The Effects of Reusing Cobalt-Chromium Alloy Powder on Its Mechanical Properties and Grain Size: An In Vitro Study

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Purpose: To characterize material changes that may occur in virgin cobalt-chromium (Co-Cr) alloy powder when it is blended with alloy powders that have been reused multiple times. ***Materials and Methods:*** Initially, 20 kg of virgin Co-Cr powder was loaded into a laser-sintering device. The tensile test specimens were fabricated in the first (Group 1), fourth (Group 2), seventh (Group 3), tenth (Group 4), and thirteenth (Group 5) production cycles (N = 15). Prior to fabricating the specimens, powder alloy samples were collected from the powder bed for analysis. The tensile strength, elastic modulus, and percent elongation were calculated with tensile testing. Scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM/EDS) and laser particle size distribution (LPSD) were used to analyze the alloy powder samples. The fracture surface of one tensile test specimen from each group was examined via SEM/EDS. One-way ANOVA followed by Dunnett T3 test was used for statistical analysis (α = .05). ***Results:*** No difference was observed between groups in terms of tensile strength. A statistically significant difference was observed between Groups 1 and 2 in terms of percent elongation. Groups 2 and 4 were statistically significantly different in terms of both elastic modulus and percent elongation ($P \leq .05$). SEM images of the powder alloy showed noticeable differences with increasing numbers of cycles. SEM images and the EDS analysis of the fractured specimens were in accordance with the strength data. ***Conclusions:*** Reusing Co-Cr alloy powder increased the particle size distribution. However, there was no correlation between increased cycle number and the mechanical properties of the powder. *Int J Prosthodont 2024;37(suppl):s187–s193. doi: 10.11607/ijp.8905*

The popularity of laser-sintering/laser-melting methods used in the production of metal-ceramic substructures has significantly increased due to its numerous advantages.[1] One of the advantages is the possibility of reusing alloy powders.[2] As a result, this method is much more cost-effective compared to other manufacturing techniques. The reusability of alloy powder is also important from an environmental sustainability perspective, as almost no residual material is formed.[3]

During the laser-sintering/laser-melting process, alloy powder is spread across the entire build platform at a thickness predetermined by the user or manufacturer. Laser energy is used to selectively fuse the alloy powder either partially (laser sintering) or completely (laser melting) to create a solid structure. This process is repeated layer by layer until the desired object is formed.[4–7] Once the object is fully formed, the remaining unused metal powders on the build platform are collected, passed through a sieve, and then returned to the metal powder bed for reuse.[8,9] This blending process is repeated after each production cycle. The initial alloy powder in the bed is cycled over and over until a brand-new metal powder (virgin powder) is added to the

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Fig 1 Powder bed and build platform of the DMLS device just before loading the alloy powder.

Table 1 Composition of Alloy Powder

Alloy powder	Co	Cr	Mo	W	Si	Fe	Mn	Nb
Adorbond CC Plus-Pulver (10–30 mm)	63.6	24.8	5	5.5	1.1	< 1	< 1	< 1

Co = cobalt; Cr = chromium; Mo = molybdenum; W = tungsten; Si = silicon; Fe = iron; Mn = Manganese; Nb = niobium.
Data are presented as wt%.

powder bed, mostly because insufficient alloy powder is left. This type of workflow is referred to as the *single batch strategy* in the literature, and different lots of alloy powders can be used.

In single batch powder reuse strategy, the amount of reused alloy powder in the powder bed increases gradually after each production cycle. As demonstrated in previous studies, the exposure of adjacent alloy powder to heat from the laser energy used during the sintering process can cause the alloy powder to agglomerate. This deforms the spherical shapes of the particles, which become contaminated with gases (nitrogen, oxygen, and moisture), resulting in altered flow properties.[2,9,10] The effect of these changes in alloy powder was investigated in previous studies. However, most of the studies were conducted using alloy powders that are not used for building dental restorations.[11–17] There are limited studies in the literature about the effect of reused cobalt-chromium (Co-Cr) alloy powders on sintered structures. Leban et al[2] reported that reusing Co-Cr alloy powder increased the hardness and porosity of the manufactured objects. However, there was no significant effect on particle size distribution and corrosion resistance. Okazaki et al[18] claimed that laser sintering up to 20 times had no significant effect on the chemical composition of cobalt-chromium-molybdenum (Co-Cr-Mo) alloys. Aldhohrah et al[19] reported that alloy powder with different recycling times released significantly more Co and Cr ions and showed higher cytotoxicity compared to the unused alloy powder. Albayrak et al[8] observed that reuse of Co-Cr alloy powders up to 30 times had no effect on metal-ceramic bond strength.

