Structural and tribological properties of the re-casted dental NiCrMo alloy

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Abstract. The crisis related to the COVID 19 pandemic caused an increase in nickel prices on the global markets. From this perspective, it seems promising to search for the possibilities of effective recycling of nickel-based alloys as biomaterials. The topic of the recasting of Ni-Cr dental alloys is currently being broadly described in the literature. Nonetheless, there are still no conclusive results on the impact of recasting on the quality of the cast dentures. Considering the aforementioned, for research, the effect of recasting on the wear resistance and microstructure of NiCrMo dental alloy was investigated. The Heraenium NA alloy was used for testing. Abrasion resistance was tested by the ball on disc method. Microstructure and wear trace were observed using an optical microscope and a scanning electron microscope. The tests showed a higher wear resistance of the re-casted material. The average coefficient of friction for the initially cast alloys was 0.664, while for the remelted samples the mean value was 0.441. The tested samples are characterised by an abrasive-adhesive wear mechanism. Piling up of the wear tracks edges was observed – the highest for H100. For the H100 samples, a slightly lower average hardness value (HV10) was observed – 226 compared to 233 (HV10) for the samples made from the re-casted alloy (H0). The presence of a dendritic structure of alloys was demonstrated. Blocky eutectic precipitations are visible against the matrix. The observed growth of interdendritic precipitations constitute a natural barrier for the counterpart material and increases its tribological properties. Obtained results suggest that alloy recasting does not constitute a limitation to its use.

1. Introduction
The material properties of fixed and removable prosthetic restorations (obtained in the process of precision casting) and their design are decisive when it comes to durability under conditions of a complex state of biomechanical loads. The mechanical stresses occurring during chewing are mainly responsible for damage and failure of prosthetic treatment. The basic parameter determining the resistance of a prosthetic structure to damage is its mechanical strength.

Depending on the size, duration and place of occurrence, the clamping forces result in a different degree of stress concentration in the hard tissues of the tooth and prosthetic restorations. This often causes damage to the fixing elements of the prosthesis or damage to the entire prosthesis. There are two types of dentures damage: i) extraoral – arises as a result of mechanical damage, i.e., violence, diseases;
ii) intraoral – including operational damage: wear of the prosthesis by friction and corrosion, changes in the conditions of the prosthetic base causing inaccuracy in the adhesion of the plate and uneven loading of the plate, lack of strain relief, short-circuit and non-short-circuit para-functions [1-3].

Despite the great popularity of precious metal alloys, the nonprecious Co-Cr and Ni-Cr ones are often used interchangeably for dentures because of their good mechanical properties and low cost [4,5]. Due to questioning the use of nickel alloys as biomaterials and their potentially harmful effects on human tissues, nickel-based alloys are still widely used to manufacture the substructures of ceramic crowns and bridges. These materials are characterised by a higher elasticity modulus than the gold alloys and thus thinner cross-section of the alloy can be used to reduce the destruction of the healthy tooth during crown manufacturing [6].

Starting from the end of 2017, nickel prices have been steadily increasing. The dynamics of growth has increased even more in the last two years. The prices of other metals are also rising. This is related, inter alia, to the crisis on global markets caused by the COVID19 pandemic. The demand for nickel is growing very quickly and the supply is relatively slow. Facing such a strong global economic situation, the growing demand from the construction industry and the electromobility revolution, as well as the currently difficult trade policy, a systematic and further increase in the prices of this metal is expected. From this perspective, it seems promising to search for the possibilities of effective recycling of nickel-based alloys as biomaterials.

Literature data and the dentists’ practice indicate that the quality of prosthetic restorations can be influenced by the use of remelted materials for casting [2,3,7,8]. These materials can be both metals and their alloys that have already been used in the casting process (e.g., casting channels) as well as residuals from the prosthetic. Such a procedure is a quite common method of additional cost reduction in prosthetic laboratories, but statistical data on this subject are not published. However, from the point of view of the producers and researchers, this case may be seen differently. Some manufacturers of dental alloys permit the use of once melted alloys but not less than the 50% addition of the brand new material. They also require that the material must come from the same batch. Another group of manufacturers do not allow using remelted material (e.g., Heraeus Kulzer Co.) or do not provide any information on the use of dental alloys obtained from recycling [4].

A recasting of Ni-Cr dental alloys is the current topic in the literature. Researchers examine the effect of using re-casted materials on properties such as chemical composition and precipitations formation and microstructure and its influence on mechanical properties, including testing of metal-ceramic bond strength. In tribological properties, research related to surface metrology is also very important, which is closely connected to the microstructure. Also in post-operational or post-mortem cases [9,10].

