ISSN 1848-0071
616.314+546.82=111
Recieved: 2015-11-17
Accepted: 2015-12-18
Review

METALLIC MATERIALS FOR USE IN DENTISTRY

LJERKA SLOKAR, JOSIP PRANJIĆ, ANDREJA CAREK[1]

Faculty of Metallurgy, University of Zagreb, Sisak, Croatia
[1]School of Dental Medicine, University of Zagreb, Croatia
e-mail: slokar@simet.hr

Dentistry as a branch of medicine has an important role in the health of the human, while applying new technologies the maintaining of oral health is much more effective. For that purpose many dental products are used, such as crowns, bridges, implants, which are made of various metallic materials the mostly by casting or forging. They have to possess an adequate properties among which a biocompatibility, hardness and strength are the most important. Metal as an individual element with its properties does not meet certain conditions, therefore, the process of alloying results in different alloys that may be applied in oral environment. The most common classification of metallic materials for use in dentistry divides them in: noble and non-noble alloys and dental amalgames. Further, development of new technologies provides a new metallic materials with more adequate properties. Among them, titanium and titanium-based alloys stand out as materials of future in dentistry. Also, progress in computer technology results in faster production of economic dental products of much more quality.
Key words: metallic materials, dentistry, structure, properties.

Metalni materijali za primjenu u stomatologiji. Stomatologija kao grana medicine ima značajnu ulogu u zdravlju čovjeka, a primjenom novih tehnologija održavanje oralnog zdravlja je puno učinkovitije. U tu svrhu upotrebljavaju se dentalni proizvodi, poput krunica, mostova, nadomjestaka, koji se izrađuju od različitih metalnih materijala najčešće lijevanjem ili kovanjem. Oni moraju posjedovati odgovarajuća svojstva, među kojima su najvažnija: biokompatibilnost, tvrdoća, čvrstoća. Metal kao zaseban element sa svojim svojstvima ne zadovoljava u potpunosti tražene uvjete, te se stoga postupkom legiranja dobivaju različite legure koje se mogu primjenjivati u oralnoj sredini. Najčešća podjela metalnih materijala koji se primjenjuju u stomatologiji je na: plemenite i neplemenite legure, te dentalne amalgame. Nadalje, razvojem novih tehnologija omogućeno je dobivanje novih metalnih materijala s još pogodnijim svojstvima. Tu se svakako ističu titan i legure na bazi titana kao materijali budućnosti u stomatologiji. Također, napredak u računalnoj tehnologiji rezultira bržom proizvodnjom kvalitetnijih i ekonomičnijih dentalnih metalnih proizvoda.
Ključne riječi: metalni materijali, stomatologija, struktura, svojstva.

INTRODUCTION

Metallic materials in dentistry are applied as internal and/or external structural component of many prosthetic restorations. They have wide indication field due to their good mechanical properties contribute to the strength of the structure, and the ability to resist the plastic deformation under the applied load. Metals and their alloys have properties, such as: a high elastic modulus and load carrying capacity that make them desirable materials in dentistry. In addition, if they are implanted into the body, or if they come into contact with the tissue, must have other properties such as: biocompatibility, resistance to corrosion, high static and dynamic strength and toughness, and must not release metal ions in the environment in which they are located. The most important mechanical properties in clinical practice are: elastic modulus, tensile strength and hardness. [1]

The primary goal of dentistry is to maintain or improve the oral health of the patient, which includes a variety of dental materials. Dental casting alloys must satisfy certain criteria, which must be a balance of factors that influence its application. It is therefore important to know the properties of dental materials, in order to understand their behavior in the oral cavity and predict the outcome of the patient's health. [2]

Although, use of dental casting alloys is decreased in the last few years, due to the increased demands of patients for aesthetics in regard to service life, knowing and understanding of the structure and properties of cast metal and alloys is necessary to ensure the quality and characteristics of dental products.

So far, the main application of dental casting alloys was for production of partial denture frameworks, base for crowns and bridges for metal-ceramic restorations as the most durable aesthetic substitute for natural teeth. [3]

HISTORICAL DEVELOPMNET OF METALLIC MATERIALS IN DENTISTRY

In the 7th century BC Etruscans used the ivory and gold-rimmed bone supported as core of the teeth. In 1800s, metallic substitutes were made by pressing of aluminum, amalgam, gold made metallic substitutes, lead, platinum and silver in dental cavities. Although dentures and other dental restorations were made from metals for centuries, technology of precision casting was not possible until the 20th century, precisely in 1907. when Taggot introduced the method of precision casting for the production of crowns and bridges. Electric furnaces and equipment for casting began to be used in the early 1900s, and soon after that, casting technologies rapidly progressed. However, successfully casting of titanium, one of the most biocompatible metal for use in dentistry, was not achieved until the 1970s because of its high reactivity with oxygen and sensitivity of casting technique. Subsequently several technologies were developed, such as CAD/CAM (*Computer aided design/computer aided manufacturing*), laser sintering, laser welding to facilitate production of metallic materials for use in dentistry. [4].

Although many methods for producing the dental materials are available, the best and most popular method, especially for making crowns, is casting. The impression of the prepared tooth is replicated in a refractory mold and the required sample is made of wax. Then the samples are invested in the investment material and burned. In such prepared mold, molten metal or alloy is casted under pressure by a centrifugal force.

The historical development of metallic materials in dentistry was influenced by many factors, and the most important are: the technological changes of dentures, progress in metallurgy and price changes of the precious metals.

