

## DENTAL MATERIALS – CHALLENGE AND USAGE OF THE LATEST INVENTIONS

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### ABSTRACT

This paper describes a short overview of the history and classification of different materials used in dentistry, and represents the challenge and usage of the latest inventions in the field of dental materials, with special focus on gold-based alloys. Chapter 1 gives an introductory overview of dental materials' historical evolution; chapter 2 contains a review of dental material's classification, and chapter 3 shows new approaches in the production, characterisation and uses of gold-based alloys in dental applications. Moreover, the future role of Au in restorative and conservative dentistry is discussed compared to alternative materials. Namely, today the science of dental materials generally encompasses some of the properties of natural oral tissues compared to the synthetic materials used for prevention and restoration in dentistry.

**Key words:** dental materials, properties, gold-based alloys

### 1. INTRODUCTION- HISTORICAL BACKGROUND

Dentistry, as a speciality, is believed to have begun about 3000 B.C. Gold bands and wires are examples used by the Phoenicians (after 2500 B.C.) (1). Although inscriptions on Egyptian tombstones indicate that tooth-doctors were considered to be medical specialists, they are not known to have performed restorative dentistry. However, some teeth found in Egyptian mummies were either transplanted human teeth or tooth formed of ivory.

Modern dentistry began in 1728, when Fauchard published a treatise describing many types of dental restorations, including a method for the construction of artificial dentures made of ivory. At that time, gold foil had also been employed for dental restorative purposes. The dentists of Prussia in 1750 used foil to cap the pulp chamber. Using fillings from silver coins mixed with mercury, Taveau (1816) developed in France what is most likely the first dental amalgam (2). Many dentists criticized the poor quality of the early amalgam restorations. This controversy led to the “amalgam war”, during which heated debates occurred over the benefits and drawbacks. Research

over the next years greatly improved the handling properties and clinical performance of amalgam-filling materials.

In 1885 Logan patented porcelain fused to a platinum post, replacing the unsatisfactory wooden posts used previously to build-up intraradicular (within the tooth root) areas of teeth.

Up to this point, we have focused primarily on the historical evolution of direct filling materials and some indirect materials. Prior to the 20<sup>th</sup> century, fillings were of rather poor quality and did not fit well within the teeth. However, a refined method for producing cast inlays was developed in 1907 (3). Cast alloys were then introduced later, further developing the required technology. Commercially-pure titanium, noble alloys, and base-metal alloys of nickel-chromium, cobalt-chromium, or cobalt-nickel-chromium are now available for use in the production of cast inlays, onlays, crowns, and frameworks for fixed all-metal or metal-ceramic-dentures, and removable dentures.

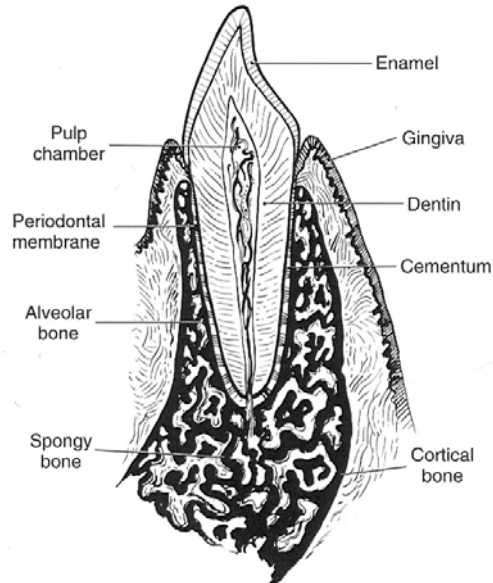
Little scientific information about dental restorative materials has been available until recently. Prior to this knowledge, the use of these materials was entirely an art, and the only testing laboratory was the mouth of the patient. Today, despite the availability of sophisticated technical equipment and the development of standardized testing methods for evaluating the biocompatibility of preventive and restorative materials, this testing sometimes still occur in the mouths of patients.