During the use of dentures, due to frictional forces, metal particles may be released into the oral cavity. In the case of nickel alloys, their chemical compounds can have a negative influence on the human organism [11,12]. The analysis of the impact of recasting on the wear resistance of NiCrMo alloys will allow investigation, whether “recycling” in this type of alloys does not lead to a decrease of abrasion resistance and hence a potential increase in the risk of an allergic reaction, can occur.

2. Materials and methods

Samples preparation
Specimens for all tests were made of the Heraenium NA alloy (Heraeus Kulzer GmbH, Germany), whose chemical compositions were as follows (by weight): Ni-59.3% Cr-24% Mo-10% Fe-1.5%, Mn-1.5%, and Ta-1.5% Si-1.5% Nb-1.0%, according to the manufacturer’s data [13]. The mentioned alloy is used for casting crowns and bridges. The castings were made using a disposable alloy with a starting composition of 100%, and 0% of the brand new material made up to 100% by the re-casted material according to Table 1. All materials came from the same batch. Castings were carried out in a professional prosthetic laboratory according to the procedures applied to manufacture dental crowns and bridges. The vacuum pressure casting method (Nautilus, Bego Co.) and the ceramic crucibles (Nautilus) were used.
The test samples were in the form of cylinders with a diameter of 5 mm and a height of 6 mm. After removing the ceramic shell and cutting off the gating system elements, the surface of the samples was sandblasted.

The cast samples were mounted into an acrylic resin (VariDur10, Buehler GmbH). Then, they were ground on diamond wheels corresponding to sandpaper with grit from 220-1200 on rotary grinders and mechanically polished using SiO₂-based suspensions on Buehler discs, allowing to obtain a surface roughness of 6, 3 and 1 μm, respectively. To reveal the components of the microstructure, the samples were etched with aqua regia. Prepared samples were cleaned in ethyl alcohol in an ultrasonic cleaner and dried using compressed air.

**Table 1. Characterisation of the specimens.**

| Cast specimen type | Sample characterisation                                                                 |
|--------------------|-----------------------------------------------------------------------------------------|
| H100               | Castings made of 100% of the brand new alloy                                             |
| H0                 | Castings made of 0% of the brand new alloy – re-casted H100 alloy (100% portion of the already melted alloy comes from material H100) |

**Tribological tests**

Wear resistance was tested by the ball on disc method, which is a commonly used method to determine the tribological properties of the surface layer of engineering materials, including those used in dentistry [14,15]. The measurements of the friction and wear coefficients were carried out in conditions of technically dry friction on an Antonpaar Nano-Tribometer NTR2 (CFM Instrument). A tungsten carbide ball with a diameter of ϕ= 0.5 mm and 100 mN contact force was used as a counter-sample. The wear trace was measured with a profilometer (Taylor Hobson model Form Talysurf Series 50 mm Intra profilometer). The measurements provided profilograms enabling determination of the mean wear of the wear trace. The wear was defined as the mean surface of the cross-section of contact between the sample and the counter sample.

The microstructure of the specimens and the wear trace were observed using the Nikon MA200 optical microscope as well as the Carl Zeiss Ultra Plus scanning electron microscope with the Bruker EDS microanalyzer.

**Hardness measurements**

Hardness measurements were performed on Vickers hardness tester FV-700 with an automatic ARS 900 system from Future – Tech Corp., at a load of 98.07 N for transverse and longitudinal specimens. The 20 hardness measurements for each melt were performed.

**3. Results and discussion**

**Wear resistance**

Tribological tests showed that the average coefficient of friction (μ) for the H100 alloys was 0.664 (± 0.082); for H0 the mean value was lower – at the level of 0.441 (± 0.128). Moreover, the graph of changes in the coefficient of friction (Figure 1) as a function of the number of cycles shows a clear decrease in μ values for alloy H0 after about 1500 cycles. According to the work [16] greater stability of the friction coefficient during the test may indicate a more plastic nature of the material. Temporary increases in this coefficient (Figure 1) indicate that secondary wear products get into the path of direct interaction between the sample and the counter sample [17]. As a result of these processes, scratches or plastic deformations in the form of grooves occurred, which are caused by the rolling of secondary wear products over the sample surface. Over time, wear products are pressed into the alloy surface. Observed stabilisation of the friction coefficient (Figure 1) is related to the increase in the contact area between mating surfaces.
Figure 1. Results of measurements of the friction coefficient for the Heraenium Na alloy – H100 and H0 specimens.

Wear trace analysis by SEM
The analysis of the wear profiles, determined from the 20 measured profilograms (Figure 2), together with the wear trace – SEM images (Figure 3) indicate that the recasting of the Heraenium NA alloy resulted in a reduction of wear compared to the primary castings. The tested samples were characterised by an abrasive-adhesive wear mechanism. An accumulation of the wear tracks edges was observed – the highest for H100. In this case, the occurrence of continuous scratches along the wear traces can be observed (Figure 3a); on the other hand, for H0 castings, plastic smudging of the material dominates on the wear track (Figure 3b).

