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Assessment of Dental Alloys by Different Methods

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Abstract

Alloys are used in various areas of dentistry. The field of dental alloys is a very extensive one, encompassing both the materials themselves as well as the manufacturing methods, which are constantly developing. Our chapter focuses on corrosion and biocompatibility assessment, using various methods. At present there is no perfect dental alloy. Superalloys for dental use are not yet available, and only few studies concerning the new generation of superalloy candidates for medical applications have recently been developed, with promising results.

Keywords: dental alloys, corrosion, sintering, laser welding, cytotoxicity

1. Introduction

Alloys are used in various areas of dentistry. Iron-based alloys are used for orthodontic wires and tools. Noble-metal alloys and base-metal alloys are used for manufacturing crowns, inlays, partial fixed dentures, and metallic frames of removable partial dentures. The field of dental alloys is a very extensive one, encompassing both the materials themselves as well as the manufacturing methods, which are constantly developing [1].

However, superalloys for dental use are not yet available, and only few studies concerning the new generation of superalloy candidates for medical applications have recently been developed. Three superalloy candidates [2] for medical application were assessed by means of corrosion behavior, cation release, and biological evaluation for a prolonged contact with skin, in comparison with two reference austenitic stainless steels 316L and 904L. The three

superalloy candidates assessed were X1 CrNiMoMnW 24-22-6-3-2 N, NiCr21 MoNbFe 8-3-5 AlTi, and CoNiCr 35-20 Mo 10 BTi. Several electrochemical parameters were measured and determined (E_{oc} , E_{corr} , i_{corr} , b_a , b_c , E_b , R_p , E_{crev} , and coulometric analysis) in order to assess corrosion behavior. The cation release evaluation and in vitro biological characterization have also been carried out. In terms of corrosion, the results reveal that the 904L steels presented the best behavior followed by the super austenitic steel X1 CrNiMoMnW 24-22-6-3-2 N. For the other two superalloys (NiCr- and CoNiCr-type alloys) tested in different conditions (annealed, work hardened, and work hardened + age hardened), their behavior to corrosion was found to be weak and close to the other reference stainless steel, 316L. As far as extraction is concerned, a mixture of cations in relatively high concentrations was noted, and, therefore, a cocktail effect was not excluded. The results obtained in the biological assays WST-1 and TNF- α were in correlation with the corrosion and extraction evaluation [2]. The encouraging results of this study may support the development of superalloys for medical applications.

2. Classification of dental alloys

Commonly used dental alloys may be classified as shown in Table 1

Noble alloys	Base metal alloys
With a high gold content	Ni-Cr alloys
With a low gold content	Co-Cr alloys
Based on Ag-Pd (with and without copper)	Titanium alloys
Palladium-based (with increased content of Pd, based on Pd-Cu and Pd-Ag)	

Table 1. Classification of dental alloys

At present, there is no perfect dental alloy. Alloys are mixtures of two or more metals. Metals, when melted, are usually inter-soluble; once the mixture has cooled, the result is a solid solution with higher values of hardness, resistance, and flexibility than the initial pure metals from which it was derived. The grain-type structure of the alloy predisposes to corrosion, which is quite an issue in the case of dental alloys. Other shortcomings involve biocompatibility and manufacturing technology, which, in case of casting, is quite laborious.

3. Corrosion assessment

Corrosion characterizes the chemical reactivity of metals and alloys, which results in a visible alteration of the material and affects the function of a metallic component or of the entire

system, since the results of corrosion are metallic compounds. Such compounds are more stable than the metals concerned.

A major necessity that concerns any material of metallic nature used in the oral cavity is good resistance to corrosion.

Corrosion that occurs in the presence of atmospheric moisture or water is an electrochemical (galvanic) corrosion. The oral cavity provides an ideal environment for conducting electrochemical corrosion phenomena.

In the case of dental alloys, corrosion causes an unaesthetic change of the alloy surface. Metal restorations (crowns, inlays, amalgam fillings) are charging electrically in the oral environment, the degree of damage on the restoration depends on the metallic material (type of alloy), the presence on the surface of the restoration of soft or hard deposits, the connection with anatomical substratum, the existence of fractures in the veneering material, the age of the restoration, and the composition of saliva [3].

Metals and alloys are good electricity conductors, most of the corrosion processes involving the formation of an electrolytic cell, as the first stage of the process. Conditions for the formation of an electrolytic cell in the oral cavity include the presence of two or more metals with different electrode potentials and of an electrolyte (saliva and tissue fluids are good electrolytes). The two materials must be immersed in an electrolyte and must be in electrical contact for current to flow [1].

Bimetallic devices may present signs of corrosion after variable time [4]. Such degradations are quite frequent in the oral cavity, fortunately at a smaller scale in case of noble dental alloys [5], but may occur in various other situations (Figure 1). Such degradations correspond to the galvanic corrosion type.



Figure 1. Bimetallic wrist bracelet made of bimetallic rings gold/steel after corrosion in saline solution

Numerous factors influence the galvanic corrosion: internal factors (metal related) and external (electrolyte related).

Parameters related to the material (composition, structure, impurities, surface condition, etc.) [6]:

The nature of the metal: metals and alloys which when inserted into the oral cavity have a good stability are copper, silver, molybdenum, iridium, and palladium. Gold and platinum are very stable; copper and iron are relatively stable; chromium, zinc, and aluminum are very unstable.

The tendency of a metal to corrode is given by its electrode potential, as metals with increased negative potential are more likely to corrode, while metals with high positive values are much less reactive and are also called noble metals.

At first sight it seems incomprehensible why chromium, having one of the most negative potential values, is used as a component of many dental alloys. This apparent contradiction is explained by the fact that despite being electrochemically active, chromium reacts by forming a layer of oxide that protects the metal or alloy from further decomposition [7, 8].

The metal's structure depends on:

Grain size: if there is a precipitation of impurities between grains, the larger the grains, the more intense is corrosion along them.

Structural heterogeneity: the more homogeneous the distribution of metallic atoms in an alloy, the less present is the tendency to corrode. That is why most manufacturers submit the alloys to a homogenizing treatment using heat, in order to minimize the possibility of electrochemical corrosion.

The surface condition depends on the following: the polishing degree, surface properties, absence of pores or cracks in the primary protective layers. Deformations, and mechanical tensions in the metal contribute to decreasing the potential, as fatigue is more accentuated in corrosive environment [1].

Parameters related to the nature of the electrolyte (composition, concentration, temperature, oxygen content, pH, heterogeneity, etc.):

Chemical: pH- corrosion is poor in a neutral environment, generally high in acidic environment, and variable in basic environment; oxidants present in the solution determine, most frequently, an increase of the electrode potential [9].

Physical: temperature may have an important indirect effect; the movement of the solution may cause variations by changing concentration of the metal's specific ions, in the vicinity of the electrode surface, duration of exposure being a key factor.

Parameters related to topography (surface ratio of the two materials, geometric distribution, etc.) may also play a role in developing corrosion.

Corrosion effects

Chemical effects are manifested by loss of metallic luster and brown coloration of the surface.

The physical and mechanical effects, leading to the deterioration of mechanical properties, are the following:

Uniform corrosion decreases the metal thickness.

Localized corrosion in the form of plates or punctiform.

Intercrystalline corrosion: metal corrodes in depth.

Selective corrosion: only a component of the alloy is involved.

Biological effects of galvanic microcurrents translate as:

Subjective symptoms: metallic taste due to the release of ions, reflex salivation or xerostomia, burning sensation, headache due to the occurrence of galvanic current, and trigeminal neuralgia.

Objective symptoms: gingivitis and glossitis, hypertrophy and turgescence of taste papillae, erosions and ulcers of the oral mucosa, late leukoplasia, and changes of blood chemistry.

General manifestations: fatigue, dyspepsia, and headache.

An unwanted effect is an increased charge of metal ions, with negative effects, in particular regarding heavy metals like mercury and nickel [1].

Galvanic corrosion is rare in case of noble dental alloys. However, incorrect manufacturing technology or improper finishing may have unwanted results.

3.1. Corrosion of noble alloys due to incorrect manufacturing technology

A combined fixed prosthetic restoration of four elements consisting of a metal-ceramic part (23-24) and a cast part (25-26), bonded after firing the ceramics, presented a significant corrosion shortly after luting.

The two parts were made following strictly all the rules, using noble alloys with high content of gold (Table 2), bonded by soldering in the oven using a gold-enhanced content alloy.(Table 1). Restoration was then finished and luted.

Technique	Alloy	Manufacturer	Au	Pt	Pd	Ag	Cu	Zn	In	Cd
Metal-ceramic	Esteticor Royal	Cendres et Metaux	810	118	20	32	2	1	17	0
Conventional	Qualigold 4	Qualident	685	23	42	125	103	22	0	0
Soldering	Esteticor R No.2	Cendres et Metaux	785	0	20	25	X	X	0	X

Table 2. Composition of the alloys used for the fixed prosthetic restoration

One week after luting, we noticed the appearance of intense colored deposits, irregular in some superficial parts of the cast area. The restoration was removed from the mouth.