The next great advance in the knowledge of dental materials and their manipulation represents the usage of suitable standards. In 1928, the Dental Research Fellowship was created by the American Dental Association (ADA) (4). The work at the ADA is divided into a number of categories, including measurements of clinically-significant physical and chemical properties of dental materials and the development of new materials, instruments, and test methods. However, when the ADA Council on Dental Materials and Devices was established in 1966, it assumed responsibility for standard development and initiated the certification of products. These standards identify the requirements for the physical and chemical properties of a material that ensure satisfactory performance if the material is properly manipulated and used by the dental laboratory technician and the dentist.

## 2. CLASSIFICATION OF DENTAL MATERIALS

Nowadays four groups of materials are used in dentistry: metals, ceramics, polymers, and composites (5). Despite recent improvements in the physical properties of these materials, none of these are permanent. Dentist and material scientists continue research in the 21<sup>st</sup> century for the ideal restorative material. An ideal restorative material would be biocompatible, bond permanently to tooth structure or bone, match the natural appearance of tooth structure and other visible tissues, exhibit properties similar to those of tooth enamel, dentin, and other tissues, and be capable of initiating tissue repair or regeneration of missing or damaged tissues.

Historically, a wide variety of materials have been used as tooth crown and root replacements, while restorative materials for the replacement of missing portions of tooth structure have evolved more slowly over the past several centuries.



*Figure 1: Schematic illustration of cross-sectional view of a natural anterior tooth and supporting tissues (6)*

Figure 1 is a schematic cross-section of a natural tooth and supporting bone and soft tissue (6). Under healthy conditions, the part of the tooth that extends out of adjacent gingival tissue is called a clinical crown, and that below the gingival is called the tooth root. The crown of a tooth is covered by enamel and the root is covered by cementum, and it consists of dentin and tissue within one or more root canals.

Dental materials may be classified as preventive materials, restorative materials or auxiliary materials.

Preventive materials include pit and fissure sealants, sealing agents that prevent leakage, materials that are used primarily for their antibacterial effects, and liners, bases, cements etc. In some cases a preventive material may also serve as a restorative material that may be used for a short-term application.

Restorative materials consist of all synthetic components that can be used to repair or replace tooth structure including primers, bonding agents, liners, cement bases, amalgams, resin-based composites, hybrid ionomers, cast metals, metal-ceramics, ceramics, and denture polymers (7). These materials can also be designed as controlled-delivery devices for the release of therapeutic or diagnostic agents. Restorative materials may be used for temporary, short term purposes (temporary cements, and temporary crown and bridge resins) or for longer-term application (dentin bonding, agents, inlays, onlays, crown, removable dentures, fixed dentures, and orthodontic appliances). These materials may further be classified as direct restorative materials or indirect restorative materials, depending on whether they are used – intraorally to fabricate restorations or prosthetic devices directly on the teeth or tissues or extraorally, in which materials are formed indirectly on casts or other replicas of the teeth and other tissues. An ideal restorative material would be biocompatible, bond

permanently to tooth structure or bone, match the natural appearance of tooth structure and other visible tissues, exhibit properties similar to those of tooth enamel, dentin and other tissues, etc.

Auxiliary dental materials are substances that are used in the process of fabricating dental prostheses and appliances but that do not become part of these devices. These include acid-etching solutions, impression materials, casting investments, gypsum cast and model materials, dental waxes, acrylic resin for impression and bleaching trays, acrylic resins for mouth guards and occlusion aids, and finishing and polishing abrasives.

The performance of all dental materials whether ceramic, polymeric, or metallic is based on their atomic structure. Namely, the collective physical and chemical reactions of the atoms determine the properties of material. This is concerned with the microstructural features of the materials and with the dependence of properties on these internal structures. Knowledge in this field is derived from physical chemistry, solid-state physics, polymer science, ceramics, engineering mechanics, and metallurgy. Because fundamental principles of the physical sciences, engineering and microstructure influence the properties of all materials, it is logical to study the microstructural characteristics before proceeding to the macrostructural features.

