



Physico-mechanical properties and prosthodontic applications of Co-Cr dental alloys: a review of the literature

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Cobalt-Chromium (Co-Cr) alloys are classified as predominantly base-metal alloys and are widely known for their biomedical applications in the orthopedic and dental fields. In dentistry, Co-Cr alloys are commonly used for the fabrication of metallic frameworks of removable partial dentures and recently have been used as metallic substructures for the fabrication of porcelain-fused-to-metal restorations and implant frameworks. The increased worldwide interest in utilizing Co-Cr alloys for dental applications is related to their low cost and adequate physico-mechanical properties. Additionally, among base-metal alloys, Co-Cr alloys are used more frequently in many countries to replace Nickel-Chromium (Ni-Cr) alloys. This is mainly due to the increased concern regarding the toxic effects of Ni on the human body when alloys containing Ni are exposed to the oral cavity. This review article describes dental applications, metallurgical characterization, and physico-mechanical properties of Co-Cr alloys and also addresses their clinical and laboratory behavior in relation to those properties. [J Adv Prosthodont 2014;6:138-45]

KEY WORDS: Co-Cr alloys; Base metal alloys; Physical properties; Mechanical properties; Metallurgical characterization

INTRODUCTION

The application of predominantly base-metal alloys in removable and fixed prosthodontics has become more popular since the 1980s, due to the increasing cost of noble metals, especially after the global financial crisis of 2008. Cobalt-Chromium (Co-Cr) alloys are among the best-known base metal alloys in dentistry with various and successful clinical applications.

Most of the Co-Cr alloys currently used in industrial and biomedical fields evolved from the work of Elwood Haynes at the turn of previous century. Initially, he demonstrated that the binary Co-Cr alloy possesses high strength and resists stain, and he subsequently identified molybdenum (Mo) and tungsten (W) as powerful strengthening agents for these alloys. Because of their stainless nature and permanent 'star-like' luster, Haynes named them *Stellite alloys*, based on the Latin word *Stella*, which means 'star'.¹

Co-Cr alloys can be generally described as alloys that have high strength, are heat-resistant and non-magnetic, and have favorable resistance to wear, corrosion, and tarnish.¹ They possess excellent biocompatibility^{2,3} and corrosion and tarnish resistance,^{4,5} while the high modulus of elasticity (E) provides the requisite strength and rigidity without the need for heavy cross-sections, thus reducing the weight of metal substructures. Currently, biomedical applications of Co-Cr alloys are mainly related to the fabrication of orthopedic prostheses for knee, shoulder, and hip replacement as well as for use as fixation devices for fractured bones (joint endoprostheses).⁶

The first known dental application of Co-Cr alloys

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(along with Ni-Cr alloys) was in the 1930s, for the fabrication of removable partial denture (RPD) frameworks. Since then, both Co-Cr and Ni-Cr base-metal alloys have become increasingly popular compared with conventional Type IV gold alloys, which were predominant metals previously used for RPD framework fabrication.⁶ In addition to the excellent mechanical and stain-resistant properties of Co-Cr alloys, they have almost half the density of Au-based alloys, and thus the weight of fabricated dental restorations and frameworks becomes significantly lighter.

In 1984, the ADA⁷ proposed a simple classification for all dental casting alloys. Three categories were described: high noble (Au > 40 wt% and noble metal content > 60 wt%), noble (noble metal content > 25%), and predominantly base metals (noble metal content < 25%). The last includes Co-Cr alloys, which are composed of 75 wt% or more of base metal elements or less than 25 wt% of noble metal elements (Au + Ir + Os + Pt + Rh + Ru),^{7,8} although in practice neither Ni-Cr- nor Co-Cr-based alloys contain noble metals.⁹

The use of Co-Cr-based alloys for metal ceramic applications was first mentioned in the 1959 Weinstein patent for dental porcelain. The elemental composition that was suggested in that patent was: (% wt) Co 62.55, Cr 27.00, Mo 6.00, Ni 2.00, Fe 1.00, Si 0.60, Mn 0.60, and C 0.25.² Intensive research into applying such alloys for the fabrication of fixed restorations did not begin until the 1970s, when stimulated by the rapidly escalating price of Au.

Today, Co-Cr-based alloys are almost exclusively used for the production of metallic frameworks of RPDs and, more recently, as possible alternatives to Ni-Cr alloys for the production of PFM restorations, since they are free from the risk of Ni-related allergic responses and/or Be-related toxic consequences. The aim of this article is to describe the properties of Co-Cr-based alloys and their laboratory and clinical behavior.