Figure 2. The wear tracks on both types of samples after the 5000 cycles test.

Figure 3. SEM images of wear tracks of NiCrMo alloy: a) H100 sample; b) H0 sample.
**Hardness measurements**

The hardness HV10 (Figure 4) of the samples reaches an average value slightly higher than the one declared by the manufacturer (185 for Heraenium NA alloy). For the H100 samples, a slightly lower average hardness value (HV10) was observed – 226 compared to 233 (HV10) for the samples made from the re-casted alloy (Figure 4). These differences are not statistically significant. The increase in hardness caused by subsequent remelting was already observed in other works [7]. The differences in hardness values reported by these authors were however statistically significant (between the first and third cast) and closely related to the change in chemical composition and diverse types of secreted phases that occur during alloy recasting.

The results of the research of Palaskar et al. [18] presents a different opinion. Work shows no differences between the hardness of the new alloy and the re-casted alloy. He also said that the recasting of dental casting NiCr alloy is greatly beneficial both economically and environmentally.

![Figure 4. Vickers hardness (HV10) of NiCrMo alloy: H100 – cast made of brand new alloy and H0 – re-casted alloy](image)

**Microstructure analysis**

The analysis of the microstructure of the casting showed that the Heraenium NA alloy was characterised by a typical dendritic structure. The presence of interdendritic precipitations along the crystallite boundaries (Figure 5) was found for both studied groups. The images obtained from the optical microscope showed that the microstructure of the H0 samples is coarser than H100. In addition, it was observed that prolonged cooling (during the vacuum-pressure method) favours the creation of a large number of precipitations of large sizes and slightly elongated shapes. Precipitations occurring in the background of a nickel-rich matrix are more extensive in the case of re-casted materials, which is particularly visible in Figure 6 c,d,e,f.

This may indicate the presence of undissolved, refractory compounds (carbides, oxides, intermetallic phases) remaining from previous manufacturing processes that increase the size of the crystal nuclei [19]. According to [20] the greater number of precipitations, especially large-sized, can contribute to a reduction in strength properties and corrosion resistance. For both tested castings (H100 and H0) blocky eutectic precipitations are rich in molybdenum, niobium and silicon (Figure 6).

Analysis of the microstructure and the results of tribological tests indicate that interdendritic precipitations constitute a natural barrier for the counterpart material. Comparable results were found in the works of other authors [21,22] on dental cobalt alloy. However, no clear difference in the microstructure was observed by these authors, only the increase in hardness of castings with the addition of recasting materials was noted. The next stage of the research should be the hardness and microhardness analysis of castings and corrosion resistance tests and linking the results with structural and tribological tests. Because some authors indicate that the greater number of precipitations, especially large-sized, can lead to a reduction in mechanical properties and corrosion resistance of NiCrMo dental alloys [20,23].
Figure 5. Representative maps of elements distribution in matrix and precipitations in the Heraenium NA alloy; H100 sample.
Figure 6. Microstructure NiCrMo alloy: a), c), e) H100 sample; b), d), f) H0 sample.

4. Conclusions
A comparative analysis of the friction coefficients demonstrates that the lowest mean friction coefficient is exhibited by H0 specimens ($\mu=0.441$), followed by (a relatively higher value) H100 specimens ($\mu=0.664$). The highest wear resistance, as shown by the results of the tribological test was observed for the re-casted alloy. Generally, the tested materials exhibit an abrasive wear nature. Moreover, adhesive phenomena connected with plastic deformation can be observed in the case of H0 samples. The growth of interdendritic precipitations as a result of re-casting of the Heraenium NA alloy is a natural barrier for the counter sample material and reduces the alloy wear. Obtained results suggest that alloy recasting...
does not constitute a limitation to its use. However, further tests are necessary to check the influence of the microstructure of the re-casted alloy on corrosion resistance or the adhesion to dental porcelain.