The chemical and mechanical analysis of reused alloy powders and objects fabricated from only reused alloy powders rather than blended alloy powders does not replicate routine laboratory practice. Thus, it is necessary to conduct studies to understand how mixing reused alloy powders with virgin powders (blended alloy powders) affects the mechanical properties of metal-ceramic substructures, since according to ISO 22674, a metal-ceramic substructure must conform to certain mechanical properties if it is meant to be used in clinical practice.[20] Therefore, the objective of the study was to investigate the mechanical properties (tensile strength, percent elongation, and elastic modulus) of specimens fabricated with virgin and blended Co-Cr alloy powder. The null hypothesis of the study was that there would be no difference between virgin Co-Cr alloy powder and blended Co-Cr alloy powder in terms of mechanical properties.

MATERIALS AND METHODS

The current study was designed according to CRIS (checklist for reporting in-vitro studies) guidelines.[21] The sample size per group was determined using power analysis, G*Power v.3.1 (F test, fixed effects, omnibus, one-way, effect size .5, =.05, power = 0.9, number of groups = 5, minimum total sample size = 75).

Tensile test specimens in the shape of a dumbbell were created using 3D software (Solidworks Premium, Dassault Systèmes) in accordance with ISO 22674-2022. The test specimens were fabricated in a large-scale dental laboratory. First, the alloy powder bed of the direct

Fig 2 Tensile test in progress.

Table 2 Mechanical Properties

Group	Tensile strength, MPa	Elongation, %	Elastic modulus, GPa
Group 1	989 ± 105^{A}	8 ± 1.1^{A}	126 ± 24.8^{A,B}
Group 2	1,055 ± 60^{A}	9.7 ± 1.2^{B}	110 ± 13.7^{B}
Group 3	1,030 ± 93^{A}	8.14 ± 1.6^{A,B}	132 ± 36.8^{A,B}
Group 4	1,067 ± 49^{A}	7.8 ± 1^{A}	137 ± 17.4^{A}
Group 5	964 ± 143^{A}	8 ± 1^{A,B}	122 ± 28.4^{A,B}

Data are presented as mean ± SD. Different uppercase letters represent statistically significant differences in the same column ($P \leq .05$).

metal laser-sintering (DMLS) device (EOSINT M 270, EOS) was thoroughly cleaned with a vacuum cleaner before loading 20 kg of virgin Co-Cr alloy powder (Adorbond CC Plus-Pulver, 10–30 µm, Ador Edelmetalle) (Fig 1). The composition of the alloy powder is described in Table 1.

The build platform of the DMLS device was expected to be fully loaded to start each production cycle. Following each production cycle, the remaining non-sintered alloy powder on the build platform was collected, sieved (sieve pore size = 80 mm), and mixed with the alloy powder in the powder bed for the next production cycle. The production cycles were continued in laboratory routine until there was insufficient alloy powder in the powder bed to complete the fabrication of objects on the fully loaded build platform. Tensile test specimens in Group 1 served as the control group and were fabricated in first production cycle. The specimens in Groups 2, 3, 4, and 5 were fabricated in the fourth, seventh, tenth, and thirteenth production cycles, respectively. All specimens were fabricated with 30-mm layer thickness. The process parameters of the DMLS device used in the study was as follows: scan speed = 7 m/sec, production speed = 20 m^3/sec, spot laser diameter = 100 to 500 mm, laser beam power = 120 to 220 W, hatch distance = 0.08 to 0.1 mm. Powder alloy samples were collected for each group from the powder bed for analysis prior to fabrication of the specimens.