An important, recent event in the field of dental metallic materials is the development of composites materials produced by the powder metallurgy and sintering respectively. These composites consist of sintered high precious alloy in the form of a "sponge" in which almost pure gold is infiltrated. The resulting composite of two metallic gold materials is not casted but sintered in a refractory mold. [2]

METALLURGY OF DENTAL METALLIC MATERIALS

All metallic materials used for making the dental restorations are produced by mixing in the molten state and casting into a mold in which solidify. Some substitutes may be made of cast or molded parts into a form that is very close to the final, while others are subjected to a series of thermomechanical procedures from an initial ingot to produce the final product. Differences in the microstructures can have a significant impact on the rate of wear and corrosion. In order to understand why the particular alloy is used and how it is able to behave in vivo, it is crucial to understand the physical metallurgy of metallic materials used in dentistry. [4]

During the cooling of molten metal in the mold, solidification begins usually at the surface. If the mold is very hot, there are few places where the metal begins to stiff, or where it starts to form the nucleus and grows. If the mold is cold, there is much room for the development of the nucleus. For most metallic systems, solid phase increases as the advancing front with side branches, which is reminiscent of the front, called dendritic growth. Solidification continues to encounter two nucleuses, which then form the border. Each of these places is called a growth or crystal or grain, and every boundary is boundary of crystal or grain boundaries. At the microscopic level, clearly visible areas can be identified as dendrites, the interdendritic area and grain boundaries. To achieve a fine grain and nondendritic structure of castings used in dental medicine, it is necessary to add various alloying elements. Thus, alloys are mixtures of several elements in a solid solution, sometimes with the precipitated intermetallic compounds. For elements of similar atomic charge, diameter and crystal structure there is no limit of solubility of one element in another and, therefore, they solidify as a single phase. For example, copper and nickel are completely soluble. Melting point of nickel is higher than that of copper, so in the first solidified phase the more of nickel will be represented, and the later solidified phase will be richer in copper. Thus, the casted implants can have a pronounced dendritic structure, with differences in chemical composition on the macroscopic level. Casted products can be subjected to the subsequent heat treatment known as homogenization or solution annealing in order to ensure an uniform chemical composition by atomic diffusion. Small differences in the diameter of atoms of two (or more) elements in the single-phase or two-phase alloys allow the strengthening. The presence of large atoms in the lattice of smaller ones causes localized stress in the lattice, so that the atoms are under the influence of local compression. Similarly, several small-sized atoms in the lattice will be influenced by localized stress. This stress can increase the strength of the metal by a mechanism known as a solid solution strengthening. Elements with very different properties and crystal structures have limited solubility. In many alloys systems, the precipitation of secondary phase is used as the strengthening mechanism, known as precipitation hardening. In some alloys such as cobalt alloys, carbides have beneficial effect on the wear and strength. In contrast, they have an adverse effect on the corrosion resistance of stainless steel. [4]

Production of dental metallic materials

Some metallic products for use in dentistry can be produced by casting in nearly final form, and used in as cast or heat-treated state. However, castings are often subjected to the mechanical methods of rolling or drawing, and then are heated with the aim of yielding the stress. This results in the formation of new crystals with dislocations. By controlling the temperature and time the soft metals with fine grains that are suitable for cold working can be achieved. Dental metallic products can be also produced by cold or hot forging and by powder metallurgy. In the latter case, the fine powder is usually produced by melting the alloy and atomizing it. Thereafter is compacted into the almost final shape, and is subjected to the controlled high temperature and pressure in the sintering process. [4]

The characteristics of the surface are very important factor in the use of materials in the oral cavity, as they may affect the ability of polishing, the appearance of scratches etc. Therefore, surface treatment during production has a major influence on the wear and corrosion resistance. After casting, casted product has a matted surface originating from the investment material, so it has to be abrasive blasted or sandblasted with purpose of removing the particles of investment material from the castings surface. For example, on the steel castings that would be used as implants, first the mechanical then the electrolytic polishing is carried out. However, the surface of metallic materials can be treated by ion implantation, plasma or ion nitrating, or coating by the hard ceramic materials in order to improve the wear resistance. Since the 1980s a number of methods are used to modify the surface to ensure the biological bone growth from the surface of the porous metal material. In most cases, the final stage is passivity in nitric acid, which increases the thickness of the passive film, and any impurities from the surface are removed. [4,6]

As in many other industries, the production phases are increasingly automated in dental technology too. Since the cost of laboratory work has become a major factor in the planning of treatment and therapy, automation would allow a more competitive production and profits. Therefore, advances in computer technology enable cost-effective production of individual pieces. In recent years, the dental products, especially titanium and its alloys, and cobalt-chromium alloys, are increasingly produced or processed, with the help of computers, especially by CAD/CAM technique. It provides a new, almost without faults, industrially processed and controlled materials, increased the quality and reproducibility, as well as increased the efficiency and precision of the finished product. Due to the continuous development of computer technology, development of new methods of production and processing, which will further reduce the costs is expected. [7]

METALS IN DENTAL MEDICINE

Metals and alloys have an important role in dental medicine. The different metals are used in all aspects of dentistry, including dental laboratories, direct and indirect dental restorations and instruments for the preparation and manipulation of teeth. Although the latest trends go to metals free restorations, they remain the only clinically proven material for the base of the long span bridge and for partial denture framework in dental medicine. [2,8]

Gold (Au). Gold is used in dentistry because of its good properties and aesthetics. It is corrosion stable, with no change in color, and has a sufficient hardness, elasticity and oligodynamic action. Also, it is chemically inert, non-allergenic and it is easy to work with. Gold is noble metal that provides high resistance to corrosion and wear, and slightly increases the melting range of the alloy. Gold improves the workability, the ability of polishing, increases the density and ductility of alloy to which is added. Also increases the coefficient of thermal expansion of palladium alloys. However, if it is present in sufficient quantities, gold gives a pleasant golden yellow color to alloy, which can be easily neutralized by adding a "white" metal, such as palladium or silver.

Palladium (Pd). Palladium is a noble metal of the platinum group in the periodic table of elements. If it is added to the gold alloys, palladium increases the strength, hardness, resistance to corrosion and tarnishing. In addition, it increases the elastic modulus, strength and hardness of gold alloys and reduces their density. Palladium increases melting range and improves its resistance to sag. It has a great ability of bleaching, so that the alloy with 90% gold and 10% of palladium has platinum color.

Platinum (Pt). Platinum is a precious metal that belongs to the platinum group of elements. Platinum increases the melting range, strength, hardness and elastic modulus of gold alloys, and improves their resistance to corrosion, tarnish and sag. It gives the white color to alloys, and because of the high density platinum increases the density of non-gold based alloys.

Iridium (Ir) and Ruthenium (Ru). Iridium and ruthenium are precious metals belonging to the platinum group. If added to the gold or palladium based alloys they reduce the grain size in order to improve the mechanical properties and resistance to tarnishing.

