a result of an additional impact of hard carbide phase loosely rolling between mating surfaces of specimen and counterpart with wearing surfaces. Such behaviour causes increased abrasive wear effect in alloys being tested. The scratches are caused by rolling carbides on the specimen mating surface or plastic deformation of matrix fragments leaving specific traces in the form chases. The chases are clearly visible on wear trace profile (Fig. 5). The authors of studies [3, 23] also confirm in their tests that the abrasive wear is the prevailing factor causing the destruction of the top layer of CoCrMo casting alloys.

Figure 7 illustrates the results for volumetric wear for tested materials. When comparing the tested materials, it is possible to observe higher wear resistance of R1 control material by about 14% in relation to R2 alloy. However in case of addition of two times remelted
material to the fresh alloy (R3 specimen) its wear resistance will be reduced by about 34% in relation to R1 control specimen.

As described in literature [23], abrasive wear of cobalt alloys is determined by hard carbide particles or hard protrusion which are depressed by the counterpart and moved in relation to mating surfaces thereafter. From data available in literature [22] it appears that wear intensity in high carbon CoCrMo alloys is significantly lower than in low carbon alloys due to the fact that low carbon CoCrMo alloys are characterized by low volume percentage of carbides. The value of friction coefficient is affected by the environment (liquid medium) contacting and interacting with an active surface. For instance 0.36%NaCl environment increases the friction coefficient in high carbon cobalt casting alloys and its reduction in case of low carbon alloys [23]. However this trend is completely reversed in different medium (e.g. in 50% bovine serum or Dulbecco’s Modified Eagle’s Medium).

The values of friction coefficients obtained by the authors of the present article is similar to the data available in literature [23] obtained from tests performed for high carbon alloys (µ=0.19÷0.25) and for low carbon alloys (µ=0.27÷0.28) in various liquid media (but other than artificial saliva).

However the authors of the present article were unable to make any references in wider form because the scientific studies in the scope of tribological measurements for recast CoCrMo alloys in artificial saliva environment still remain to be realized. So called wear factor K considering the force and sliding distance applied in course of test is specified as a comparative wear measure by the authors engaged in the scope tribological wear research [18, 23]:

$$K = \frac{\text{Wear volume}}{\text{Applied force} \times \text{sliding distance}} \left[ \text{mm}^3 \text{N}^{-1} \text{m}^{-1} \right]$$

The table No 4 presented below contains the values of wear factors for all tested groups. Iijima et al. [7] emphasize the fact that the wear factor is an important feature characterizing the tribological properties of materials used for the production of prosthetic apparatuses. Furthermore they indicate to a serious problem occurring in the greater part of research studies in the scope of prosthetic dentistry i.e. the fact that the tribological properties are neglected by the scientists concentrating on the examination of strength and corrosion properties.

Significant differences between R1 and R2, R2 and R3 as well as R1 and R3 groups (p<0.05) have been demonstrated in course of statistical analysis of wear volume carried out in the form of U Mann-Whitney test:

<table>
<thead>
<tr>
<th>Groups</th>
<th>Wear factor K [mm³/N·m⁻¹]</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Never cast (R1)</td>
<td>2.25×10⁴</td>
<td>0.26×10⁴</td>
</tr>
<tr>
<td>Cast once (R2)</td>
<td>2.58×10⁵</td>
<td>0.31×10⁴</td>
</tr>
<tr>
<td>Cast twice (R3)</td>
<td>3.02×10⁵</td>
<td>0.57×10⁴</td>
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the value $\tau$ has been recorded in each group when a specimen under test achieved specimens group with the addition of remelted alloy, one case of case and even significantly exceeded in certain cases. Only in R2 and R3 ceramic bond demonstrate that this minimum value has been achieved MPa in three point bending test. The mean strength values for metal-

This standard assumes the minimum strength on the level of $\tau$ ceramic systems carried out in accordance of ISO 9693 procedures. In case of of Kruskal-Wallis test more prudence is necessary when drawing any substantive conclusions from performed tests due to greater probability of type I and II errors.

Figure 8 illustrates the variations of bond strength for metal-ceramic systems carried out in accordance of ISO 9693 procedures. This standard assumes the minimum strength on the level of $\tau=25$ MPa in three point bending test. The mean strength values for metal-ceramic bond demonstrate that this minimum value has been achieved and even significantly exceeded in certain cases. Only in R2 and R3 specimens group with the addition of remelted alloy, one case of case has been recorded in each group when a specimen under test achieved the value $\tau<25MPa$. The production of prosthetic apparatuses with permanent porcelain coat is a difficult process due to different nature of chemical bonds occurring in the both materials. This process in large part depends on manual skills of dental technician who should uniformly apply the dental porcelain onto metal substrate in a manner ensuring complete wetting of metal substrate and the thickness of individual ceramic layers being applied should be not excessive in order to avoid the weakening of metal-ceramic bond structure by pores occurring in course of porcelain firing process. Therefore the failure to achieve the minimum value of 25Ma for said two specimens could probably caused by excessive porosity in ceramic structure created in application phase but not by the addition of recast material.

In summary, no deterioration has been observed in metal–ceramic bond strength for alloys containing recast materials be even an insignificant growth. Comparing the results obtained for R2 group and for R1 control group, it can be observed that dental porcelain bond strength is 17% higher in R2 group. In case of comparison between R1 and R3 group the bond strength is increased in R3 alloy. However no statistically significant changes have been indicated by means of U Mann-Whitney test at significance level $\alpha=0.05$. The power of U Mann-Whitney test is the high-

Figure 9 presents SEM microphotographs of the cross-section of the metal-ceramic systems after debonding for dental porcelain on metal substrate. The adhesive-cohesive fractures have been obtained in almost all tested groups of alloys on the metal substrate end. The cohesive fracture has been obtained in several cases (Fig. 9c) for R3 test group, with the fracture occurring within ceramic or metal oxides transitionlayer.

Ucar et al. [19] suggest that porcelain veneers on recast metals may result in changed composition of surface metal oxide and consequently in a critical impact on metal–ceramic bond strength. Their three point bending tests for NiCrMo demonstrated that use of recast base metal alloy with fresh alloy reduces the metal alloy–ceramic material bond strength but they did not achieve any statistically significant difference in metal–ceramic bond strength for alloys containing recast material.

**4. Summary and conclusions**

The alloys produced by the authors with the addition of recast materials meet the quality requirements applicable to prosthetic dental elements in the scope of their quality and durability and can be used in prosthetic dental laboratories. After applying remelting materials, in spite of small increase in hardness wear increased, preferably while affected the adhesion of dental porcelain. Hence, one can predict that such a material is certainly better suited to veneering than abrasion working elements.

On the basis ofits ownresearchfound that the production of durable prosthetic castings is possible provided that relevant procedure is adhered to, i.e. at least 50% of brand new must be used and remaining part of alloy may be casted once or twice. In the present study, the alloys with 50% addition of recast materials have been tested up to the second generation level only. Therefore the authors suggest the recasting of alloy addition to the level of determined number of generations as well as the testing of effect of increased number of recasting processes on the alloy properties. The recasting procedure may reduce the costs of CoCrMoW castings and may be safely used in dentistry.

**References**


