



## Metals in Prosthodontics: A Review

**Arunoday Kumar<sup>1</sup>, Babina Chirom<sup>1</sup>, Manawar Ahmad<sup>2</sup>, Hina Naim<sup>2</sup>,  
Nanditha Kumar M<sup>3</sup>, Mahesh Mundathaje<sup>4</sup>, Sharon Saldanha<sup>4</sup>**

*Department of Prosthodontics and Crown & Bridge, Dental College, RIMS, Manipur, India*

*2. Department of Prosthetic Dental Sciences, College of Dentistry, Jazan University, Kingdom of Saudi Arabia.*

*3. Department of Prosthodontics, JSS Dental College and Hospital, JSS Academy of Higher Education and Research, Mysore, India.*

*4. Department of Prosthodontics and Crown & Bridge, Manipal College of Dental Sciences, Mangalore, Manipal Academy of Higher Education, Manipal, India*

**Corresponding Author: Arunoday Kumar,  
[dr.arunodayk@gmail.com](mailto:dr.arunodayk@gmail.com)**

### **Introduction:**

In dentistry, metals represent one of the four major classes of materials used for the reconstruction of damaged or missing oral tissues. Although metals are readily distinguished from ceramics, polymers, and composites, it is not easy to define the word metal because of the wide variation in properties of metallic materials. The Metals Handbook (1992) defines a metal as "an opaque lustrous chemical substance that is a good conductor of heat and electricity and, when polished, is a good reflector of light."<sup>1</sup>

An alloy is a substance with metallic properties that consists of two or more chemical elements, at least one of which is a metal. Gallium and mercury, elements commonly used in dental alloys, are liquid at body temperature. However, all metals and alloys used as restorative materials in dentistry are crystalline solids. Metals can also be described in terms of qualitative and quantitative properties such as their luster, malleability, ductility, electrical conductivity, thermal conductivity, specific gravity, and ability to make a ringing sound when struck.<sup>1</sup> With the exception of pure gold foil, commercially pure (CP) titanium, and endodontic silver points, materials used for dental restorations, partial denture frameworks, orthodontic wires and endodontic instruments are alloys. The wide variety of complex dental alloy compositions are (1) Dental amalgams containing the major elements mercury, silver, tin, and copper, (2) Noble metal alloys in which the major elements are some combination of gold, palladium, silver, and important secondary elements including copper, platinum, tin, indium, and gallium, and (3) Base metal alloys with a major element of nickel, cobalt, iron, or titanium and many secondary elements that are found in the alloy compositions. Moreover CP titanium, which is classified in four different grades, may also technically be considered as an alloy, because small percentages of other elements are allowed as impurities as specified by a standard set by the American Society for Testing and Materials (ASTM) for each grade.<sup>1</sup>

Dental casting alloys play a prominent role in the treatment of dental disease. This role has changed significantly in recent years with the improvement of all-ceramic restorations and the development of more durable resin-based composites. However, alloys continue to be used as the principal material for fixed prosthetic restorations and will likely be the principal material for years to come. No other material has the combination of strength, modulus, wear resistance, and biologic compatibility that a material must have to survive long term in the mouth as a fixed prosthesis.<sup>2</sup>

Although uses for pure metals such as gold foil and platinum foil exist in dentistry, the main role for metals in dentistry has been in alloys. Alloys are mixtures of metals and nonmetals. Alloys are used for fixed prostheses rather than pure metals because pure metals do not have the appropriate physical properties to function in these types of restorations. For example, the tensile strength of pure gold is 105 MPa. By adding 10 wt % of copper, this strength increases to 395 MPa. With the appropriate addition of other elements and proper casting conditions, the strength increases to over 500 MPa. Even more impressive is the increase in hardness: from 28 kg/mm<sup>2</sup> for pure gold to nearly 200 kg/mm<sup>2</sup> for a typical gold-based casting alloy. Thus, the use of alloys provides physical and biologic properties that are required for successful, long-term fixed prostheses.<sup>2</sup>

Most metals have a "white" appearance (e.g., aluminum, silver, nickel, palladium, tin, and zinc). However, there are slight differences in hue and chroma among the white metals. Two non-white metals in the periodic table are gold and copper, both of which are important components of cast dental alloys. The properties of the pure elements do not change abruptly from metallic to non-metallic as one moves to the right side of the periodic chart rather, the boundary between metals and nonmetals is somewhat arbitrary and the elements near the boundary exhibit characteristics of both metals and nonmetals.