Silver (Ag). Although silver is a valuable element, it is not considered as noble in the oral cavity. Silver decreases the melting range, improves viscosity, helps to control the coefficient of thermal expansion of the gold and palladium based alloys. Silver has a high affinity for the absorption of oxygen, which can cause porosity during casting. However, by the addition of small amounts of zinc or indium this absorption can be controlled. In the presence of sulfur, silver corrodes and darks.

Aluminum (Al). Aluminum is a metal that is added to nickel based alloys to reduce the melting range. It solidifies the alloy and affects on the formation of oxides. It is one of the elements, besides the Co-Cr alloys, which is "etched" on the surface of the alloy with the aim of creating the micro-mechanical retention.

Beryllium (Be). Such as aluminum, beryllium decreases the melting range of nickel-based alloys, improves castability and the ability of polishing and it helps to control the formation of oxides. However, biological properties, as health safety for the patients and technicians, are questionable when working with alloys containing the beryllium.

Boron (B). Boron is deoxidation agent. It increases the hardness of nickel-based alloys, reduces the surface tension of the molten alloy, improves its castability and reduces the ductility of the alloys to which is added.

Chromium (Cr). Chromium is a metal that improves solid solution hardening. Because of its passivating effect it contributes to the corrosion resistance in nickel and cobalt based alloys and provides their resistance to tarnishing. However, chromium forms a brittle sigma phase, which leads to the breaking of the castings. For this reason, its content in these alloys is limited to 28 - 29%.

Cobalt (Co). Cobalt is added to palladium alloys to increase the coefficient of thermal expansion. Furthermore, it strengthens the alloy, increases the hardness and modulus of elasticity. Cobalt-based alloys are an alternative to nickel-based alloys, but they are more difficult to process.

Copper (Cu). Copper is added for hardening and strengthening of the alloy and can reduce the melting range. In the interaction with platinum, palladium, silver and gold, it provides the ability of thermal processing of alloys based on gold, silver and palladium. Copper slightly decreases the density, and can improve the passivity of Pd-Cu alloys.

Gallium (Ga). Gallium is added to the non-silver ceramics to compensate the reduced coefficient of thermal expansion that is the result of the silver absence.

Indium (In). Indium has different functions in metal-ceramic gold-based alloys. It decreases the melting range and density of alloy, improves viscosity and has beneficial effect on strengthening and hardening. Indium is added to alloys with a high silver content to increase the resistance to tarnishing.

Iron (Fe). Iron is added to the gold alloys for metal-ceramic system for hardening and strengthening and for bonding the oxygen to oxides. Also, the iron is the base of several types of metallic alloys. It has good complements with nickel and together enhance the ability of processing of the alloy in cold state.

Manganese (Mn). Manganese binds the oxygen in cobalt and nickel based alloys. However, if present in high concentrations, it is health risky for the patient, and can cause the Parkinson's disease.

Molybdenum (Mo). Molybdenum improves the corrosion resistance, forms the oxides, and has a beneficial effect on thermal expansion coefficient of nickel-based alloys.

Nickel (Ni). Nickel has a coefficient of thermal expansion close to that of gold, and therefore it forms the basis of many alloys. In addition, it provides the corrosion resistance and allows the elasticity and toughness to alloys. However, nickel is not completely safe for the patient's health, especially for the female population, because it can cause allergies and dermatitis.

Tin (Sn). Tin helps the hardening of alloys and decreases the melting range. It is one of the key trace elements for oxidation of Pd-Ag alloy.

Titanium (Ti). Titanium is non-precious metal. Numerous studies prove its good biocompatibility and resistance to corrosion. It reduces the melting range and improves the castability. Also, it increases the hardness of the alloy and forms the oxides at high temperatures.

Zinc (Zn). Zinc enhances castability and contributes to the hardness when combined with palladium. It helps to reduce the melting range of the alloy and reduces the gaseous porosity. [1-3,9]

CLASSIFICATION OF METALLIC DENTAL MATERIALS

Metallic materials used in dentistry, particularly alloys, can be divided in several ways (e.g. regarding to application, the main element, producing method etc.)

Metals classified as noble are: gold, copper, mercury, platinum and platinum group of metals (ruthenium, palladium, osmium, rhodium and iridium). Precious alloys may contain non-precious elements (about 10%), but the content of the precious metals may not be less than 75%. If the content is still lower, the alloys are named as reduced precious alloys or alloys of reduced gold content. Corrosion resistance and stability in the mouth are the main characteristics of noble alloys.[9]

Today, the most used alloys in practice are obtained by casting (Table 1). They have to possess certain properties, such as biocompatibility, minimal reactivity with the material of the mold, must be easily melted, casted, joined, polished, must have high strength, good wear, corrosion and tarnishing resistance, and should be inert in the oral cavity. [2]

Table 1. Classification of casting alloys for metal ceramic prosthesis and partial dentures [2]
Table 1. Klasifikacija lijevanih legura za zubarske proteze [2]

Metal Type	All-metal prostheses	Metal ceramic prostheses	Partial denture frameworks
High Noble (HN)	Au-Ag-Pd	Pure Au (99.7%)	Au-Ag-Cu-Pd
	Au-Pd-Cu-Ag	Au-Pt-Pd	
	HN metal ceramic alloys	Au-Pd-Ag (5-12 wt. % Ag) Au-Pd-Ag (>12 wt. % Ag) Au-Pd	
Noble (N)	Ag-Pd-Au-Cu	Pd-Au	
	Ag-Pd	Pd-Au-Ag	
	Noble metal ceramic alloys	Pd-Ag Pd-Cu-Ga Pd-Ga-Ag	
Predominantly Base metal (PB)	CP Ti Ti-Al-V	CP Ti Ti-Al-V	CP Ti Ti-Al-V
	Ni-Cr-Mo-Be	Ni-Cr-Mo-Be	Ni-Cr-Mo-Be
	Ni-Cr-Mo	Ni-Cr-Mo	Ni-Cr-Mo
	Co-Cr-Mo	Co-Cr-Mo	Co-Cr-Mo
	Co-Cr-W	Co-Cr-W	Co-Cr-W
	Cu-Al		

Noble alloys

Gold alloys. Ternary Au-Ag-Cu alloy is the oldest one used in dentistry. Copper is added to gold for increasing the strength and silver for workability. This alloy with 18-carat gold (75 wt.%) is very resistant to corrosion. Palladium and platinum are added to improve the mechanical properties. Zinc is added to improve casting of the alloy. Small amounts of ruthenium or iridium (0.0005 - 1%) are added to promote the nucleation centers development. In addition, they form a fine-grained structure in the alloy.