Surface analysis

The superficial analysis of the cast part (Figure 2) by the scanning electronic microscope (SEM) showed three different areas:

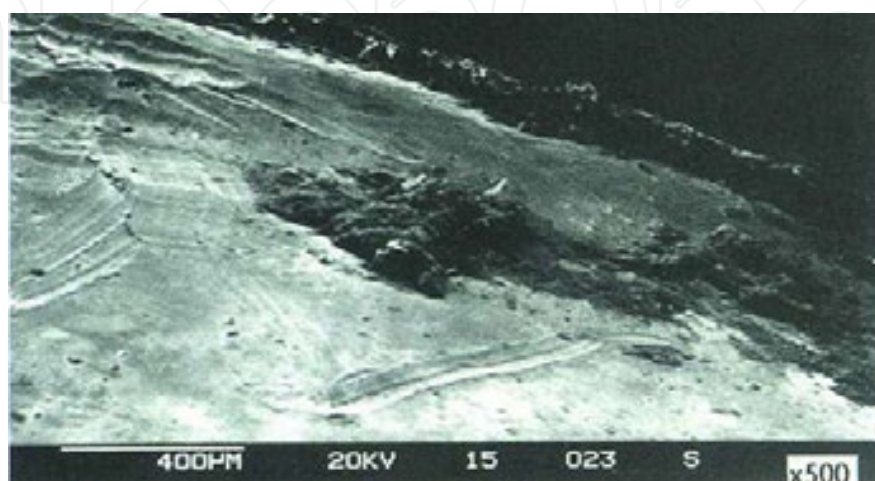


Figure 2. SEM observation (500 x magnification) of the corroded crown surface

Areas with no deposits and corrosion-free deposits

The spectrum obtained by energy-dispersive X-ray spectroscopy (EDX) reflects a normal nominal alloy composition (Figure 3).

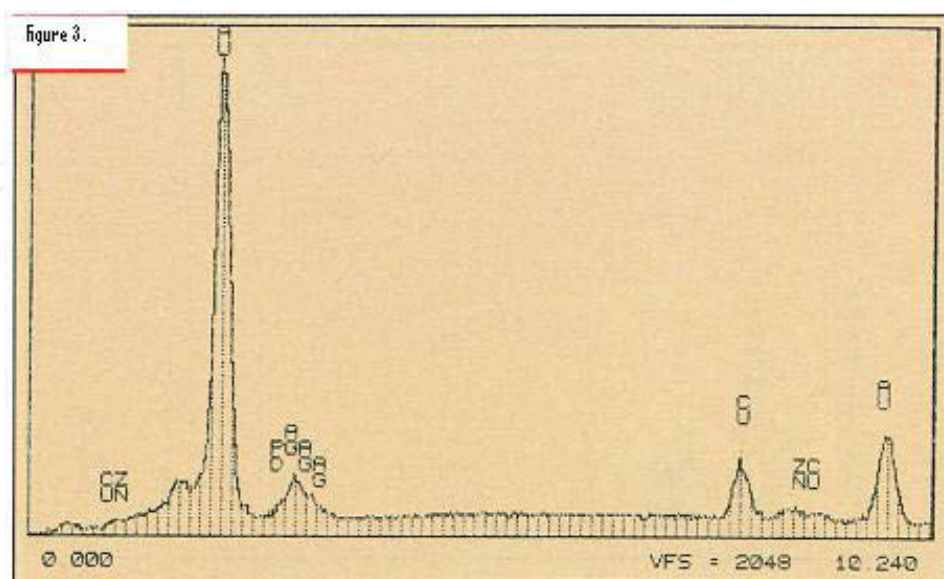


Figure 3. Energy-dispersive X-ray spectroscopy of the cast alloy

Black-bluish colored areas, without deposits

In these areas the laser ionization surface analysis revealed formation of copper and silver sulfides. Sulfur concentration decreases rapidly depending on the analysis depth.

Areas characterized by relatively thick whitish deposits

In these areas, the analysis shows the presence of sulfur, sodium and, potassium chlorides, as well as calcium phosphates (Figure 4). We also noticed a high concentration of copper (Figure 4) compared to that measured at the nominal composition (Figure 3).

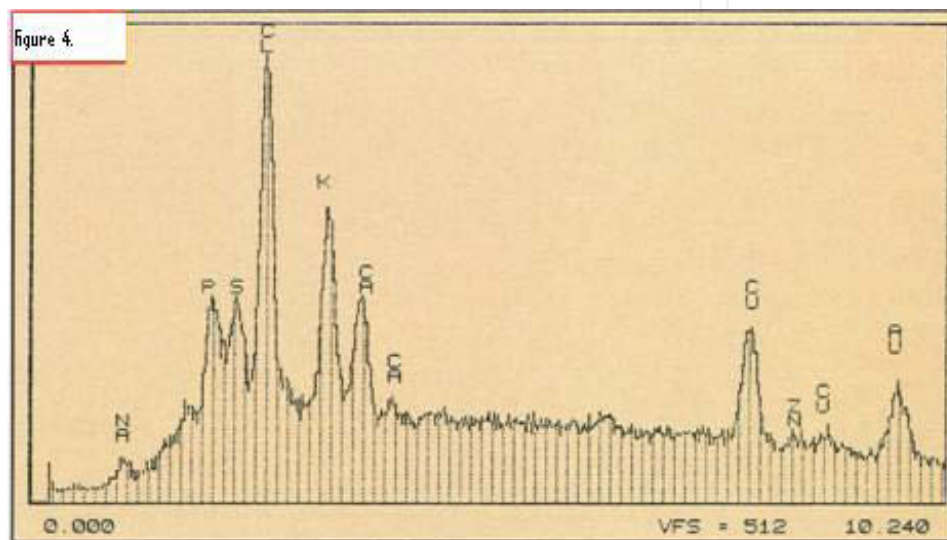


Figure 4. Energy-dispersive X-ray spectroscopy of the whitish deposit

Section analysis

Energy-dispersive X-ray spectroscopy shows that the segregations are nodules of copper and zinc oxide (Figure 5, 6).

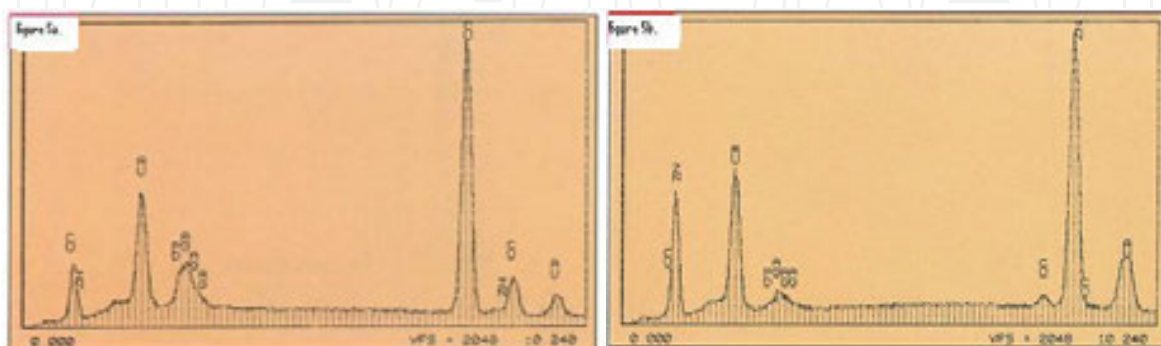
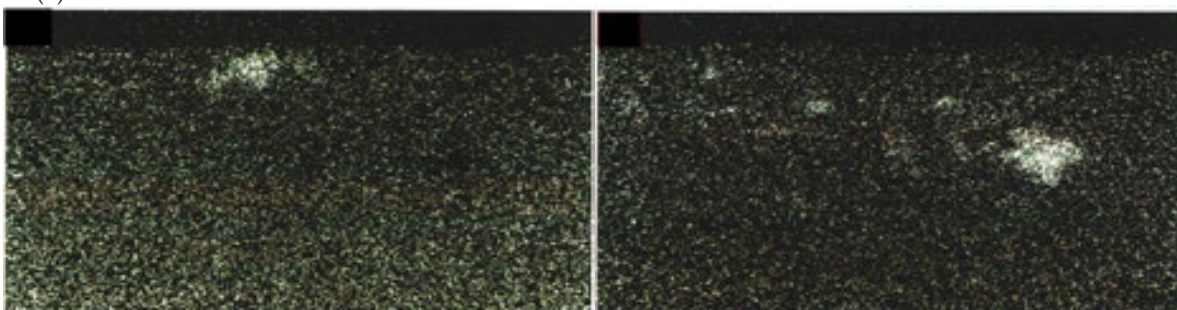


Figure 5. Energy-dispersive X-ray spectroscopy of a segregation consisted mainly of copper oxide (a) and of zinc oxide (b)



Optical microscopy of a metallographic section of the cast part does not reveal defects in the internal structure of the a correct soldering [1]. Cpy, with a 5000x magnif order of 10-20 microns (Figure 7).