### 3. THE CHALLENGE AND USAGE OF THE LATEST INVENTIONS

Gold is the oldest dental restorative material. Early dental applications were based on aesthetics, rather than masticatory ability. The use of gold in dentistry remains significant today (8). In conservative and restorative dentistry, as well as in orthodontics, gold is used either as a pure metal, or alloyed together with noble metals and base metals. However, with an increasingly wide range of alternative materials available for dental repairs, it is considered appropriate to review the new gold-based dental technologies.

An interesting new variation on Au dental alloys is the development of an extremely high gold content alloy (99.7% Au), with small additions of indium (0.2%) and zinc (0.1%) – (9). It has been claimed that the high gold content means that this alloy imparts a warm, dentin-like colour to the porcelain. Because of this feature, there is a complete elimination of gingival “black line disease” associated with traditional porcelain-fused-to-metal fixed restorations. The lower strength of this alloy means that it is unsuitable for long span bridgework. For several years, other extremely high gold content alloys (98.2% Au) with additions of Ti, Ir, Rh and/or Nb have been used – (10). They are fine grained, have sufficient strength for crown and bridgework, but they have to be melted and cast under a protective gas atmosphere.

Over recent years pure gold has also been used through the electroforming process (11). Electroformed inlays and onlays are suitable to be cemented into cavities after they have been veneered with porcelain. Tooth restorations such as porcelain-veneered copings for crowns and bridgework can be electroformed with pure gold. The major advantage of the process is that the production of a very precise coping of pure-gold, which does not change its dimensions during firing on porcelain, can be achieved with only one piece of equipment and there is no further need for wax-modelling, investing, preheating of moulds, and casting. Electroforming baths suitable for dental restorations

are non-cyanide and contain a gold sulphite electrolyte. Electroformed pure-gold has a hardness of 100 HV and purity between 99.9 and 99.99%. The crystal structure of the deposit shows a very fine grain size of less than 1  $\mu\text{m}$ . After firing on porcelain, recrystallisation leads to a very acceptable average grain size of 50  $\mu\text{m}$ . Contrary to this cast pure gold is coarse grained with typical grain size of 400  $\mu\text{m}$ . A further advantage of electroformed parts is the absence of dark oxides, which are formed during porcelain firing on the surface of alloys. Namely, there are a wide range of dental applications for electroformed pure gold in crown- and bridgework. Various methods are available to join cast pontics together with electroformed copings. These methods include sintering, lasering/soldering, sticking, cast-on and galvanizing-in techniques. It is considered that the sintering technique with electroformed bridgework is the most precise method with strengths similar to those achieved by full cast bridgework. Electroformed copings used in modern telescopic removable prostheses and fixed prostheses are playing an important role as a secondary structure. Long-span bridges from one piece castings are critical with respect to their fit at the abutment crowns. To overcome this problem, coping are positioned onto the prepared stumps and cemented to the framework within the mouth. This method is also very important in the case of implants, because they can become detached if they are exposed to lateral stresses.

One further application for gold in dentistry is plating or gliding other metallic components. Partial dentures are mainly cast from cobalt/chromium alloys. Fixing to the residual dentition can be performed either by clasps which are fabricated in one-piece cast together with the connector part or by telescopic crowns, which have to be soldered or welded onto the connector. In order to mask the white colour of the Co/Cr alloy, and especially to visually mask the joint, a yellow gold layer is deposited onto the surface of the denture by using cyanidic gold electrolytes. If gilding is used, the thickness of the layer is only 0.1 to 0.2  $\mu\text{m}$ , and therefore the durability may be unacceptable because of abrasion occurring during use. Gold-plating with layers of 5  $\mu\text{m}$  thickness and greater are, therefore, recommended. Plated layers are relatively hard (HV 140-180) and have a density of 16.5 to 17.5  $\text{g}/\text{cm}^3$ .