Figure 1. Metallic gold crown [10]
Slika 1. Metalna zlatna krunica [10]

Gold alloys can be classified as:
- (1) alloys with high gold content; they are golden yellow colored; show good castability and solderability; used for metals fused to polymer veneers system;
- (2) alloys with reduced gold content; they are light yellow colored; show good castability and solderability; portion of the gold is compensated by the addition of palladium or silver; palladium's tendency to changing the color of alloy is compensated by adding a larger copper content;
- (3) reduced gold alloys with silver; higher gold content is compensated by the addition of palladium, which significantly increases the melting range, especially the solidus temperature;
- (4) reduced gold alloys without silver; they have a white color; used for metal-ceramic systems; silver was replaced with palladium because it causes discoloration of ceramics; however, the palladium addition increases the melting temperature of the alloy, so indium is added to decrease it.[4,9]

The chemical compositions of these types of alloys are showed in Table 2. [9]

Table 2. Chemical compositions of gold alloys, wt. % [9]
Table 2. Kemijski sastav slitina na bazi zlata, tež. % [9]

Alloy/element	Au	Pt	Ag	Cu	Pd	Sn	In
(1)	70-80	1-5	10-15	5-10	-	-	-
(2)	55-60	-	0-25	10-12	5-10	-	-
(3)	0-50	-	0-20	-	0-30	0-5	-
(4)	50	-	-	-	0-40	-	0-10

Palladium alloys. Melting point of pure palladium is 1552 °C and is too high for dental casting devices. Certain larger percentage of silver or copper, and other elements such as gallium, indium and tin, should be added to reduce the melting temperature of the alloy to 1200 - 1400 °C. These base metals are used for the formation of oxide on the surface of the metallic part of crowns or bridges that are necessary for binding of the alloy and the ceramic after appropriate heat treatment. In most cases, the alloys that do not contain copper are more resistant to corrosion. Most used palladium alloys are Pd-Ag and Pd-Cu alloy. Their chemical compositions are listed in Table 3. [4,9]

Table 3. Chemical composition of the alloy of palladium, wt. % [9]
Table 3. Kemijski sastav slitina na bazi paladija, tež. % [9]

Alloy/element	Pd	Ag	Cu	Sn+In	Ga
Pd-Ag	0-60	0-30	-	10-12	-
Pd-Cu	80	-	10	-	10

Pd-Ag alloys are economical, unlike the Pd-Cu alloys that have the highest melting temperature among the all noble alloys, and they are difficult to cast and solder. Both types of alloys are used for metal-ceramic systems. [9]

Silver-palladium alloys. Pd-Ag (53 - 61% Pd and 28 - 40% Ag) were the first precious alloys on the market that did not have gold in its composition. In these alloys the content of the precious metal is the lowest among the all other precious alloys. Indium and tin are added to form the oxide needed for the binding of the ceramic and to increase the hardness, while the ruthenium is added to improve the castability. Because of the higher content of palladium the coefficient of thermal expansion is reduced. This can be prevented by increasing the content of silver that also reduces the melting range. These alloys are gray colored, and by the alloying the color durability and the hardness compared to the silver are increased, and the melting point when compared to palladium is decreased. The maximum content of non-precious components (Zn, Sn, Cu, Ni, Mn, Si) is limited to 10% to achieve better mechanical properties. Regarding to microhardness, precious alloys can be divided into 4 types: soft alloy, medium-hard, hard and extremely hard alloys. [2,9]

The most important physical and mechanical properties of noble metal alloys include:
- biocompatibility
- good corrosion and tarnishing resistance
- melting temperature at 1000 °C, molding temperature higher for 75-150 °C
- density of about 15 g/cm^3
- hardness, from soft to extremely hard
- elongation, as a measure of ductility, 20 - 39%
- coefficient of linear thermal expansion in the range of 14 - 18 · 10^{-6} / °C
- tensile strength ranging from 103 to 572 MPa. [2]

Non-precious alloys

This group of alloys is based on the non-precious metals, such as chromium, nickel, iron, tin, lead, magnesium and titanium. These alloys are introduced in dentistry as an alternative to gold alloys after significant increase in gold price. Generally, non-precious alloys, besides they are more economical, they are characterized by: high hardness, resistance to discoloration and corrosion, high rigidity, low elasticity, low thermal conductivity, low density, platinum color. The alloys that are commonly used are Ni-Cr and Co-Cr based alloys. [2,9]

Ni-Cr alloys. Nickel content in these alloys is 70 to 90% and chromium from 13 to 20%. The balance is iron, aluminum, molybdenum, beryllium, silicon and copper. The alloys based on Ni-Cr have great strength and hardness, and due to a large melting range it is necessary to use the high-frequency melting furnace. Despite the local fracture corrosion, these alloys are considered to be stable in the mouth. Due to the nickel content, the elasticity and processing in the cold state are increased. However, nickel is considered as an allergen and it is increasingly replaced by cobalt. Ni-Cr alloys are characterized by high elastic modulus, high hardness and tensile strength, lower density, relatively low cost and high ductility when compared to the Co-Cr alloys. [2,9]

Co-Cr alloys. The discovery of proper casting techniques and materials for making models resistant to high melting temperatures was enabled the use of cobalt-chromium alloys in dental medicine. After introducing, their application in dentistry is constantly growing, and the reasons are the numerous. For example, they are lighter than gold alloys, and mechanical properties and corrosion resistance are the same or even better. The big advantage that ensures the wide application in economically weaker countries is their low price. However, due to the complex procedures of technical appliances, high melting temperatures requiring the use of special casting devices, and high hardness, their application is still difficult. Co-Cr based alloys are mostly used for base frameworks of removable partial dentures, as well as for base of crowns and bridges in metal-ceramic systems.[9]

Cobalt possesses a good corrosion resistance and can be used in multi-phase alloys to improve their mechanical properties. Chromium is the primary alloying element in a wide variety of cobalt superalloys, and is preferably added to improve corrosion resistance. In addition, it contributes by a solid solution hardening. [4]