Figure 5. Energy dispersive X-ray spectroscopy of a segregation consisted mainly of copper oxide (a) and of zinc oxide (b)

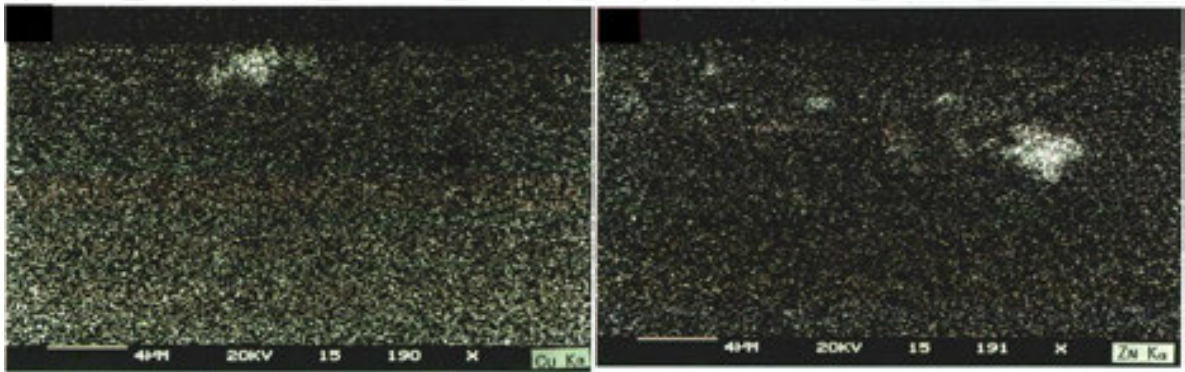
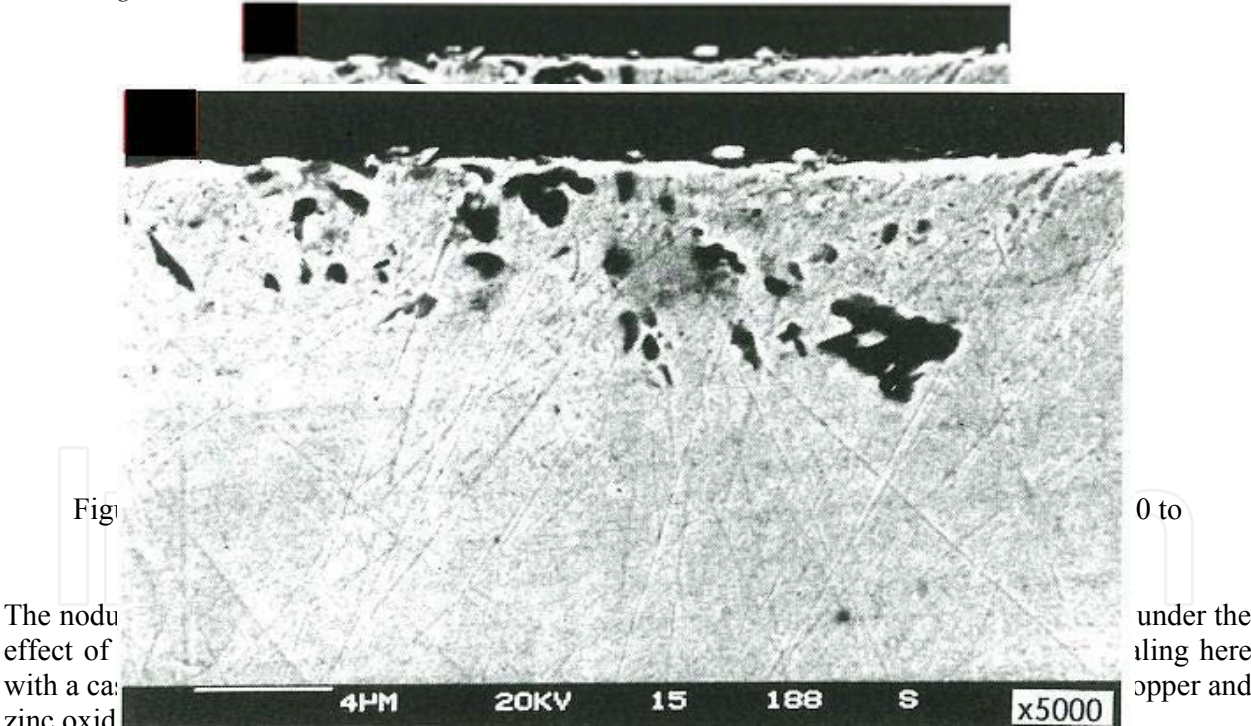


Figure 6. Picture of the copper density and of zinc density observed on the same area and same magnification as illustrated in Figure 7



Thus, a mixed potential (corrosion potential) has been created on the same surface due to the areas of different chemical composition [9]. In this case, the anodic parts are areas consisting of copper and zinc oxide nodules. We cannot take into account the galvanic corrosion between the metal-ceramic and the base parts, because the origin of the corrosion is located above the base metal. The corrosion is under the effect of heat treatment represented by secondary bonding in the furnace [10]. We are dealing here with a case of localized corrosion [7] in which the less noble parts of the surface consist of copper and zinc oxide nodules.

Thus, a mixed potential (corrosion potential) has been created on the same surface due to the areas of different chemical composition [9]. In this case, the anodic parts are areas consisting of copper and zinc oxide nodules. We cannot take into account the galvanic corrosion between the metal-ceramic and the cast parts, because the localized corrosion described above could have also occurred in the absence of the metal-ceramic part.

A galvanic cell can still accompany a localized corrosion process. In this case, the main cause of corrosion is the appearance of a mixed potential on the surface of the cast part.

The same bridge rebuilt with the same materials, but with a correct finishing phase, including a deoxidation in an etching salt and planted to the same patient has not shown signs of corrosion [11].

The omission of certain technological phases can have severely adverse consequences to the quality and durability of prosthetic restorations. In this case, the consequence was the occurrence of a localized corrosion following luting in the mouth.

3.2. Surface condition influence on galvanic corrosion

In order to illustrate the importance of the surface condition on galvanic corrosion, we performed tests in sections consisting of two plates of different noble dental alloys, joined by a solder point (Figure 8).



Figure 8. The corrosion test samples are two plates of noble alloy connected by soldering

The two chosen alloys (Table 3) are an alloy for the metal-ceramic technique (Qualiceram 3, Qualident) and an alloy for the conventional technique (Qualigold 4, Qualident).

The two alloys are characterized by very different electronic properties. The secondary soldering was done with a noble gold soldering alloy (Table 3).

Type	Alloy	Au	Pt	Pd	Ag	Cu	Zn	In
Metal-ceramic alloy	Qualiceram 3 (Qualident)	84,4	7,9	4,6	0	0,4	0	2,6
Conventional alloy	Qualigold 4 (Qualident)	68,5	2,3	4,2	12,5	10,3	2,2	0
Soldering alloy	Qualisold S2 (Qualident)	75	0	0,3	4,8	11,4	3	5,5

Table 3. Composition % weight of the couples tested for corrosion

Five samples were prepared by soldering in the oven at 860°C. The sections then underwent different surface treatments (Table 4): no treatment (1), cleaning by a slight polishing with a polishing paste (2 and 3), chemical etching in a hot etching salt (4) and abrasion with ceramic abrasive disks followed by polishing and chemical etching (5).

Sample	Couple	Surface treatment after soldering
1	Qualiceram 3/Qualigold 4	No treatment
2	Qualiceram 3/Qualigold 4	Cleaning by brush and polishing paste
3	Qualiceram 3/Qualigold 4	Cleaning with rubber and then with polishing paste
4	Qualiceram 3/Qualigold 4	Chemical etching in a hot etching salt
5	Qualiceram 3/Qualigold 4	Abrasion with ceramic abrasive disks followed by polishing and chemical etching

Table 4. Defining the surface treatments after soldering, before the corrosion testing

Human artificial saliva may vary to a considerable degree and is dependent on the age and sex of the patient, time of day, eating habits, medication and oral hygiene [12]. The corrosion test consisted in immersion of the samples in Fusayama artificial saliva (detailed composition in Table5) at 37°C for 30 days. We selected Fusayama artificial saliva because it was shown to produce results that were consistent with the clinical experience of dental alloys. The pH of such solution is about 5.6 [13].

The test results are illustrated in Figure 9.

Samples 1, 2, and 3. The samples subjected to only a slight polishing or no treatment have significant corrosion product deposit.

NaCl	0,40 g/l
KCl	0,40 g/l
CaCl ₂ ·2H ₂ O	0,79 g/l
NaH ₂ PO ₄ ·H ₂ O	0,69 g/l
Urea	1,00 g/l
Na ₂ S·9 H ₂ O	0,005 g/l
NH ₂ CONH ₂	1.00 g/l
Distilled water	Up to 1000 ml

Table 5. Artificial saliva Fusayama type

The blue stains show the formation of copper-based compounds, deriving from the alloys for the conventional technique.

Sample 4. The sample subjected to chemical etching reacted very little. Only a slight gloss change is visible.

Sample 5. The sample subjected to surface abrasion, and then to a polishing followed by chemical etching showed no sign of corrosion or any other change.

We also observed that areas protected by a fusing agent during soldering were not corroded.



Figure 9. Illustration of galvanic corrosion observed in the 5 samples (1-5)

The corrosion observed on the artificially created surface shows that the passivity and non-passivity phenomena of the surfaces strongly influence the formation and functioning of a cell.

Soldering, which is linked to a thermic treatment, produces a more or less thick layer on the surface, layer consisting of various oxides. In case of alloys for the conventional technique, this layer is typically a few tenths of microns thick and contains highly corrosive oxides in saliva (as copper oxide, zinc, etc). Thus, the behavior of samples 1, 2, and 3, conditioned by nonremoval of the oxide layer, is under anodic control and leads to a significant corrosion despite the nobility of the two alloys [14].

Sample 4, for which this layer has been practically eliminated, reacted very little. Sample 5, for which the layer was completely removed, did not react at all and did not show any effect of corrosion.

For the noble dental alloy combinations, a surface treatment that removes the oxide layers properly is essential to prevent the consequences, sometimes catastrophic, of the galvanic corrosion incidence [14].

3.3. Corrosion due to improper melting conditions

Only a few months after luting, we noticed a severe color change and the loss of the metallic shine in case of four-element bridge (Figure 10). Its surface presented dark and shiny areas. The bridge (23-26) was manufactured using a low-gold-content conventional class E alloy (Au, Ag, Pd, Cu, Zn). We decided to remove it and have it analyzed for determining the causes that lead to its failure.



Figure 10. The deteriorated surface of the four-element bridge

For analytic purposes, we prepared two samples, one part of the bridge (24-25) was used to analyze the damaged surface using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), without any surface alteration.

The second part of the bridge (26) was transversally sectioned in order to observe the superficial structure of the alloy.