New-standard specifications are continually being developed to apply to new programme areas (12). Existing specifications are periodically revised to reflect changes in product formulations and new knowledge about the behaviour of materials in the oral cavity. On the other hand, we must know that no restorative materials and dental device are absolutely safe. Safety is relative, and selection and use of dental materials and devices are based on the assumption that the benefits of such use for the known biological risks. However, there is always uncertainty over the probability that a patient will experience adverse effects from dental treatments. Namely, there are two main biological effects: allergic and toxic reactions. This means that besides functional performance and aesthetics, biocompatibility is an important requirement for future dental restorative materials. Namely, for several years research teams have been attempting to find a correlation between the corrosion behaviour and the cytotoxic effects of dental alloys. However, it is reasonable to state that the relationships between corrosion, the released corrosion products and the cytotoxic have not yet been clearly established. It is necessary to obtain information about dissolution behaviour to predict the biocompatibility properties of a material. For this reason we have prepared Au-Pt

alloy with nominal composition: 87.3 wt.% Au, 9.9 wt.% Pt, 1.7 wt.% Zn, 0.2 wt.% Ir, 0.2 wt.% Rh, 0.1 wt.% In (13). In the research work, microstructures of Au-Pt alloy were compared before and after conditioning for biocompatibility testing, in order to identify those phases and microelements responsible for the alloy's corrosive behaviour. Microstructural characterization was carried-out by means of optical and scanning electron microscopy, in addition to energy dispersive X-ray (EDX) analysis. X-ray diffraction (XRD) was applied to determine the phase's composition and their portions within the alloys. Additionally, simultaneous thermal analysis (STA) was used to identify the temperatures of phase transformations.