The first cast cobalt-chromium alloy (30% Cr, 5% Mo with small portions of Ni and C) dates back to the year 1911. and Haynes named it "stellite". Later, in 1926 alloy of similar chemical composition is patented under the name vitallium, and it has become one of the major cobalt alloy for dental implants. The typical microstructure of cast and wrought Co-Cr-Mo alloys are shown in Figure 2. [4]

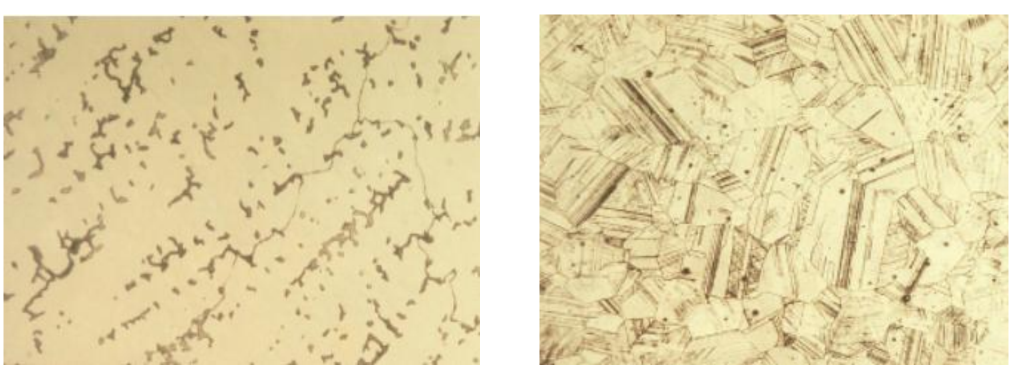

Figure 2. Microstructure of as cast and wrought Co-Cr-Mo alloy, 200x [11]
Figure 2. Mikrostruktura lijevane i kovane Co-Cr-Mo slitine, 200x [11]

The microstructure of the cast alloy consists of carbides and large grains, as opposed to the wrought alloy that possesses a better resistance to wear and fatigue. As cast Co-Cr-Mo alloys are used for complex designs and applications (Figure 4).[11]

Figure 3. Applications of Co-Cr-Mo alloys [11]
Figure 3. Primjena Co-Cr-Mo slitine [11]

In general, Co-Cr alloys are very hard and brittle and they are not easy to solder and weld. Due to the high hardness they are difficult to cut, grind and polish. The mechanical properties and castability are determined by cobalt, while chromium increases the corrosion resistance. The most important properties of these alloys are summarized in Table 4. Co-Cr alloys are cheaper than gold alloys, and therefore more economical. [2,9]

Table 4. The properties of Co-Cr alloys [2,11]
Table 4. Svojstva Co-Cr slitina [2,11]

Melting temp., °C	Density, g/cm^3	Yield strength, MPa	Tensile strength, MPa	Hardness, HVN	Elongation, %
1250	8,8	470 – 710	685 – 870	264 – 432	1,6 – 3,8

Because of the high melting point of the Co-Cr alloy, melting can be performed only by an induction technique. These alloys are not viscous so the casting is preferably performed in the furnace under pressure. Due to their high hardness a method of electrolytic method for polishing must be employed. [2]

Co-Cr-Ni alloys. These alloys have been launched in the 1950's. Their typical chemical composition is: 40% Co, 20% Cr, 15% Ni, 15.8% Fe, 7% Mo, 2% Mn, 0.16% C and 0.04% Be. They have excellent resistance to corrosion and tarnishing. Hardness, yield strength and tensile strength are the same as for stainless steel, while the ductility is higher in softened condition, but it is less after hardening. [2]

Ni-Ti alloys. These alloys typically contain 54% Ni, 44% Ti and 2% or less of cobalt. The crystal structure at high temperature is cubic volume-centered and corresponds to the austenitic phase. When cooled through a critical temperature range these alloys show a significant change in the elastic modulus, yield strength and the electrical resistance as a result of changes in the electron bonds. Cooling through this area leads to changes in the crystal structure, known as a martensitic transformation. Ni-Ti alloys show two closely related and unique properties, such as: shape memory effect and superelasticity. Cobalt helps to reduce the temperature of the phase transition, which can be close to the temperature in the oral cavity. Shape memory effect is achieved by establishing a shape at a temperature near 482 °C, and then by cooling and forming of the second form. Superelasticity can be achieved when the phase transition is induced by stress. These alloys have a variety of applications, particularly in orthodontics. However, they are difficult to shape and cannot be joined by soldering or welding. [2,12]

Titanium and titanium-based alloys. Titanium is a very popular metal in dental medicine and it is an integral part of dental treatment since the 1960s due to its good properties, such as low density (4.51 g/cm^3), low elastic modulus (110 GPa), and compatibility with the tissues of the mouth. The high price of precious metals and the potential health harmfulness of some metals have led to the widespread use of commercially pure titanium (CP Ti) and its alloys, especially for dental implants and crowns (Figure 4). The main advantage of the titanium implant is based on good osseointegration with the bone of the jaw. Due to the low density it is applied to produce the high-strength and lightweight dentures. [2,13-15]

Figure 4. Titanium dental implants and crowns [16-18]
Figure 4. Titanski zubni implantati i krunice [16-18]

Titanium is considered as the most biocompatible among the all metals. When the patient is allergic to nickel, titanium is an excellent choice. At room temperature it is stable as a ductile metal, but of low-strength, while during the heating to a temperature above 883 °C titanium transforms into the hard, brittle form. Namely, the transformation of the hcp lattice of alpha phase (α) in the bcc lattice of beta phase (β), which remains stable up to the melting temperature of 1672 ° C, then occurs.