The surface analysis performed with retrodiffused electrons (Figure 11) and energy-dispersive X-ray spectroscopy (EDX) (Figure 12) shows that the coloration is associated with a nonhomogeneous surface composition. We noticed areas without sulfur (area 1, Figure 12), areas rich in copper and sulfur (area 2, Figure 12), and areas rich in silver and sulfur (area 3, Figure 12).

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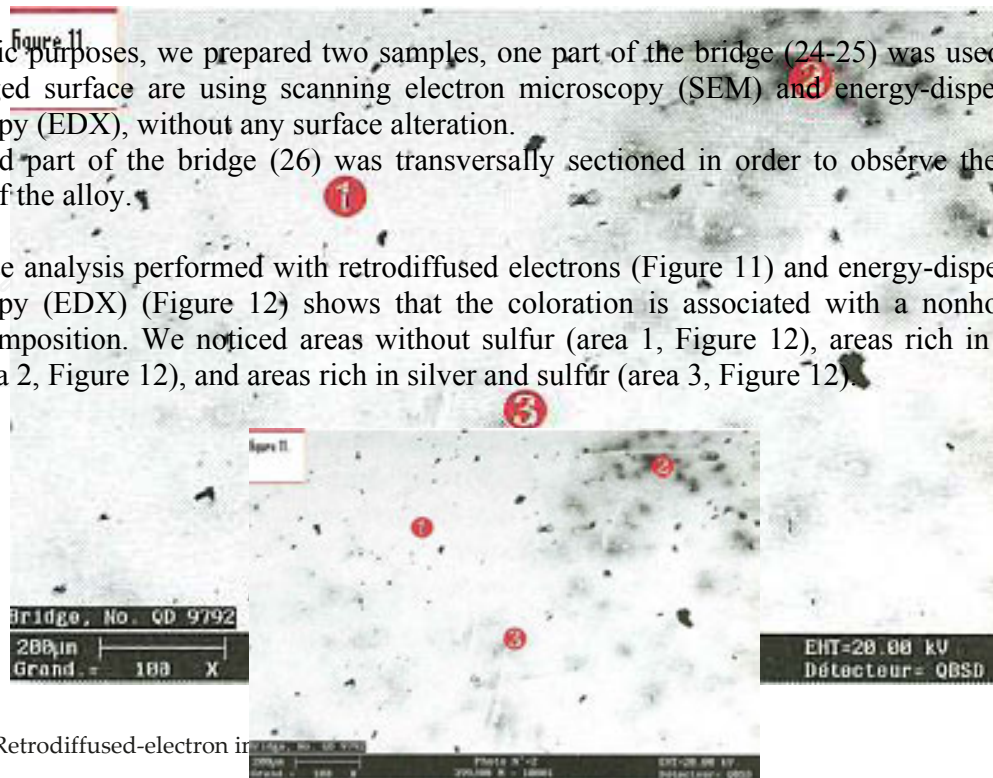


Figure 11. Retrodiffused-electron image (chemical contrast) of the 25-crown surface

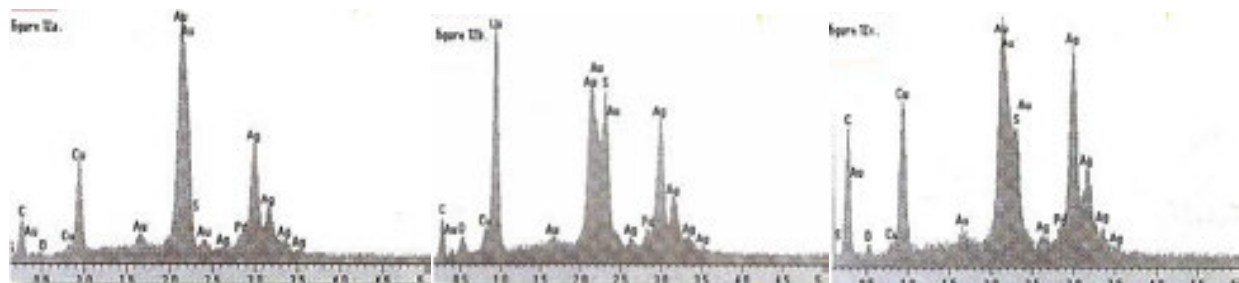


Figure 12. EDX spectrum of (a) area 1 (without sulfur), (b) area 2 (rich in copper and sulfur), and (c) area 3 (rich in silver and sulfur)

Retrodiffused electron observation and the location of the elements (Au, O, Cu, S and Ag) (Figure 13) indicate that the shine loss in area 2 was characterized by excess of sulfur and copper. The presence of oxygen was associated with copper localization.

SEM section analysis using secondary electrons (Figure 14) shows a very important millimetric internal porosity. The porosity area is localized on the external part, in some areas merging to the surface. SEM analysis with retrodiffused electrons (Figure 14) shows a dendritic nonhomogeneous structure, close to the surface.

The main alloy elements (Au, Ag, Cu) are positioned close to the surface, mainly in the proximity of the porosity areas, in a nonhomogeneous way. This nonhomogeneity is more important in the sub-superficial darkened areas than in the sub-superficial shiny areas. The

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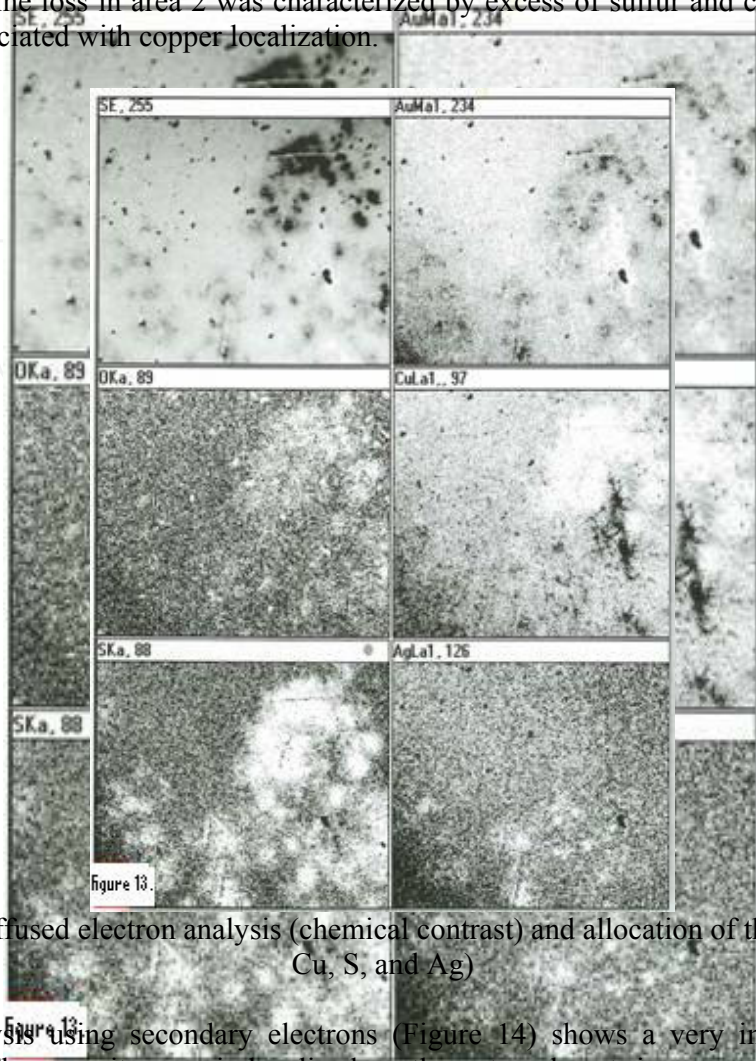


Figure 13. Retrodiffused electron analysis (chemical contrast) and allocation of the elements (Au, O, Cu, S, and Ag)

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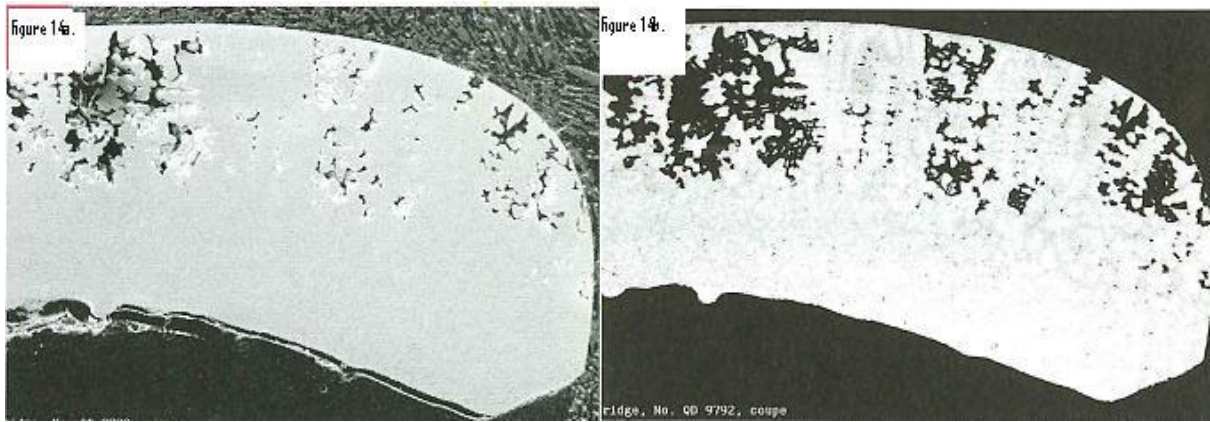


Figure 14. Section observation with (a) secondary electrons (topographic contrast) and with (b) retrodiffused electrons (chemical contrast)

porosities are colored in black and are characterized by the presence of tiny inclusions very rich in Cu (Figure 16).