To determine a random tensile test order, a randomization chart was created using a free internet program.[22] The software automatically generated a testing order for all 75 test specimens. Tensile testing was performed by the same operator on the same day with a universal testing machine (M500-25 kN, Testometric) with a crosshead speed of 1 mm/minute until fracture (Fig 2). The equipment software calculated the tensile strength, elastic modulus, and percent elongation values directly (Wintest Analysis, Testometric). Scanning electron microscopy (SEM) (FEG-SEM Inspect F50, FEI) and laser particle size distribution (LPSD) analyses (Mastersizer 3000, Malvern Panalytical) were performed for the alloy powder samples. For LPDS analyses, three measurements were taken for each group of alloy samples, and the mean of the three measurements was regarded as the average particle size of that group. The fracture surface of one tensile test specimen for each group was examined by SEM/energy dispersive x-ray spectroscopy (EDS) for fracture surface analysis.

One-way ANOVA followed by Dunnett T3 test were used for statistical analysis ($\alpha = .05$) using a statistical software (SPSS Statistics v21.0, IBM).

RESULTS

A total of 15 tensile test specimens per group were assessed. No specimen was excluded. The means and SDs of tensile strength, percent elongation, and elastic modulus for the groups are presented in Table 2. No difference was observed between groups in terms of tensile strength. A statistically significant difference was observed between Groups 1 and 2 ($P = .003$) in terms of percent elongation. Group 2 and 4 were statistically significantly different in terms of elastic modulus ($P = .038$) and percent elongation ($P = .001$).

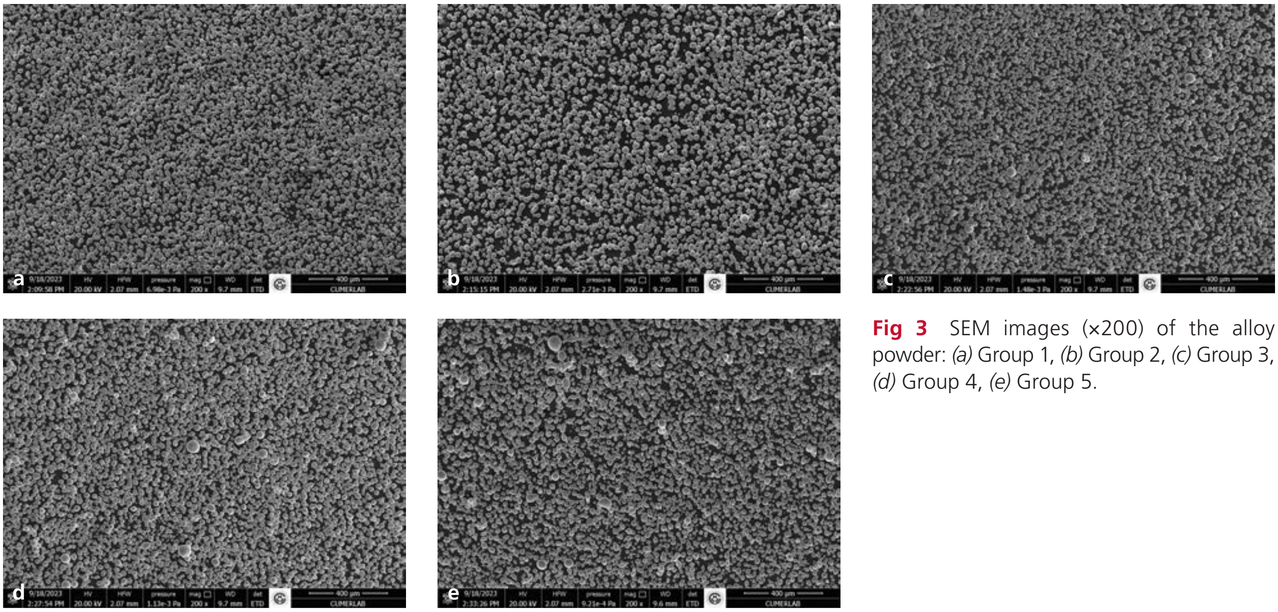

Fig 3 SEM images (×200) of the alloy powder: *(a)* Group 1, *(b)* Group 2, *(c)* Group 3, *(d)* Group 4, *(e)* Group 5.