PROPERTIES OF Co-Cr ALLOYS FOR THE PRODUCTION OF RPD FRAMEWORKS

Table 1 gives the elemental composition of representative commercial alloys used for the fabrication of RPDs. All alloys were found to be in compliance with ISO 6871-1:1994 requirements,⁸ which means that the sum of Co, Cr, and Ni should not be less than 85 (%wt), while that of Cr and Mo should not be less than 25 and 4 (%wt), respectively. These restrictions explain the small variations in commercial alloys shown in Table 1. Si and Mn are also added in small amounts, along with Fe, Ni, and C, in Co alloys. This composition is considered as the basis for the modified alloys that have been developed by the addition of one or more elements, such as Ga, Zr, B, W, Nb, Ta, and Ti, to achieve a desirable range of properties.^{5,10} Based on Table 1, and since Co is the predominant metal element, it is important to mention that the alloy should be referred to as a Co-Cr alloy instead of a Cr-Co alloy. Unfortunately, it is still seen, in some textbooks, that these terms are used interchangeably, which might be interpreted incorrectly, because alloys should start with the name of the predominant element.

In the alloys presented in Table 1, Co was the main constituent, with Cr and Mo the primary alloying elements. From a metallurgical standpoint, Co introduces to its alloys an unstable, face-centered cubic crystal (fcc) structure resulting from the fact that pure Co, if cooled extremely slowly, transforms from an fcc to a hexagonal close-packed (hcp) crystal structure. The transformation temperature is 417°C for pure Co but is higher for Co alloys. The unstable fcc structure is usually retained at room temperature, due to the slow reaction rate of the fcc ↔ hcp transformation. The retained unstable fcc structure is believed to be associated with some characteristic properties of Co alloys, such as high yield strength, high work-hardening rates, limited

Table 1. Composition of Co-Cr partial denture alloys as provided by the manufacturers

Elements	Wironit LA*	Wironium plus*	Suprachrome†	Vitallium‡	Brealloy F400§
Co	63.5	62.5	63.6	63.4	64.7
Cr	29.0	29.5	28.5	29.0	29.0
Mo	5.0	5.0	6.0	5.2	5.0
Si	1.2	<1.0	<1.0	<1.0	0.5
Mn	<1.0	<1.0	<1.0	<1.0	0.4
Fe	-	<1.0			
Ta	<1.0	<1.0			
C	<1.0	<1.0	<1.0	<1.0	0.4
N	<1.0	<1.0		<1.0	

* Bego, Bremen, Germany; † Jelenco, San Diego, CA, USA; ‡ DENTSPLY Prosthetics' Austenal, USA; § Bredent, Senden, Germany.

Table 2. Mechanical properties and ISO 6871-1 requirements of cobalt-chromium partial denture alloys

Brand Name	Modulus of Elasticity (GPa)	Yield Strength* (MPa)	Tensile Strength (MPa)	Elongation (%)	Vickers Hardness
Wironium	220	640	940	10.0	360
Wironium plus	220	700	1000	13.0	340
Suprachrome	200	600		9.0	410
Vitallium	200	680	960	10.0	395
Brealloy F400	220	700	900	4.0	400
ISO 6871-1:1994		>500	-	>3.0	

* 0.2 offset.

fatigue damage under cyclic stresses, and the ability to absorb stresses (through transformation of fcc to hcp structure).¹

Cr is the primary alloying element and is added to increase strength due to carbide formation and solid solution strengthening and to enhance resistance to corrosion and oxidation. M_7C_3 and $M_{23}C_6$ (where M stands for any metal) are known as Cr-rich carbides,^{1,11} although MC and M_6C types have also been detected in Co alloys.⁵ Despite the positive effects in terms of mechanical and electrochemical properties, the addition of Cr should be made with care to avoid the formation of the hard and brittle Cr-rich sigma phase, which decreases corrosion resistance due to local Cr depletion around the sigma phase precipitates. Mo is added to provide additional strength due to solid solution strengthening, while also participating in the formation of carbides promoting the precipitation of M_6C , and, in addition, enhancing the corrosion resistance of the alloys. W has the same effect on the properties of Co-Cr alloys and thus is sometimes used instead of Mo. However, since Co-Cr alloys are hardened primarily by carbide formation, the C content is of primary importance. However, the ISO specification does not force manufacturers to provide the exact composition of trace elements. Therefore, the elements with composition less than 1% by weight must be presented in the list but with '< 1%' identification. Only one manufacturer provides the exact composition of C, and thus the effect of C content cannot be correlated with the mechanical properties given in Table 2. Several carbides, including MC, M_6C , M_7C_3 , and $M_{23}C_6$, have been detected in dental Co-Cr alloys.^{5,11} Although carbide formation is the primary strengthening mechanism,¹¹ solid solution and intermetallic compound formation strengthening also occurs. Fig. 1A demonstrates the microstructure of a cast Co-Cr alloy comprised of a cored fcc solid solution matrix interspersed with a second phase (white areas) occupying the interdendritic spaces.¹²