The elements carbon, boron, and silicon are often combined with metals to form commercially important engineering materials. Silicon and germanium are termed semi-conductors because their electrical conductivity is intermediate between that of a metal and that of an insulator. These two elements form the basis for many electronic devices. However, in dentistry the most common casting alloys used for dental appliances and prostheses are based on a majority of one of the following elements: cobalt, gold, iron, nickel, palladium, silver, and titanium.<sup>1</sup>

Review of Literature:

In the study **Tarnish and Corrosion Behaviour of Dental Gold Alloys** by **Leon W. Laub and John W. Stanford** in the year **1981** has shown that approximately two hundred casting alloys containing varying amounts of noble metals are being marketed for dental prostheses. Among the important characteristics of these materials are tarnish and corrosion resistance in the oral environment. Composition restrictions are not sufficient to assure *in vivo* alloy stability - alloys containing 75 per cent noble metals by weight have been found to tarnish, whereas alloys containing 52 per cent noble metals have not. Furthermore, procedures for screening new alloy formulations prior to marketing have not yet been standardized.

**Katsuhiro Yasuda** conducted the study titled **Age-Hardening And Related Phase Transformations in Dental Gold Alloys** in the year **1987** has attempted to show that **transmission electron microscopy** (TEM) is a powerful tool for studying age-hardening mechanisms in dental gold alloys. In particular, high resolution TEM coupled with electron diffraction are extremely effective in helping to elucidate the structural changes, down to the

scale of inter atomic distances that are associated with a phase transformation during age-hardening, even though the results are still mainly of a qualitative nature. The author hopes that this article will provide future researchers in this field with a better understanding of the need for fundamental studies, which will ultimately result in a more effective utilization of dental alloys for the best patient care.

**In the year 1988 a study titled *The Electroforming Of Gold And Its Alloys* by *Anselm T. Kuhn & Leslie V. Lewis* has shown that** after a very slow start, the electroforming of gold and its alloys is a technology capable of considerable further development and that as this takes place, so will the scale of its use increase. Electroforming can be described as a manufacturing process based on the electro deposition of a metal. Unlike electroplating, however, where the deposited metal covers a substrate, in electroforming, at the end of the deposition process, that substrate (which is known as the mandrel), is removed, leaving the electro deposit as an object in its own right. Thus electroforming, though it superficially resembles electroplating, is in fact a far more advanced technology. Not only is the preparation of the mandrels a complex procedure, but also many of the difficulties inherent in electrodeposition, such as current distribution and the incidence of internal stress, become critically obvious in electroforming, whereas in electroplating, this might not have been the case. For every hundred companies in the electroplating industry, perhaps one might include electroforming among their activities.

**In the study *Casting Alloys: The Materials and the Clinical Effects* by *Morris, Manz et. al.* in the year 1992** has estimated that 96% of adults in the United States between the ages of 18 and 65 have one or more carious or filled teeth, with an average of almost 10 decayed or filled teeth for each adult (Miller *et al.*, 1987). The best treatment for carious teeth, to prevent loss and restore masticatory function, often involves the use of cast dental restorations. The chemical compositions of noble and base metal dental alloys and, based on 72-month data from a 10-year clinical study (Morris *et al.*, 1986), will summarize the clinical behavior of alloys with "representative formulations". "Noble" refers to metals with marked resistance to oxidation and chemical reaction. Silver is not considered noble in the context of dental casting alloys. "Precious" refers to an economic value. The American Dental Association has stated that "semi-precious" has no meaning in dentistry because no definition has been agreed on (ADA, 1984). "Base metal" refers to metal elements that are chemically reactive to their environment (Phillips, 1991).