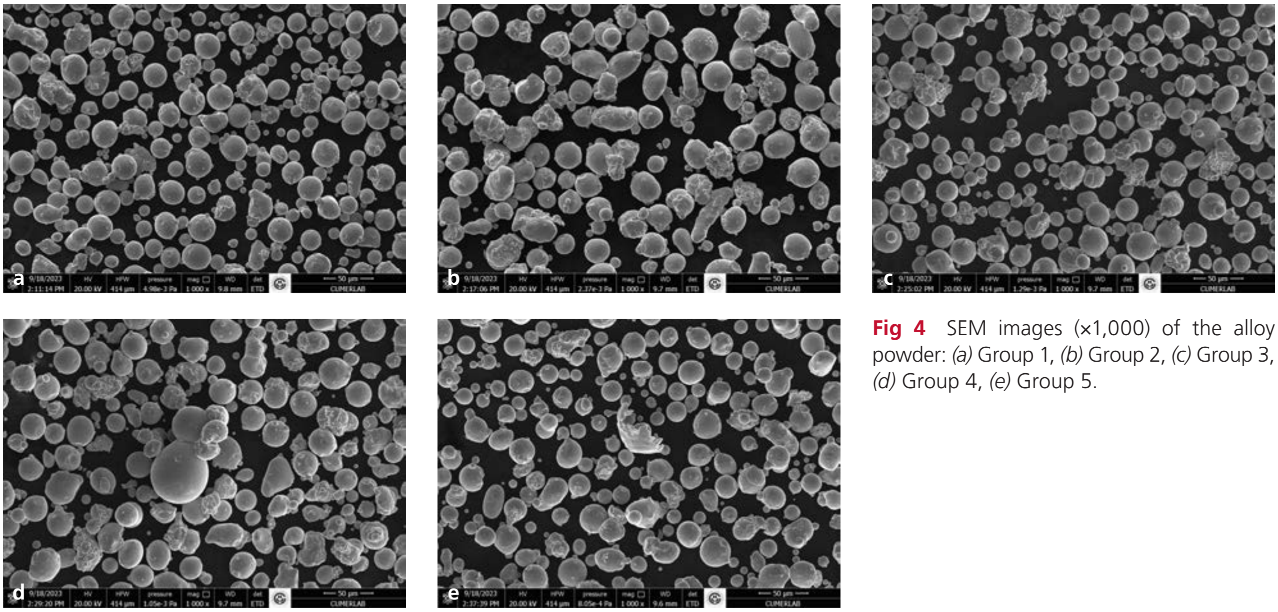

Fig 4 SEM images (×1,000) of the alloy powder: *(a)* Group 1, *(b)* Group 2, *(c)* Group 3, *(d)* Group 4, *(e)* Group 5.

Table 3 Laser Particle Size Distribution

Groups	d10, μm	d50, μm	d90, μm
Group 1	15.4 ± 0.08	23.6 ± 0.08	35.0 ± 0.05
Group 2	15.4 ± 0.01	23.6 ± 0.009	35.2 ± 0.005
Group 3	15.4 ± 0.02	23.8 ± 0.02	35.8 ± 0.01
Group 4	15.3 ± 0.01	24.1 ± 0.01	37.2 ± 0.01
Group 5	15.3 ± 0.02	24.1 ± 0.04	38.1 ± 1.7

Data are presented as mean ± SD.

Figures 3 and 4 show SEM images of the alloy powder samples from each group. The SEM images clearly show that as the number of cycles increased, the grain size of the alloy powder increased due to agglomeration. LPSD analysis supports the SEM images of the alloy powder. Mean particle size distribution increased as the cycle number increased (Table 3). Higher magnifications revealed deformation of the alloy powder grains, possibly due to multiple exposures to laser energy. SEM images of the fractured surface showed no obvious differences between the groups (Fig 5).