There are 4 types of CP titanium for dental applications, which contain small amounts of iron, nitrogen and oxygen. As their content increases from Type 1 to 4, so does the strength. In order to improve its primarily mechanical properties titanium is alloyed by different elements. The most used alloy is Ti-6Al-4V containing 90% Ti, 6% Al and 4% V. However, because of proven health damaging of aluminum and vanadium, titanium is nowadays alloyed by other elements, such as Nb, Ta, Zr, Mo or Sn, resulting in new alloys with a lower elastic modulus, a higher fatigue strength and a better biocompatibility and more aesthetical acceptability as well. In addition, the melting temperature is decreased by alloying. [2,4,9,19-25]

Titanium is electrochemically very active. The consequence of this is its high reactivity to oxygen resulting in a stable passive oxide film that makes titanium resistant to electrochemical corrosion. Titanium and its alloys are produced by centrifugal or vacuum-pressure casting. Although these are cost-effective, biocompatible and easily available materials, there is a need to find appropriate techniques for easier casting, processing, welding, in order to obtain a more diverse applications. [4,14,15]

Stainless steel. Stainless steel, which is used in dental medicine, has chemical composition: 17-19% Cr, 13-15% Ni and 2-3% Mo for improving the corrosion resistance and the carbon content is below 0.03%. Besides the mechanical strength, corrosion resistance is the most valuable feature of stainless steel. The addition of a minimum of 12% Cr makes steel a stainless, due to the formation of stable and passive oxide film. Since chromium has a cubic volume-centered structure (bcc), if added, it stabilizes a bcc structure of iron. However, carbon has a high affinity to the chromium, and forms carbides of $Cr_{23}C_6$ type. This leads to the precipitation of carbon in the carbides area wherein the chromium concentration decreases as it enters the carbide, resulting in decreased the corrosion resistance around carbide. If the content of chromium is reduced to <12%, it is not enough for repassivation and stainless steel becomes susceptible to corrosion. Stainless steel is the most commonly used for crowns (Figure 5) and in the orthodontics. [4,9]

Figure 5. Stainless steel crowns [26]
Figure 5. Krunice od nehrđajućeg čelika [26]

Dental implants made of stainless steel are produced by casting or punching. The costs are low because the complex methods of shaping are not required. The main advantage of stainless steel is availability in sufficient quantities, while its main disadvantage is a low resistance to edge corrosion. [4,9]

Dental amalgams

Dental amalgam, an alloy of mercury and one or more metals, e.g., silver, tin, copper, is the oldest filling material for the posterior teeth. Mercury has to be very clean and free of harmful ingredients. Silver contributes to the total resistance of the alloy and reduces spillage edge of parts fillings. In addition, silver facilitates the handling of amalgam and coordinates the expansion of the volume. Amalgams with lower silver content are hardened slowly and they are less resistant to compression, but they are more contracted during the hardening when compared to the amalgam with a greater amount of silver. Tin takes up a quarter of the amalgam alloy, reduces its mechanical resistance and expansion. Unlike silver, tin increases spilling amalgam in the cavity. Copper contributes to the hardness of the amalgam alloy, and prevents its excessive expansion in the cavity. Although the tendency in recent times is put it out of use, because of environmental reasons and the growing use of modern materials, amalgams are still used for filling in primary and young permanent teeth. Dental amalgams are characterized by good mechanical properties, while some modern amalgams show antibacterial activity too. Advantages of the amalgams when compared to the other materials include:

- easy to handle, i.e. the dry work area is not required and time of manipulation is short
- easy production, which excludes several working phases in contrast to composites
- excellent resistance to masticatory forces
- ease of use in ordination conditions
- affordable price.

However, they have drawbacks such as:

- bad aesthetics
- chemical and micromechanical bond to enamel and dentin is not possible
- extensively grinding of healthy hard tissue due to retention of the amalgam is necessary
- possible toxicity due to the high mercury content. [9,27-29]

Since there are ongoing concerns about the toxicity of dental amalgams, they are constantly evolving and improving. Among the most important advances in the development of amalgams is discovery of so-called "Non-$\gamma2$" amalgam and amalgam packaging in capsules in exactly dosed ingredients. According to the number of chemical elements, dental amalgams may be: binary, ternary, quaternary, while according to the copper content they are divided into: conventional dental amalgams and amalgams with a high portion of copper.

Proportion of copper in the conventional dental amalgams is up to 3%. However, because of insufficient strength and tendency to corrosion due to $\gamma2$ phase (Sn_8Hg), in the amalgam alloys the content of copper is increased, leading to elimination of this phase. These amalgams are called "non-$\gamma2$" amalgams. In the dental amalgams with a high content of copper $\gamma2$ phase is completely removed. This type of amalgam can be classified, depending on the copper content, as: mixed amalgam alloys and dental amalgams with a very high portion of copper. Mixed amalgam alloys contain about 9% copper. The $\gamma2$ phase is formed in the process of amalgamation, but the final alloy does not contain it. Dental amalgams with a very high portion of copper contain 9-28% of this element, and the $\gamma2$ phase in this type of amalgam is not formed. [9,28]

According to investigations, the amalgam alloys are more resistant to compression then to tensile and bending loads. For this reason, the cavity must be designed in such a way that fulfills are exposed to compression forces. The average resistance to pressure of the amalgam alloy is about 275 MPa, and some even up to 550 MPa. In comparison, the resistance of these alloys to tensile load is 55 - 62 MPa.[9]

PROPERTIES OF METALLIC DENTAL MATERIALS

For use of metal in dental medicine it is very important to know its properties, which depend on its crystal structure. Properties are determined by the strength of bond (metallic) that links the atoms, and in dental metals a strong metal bond is present. The physical properties are very important in dental researches, because they provide information necessary to evaluate the characteristics of materials and their improvement during development. If some alloy could be used in dentistry, it has to meet a certain requirements, such as: appropriate physical and chemical properties, technical workability and suitability for clinical use. Physical and chemical properties include:

- homogeneous fine-grained structure
- self-hardening after casting,
- high strength values,
- the possibility of soldering
- corrosion resistance.

Technical workability of dental metal or alloy means:

- the possibility of arc and induction melting,
- the achievement of a low viscosity melts by simple casting technique,
- the ability of processing by standardized technique,
- a wide tolerance of processing with a minimal risk
- economic viability.