Table 2 shows selected mechanical properties of the commercial alloys from Table 1, along with ISO specifications for yield strength and elongation, for comparison purposes. Although the alloy products can satisfy these two requirements, the clinical importance of each mechanical

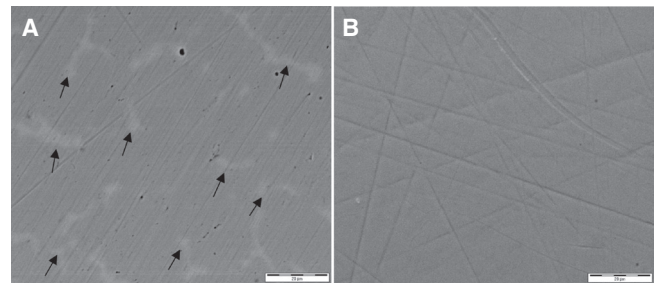


Fig. 1. Backscattered electron images (BEI) from the surface of a Co-Cr alloy manufactured by conventional casting (A) and selective laser melting (SLM) techniques (B). A second Mo-rich phase (white areas/black arrows) occupies the interdendritic spaces in the cast alloy. A homogeneous single-phase microstructure is shown for the Co-Cr alloy manufactured by the SLM technique.

property is of paramount significance from the standpoint of design and the selection of an appropriate alloy corresponding to clinical demands. Especially for RPDs, the retentive clasp arms must be capable of flexing, preserving their original shape and satisfactorily retaining the prosthesis. Clasps manufactured from alloys with higher yield strength demonstrate increased resistance to plastic deformation, while elongation is associated with the extent of plastic deformation of the clasp before fracture. Although not included in the specifications, the highest E of Co-Cr-based alloys (200-220 GPa) compared with those of cpTi (110 GPa)¹³ and Type IV gold alloy (81-90 GPa)⁹ provides the casting frameworks and especially the clasps with increased rigidity, giving the advantage of thinner cross-sections. The last two properties give Co-Cr-based alloys the ability to overcome the unavoidable plastic deformation of clasps produced by Type IV gold alloys after long terms in service.

Co-Cr-based alloys possess better biocompatibility as well as higher resistance to corrosion and tarnish compared with Ni-Cr-based alloys.^{2,3} The long-time preservation of a polished shine is a distinct advantage of Co-Cr alloys in the production of removable prostheses.¹⁴ *In vitro* studies^{15,16}

have shown favorable long-term corrosion behavior for four Co-based alloys. The average substance loss, in a solution of lactic acid and sodium chloride, of the tested alloys after 35 days ranged from 0.43 to 34.9 g/cm², while the Ni-Cr-Mo alloys exhibited a wide range of corrosion resistance, between 0.65 and 3261 g/cm², denoting that Ni-based alloys are more prone to ion release compared with Co ones. The Be content of Ni alloys showed extremely high ion release in the same solution.^{15,16} These results are supported by the findings of Okazaki and Gotoh,¹⁷ who pointed out the low release rate of Co, Cr, and Mo from a cast Co-Cr alloy in a vast variety of testing solutions such as PBS (-), calf serum, 0.9% NaCl, artificial saliva, 1% lactic acid, 1.2% L-cysteine, and 0.01% HCl. Ion release rates from cast Co-Cr-based alloys are also decreased, from 0.28 wt% to 0.06 wt% toward a lower C content.¹⁸ However, this is counteracted by the adverse effect on mechanical properties of the alloys.