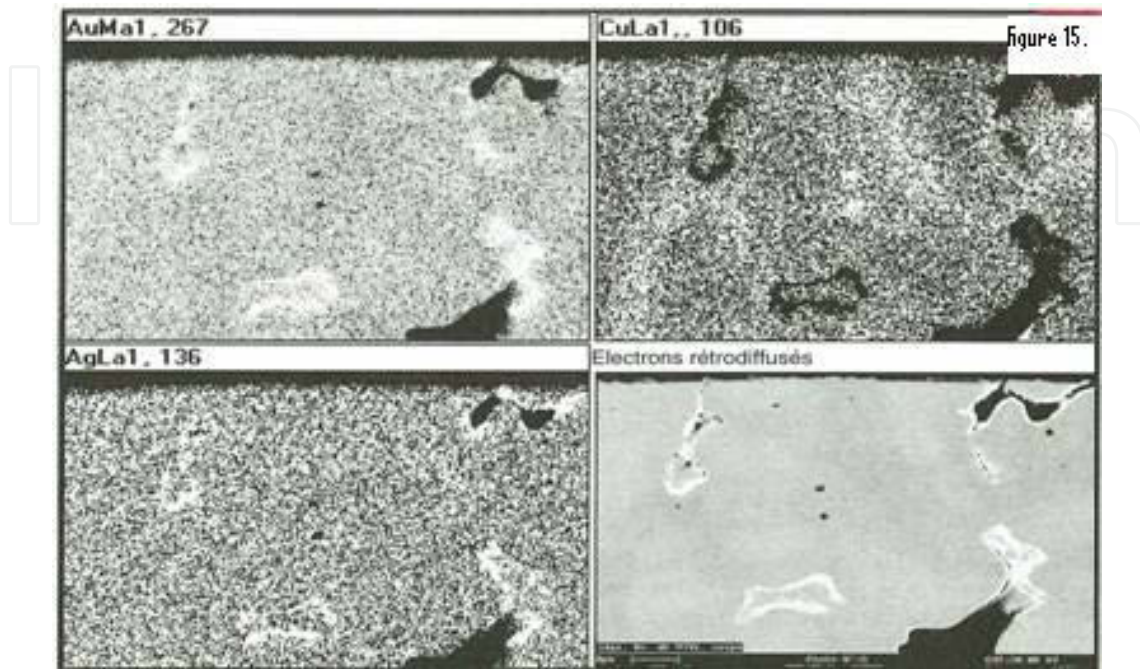


Figure 15. Observation of the sub-superficial layer of the dark area with retrodiffused electrons (chemical contrast) and element allocation (Au, Ag, and Cu)

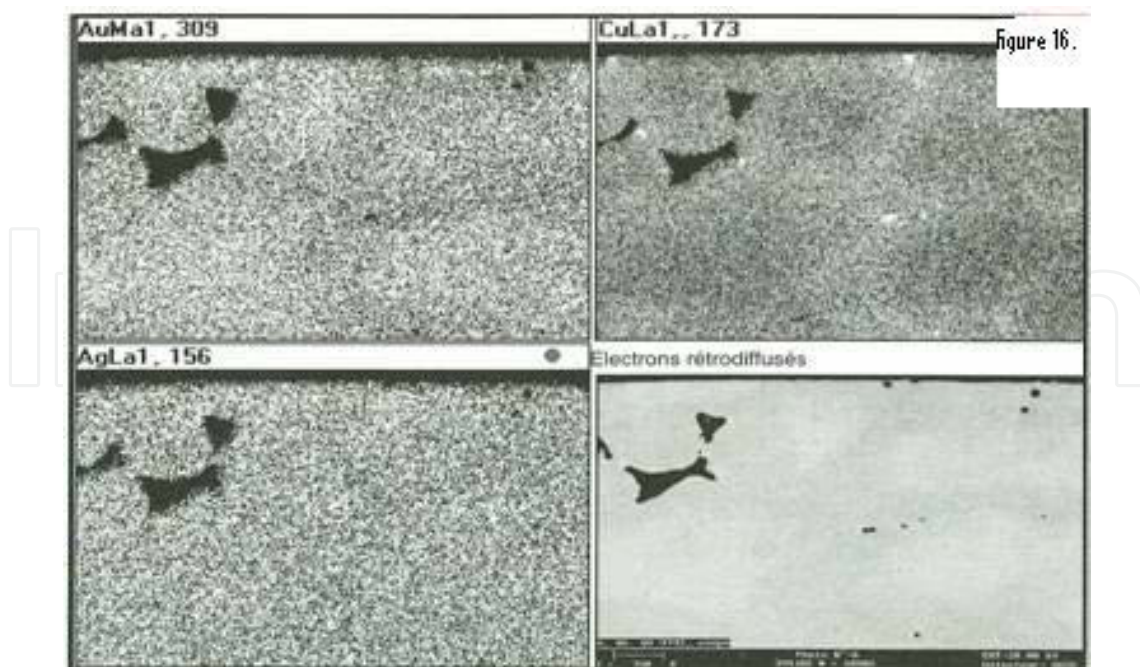


Figure 16. Observation of the sub-superficial layer of the shiny area with retrodiffused electrons (chemical contrast) and the element allocation (Au, Ag, and Cu).

Comparing the nominal chemical composition to that of the analyzed areas (areas I, II, III, and IV), we noticed differences (Table 6). As known, any change in the alloy's composition (decreasing or increasing with one or more elements) has negative consequences for the corrosion resistance [7]. The corrosion process will be accelerated by the unstable phases in the alloy structure. A galvanic cell usually appears between these unstable phases and the alloy matrix, with the appearance of subsequent selective corrosion [15, 7]. In our case, the shine loss represents its result. Composition analysis shows that sulfur and oxygen are present. Areas rich in copper or silver reacted with the sulfurous compounds in the saliva, which explains their presence in the darkened areas. In this case, a selective corrosion process is involved, with formation of insoluble chemical products (sulfides, copper, and silver) [16].

	Au*	Ag*	Cu*
I	560	243	197
II	574	237	189
III	611	354	35
IV	253	123	624
% weight			

Table 6. Relative chemical compositions in Au, Ag, and Cu measured in four areas: I and II internal composition of the matrix and external composition of the inclusions; III inclusions rich in Au and Ag (Figure 15); and IV inclusions rich in Cu (Figure 16).

The failure is due to the incorrect alloy usage. The alloy's normal melting conditions were not respected. This incorrect melting was the cause for the internal porosities and for the areas with very different superficial compositions. Furthermore, the surface was not properly polished. The surface, porous and chemically nonhomogeneous, as a result of incorrect melting and surface treatment, led to decreased corrosion resistance and subsequent degradation of the bridge, shortly after luting.

3.4. Corrosion resistance of cobalt-chromium alloys doped with precious metals

Cobalt-based alloys are often used to manufacture different types of devices implanted in the body by surgery. Their applications include hip prosthesis, knee plates, screws for osteosynthesis, and basic structures for heart valves [17]. In dentistry [17,18], cobalt-chromium alloys are mainly used for manufacturing removable partial dentures and metal ceramic fixed partial dentures. In both these cases fine framework constructions are involved. These alloys are characterized by excellent corrosion resistance and superior mechanical properties (e.g., high stiffness) [19]. The dental Co-Cr alloys have diversified over time, aiming at creating both new products and new technologies to process them [20].

A new generation of cobalt-chromium alloys enriched with precious metals (Au, Pt, Ru) are available, their goal being to improve corrosion resistance. In order to verify this hypothesis 4 different such alloys were tested [21,22].

The compositions of the commercial tested alloys and of a “classical” Co-Cr alloy are listed in Table 7.

Element	Chemical composition (wt %)				
	Co-Cr	1	2	3	4
Co	63.7	63.5	52.0	50.6	59.3
Cr	28.9	21.0	25.0	18.5	25.0
Mo	5.3		4.5	3.0	5.0
Ga		4.5	6.0		2.5
In		Trace	5.0		1.2
Au		2.0	2.0		2.0
Pt		Trace	2.0	15.0	
Ru				10.0	
Sn			1.0		
Mn	0.8	6.5	0.5	1.0	
Si			2.0	0.75	
W	0.1			0.5	4.0
Nb				0.5	
Al		2.5			
Ti				Trace	
Fe	0.4				

Table 7. Composition of the tested alloys (wt %).

Before electrochemical testing the alloys were analyzed micrographically, analysis of phases by energy-dispersive X-ray spectroscopy (EDX) was carried out, and hardness properties were also tested.

Metallographic structures of the tested alloys are shown in Figures 17-20.

The microstructures of alloys 1 and 4 showed round “inclusions” with a diameter up to 0.1 mm. The chemical analysis of these zones showed In (between 42 and 51 %), Pt (around 28 %), and Au (between 18 and 27 %).

The Vickers tests of such zones for alloy 4 gave a mean hardness value more than twice lower (147 HV) compared to the overall hardness value of the alloy (326 HV).

The hardness values are given in Table 8.