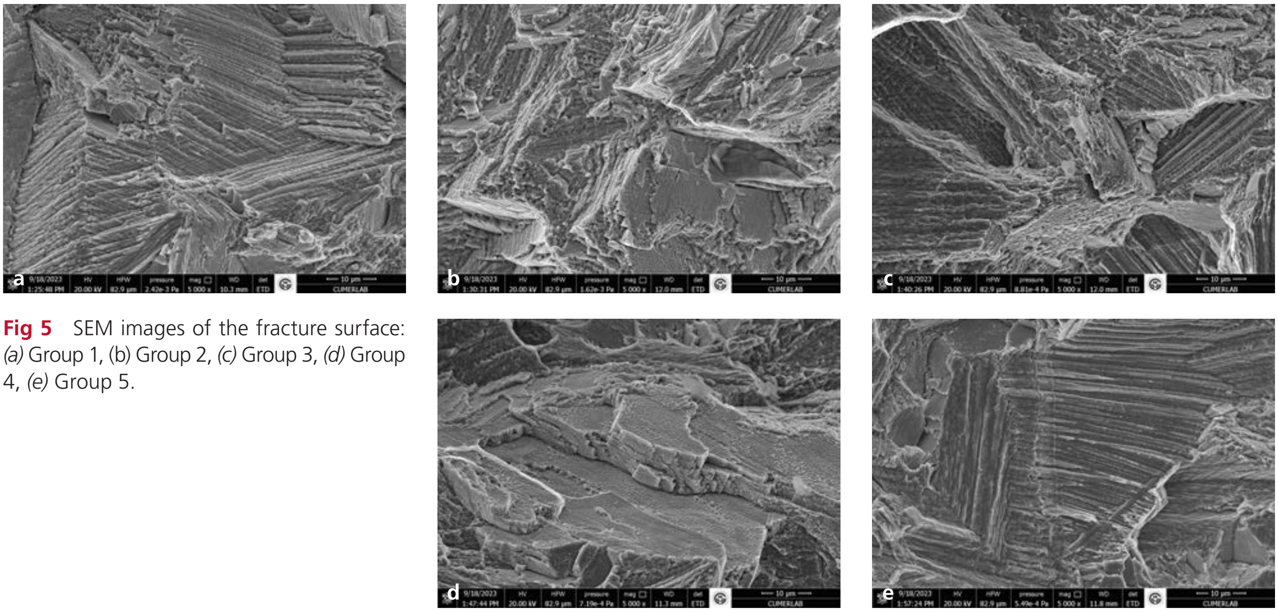

Fig 5 SEM images of the fracture surface: *(a)* Group 1, (b) Group 2, *(c)* Group 3, *(d)* Group 4, *(e)* Group 5.

DISCUSSION

This study was designed to reveal the mechanical changes in virgin Co-Cr alloy powder when blended with reused alloy powder that had been exposed to laser energy at various times during the manufacturing cycle. The null hypothesis for tensile strength results (that there would be no difference between virgin and blended Co-Cr alloys) was rejected. There were statistically significant differences between groups for elastic modulus and percent elongation.

According to ISO 22674, metallic materials are classified into six different types in increasing order from 0 to 5, with Type 0 representing materials with the least mechanical properties and Type 5 representing materials with the greatest mechanical properties.[20] If a metal-ceramic substructure is meant to be used as fixed partial denture, it must at least satisfy the mechanical properties of Type 3 materials (flexural strength > 270 MPa and percent elongation > 5). All groups in the current study satisfy the specifications of Type 3 materials. However, a Type 3 material is not suitable to use if a high level of stiffness and flexural strength are needed, such as in full-arch fixed dental prostheses with limited cross-sections.

Previous studies reported higher mechanical properties compared to the current study. Ekren et al[6] reported 1,045 MPa tensile strength, 284 GPa elastic modulus, and 28.8% elongation. Ucar et al,[5] on the other hand, reported 1,225 MPa tensile strength, 177 Gpa elastic modulus, and 3.1% elongation. Mechanical properties are affected by the laser-sintering device, alloy powder, and different device specifications that are used during the fabrication process.[5] The mentioned studies used the same laser-sintering device and the same device specifications but different alloy powder while fabricating specimens. Differences in the reported values might be attributed to different powders used in the current study.

The alloy powder used in the current study had an average particle size of 10 to 30 mm. LPSD analysis of Group 1 (virgin powder) revealed slightly higher values compared to the manufacturer's information (Table 3). It is claimed that reusing alloy powder contributes to increased particle size due to agglomeration and satellite formation, which would impair the flowability of the powder.[2] The result of the current study is in accordance with the previous studies, as Group 5 showed larger average grain size compared to Group 1 (Table 3). Satellite formations and agglomerations are evident in the SEM images (see Fig 4). In the current study, an 80-mm sieve was used for extracting macro particles from the unused alloy powders on the build platform, as suggested by the manufacturer. If an ultrasonic sieve were preferred, the pore size could be decreased to 55 mm. Obviously, alloy powder manufacturers want to diminish alloy powder waste, as the recommended sieve pore size is much larger than the average particle size of virgin powder. However, a user has to know the risks related to changes in the particle size distribution while sieving alloy powder. It may be wise to use a smaller-sized sieve equal to the initial grain size of the alloy powder.