***Katsuhiko Yasuda and Kunihiro Hisatsune* conducted the study titled *Microstructure And Phase Transformations In Dental Gold Alloys* in the year 1993** has shown that to achieve control of the mechanical properties such as strength, ductility, fracture toughness, and chemical stability in dental gold alloys, it is most important to understand the correlation between micro structural morphology and phase transformation. A coherent phase diagram gives us effective information concerning phase transformations and related micro structural features for a given alloy.

**In the year 2003 a study titled *Gold in Dentistry: Alloys, Uses and Performance* by *Helmut, Richard and Christopher* has shown that** gold is the oldest dental restorative material, having been used for dental repairs for more than 4000 years. These early dental applications were based on aesthetics, rather than masticatory ability. The early Phoenicians used gold wire to bind teeth, and subsequently, the Etruscans and then the Romans introduced the art of making fixed bridges from gold strip. During the middle Ages these techniques were lost, and only rediscovered in a modified form in the middle of the nineteenth century.

**In the study Casting alloys by John C. Wataha and Regina L. Messer in the year 2004** has shown that Dental casting alloys play a prominent role in the treatment of dental disease. This role has changed significantly in recent years with the improvement of all-ceramic restorations and the development of more durable resin-based composites. However, alloys continue to be used as the principal material for fixed prosthetic restorations and will likely be the principal material for years to come. No other material has the combination of strength, modulus, wear resistance, and biologic compatibility that a material must have to survive long term in the mouth as a fixed prosthesis.

**T.P. Chaturvedi conducted the study titled An overview of the corrosion aspect of dental implants in the year 2009** has shown that Titanium and its alloys are used in dentistry for implants because of its unique combination of chemical, physical, and biological properties. They are used in dentistry in cast and wrought form. The long term presence of corrosion reaction products and ongoing corrosion lead to fractures of the alloy-abutment interface, abutment, or implant body. The combination of stress, corrosion, and bacteria contribute to implant failure.

**In the year 2009 a study Titled the Origin of the Metallic Bond by William B. Jensen** has shown that both assumed that the weakly bound conduction electrons could be modeled using the classical kinetic theory of gases. Though this “electron-gas” model gave an adequate qualitative rationale of metallic properties, it in correctly predicted both the heat capacity of metals and the temperature dependence of their electrical conductivity. In addition, it could not explain their magnetic properties.

**In the study Tensile bond strength of composite luting cements to metal alloys after various surface treatments by Saip Denizoglu, Cem S Hanyaloglu et.al. in the year 2009** made a comparison of the surface treatments between sandblasted, etched and sandblasted etched surfaces, tensile bond strengths of sandblasted surfaces were higher and statistically significant.

**DR Prithviraj, Romesh Soni et.al. conducted the study titled Evaluation of the effect of different surface treatments on the retention of posts: A laboratory study in the year 2010** has shown that air-borne alumina particle abrasion increased the retentive strength of all the type of posts used in this study. Treating the surface of the posts with resin-primer and ethyl alcohol produced no statistically significant difference in the retentive strength.

**In the year 2010 a study titled An overview of orthodontic material degradation in oral cavity by TP Chaturvedi and SN Upadhyay** has shown that a primary requisite of any alloy metal used in the mouth is that it must not produce corrosion products that will be harmful to body. In spite of recent innovative metallurgical and technological advances and remarkable progress related to orthodontic materials, failures do occur. One of the reasons for these failures could be corrosion (material degradation) of orthodontic appliances. It causes severe and catastrophic disintegration of the metal body.

**In the study screening test for metal identification in prosthetic dentistry by Reclaru Lucien in the year 2010** shows the identification of the chemical nature of metallic restorations may provide useful information in odontological diagnosis. Dentists commonly use the splint-test for such identification. Abrasion debris is collected from the metal restoration in the patient's mouth, and the sample is then sent to a laboratory for chemical analysis.

**Shaista Afroz and Pooran Chand** conducted the study titled **Collarless metal ceramic**

**restorations to obscure the umbrella effect** in the year **2010** had concluded that desirable esthetics can be achieved by collarless metal ceramic restoration. The optical phenomenon of umbrella effect was prevented by using shoulder porcelain. It is cheaper and stronger, being more conservative, having greater longevity and being an esthetically acceptable alternative to all ceramic restorations. Also, an all-ceramic restoration with the opaque alumionous core may show a similar optical phenomenon.