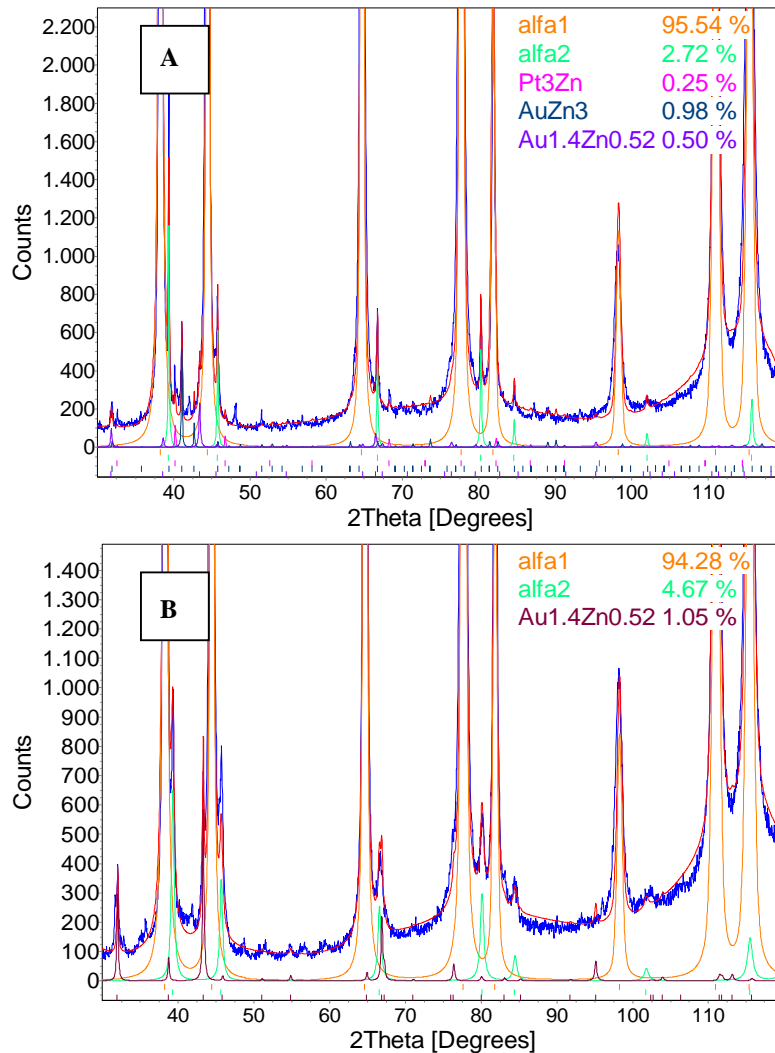


Figure 2: A) Rietveld plot for the Au-Pt alloy before biocompatibility and B) Rietveld plot for the Au-Pt alloy after biocompatibility

Our significant discovery for a lower corrosion resistance of the high noble Au-Pt alloy is the fact connected with its multi-phase microstructure and with the selective dissolution of  $\text{AuZn}_3$  and  $\text{Pt}_3\text{Zn}$  which could occur on the alloy's surface during conditioning. For the Au-Pt alloy before conditioning there are peaks of  $\alpha_1$  and  $\alpha_2$  phases and the peaks for  $\text{AuZn}_3$ ,  $\text{Pt}_3\text{Zn}$  and  $\text{Au}_{1.4}\text{Zn}_{0.52}$  (14, 15, 16) – Fig. 2A. The calculated mass ratio for the existing phases in the Au-Pt alloy is:  $\alpha_1:\alpha_2:\text{AuZn}_3:\text{Pt}_3\text{Zn}:\text{Au}_{1.4}\text{Zn}_{0.52} = 95.55:2.72:0.98:0.24:0.5$ . Contrary to this, the positions of the peaks for Au-Pt alloys after conditioning show that besides the two main phases  $\alpha_1$  and  $\alpha_2$ , the alloy contains only one minor phase for which the characteristic peaks are visible at diffraction angles of 32.0, 43.3 degrees etc. (Figure 2B). These peaks belong to the tetragonal  $\text{Au}_{1.4}\text{Zn}_{0.52}$  phase which is the only phase besides  $\alpha_1$  and  $\alpha_2$ , remained on the surface after the biocompatibility test. The calculated mass-ratio of all existing phases in the Au-Pt II AC alloy is  $\alpha_1:\alpha_2:\text{Au}_{1.4}\text{Zn}_{0.52} = 94.28:4.67:1.05$ .

Generally in dental literature, similar publications are very scarce and to our knowledge this is the first report on the microstructure of the high noble Au-Pt dental alloys and its changes during conditioning.

Nowadays, attention is increasingly focusing on the extensive range of alternative materials. These new materials include titanium and cobalt/nickel base alloys and all-ceramic crowns. The latter have excellent aesthetic properties, but do not have the long-term clinical approval that gold has. For example, zirconia has only passed clinical tests during the last 8 years. In addition, the CAD/CAM techniques associated with the use of these materials are, in many cases, prohibitively expensive. Moreover, the problems of poor aesthetics often associated with porcelain-fused-to-metal techniques might be addressed through the use of extremely high gold content alloys, which have recently been patented. It is considered that as CAD/CAM technology progresses, special high gold alloys should be developed, which are well suited to milling and grinding operations and sufficiently high strength for long span bridges and small cross sections (17). Besides long term clinical approval and longevity, the most important advantages of gold alloys are easy workability, biocompatibility, aesthetics and maximum range of indications. The development of electroforming technology with pure gold offers new opportunities for future research. For highly stressed parts in dental restorations, electroformed pure gold is still too soft and thus has limited uses. So, the future is the development increased strength through dispersion strengthening by incorporating a suspension of ceramic particles (18). Another area for electroforming research may focus on the deposition of multilayers by electrochemical structure modulation.

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