It is reported that the most common defects observed in additively manufactured objects are porosity and surface defects.[2] These defects may be more prominent with reused alloy powders.[2] Powder particles located closer to the printed object are repeatedly subjected to heat, and eventually, the particle size distribution of the fabricated object may be changed. No porosity and no surface defects were observed in specimens from any of the groups when examining SEM images of fractured surface (see Fig 5). However, the specimens in Group 2 (Fig 5b) exhibited an irregular surface in contrast to those in Group 1 (Fig 5a). Additionally, a brittle type of fracture was evident in Group 2. Group 3 specimens (Fig 5c) displayed a more irregular surface texture. In Group 4 (Fig 5d), the fiber-like structure of the fracture surface disappeared and subsequently reappeared in a Group 5 specimen (Fig 5e). Specimens from Group 1 and Group 5 exhibited similarities in both SEM characteristics and mechanical data.

Dental laboratories prefer to choose laser-sintering device production capacity according to their potential customer capacity. Thus, large-scale dental laboratories prefer to purchase laser-sintering devices with larger build platforms. The larger the build platform, the more objects can be fabricated in a single cycle. The laser-sintering device used in the current study had a build platform with 250 × 250 × 215 mm dimensions, and it could be used to fabricate approximately 500 metal substructures in a single cycle. Therefore, 20 kg of alloy powder was loaded into the powder bed to achieve at least 10 production cycles. The laser-sintering device had a powder capacity of about 60 kg, and more than 20 kg of alloy powder could be loaded to increase the number of production cycles. However, as powder alloy in the powder bed stays longer, it also has a higher chance of being contaminated with dust and humidity in the air. After discussions with the operator of the laser-sintering device, the powder bed was loaded with 20 kg of alloy powder.

Although a single batch reuse strategy was followed in the current study, alternative approaches have been described in literature.[13,23] The *frequent refreshing,* or *top-up*, strategy entails refreshing the used powder by blending it with virgin powder after a defined number of build cycles or between each cycle. Another strategy proposed by Lutter-Günther et al[23] dictates used powders with the same reuse age. The single batch strategy is predominantly favored due to its inherent traceability benefits, obviating the need for storage and control of powder batches.[13]

As the number of cycles increases, the formation of satellites and agglomerations can be observed in the SEM images of the alloy powder (see Fig 4). This phenomenon did not affect tensile strength but had an impact on both percent elongation and elastic modulus. This is not surprising, because elongation is related to a material's resistance to plastic deformation, whereas elastic modulus is resistance to elastic deformation, and tensile strength provides information about its resistance to rupture. Although all three are mechanical properties of the material, they provide information about different aspects of the mechanical behavior, so a direct correlation among them is not expected. Leban et al[2] reported that as the number of cycles increases, hardness also increases. Hardness represents resistance to plastic deformation and hence is related to percent elongation. In the present study, as the number of production cycles increases, it was anticipated that percent elongation would decrease and the elastic modulus would increase. However, an increase in the number of cycles did not reveal any gradual alterations, either in percent elongation or elastic modulus. Although the sample size in this study was determined to be sufficient based on the power analysis, the results could be different if the sample size was larger. This issue can be considered a limitation of the present study.

Because there is no study in the literature that uses the same methodology employed in the current study for evaluating the effect of reusing dental Co-Cr alloy powders, it was not possible to compare the results with previous studies. Further research on reused dental alloy is needed. Future studies can be conducted to evaluate biocompatibility and bond strength of ceramic to metal substructures fabricated with reused alloy powders. The effect of more than 13 cycles should also be evaluated.

CONCLUSIONS

Within the limitations of the current study, it can be concluded that reusing Co-Cr alloy powder up to 13 times does not have a significant effect on the mechanical properties considered in the current study. However, particle size distribution was increased after reuse.

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