In the year **2011** a study titled **Microstructure, mechanical performance and corrosion properties of base metal solder joints** by **Sujesh Machha, M Vasanth Kumar et.al.** has shown that tensile strength and percentage of elongation were higher in the one-piece casting group followed by laser fusion and gas oxygen soldered joint, when nickel chromium alloy and solder were tested. The laser fused joints exhibited better hardness, possessed better microstructure and had a high corrosion resistance. Gas oxygen soldered group showed joints with greater porosity and exhibited least corrosion resistance. Consequently, laser fusion, which is a recent introduction to the field of prosthodontics, produces joints which have properties between the one-piece casting and the gas oxygen torch soldering. The technique produces joints which possesses superior mechanical properties compared to those fabricated by conventional methods.

In the study **Evaluation and comparison of castability between an indigenous and imported Ni–Cr alloy** by **Ganesh Ramesh, Padmanabhan TV et.al.** in the year **2011** conclude that the castability of the indigenous alloy is on par with the imported alloy.

■ **Kaushal K Agrawal, Arvind Tripathi et.al.** conducted the study titled **A study to evaluate the effect of oral stereognosis in acceptance of fixed prosthesis** in the year **2011** had concluded that one-day interval for both type of cast metal crowns was found to be insignificant in all subjects. Oral stereognostic score of cast metal crown resembling original tooth was found to be significantly higher than oral stereognostic score for cast metal crown with morphology confirmed to ideal contours. Satisfaction level of subjects for cast metal crown with morphology resembling original tooth was found to be significantly higher than satisfaction level for cast metal crown with morphology confirmed to ideal contours. Oral stereognostic score and satisfaction score were found to be higher for cast metal crown with morphology resembling to original tooth due to recognition and discriminatory ability of subjects and recall-memory. There was no significant difference in oral perception and satisfaction level between male and female.

In the year **2011** a study titled **Oxidation heat treatment (OHT) affecting metal-ceramic bonding** by **Shraddha Rathi, Hari Parkash et.al.** concluded that there is neither any significant effect of OHT on the metal- ceramic bonding nor micro abrasion of the metal substructure affects metal- ceramic bonding.

In the study **An alternative treatment of occlusal wear: Cast metal occlusal surface by Sandeep Kumar, Aman Arora et.al.** in the year **2012** has described a technique that uses the custom made occlusal portions as the patterns for casting base metal occlusal surfaces. Acrylic resin is attached to the metal occlusal surfaces via direct resin processing. During recall evaluation, the patient was satisfied with the functional efficiency of the denture and did not report any problem associated with the metal occlusal denture.

**Thakur Prasad Chaturvedi and Ram Sagar Dubey** conducted the study titled **Corrosion behavior of titanium wires: An in vitro study** in the year **2012** showed degradation of titanium wires by electrochemical attack when they were placed in the hostile electrolytic environments provided in the experiments. Surface analysis of titanium wires showed pitting and localized attacks on the surface. Pitting corrosion was found in the titanium wires.

In the year **2012** a study titled **The effect of remelting various combinations of new and used cobalt–chromium alloy on the mechanical properties and microstructure of the alloy** by **Sharad Gupta and Aruna S Mehta** has concluded that repeated remelting of base metal alloy for dental casting without addition of new alloy can affect the mechanical properties of the alloy. Microstructure analysis shows deterioration upon remelting. However, the addition of 25% and 50% (by weight) of new alloy to the remelted alloy can bring about improvement both in mechanical properties and in microstructure.

In the study **The influence of metal substrates and porcelains on the shade of metal-ceramic complex: A spectrophotometric study** by **Kavitha Janardanan, Sreelal Thankappan Pillai et.al.** in the year **2012** had concluded that the variations in metal-ceramic alloy and porcelain can influence the shade of a metal-ceramic restoration. Color index value was the highest for gold alloy.

**Onur Geckili, Hakan Bilhan et.al.** conducted the study titled **The effect of urea on the corrosion behavior of different dental alloys** in the year **2012** indicate that elevated urea levels reduced the corrosion susceptibility of all alloys, possibly through adsorption of organics onto the metal surface. This study indicates that corrosion testing performed in sterile saline or synthetic saliva without organic components could be misleading.