For use of metal or alloy in clinical applications it has to:

-possess the hardness, strength and ductility determined by a specific clinical indication,
-have an aesthetically acceptable color,
-be a biocompatible. [6,9,30]

Hardness. One of the most important properties of dental materials is hardness. It represents the resistance of a material to penetration of another much harder indenter. There are different procedures for testing the hardness, and in dentistry the most common are Knoop and Vickers methods. In this case, the hardness is expressed by Knoop (HKN) (Table 5) or Vickers (HVN) number. [6,9,31]

Table 5. Knoop hardness of dental materials [9,15]
Table 5. Knoopova tvrdoća zubarskih materijala [9,15]

Dental material	HKN
Dentin	68
Enamel	350
Amalgam (Ag-Sn-Hg)	110
22-carat gold alloys	85
Titanium	170
Co-Cr alloys	420
Composite material	90

It should be noted that even small differences in the composition of cobalt-based alloys have an effect on their hardness values. Cobalt-chromium alloys are for one third harder than gold alloys used for the same purpose. This enables a production of a smaller and thinner denture bases and other dental elements. However, because of the high hardness these alloys are more difficult to handle. [9]

Strength. The strength is the resistance of a solid material to plastic deformation and fracture. It contains a number of mechanical properties such as: viscosity, coefficient of strengthening, tensile and bending strength. Strength characteristics depend on the nature of the atomic bonds in the crystal and the crystal lattice defects.

The tensile and yield strength are the most important mechanical properties that value the resistance of the dental materials. These properties are very important in terms of the development of partial dentures especially clasps and sublingual arches because they indicate the permanent deformation. If that property is poor, clasp would be broken during the activation. The final tensile strength of non-precious alloys varies ranging from 640 MPa to 825 MPa. The hard gold alloys for partial dentures have similar values of tensile strength.

Elongation is an important property of a metallic material that is applied in dentistry. The percentage of elongation is an indicator of the relative brittlement or implant's flexibility. This property is particularly significant for a clasp in the partial dentures. Elongation and ultimate tensile strength affect the ductility of each material. Also should be noted that the small micro-porosity of alloy significantly changes its ductility. Percentage of elongation of alloy in large extent depends on the casting conditions. It is therefore very important to control the temperature of melting and casting of these alloys. [9,32]

Elastic modulus. This property is very important when selecting materials in dentistry. In order to ensure the positive therapeutic effect, dental material must possess a elastic modulus value equal or similar to the modulus of dentin (15 - 25 GPa) or enamel (83 GPa) depending on application (Table 6). [9,33]

Table 6. Elastic moduli of dental materials [9,33]
Table 6. Elastični moduli zubarskih materijala [9,33]

Dental material	Elastic modulus, GPa
Dentin	15 – 25
Enamel	83
Amalgam (Ag-Sn-Hg)	27,6
22-carat gold alloys	96,6
Titanium	110
Co-Cr alloys	228
Composite material	16,6

Higher value of the elastic modulus indicates a higher stiffness and lower flexibility of the cast construction of partial denture or other prostheses. Alloys with a high elastic modulus allow the production of smaller restorations. The implant becomes a lighter by reducing the thickness. Stiffer and inflexible denture base framework ensures the uniform distribution of masticatory and parafunctional loads on the stronghold of teeth and denture bearing area.

Elastic modulus of non-precious metallic alloys is at least twice higher than the modulus of gold dental alloys. This should be considered when selecting the alloys for partial dentures frameworks and other restorations. [9,21,30].

Biocompatibility. Biocompatibility of material is one of the determining characteristics for its application in clinical practice. It depends on the mechanical and corrosion properties of materials and tissues. Surface chemistry of dental material, its topography, roughness and types of integration with tissue are correlated with the response of the host, i.e. the oral cavity. Biocompatibility of the metallic implant and its structure are important for the proper functioning of the prosthesis and other restoration in oral cavity. [4,16]

Indicators of biological compatibility of dental materials are: biocompatibility, biofunctionality and biodegradation. A biological inert behavior of material in the body indicates its biocompatibility. Dental materials should not be a toxic for the patient, therapist or technician and may not cause the irritation of oral and other tissues, allergic reactions and may not be a cancerous. Biofunctionality of material is expressed by its efficiency and performance of functions over time, while changes that occur in the material under the influence of the surrounding environment indicate a biodegradation.

The corrosion of dental metallic materials is the result of various factors. It depends on the combination of used alloys, their chemical composition, concentration of electrolytes, oral hygiene, diet, activity of proteins, microorganisms and temperature in the mouth. The most common cause of biological corrosive action is based on the release of component ions in the corroding alloy. The eluted ions from the alloy are harmful to the surrounding tissues in the form of allergic reactions, toxic and carcinogenic effect. Biocompatibility of the alloy and its components determines the ability of the implanted material to perform its therapeutic function and physically replace the damaged or destroyed tissue. So, biocompatible metallic dental material should not cause irritation in the mouth or be subjected to biodegradation, must not be a toxic or carcinogenic, and may not cause an allergic reactions.

In general, the metals can be a stable passive, meaning that if broken the protective oxide layer will be spontaneously renew, or may be unstable when the passive layer cannot be renewed, which results in exposing of metal to active corrosion. That depends on the oxidation or reduction potential of the environment.

A problem that might occur in some alloys for basic dental parts containing beryllium is its evaporation. Namely, vapor is harmful for dental technicians exposed to dust and fumes during the various processes of casting and machining of alloys. Exposure to vapors of beryllium can lead to acute or chronic infection (dermatitis, pneumonia). Furthermore, the problem may be patient’s allergy to the nickel. Exposure to nickel leads to various diseases, such as dermatitis, lung and sinus carcinoma, loss of sense of smell, asthma, pneumoconiosis.

Dental metallic materials are constantly exposed to saliva, to the changes of conditions in the oral environment with frequent changes of alkaline and acidic conditions caused by intake of various food ingredients and liquids. It is therefore very important to choose an alloy that is chemically resistant to their effects, and is not susceptible to electrochemical corrosion. In addition, dental alloys are exposed to masticatory forces in different directions and intensity. Therefore they have to be very strong in order to prevent the deformation of the metallic construction or rupture. From the above it can be concluded that the metallic material used for dental therapy should not be chemically, electrochemically or mechanically dissipated in the mouth. [9,15]

CONCLUSION

In dentistry pure metals are apply rarely because they cannot meet required high demands. For example, gold has too low hardness, silver easily oxidizes and palladium has a high melting point. Therefore metals are alloyed by other metals or non-metals resulting in alloy of metallic character. By alloying is therefore exploited the good properties of each, and the reduced negative properties of alloy components.