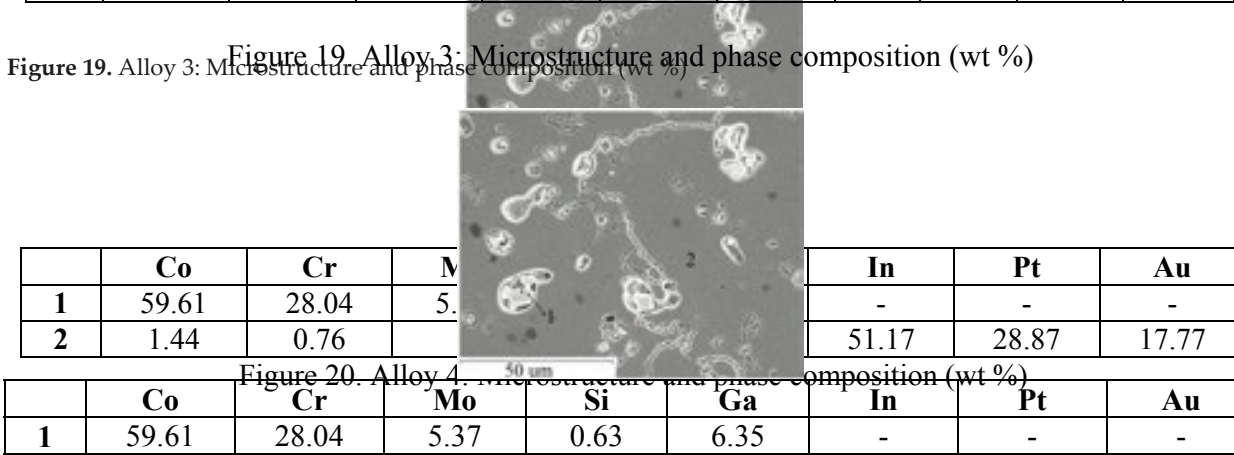
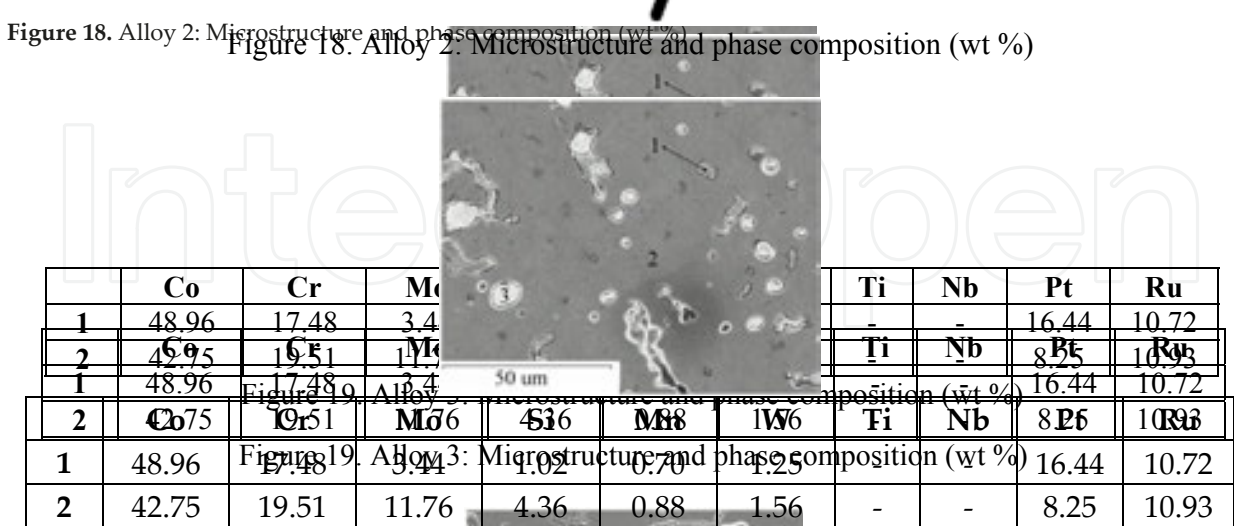
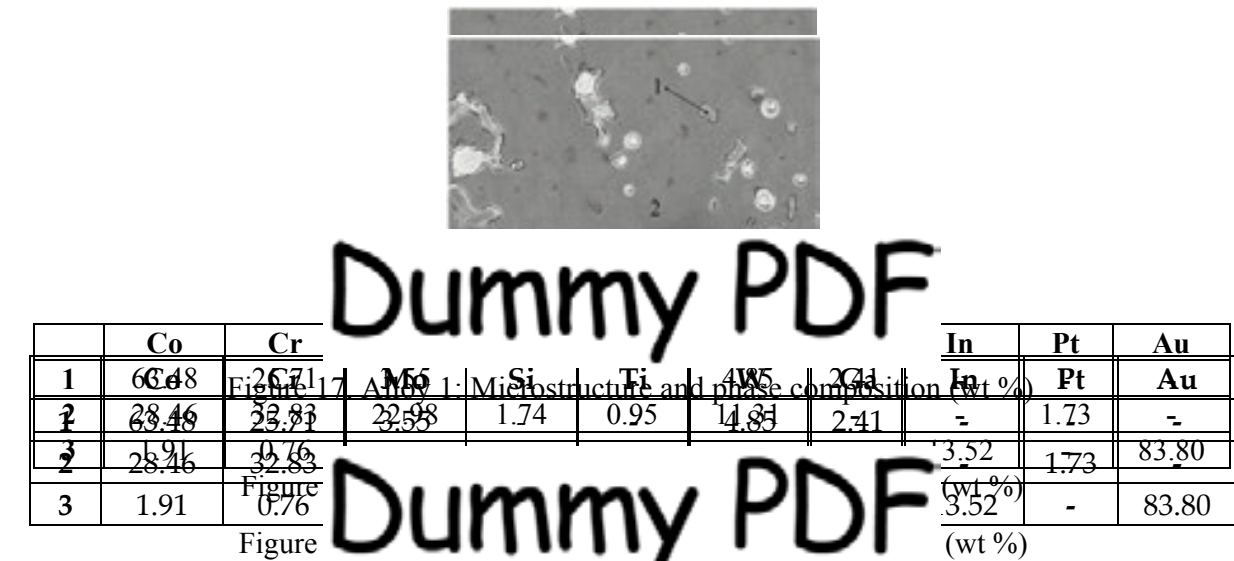
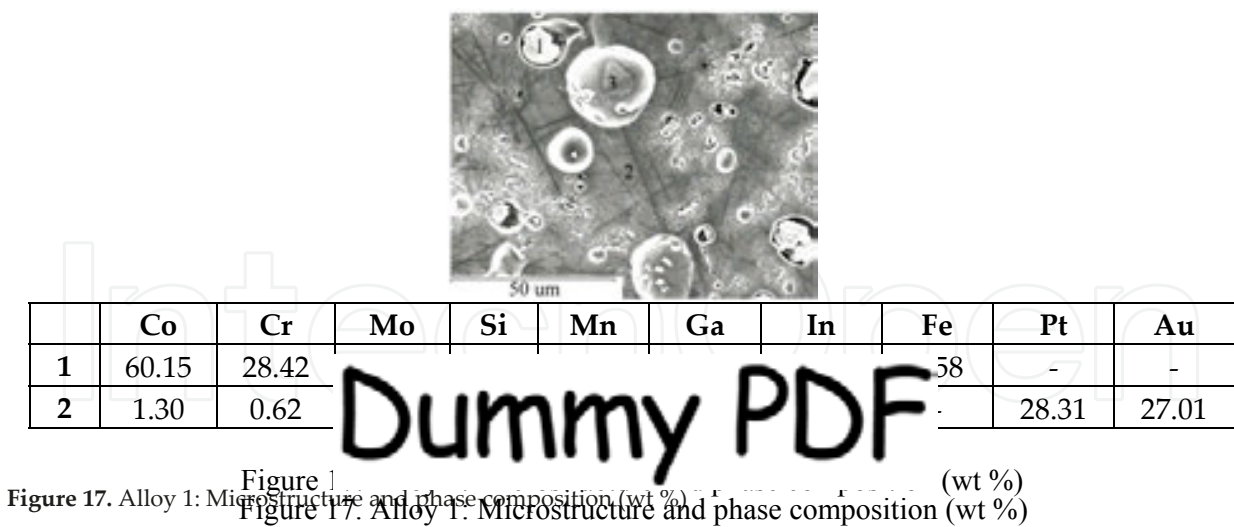


Figure 19. Alloy 3: Microstructure and phase composition (wt %)

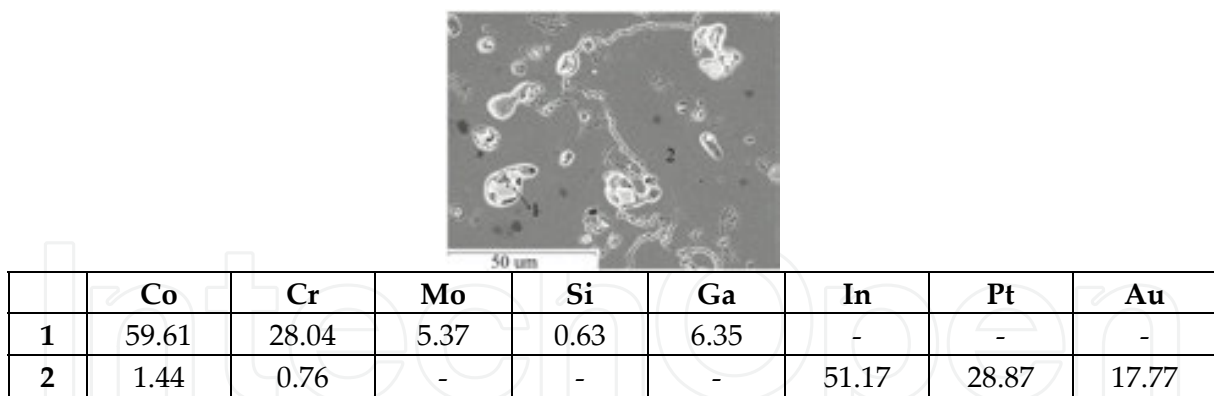


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The microstructures of alloys 1 and 4 showed round “inclusions” with a diameter up to 0.1 mm. The chemical analysis of these zones showed In (between 42 and 51 %), Pt (around 28 %), and Au (between 18 and 27 %).

The Vickers tests of such zones for alloy 4 gave a mean hardness value more than twice lower (147 HV) compared to the overall hardness value of the alloy (326 HV).