In the year **2012** a study titled **A finite element thermal analysis of various dowel and core materials** by **Shanti Varghese, Padma Ariga et.al.** has shown that non-metallic dowel and core materials such as fibre reinforced composite dowels (FRC) generate greater stress than metallic dowel and core materials. This emphasized the preferable use of the metallic dowel and core materials in the oral environment.

In the study **Evaluation of flexural bond strength of porcelain to used nickel–chromium alloy in various percentages** by **Madhav VNV, Padmanabhan TV et.al.** in the year **2012** has shown that fresh nickel–chromium alloy shows the greatest porcelain adherence. There is no significant change in bond strength of ceramic to alloy with up to 75% of used nickel–chromium alloy. At least 25%– of new alloy should be added when recycled nickel–chromium alloy is being used for metal ceramic restorations.

**Mirza Rustum Baig and Rajan Gunaseelan** conducted the study titled **Intraoral framework pick-up technique to improve fit of a metal-resin implant prosthesis** in the year **2012** proposed technique uses a custom cast frame in combination with prefabricated milled abutments to create a retrievable metal-resin fixed complete denture. The technique may be useful in situations where screw-retention is intended and a cost-effective option is desired. Long-term clinical studies evaluating the success rates of this treatment modality in comparison with conventional options are required, before recommending it for routine use in clinical practice.

In the year **2012** a study titled **Evaluation of resistance to displacement of metal posts with different lengths** by **Ana Paula Farina, Douglas Cecchin et.al.** Concluded that metal

retainers of 2/3 and 1/2 the length of the root portion showed higher resistance to displacement values when compared with the group that had been prepared for 1/3 of the root length.

In the study **Alternative anterior esthetics: A case report** by **Manish Khan Katyayan and Preeti Agarwal Katyayan** in the year **2013** has shown that due to the rise over the years in patient emphasis on better esthetic outcomes, veneering the metal base of a restoration with composite resin or porcelain is widely used in dentistry. For the preservation of the opposing natural dentition and the potential for repair, the use of composite veneering materials has been suggested because of their resilience, low abrasive properties, and superior repair potential. Composites are not as popular as porcelain, but they are still widely used to cover metal because of low cost and because the laboratorial procedures are faster and simpler.

**Deepak K, Ahila SC et.al.** conducted the study titled **Comparative evaluation of effect of laser on shear bond strength of ceramic bonded with two base metal alloys: An in vitro study** in the year **2013** has shown that the shear bond strength between ceramic bonded with Ni Cr alloys using the Laser etching as surface treatment was  $49.12 \pm 7.12$  MPa and for Co Cr alloys  $50.04 \pm 4.27$  MPa. Laser surface treatment produces an excellent surface roughness and achieved good shear bond strength values and aid in achieving a better bond strength between metals and ceramic.