Since there are on the market a lot of different materials, the dentists have difficulties to choose the right one. Hence they should keep the guidelines, such as:

- it is necessary the thoroughly knowledge of the alloy
-it is necessary to avoid a choosing the alloy based on the color, unless other factors are the same
-it is necessary to know the chemical composition of the alloy and to avoid the elements which could cause the allergic reaction of the patient
-if it is possible, single-phase alloys should be used
-only proven materials produced by known manufacturers should be used
-only alloys resistant to corrosion should be used, which is proved by investigations
-long-term clinical performance should be in focus
-finally, it is important that the dentist takes over responsibility and be responsible for the safety and effectiveness of any intervention.

By knowing the basic properties of the alloy such as: strength, hardness and melting range the best suited alloy for the patient and certain application could be determined. Today, of course, advances in technology, enable the production of alloys with improved properties. Taking into account all metallic materials, which have so far been applied in dentistry and which are currently in use, the biggest advantage may be given to titanium and titanium based alloys due to their superior properties, the economy factor and the most important fact that they are not harmful to the patient.

REFERENCES

[1] Z. Kralj, Usporedba metal-keramičkih i cirkonij oksidnih fiksnoprotetskih radova, magistarski rad, Stomatološki fakultet, Zagreb, 2011.

[2] http://indiandentalacademy.blogspot.com/2013/08/alloys-used-in-dentistry.html

[3] http://pocketdentistry.com/structure-and-properties-of-cast-dental-alloys-2/

[4] http://monographs.iarc.fr/ENG/Monographs/vol74/mono74-6.pdf

[5] http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Phases_of_Matter/Solids/Crystal_Lattice/Closest_Pack_Structures

[6] L. Wang, P.H.P. D'Alpino, L.G. Lopes, J.C. Pereira, Mechanical properties of dental restorative materials: relative contribution of laboratory tests, Journal of Applied Oral Science, 11 (2003) 3, p. 162-7

[7] F. Bauer, J. Schweiger, D. Edelhoff, Digital dentistry: an overview of recent developments for CAD/CAM generated restorations, British Dental Journal, 204 (2008), p. 505-511

[8] W.J. O'Brien, Dental Materials and Their Selection, 3rd ed., Quintessence Publishing Co, Inc., Hanover Park, 2012.

[9] V. Jerolimov i suradnici, Osnove stomatoloških materijala, Stomatološki fakultet, Zagreb, 2005.

[10] www.mojstomatolog.com.hr/fiksni-nadomjesci

[11] https://www.google.hr/url?sa=t&rct=j&q=&esrc=s&source=web&cd=4&cad=rja&uact=8&ved=0CDMQFjADahUKEwiTw6_d6cjHAhXDXRQKHRibAJg&url=http%3A%2F%2Fnebm.ist.utl.pt%2Frepositorio%2Fdownload%2F2703%2F2&ei=w8feVdPVMsO7UZi2gsAJ&usg=AFQjCNGiz7wgSPFtpRHKep87Qi4fif2l0w

[12] S.A. Thompson, A Review: An overview of nickel-titanium alloys used in dentistry, International Endodontic Journal, 33 (2000), p. 297-310

[13] B.D. Ratner, A.S. Hoffman, F.J. Schoen, J.E. Lemons, Biomaterials Science: An Introduction to Materials in Medicine, Elsevier, Oxford, 2013.

[14] American Dental Association, Titanium applications in dentistry, JADA, 134 (2003), p. 347-349

[15] M. Özcan, C. Hämmerle, Review: Titanium as a Reconstruction and Implant Material in Dentistry: Advantages and Pitfalls, Materials 5 (2012), str.1528-1545; doi:10.3390/ma5091528

[16] http://www.aaid-implant.org/about-dental-implants/what-are-dental-implants/

[17] http://www.beavertondentaloffice.com/wp-content/uploads/2014/06/Root-Form-Titanium-Implant.jpg

[18] http://www.datron.com/applications/dental-milling.php

[19] Su. Gosavi, Si. Gosavi, R. Alla, Titanium: A Miracle Metal in Dentistry, Trends in Biomaterials and Artificial Organs, 27 (2013) 1, p. 42-46

[20] J. Živko Babić, M. Medić-Šarić, A. Mornar, et al., Anodic Sampling of Titanium by Thin-Layer Chromatography, Journal of Planar Chromatography, 16 (2003), p. 63–65

[21] D. Stamenković i sar., Gradivni stomatološki materijali – dostignuća i

perspektive. Stomatološki fakultet, Beograd, 2007, p. 131–50.

[22] http://www-key-to-metals.com/Artcile 20.html

[23] M. Niinomi, D. Kuroda, M. Morinaga, Y. Kato, T. Yashiro, Non-aerospace Application of Titanium, TMS, Warrendale, SAD, 1998.

[24] Y. Oshida, Bioscience and Bioengineering of Titanium Materials. Elsevier, Amsterdam, 2007.

[25] A. Zhecheva, W. Sha, S. Malinov, A. Long, Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods, Surface & Coatings Technology, 200 (2005) 7, p. 2192–2207.

[26] http://doctorspiller.com/Crowns/crowns_3.htm

[27] A. Knežević, Z. Tarle, A. Meniga, V. Pandurić, J. Šutalo, Najčešće rabljeni materijali za naknadu tvrdoga zubnog tkiva, Acta Stomatologica Croatica, 34 (2000) 4, p. 379-385

[28] https://prezi.com/1-9vmcwawzyi/dentalni-amalgami/

[29] N. Galić, J. Šutalo, G. Prpić-Mehičić, I. Anić, Dentalni amalgam, Acta Stomatologica Croatica, 28 (1994) 2, p. 147-153

[30] Kikuchi, Y. Takada, S. Kiyosue, M. Yoda, M. Woldu, Z. Cai, O. Okuno, T. Okabe. Mechanical properties and microstructure of cast Ti-Cu alloys, Dental Materials, 19 (2003) 3, p. 174–181.

[31] M. Franz, Mehanička svojstva materijala, FSB, Zagreb, 1998.

[32] S.Rešković, Ispitivanje materijala, Interna skripta, Metalurški fakultet, Sisak, 2012

[33] A. Ćatović, J. Vukšić, D. Seifert, L. Bergman-Gašparić, Suvremeni sustavi nadogradnje avitalnih zuba – estetska i biomehanička učinkovitost, Medix, 71 (2007), p. 157-158