Electrochemical measurements were conducted in artificial saliva of the Fusayama type (Table 4) using the rotating electrode technique. The cathodic and anodic potentiodynamic polarization curves were measured from -1000 mV to +1250 mV vs. saturated calomel electrode (SCE).

Alloys	1 overall	2 overall	3 overall	4 overall	4 zone 2
HV _{0.2}	333	435	338	326	147

Table 8. Vickers hardness of the tested alloys (n=5)

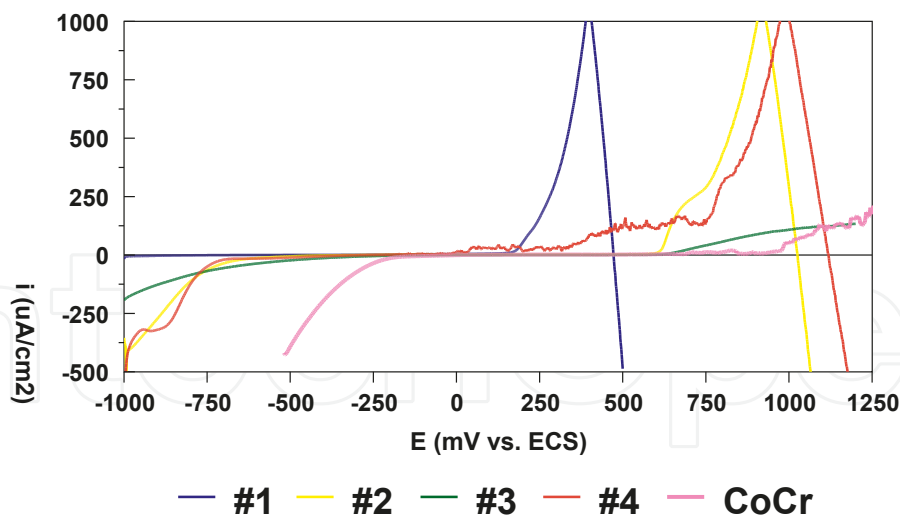


Figure 21. Potentiodynamic polarization curves in linear system of alloys #1 to # 4 in comparison with a Co-Cr alloy

The potentiodynamic curves (Figure 21) show important differences in the behavior of the 4 studied alloys (1 - 4), compared to the Co-Cr alloy. The worst behavior was shown by the alloys containing only gold (1 and 4). Au is not miscible to Co and Cr, confirming existing results [23].

Alloys 1 and 4 showed a very complex microstructure compared to the other studied alloys. The round “inclusions” with a diameter up to 0.1 mm are in part nonmiscible phases with a very low corrosion resistance. Regarding the corrosion behavior, the conventional Co-Cr alloy is the best, followed by alloys 2 and 3 (addition of, respectively, 4 % and 25 % precious metals). The worst behavior was noticed in cases of alloys 1 and 4 (with only addition of 2 % of Au). The presence of precious metals can deteriorate the corrosion behavior of Co-Cr alloys in a significant way. Gold doping, in particular, produces heterogeneous microstructures that are vulnerable to corrosive attack [21].

Scientifically speaking, Co-Cr dental alloys enriched with precious metals do not make sense. Due to their poor behavior, we conclude that using dental Co-Cr alloys enriched with precious metals, as an alternative to conventional Co-Cr alloys, is not justified [24].

4. Biocompatibility assessment

Conceived for a biological environment, dental alloys should essentially be integrated without developing adverse effects and maintaining their function without degrading within an acceptable time limit [25]. Dental casting alloys are widely used in applications that place them into contact with oral tissues for many years. With the development of new dental alloys over the past 15 years, many questions remain about their biologic safety [26].

A biocompatible material may be defined as: inert, nontoxic, non-mutagenic, non-recognizing, nonirritating, and nonallergenic [25].

The single most relevant property of a casting alloy when it comes to its biologic safety is its corrosion. The potential systemic and local toxicity, allergy, and carcinogenicity result from releasing elements into the mouth during the corrosion process. Little evidence supports concerns of casting alloys causing systemic toxicity. Local toxic effects (adjacent to the alloy) are not well documented, but it represents a higher risk, because local tissues are exposed to greater concentrations of released metal ions. Several elements such as nickel and cobalt have relatively high allergic potential, but the true risk of using alloys containing these elements is not certain. Prudence dictates that alloys containing these elements should be avoided as much as possible. Several elements in casting alloys are known mutagens, and a few, such as beryllium and cadmium, are known carcinogens in different chemical forms. Carcinogenic effects due to dental casting alloys usage have not been yet demonstrated [26].

The negative effects that the materials could have on the tissues or on the body at cellular level are precisely induced by the presence of certain components released as degradation products, especially metal cations in solution [27]. In demonstrating that the surface of the materials is degrading in contact with the biological environment due to corrosion, it still has not been established which constitutive elements of the respective materials are more apt to dissolve or in what quantity. The degradation of metallic dentures in a biological environment is accompanied by the release of cations such as Cr, Co, Ni, and Ti. Therefore, we are faced with a cumulative effect: allergic, irritating, mutagenic, and toxic [25]. The release of cations like nickel

may induce allergies. To prevent contact dermatitis, the European Directive 94/27/EC prohibits selling products that come into prolonged contact with the skin, if they release more than 0.5 $\mu\text{g}/\text{cm}^2/\text{week}$ of nickel. Some dental alloys as copper-aluminum bronzes, which appeared in the 1980's as a substitute for conventional gold-rich alloys and were used for a certain time, release about 100 times this amount [28].

The number of published studies addressing the mutagenicity of dental materials is low. So far, no published clinical reports document the carcinogenic effect of certain dental materials. The long exposure time that is necessary for a malignant tumor to show is a very aggravating factor for the clinical assessment of potential carcinogenic properties of dental materials [29].

A mutagenic substance is a substance capable of inducing mutations, in other words capable of inducing the occurrence or loss of a hereditary characteristic. For a chemical substance to become mutagenic, it should generally induce a primary DNA damage. Mutations can affect a single gene (genic mutations) or the number of chromosomes in a cell (chromosomal mutations). Several researches show that the majority of mutagens are potentially cancerous, and the majority of carcinogens have mutagenic properties [25]. According to the International Cancer Research Centre, metals are classified in two major families: metals having definite (Ni derivatives, Cr+6, Cd and its derivatives, Be and its derivatives) or potentially cancerous properties in humans and metals that have no cancerous potential. Metals not classified as cancerous but relevant as mutagens are: Sn^{+2} , Cu^{+2} , and Fe^{+2} . Metals not relevant as mutagens include Zn. Metals with none or limited references as mutagens are Cu^{+1} , Sn^{+4} , Au, Pt, Ag, Pd, In, and Ga [25].

In Europe, the main threat to health is nickel allergy. In the last years the dental alloys market has undergone dramatic changes for reasons of economy and biocompatibility. In certain countries, nickel-based, cheaper alloys have increasingly been subjected to more and more regulations or even banned. In the other countries, less expensive alloys are still the most used. Despite the restrictions imposed by the EU, the use of Ni-Cr alloys is on the increase [4]. In these current circumstances, there are some questions to be faced regarding the safety risk of nickel contained in dental alloys. In recent years, palladium and, to a lesser extent, nickel were frequently viewed as harmful when used in dental alloys [30,31]. All evidences currently available indicate that dental alloys for prosthodontic restorations are not carcinogenic [29].

Our studies are up to date, concerning cytotoxicity of dental alloys and their components involved in in vitro and in vivo tests.

4.1. Ni-Cr alloy testing for cation release

In [4] eight Ni-Cr dental alloys were evaluated for corrosion resistance (generalized, crevice, and pitting) and the quantities of cations released, in particular nickel and Cr+6 in relation with their microstructure. Cytotoxicity tests and an evaluation specific to TNF-alpha were made. The results showed that their corrosion behavior is weak and that nickel release is high. The quantities of nickel released are higher than the EU limits, in cases when contact with the skin or piercing is involved. The biological tests do not show any cytotoxic effect on HeLa and L929 cells nor any change in TNF-alpha expression in monocytic cells. The alloys do not show any

proinflammatory response in endothelial cells as demonstrated by the absence of ICAM-1 induction. Therefore no direct relationship between the in vitro biological evaluation tests and the physicochemical characterization of these alloys may be proved [4].

4.2. Ni-Cr and Co-Cr alloy assessment on cell cultures

At sufficiently high concentrations, metal ions alter cellular metabolism or lead to cell death [29].

Tests for Ni-Cr and Co-Cr dental alloys, the most commonly used in practice, were carried out [32]. The test cell cultures of pure cell line dermal fibroblasts HDFA and of those obtained from

skin biopsies were used, for both dental alloys and their eluates. The results were compared with control samples. Seven days after inoculation, the relative similarity between the Ni-Cr alloy and the Co-Cr alloy was observed. The cells did not detach from the plate and grew to

the edge of the material (Figures 22, 23). In the case of the eluates, there were no fragments detached, the cells having a relatively high confluence. The cytotoxic effects of the two alloys

seem similar, even if there are speculations in the literature according to which Ni-Cr alloys have a higher effect [33]. All the samples we used during the study maintained their initial characteristics. The cytotoxicity of the

alloys tested had minimal in vitro effects on fibroblasts from cell culture.

Alloys tested had minimal in vitro effects on fibroblasts from cell culture.

Alloys tested had minimal in vitro effects on fibroblasts from cell culture.