Clinical surveys have been undertaken to evaluate the *in vivo* consequences of RPDs made with Co-Cr-based alloys, and examined factors such as plaque, gingivitis, gingival recession, and root and coronal caries. Among them, a few have focused on Co-Cr dentures in a sizeable sample of RPD wearers.¹⁹⁻²² Some showed a high prevalence of plaque and gingivitis,^{19,20} while others showed low prevalence.^{22,23} Chandler and Brudvik²⁰ also found the same high gingivitis scores among those who were RPD wearers and those who were not. However, all seemed to agree that regular periodontal check-ups are necessary for RPD wearers to help minimize gingivitis.

Many studies have been undertaken to evaluate the longevity of RPDs during function. A survey by Yannikakis *et al.*²⁴ about partial denture repairs showed that the fracture of the metallic framework and the fracture of a wire clasp ranked second and third in order of need of repair. Additionally, the prevalence of framework fracture was almost doubled for mandibular RPDs (21.1%) compared with maxillary (10.1%) restorations.²⁴ Körber *et al.*²⁵ showed

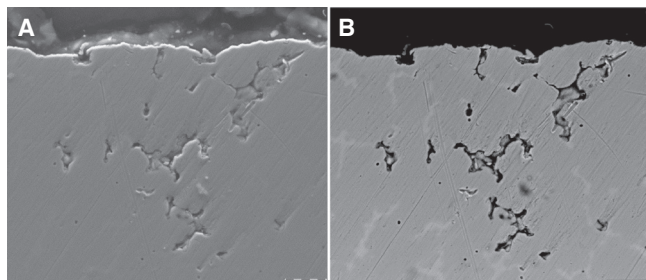


Fig. 2. Surface and subsurface interdendritic porosity formed during solidification of a Co-Cr-based alloy. (A) Secondary Electron Image and (B) Backscattered electron image. It is readily shown in the BEI that the pores follow the shape and distribution of the white Mo-rich phase.

a 40% repair rate after 5 years, of which 15% was caused by the fracture of metallic parts, while in Vermeulen's study,²⁶ fracture of the metallic parts was found in 10% to 20% after five years and in 27% to 44% after ten years.

Strain gauge analysis was used by Bates, who pointed out that clasp arms undergo high stress and low numbers of loading cycles, while connector bars are subjected to low stress with a large number of loading cycles. Based on the fact that the tip deflection for most Co-Cr clasps is in the magnitude of 0.25 mm, he concluded that fatigue seems unlikely in a sound, well-produced casting, since the developed stresses during succeeding insertions are lower than the fatigue limit of the alloy in bending, which has been estimated in the region of 480 MPa.²⁷ Therefore, fractures should be attributed to erroneously designed clasps, or to stress concentration areas such as pores developed during casting, nicks introduced during adjustment of the clasp with pliers, sharp angles introduced when joining the retentive arm, etc.²⁸ The logical assumption above has found ready verification in various studies that revealed a high percentage of porosity in Co-Cr frameworks^{14,29-36} The internal microstructure of removable partial dentures, before and after fracture occurs, has been investigated thoroughly by many authors. Radiographic and metallographic studies^{30,31} by optical and scanning electron microscopy showed interdendritic microporosity due to shrinkage.^{14,33} During the formation of the dendrites, the interdendritic spaces become isolated from the melt so that when the alloy in these spaces solidifies, the resultant shrinkage cannot be fed from the melt, and interdendritic cavities are formed (Fig. 2). The microstructure lacks a well-defined grain structure consisting of relatively few large crystals with each crystal forming a simple dendrite.

This interdendritic microporosity has been found to be responsible for altering the tensile strength, impact strength, and ductility of Co-Cr alloys³⁰ and leads to the fracture of the metallic parts of RPDs (Fig. 3), especially the clasps.^{14,30,32} In his study, Dharmar³⁰ also showed maxi-

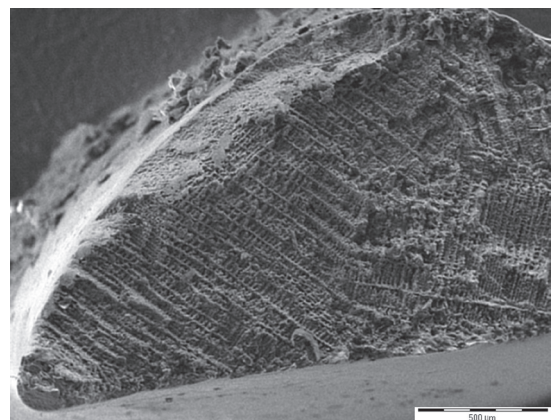


Fig. 3. Secondary Electron Image (SEI) of a fractured surface of an RPD lingual bar major connector made from a cast Co-Cr alloy. It shows extensive and coarse dendritic structure.

imum defects to the extent of 24.18% in the region of occlusal rests and minimum defects in reciprocal and retentive arms. Generally, porosity occurs in characteristic regions associated with abrupt changes in cross-sectional thickness.³¹ The problem of interdendritic porosity has been overcome in orthopedic applications by the application of special heat treatments and hot isostatic pressing (HIP). These techniques allow for the production of a homogeneous and fine grain structure with substantial increases in strength and ductility.⁶ Unfortunately, the latter cannot be used in dentistry due to dimensional constraints.