References
[1] Barclay C and Walmsley A D 2001 Fixed and Removable Prosthodontics (2nd ed., Churchill Livingstone, London)
[2] Beer-Lech K and Surowska B 2015 Research on resistance to corrosive wear of dental CoCrMo alloy containing post-production scrap Maintenance and Reliability 17 (1) 90
[3] Walczak M, Drozd K, Szała M and Caban J 2019 Influence of Recast NiCrMo Alloy Addition on Porcelain Fused to-Metal Bond Strength Marius. Chiang Mai J. Sci. 46(4) 766-777
[4] Beer-Lech K, Palka K, Skic A, Surowska B and Golacki K 2018 Effect of recasted material addition on the quality of metal-ceramic bond— macro, micro and nano study Adv. Mater. Sci. Eng. 3 1-8 DOI: 10.1155/2018/3271950
[5] Beer K, Palka K, Surowska B and Walczak M 2013 A quality assessment of casting dental prosthesis elements. Eksplotacja i Niezawodnosc- Maintenance and Reliability 15 (3) 230.
[6] Wylie C M, Shelton R M, Fleming G J P and Davenport A J 2007 Corrosion of nickel-based dental casting alloys. Dent. Mater. 22 (6) 714. DOI: 10.1016/j.dental.2006.06.011.
[7] Walczak M, Drozd K and Caban J 2019 Effect of addition of recast materials on characteristics of Ni-Cr-Mo alloys Curr. Issues Pharm. Medical Sci. 32(2) 71-76 https://doi.org/10.2478/cipms-2019-0014
[8] Vaillant-Corroy A S, Corne P, De March P, Fleutot S and Cleymand F 2018 Influence of recasting on the quality of metal alloys: A systematic review. J Prosthet Dent. 114 (2) 205-211 https://doi.org/10.1016/j.prosdent.2015.02.004
[9] Macek W, Marcińska Z, Branco R, Rozumek D and Królczyk G M 2021 A fractographic study exploring the fracture surface topography of S355J2 steel after pseudo-random bending-torsion fatigue tests Measurement 178 109443. https://doi.org/10.1016/j.measurement.2021.109443
[10] Macek W, Branco R, Costa J D and Pereira C 2021 Strain sequence effect on fatigue life and fracture surface topography of 7075-T651 aluminium alloy Mech. Mater. 160 103972. https://doi.org/10.1016/j.mechmat.2021.103972
[11] Zigante M, Rincic Milnaric M, Kastelan M, Perkovic V, Trinajstic Zrinski M and Spalj S 2020 Symptoms of titanium and nickel allergic sensitization in orthodontic treatment. Prog Orthod. 21 (1) 17. doi: 10.1186/s40510-020-00318-4.
[12] Tramontana M, Bianchi L, Hansel K, Agostinelli D and Stingeni L. 2020 Nickel Allergy: Epidemiology, Pathomechanism, Clinical Patterns. Treatment, and Prevention Programs Endocr Metab Immune Disord Drug Targets. 20(7) 992-1002. doi: 10.2174/1871530320666200128141900
[13] http://kulzer.com/ (date of access 06.08.2020)
[14] Budzynski P, Kaminski M, Wiertel M, Pyszniak K and Droździel A 2017 Mechanical properties of the stellite 6 cobalt alloy implanted with nitrogen ions. Acta Phys. Pol. A. 132 (2): 203. DOI: 10.12693/APhysPolA.132.203.
[15] Kamiński M, Budzyski P, Szala M, Turek M 2018 Tribological properties of the Stellite 6 cobalt alloy implanted with manganese ions. IOP. Conference Series Mater. Sci. Eng. 421(3). DOI: 10.1088/1757-899X/421/3/032012
[16] Walczak M and Drozd 2016 Tribological characteristics of dental biomaterials. Curr. Issues Pharm. Med. Sci. 29(4):158. DOI: https://doi.org/10.1515/cipms-2016-0033
[17] Walczak M, Caban J and Plíža P 2015 Tribological Characteristics of magnesium alloys used in means of transport TTS 12 1614-1647
[18] Palaskar J, Nadgir D V and Shah I. 2010 Effect of recasting of Nickel-Chromium alloy on its Hardness. Int J Dent Clin. 2(4) 8-11
[19] Beer - Lech K, Palka K and Borowicz J 2013 Evaluation of nickel alloy castings in their relevance to the use of post-production scrap application, Engineering of Biomaterials 121 (16) 13-18
[20] Ameer M A, Khamis E and Al-Motlaq M 2004 Corrosion behaviour of recasting Ni-Cr and Co-Cr nonprecious dental alloys. Cor. Sci. 46(11): 2825. DOI: 10.1016/j.corsci.2004.03.011
[21] Szala M; Chocyk D; Skic A; Kamiński M; Macek W and Turek M 2021 Effect of Nitrogen Ion Implantation on the Cavitation Erosion Resistance and Cobalt-Based Solid Solution Phase Transformations of HIPed Stellite 6. Materials 14 2324. https://doi.org/10.3390/ma14092324
[22] Walczak M, Pieniak D and Niewczas A M 2014 Effect of recasting on the useful properties CoCrMoW alloy. Maintenance and Reliability 16(2): 330
[22] Szala M, Beer-Lech K, Gancarezyk K, Baran K O and Pędrak P 2017 Microstructural characterisation of Co-Cr-Mo casting dental alloys. Adv. Sci. Technol. Res. J. 4(11) 76-82