Figure 22. Pure cell line of dermal fibroblasts in direct contact with Ni-Cr and Co-Cr alloys, after 7 days (10 x)

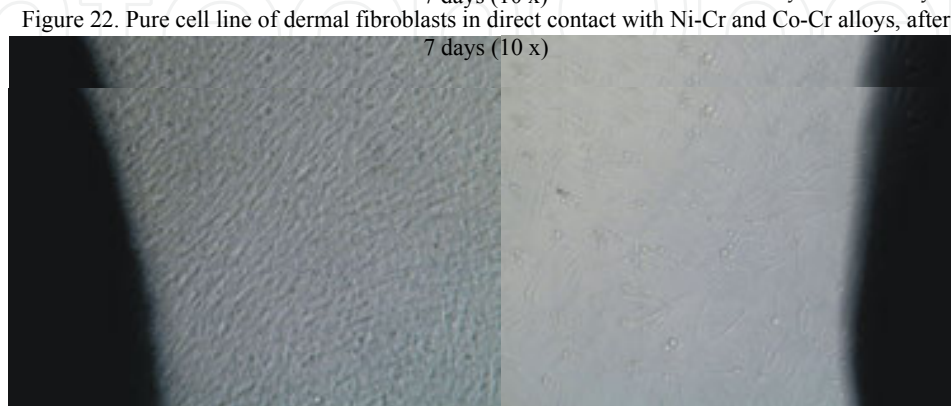


Figure 23. Primary culture of skin fibroblasts in direct contact with Ni-Cr and Co-Cr alloys, after 7 days (10 x)

4.3 In vivo tests

For in vivo testing we used the patch test (Figure 24). The patch-testing led us to the following results: sensitivity to gold, 5 %; palladium, 7 %; nickel, 30 %; and cobalt, 2 % [32]. It is not recommended to patch test an alloy before applying it ("prophetic examination") because the patch

4.3. In vivo tests

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In order to furthermore test the in vivo tolerance to metals we also used the MORA electronic device as an alternative to patch testing [34]. We considered, for testing with MORA, 55 different dental alloys, as well as the chemical elements which are components of these alloys in 100 individuals with good oral health condition. The results obtained in percentages are shown in Table 9 [35].



Figure 24. Patch test

Element	Au	Ag	Pt	Pd	Ti	Cr	Co	Ni	Cu	Ru	Zr
Well tolerated	10%	30%	10%	0%	20%	10%	0%	20%	10%	0%	40%
Intolerated	10%	20%	20%	40%	10%	30%	20%	30%	10%	10%	20%

Table 9. Results in percentages

4.4. Risk assessment of Pd genotoxicity

Regarding risk assessment of the genotoxicity of metals and metal alloys, mutagens, oncogenes, and toxic materials for reproduction, our current work is limited to the aspects of the toxicity from the point of view of the mutagenic potential of the palladium in PdCl₃ form [34].

The essays of gene mutation were conducted on cell cultures of mouse lymphoma L5178Y according to the protocol Test No. 476 OECD: In vitro Mammalian Cell Gene Mutation. The test allows the detection of chemically induced gene mutations. In the cell lines, the most commonly used genetic endpoints measure mutation at thymidine kinase (TK) and hypoxanthine-guanine phosphoribosyltransferase (HPRT) and a transgene of xanthine-guanine phosphoribosyltransferase (XPRT). The test is conducted on mouse lymphoma L5178Y. Cell L5178Y is treated with PdCl₃ until it reaches the limit of the toxicity. After several subcultures, trifluorothymidine (TFT) is added to the cultures and the cloning of mutant cells is carried out on a multiwall cell culture. At the same time there is a cloning of a sample of cells in the absence of TFT to determine how the cellular component survives the treatment. The number of mutant cells compared to the number of surviving cells allows the calculation of the frequency of transfer and is compared to untreated control cells. The results (Table 10) show that in the absence of metabolic activation no significant mutagenic effect is observed [36].

Quantity of PdCl ₂ in ug/l dose	With metabolic activity		Without metabolic activity	
	% survival	Incidence of mutation**	% survival	Incidence of mutation
0	100	97	100	155
5	189	139	112	172
10	159	136	93	185
20	155	137	76	121
45	151	151	98	170
Positive witness cells*	97	1487	55	166

*10 ug/l methylmethanesulfonate without metabolic activation; 2 ug/l cyclophosphamide with metabolic activation

**Calculated for 10⁶ cells

Table 10. Test results

5. Conclusions

The biocompatibility of dental casting alloys is a critical issue because these alloys are in long-term intimate contact with oral tissues [36].

Alloys used in dental restoration must have an appropriate corrosion resistance in order to avoid the release of cytotoxic or sensitizing elements into the biological milieu [28]. Of great importance, besides the alloy itself, are the manufacturing conditions as well as the environmental ones. The corrosion of dental alloys may be significantly increased by improper

processing (e.g., formation of pits, crevices, or gold coating). Nickel alloys are especially susceptible to lower pH [29].

Corrosion of dental alloys is a necessary but not sufficient condition for adverse tissue reactions. Good corrosion resistance should be considered important criteria for alloy selection.

Electrochemical corrosion of alloys involves the ionization of elements that are released into the environment, e.g., saliva [37]. Initially uncharged elements lose electrons and become positively charged ions as they are released into solution. Corrosion influences other properties of an alloy, such as esthetics and strength. When biocompatibility is concerned, corrosion indicates that some of the alloy components may affect the surrounding tissues. The released elements may or may not cause problems [29]. Elemental release and corrosion occurs regardless of type or composition of the alloy, but the amount may vary a lot.

One of the main factors that influence element release from an alloy is its composition. Some elements, including copper, zinc, and nickel, have higher tendencies to be released than elements such as gold and palladium [29]. Another factor influencing element lability is the phase structure of the alloy. The presence of multiple phases in an alloy shows a greater risk of element release because of the potential electrochemical corrosion among the phases [38]. Surface characteristics of an alloy, (roughness and the presence of oxides) also influence element release. Surface roughness tends to increase elemental release because it concludes in exposing more atoms to the external environment. The oral environment also influences corrosion. Reduced pH significantly increases the corrosion of some alloys, particularly nickel-based ones. Corrosion is also particularly high in crevices, gaps, and pits and in the area of the gingival sulcus ("pitting corrosion" or "crevice corrosion") [4].

Furthermore, the surface composition can be significantly different from the composition of the bulk of the alloy [39]. The surface composition may have a direct influence on which elements are released [40,41].

Non precious dental alloys (Co-Cr) compared to conventional gold alloys reveal generally an inferior corrosion resistance (pitting, crevice corrosion).

Attempts to obtain alloys with better properties by doping Co-Cr alloys with precious metals were not successful. Some cheaper alloys as copper aluminum bronze, developed to substitute gold dental alloys, proved to be a great failure.

Studies concerning superalloys as candidates for medical applications are encouraging and this may be the future in dental alloys.

The cytotoxicity of the alloys is complex and is still not fully understood. The biocompatibility of dental materials is a critical concern with the development of new products [42].

Dental alloys may, depending on their composition, damage cells in culture. It has been documented that some alloys are cytotoxic over a longer period of time in vitro [38] or change human gingival cells in vitro [41]. Cellular damage may be correlated to elemental release from

the alloys [43,44,38]. In accordance with present studies, multiple-phase alloys, which generally have higher corrosion rates, are more cytotoxic than single-phase alloys [29].

Correlations between the release of metal ions and cytotoxicity are very complex. Dental alloys that do not cause cell damage also release metal ions into the cell culture medium. Obviously, ion concentration and exposure time are not sufficient in these cases to cause cell damage. The release of metal ions is not sufficient to cause cell damage in every case. Results from in vitro tests have limited value in predicting a patient's reaction when exposed to certain alloys [29]. Most in vitro tests use only short-term exposures, in contrast with long in vivo exposure. For in vitro tests single-cell types that are often specifically altered to grow outside the body are used, and it is very uncertain if these cells react the same way as body cells. In vitro tests do not generally cover interactions between various cell types, which is a frequent feature of biological reactions in vivo. Obviously, these tests can only evaluate the general biological characteristics of materials [29].

Information on the carcinogenic activity of elements in dental alloys is incomplete or unavailable. There is little or no evidence from the dental literature that indicates that dental alloys are carcinogenic [29]. On the other hand, there is literature that documents the mutagenic potential of metal ions. Mutagenicity can be measured in bacterial systems or in mammalian cells. The reliability of these in vitro systems in predicting in vivo mutagenesis or carcinogenesis is currently limited at best [29].

Overall, there is no evidence that dental alloys cause or contribute to neoplasia in the body. As with toxic and allergic reactions, alloys must release elements for mutagenesis to occur. The form of the metal is critical to its mutagenic activity. Cr^{3+} is not a mutagen, but Cr^{6+} is. The molecular form of the metal is also important. Nickel ions are weak mutagens, but nickel subsulfide (Ni_2S_3) shows a high mutagenic potential [43]. Therefore, a metal is not mutagenic or carcinogenic per se because its mutagenicity depends on the specific form and oxidative state of the metallic element in question [29]. More recent in vitro studies with palladium and gallium chloride indicated a weak mutagenic potency of these ions [45].

It is obvious that metallic ions may act as mutagens or carcinogens in certain forms or using specific routes of exposure. Literature data were primarily determined through long-term epidemiological studies and are subject to limitations associated with these types of studies. For example, it is not correct to presume that a correlation between metal ion exposure and carcinogenesis proves a cause-and-effect relationship. Further evidence is needed, this being an active area of research, particularly regarding nickel, arsenic, cadmium, and other environmentally important metals [29].

To minimize biological risks, dental surgeons should select alloys that have the lowest corrosion potential. This goal can be achieved by using high-noble or noble alloys with single-phase microstructures. Selection of an alloy should be made on a case-by-case basis using corrosion and biologic data from dental manufacturers [29]. Success or failure depends on a variety of factors, some of them depending on the producer, some on the proper manufacture and some close related to the patient itself.

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