To find a way to solve the problem of the large grain size and its effect on the properties of the alloy, many researchers began to investigate the influence of different heat treatments. No changes in the grain structure after annealing (850°C for half an hour) and age-hardening (850°C for 5 hours) were observed compared with the original condition.³⁰ The explanation for these findings is the existence of the microporous structure of Co-Cr alloys. Such heat treatments involve the redistribution of carbides within the structure, but with a grossly dendritic and microporous structure, changes in carbide distribution become inconsequential.¹⁴ In another annealing process, using heat treatment at 704°C, 871°C, 1038°C, and 1204°C for 15 min followed by immediate quenching in water, the microstructures confirmed dissolution of the existing carbides, particularly the grain boundary morphologies.³⁷ In general, as the heat treatment temperature increased, the overall strength of the alloy decreased, while elongation slightly increased. In conclusion, it is generally accepted that heat treatments without prior plastic deformation cannot significantly alter the extent of microporosity, eliminating its adverse consequences.

In vitro tests reported that clasps produced by Co-Cr alloys showed higher fatigue resistance compared with those made of Au alloys, Ti alloys, and Ti. The latter demonstrated less loss of retention after three years of simulated use compared with those produced by Co-Cr alloys,³⁸ with the former showing lower incidence of fracture. *In vivo* results showed that there were no significant differences in fracture incidence or loss of retention between Ti and Co-Cr alloys,³⁹ indicating the inconsistency between laboratory and clinical observations.

Studies in a wet environment suggest that both water and artificial saliva reduce the fatigue strength of a Co-Cr alloy, explained by alloy corrosion, which occurs through the microcracks where clean metal surface is exposed to water. It has been accepted that the process of corrosion fatigue is controlled by localized corrosion or by the presence of hydrogen at the tip of the crack. Artificial saliva had a less reductive effect on the fatigue resistance than did water, which may be due to the inorganic compounds, such as phosphates, used in the artificial saliva.⁴⁰

Considerable research has been done in the field of repair of cobalt-based partial dentures. Several factors influence the strength of a solder joint: alloy composition, surface contamination, solder gap, heating and cooling pro-

cesses, and shape and dimension of the gap. In dentistry, the most common procedures for joining a Co-Cr alloy are soldering and brazing. According to the American Welding Society (AWS), if the joining process occurs at below 425°C, the operation is called soldering. However, if the temperature is above 425°C, it is called brazing.

Soldered joints of acceptable strength can be produced between Co-Cr alloys and solders at different melting points. A high solder melting temperature (>900°C) increases joint strength. Flux inclusions can dramatically reduce the mechanical resistance of the junction, depending on their extension with respect to the total connector area.^{41,42}

Cobalt-based alloys are usually brazed with filler metal based on the noble metals.⁴³ Brazed joints consist of dissimilar metals in intimate contact and immersed in the same electrolyte (saliva). In those cases, the possible formation of a galvanic corrosion must be considered. Studies from Heinz Luthy *et al.*,⁴⁴ including various electrochemical parameters, showed that Co-Cr-Ni alloys had the lowest nobility and underwent galvanic corrosion in a galvanic couple with gold braze, while Co-Cr-Mo alloys showed higher nobility.

This complication has been overcome by the introduction of laser welding to dental technology. Pulsed laser welding devices can be used to join broken parts of a Co-Cr removable partial denture with soldering wires with a composition similar to that of the Co-Cr alloy, thus eliminating the adverse effect of galvanic coupling. Nevertheless, laser welding demonstrates other advantages, combining a rapid, economic, and accurate way for joining metals and alloys.⁴⁵ However, laser welding is more technique-sensitive, and the optimization of the technique requires the training of the dental technician, especially for the identification of appropriate welding conditions.⁴⁶

ELEMENTAL COMPOSITION AND MECHANICAL PROPERTIES OF Co-Cr METAL CERAMIC ALLOYS

Compositions of Co-based alloys used for metal ceramic restorations are given in Table 3. Based on the International Organization for Standardization (ISO), International Standard 9693, Metal-Ceramic Dental Restorative Systems, and the ANSI/ADA Specification No. 38, which is an adaptation of the ISO 9693, there are no requirements for the chemical composition of cobalt-based alloys used for metal ceramic restorations.

Without specifications, conclusions and comparisons among various alloys cannot be made. The variability among the three main constituents (Co, Cr, and Mo) is high. Composition for Co varies from 33.9 % to 60.2%, that for Cr, from 21.4% to 30.1%, and that for Mo, from traces up to 12.7%. New metallic components are added in these alloys, such as Ce, Ga, and Nb, to provide fluidity, control thermal expansion, and modify the oxidation characteristics of these alloys to establish metal ceramic bond-

Table 3. Composition of Co-Cr metal to ceramic alloys

Elements	Wirobond 280*	Wirobond LFC*	Genesis II†	Vi-Comp‡	Callisto CP+§	IPS d.SIGN 30§
Co	60.2	33.9	52.6	55.80	40.0	60.2
Cr	25.0	28.5	27.5	25.00	21.4	30.1
Mo	4.8	5.0		3.00	12.7	<1.00
W	6.2		12.0	5.00	<1.00	
Si	<1.0	<1.0	<1.0	<1.00		<1.00
Fe		30.0	<1.0			<1.00
Ga	2.9		2.5	7.50		3.9
Cu			<1.0			
Mn	<1.0	1.0				
N		<1.0				
Al						<1.00
B					<1.00	<1.00
Ta			<1.0		<1.00	
Pd					25.0	
Ru			2.5			
Nb		<1.0	<1.0	3.00		3.2
Li						<1.00
C		<1.0				

* Bego, Bremen, Germany; † Jelenco & Co., Armonk, NY, USA; ‡ DENTSPLY Prosthetics' Austenal, USA; § Ivoclar Vivadent, Schaan, Liechtenstein.

Table 4. Physical properties for Cobalt-Chromium metal to ceramic alloys

Brand Name	Modulus of Elasticity (GPa)	Yield Strength (0.2%) (MPa)	Tensile Strength (MPa)	Elongation (%)	Vickers Hardness	CTE*10 ⁻⁶ xK ⁻¹ (25-500°C)
Wirobond C	220	540	680	11.0	280	14.0
Wirobond LFC	200	660	950	16.0	315	15.9
Genecis II	172	517	N/A	15.0	325	14.4
Vi-Comp	175	448	695	7.7	320	14.2
Callisto CP+	180	780	N/A	10.0	365	14.4
IPS d.SIGN 30	234	520	N/A	6.0	385	14.5
ISO 9693		250		3.0		-

N/A: Not available.

ing, while Ga is considered as a grain refiner.

The ISO specifications for the mechanical properties of all metallic materials agree with the requirements given in Table 4. Mechanical properties of some commercial metal ceramic alloys, as stated by the manufacturer, are also given in Table 4. Again, only the yield strength and elongation are specified as requirements for metal ceramic alloys. Yield strength is important from a clinical perspective, because the higher value of this property protects the metal-ceramic system from the initiation of plastic deformation and thus porcelain debonding, especially at the thin cervical areas. Conversely, the clinical importance of percentage elongation is questionable, since even a small amount of perma-

nent deformation may cause porcelain fracture.

Recent developments in dental technology have provided alternative production methods to conventional casting for the fabrication of FPD and RPD Co-Cr frameworks.⁴⁷ The first one is CAD-CAM technology, and the other is Selective Laser Melting (SLM), commonly known as the laser sintering technique. Both techniques are very promising for further future dental applications, especially due to the elimination of internal porosity. SLM provides a single-phase microstructure, eliminating the presence of the second Mo-rich phase and the possible consequences of galvanic coupling within alloy phases (Fig. 1B). Although SLM seems very promising, many other properties—such as fit-

ting accuracy, corrosion, metallo-ceramic bonding, etc.—should be tested to persuade the dental world that it is not expensive and reliable alternative to conventional casting. A detailed comparison among the three manufacturing methods of Co-Cr alloys is beyond the scope of this review. However, the same author is completing a soon-to-be-published comprehensive literature review comparing the three manufacturing methods (casting, CAD/CAM, and SLM).

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