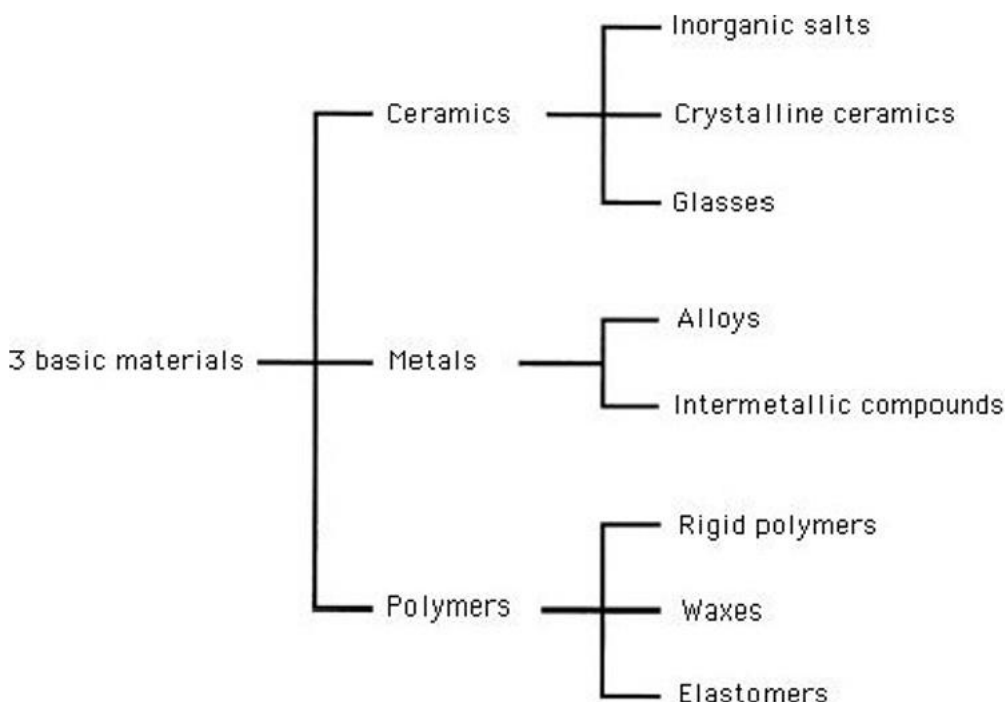
In the year **2013** a study titled **Comparison of marginal accuracy of castings fabricated by conventional casting technique and accelerated casting technique: An in vitro study** by **Srikanth Reddy S, Kakkirala Revathi et.al.** has shown that conventional casting technique produced better marginal accuracy when compared to Accelerated casting. The vertical marginal discrepancy produced by the Accelerated casting technique was well within the maximum clinical tolerance limits.

In the study **Titanium - A Miracle Metal in Dentistry** by **Sulekha Gosavi<sup>1</sup>, Siddharth Gosavi et.al.** in the year **2013** has shown that Titanium and titanium alloys, based on their physical and chemical properties, appear to be especially suitable for dental implants and prostheses. Titanium also shows a low toxicity, great stability with low corrosion rates and favorable mechanical properties compared to other metals make titanium as a miracle metal for the biomedical applications. The combination of high strength-to-weight ratio, lightweight, excellent mechanical properties (Strong), corrosion resistance, biocompatible, non-toxic, long-lasting, non-ferromagnetic, osseo integrated (the joining of bone with artificial implant), cost-efficient and long range availability makes titanium the best material choice for many critical applications.

**Harshitha Gowda BH and Satish Babu CL** conducted the study titled **Connector design in a long span fixed dental prosthesis: A three dimensional finite element analysis** in the year **2013** has shown that the cylindrical cast connectors showed less stress in comparison to triangular design and the difference in the stress distribution of cast and soldered connectors were marginal.

In the year **2014** a study titled **Casting made simple using modified sprue design: An in vitro study** by **B Eswaran Baskaran, KR Geetha Prabhu et.al.** has shown that the efficacy of a sprue design depends on how easily metal can flow through it and fill the mold cavity. The sprue must supply molten metal continuously so that the gases are forced out of the mold cavity. It should also compensate for the shrinkage of alloy in the casting as it solidifies. Ever since sprue techniques have been followed, various views are suggested regarding the selection and application of sprue designs and their mode of attachment to the pattern to be casted.

### TREE DIAGRAM CLASSIFYING THE THREE BASIC MATERIALS<sup>1</sup>



### CLASSIFICATION OF METALS ACCORDING TO PERIODIC TABLE<sup>1</sup>

Of the 115 elements currently listed in most recent versions of the periodic tables of the elements, about 81 can be classified as metals. (Additional elements that have been created with nuclear reactors have short half-lives.) It is of scientific interest that the metallic elements can be grouped according to density, ductility, melting point, and nobility. This indicates that the properties of metals are closely related to their valence electron configuration. Several metals of importance for dental alloys are *transition elements*, in which the outermost electron sub shells are occupied before the interior sub shells are completely filled.



# PERIODIC TABLE OF THE ELEMENTS

<http://www.periodni.com>

PERIOD	GROUP	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	IA	1 H 1.0079 HYDROGEN	2 He 4.0026 HELIUM																
2	IIA	3 Li 6.941 LITHIUM	4 Be 9.0122 BERYLLIUM																
3		11 Na 22.990 SODIUM	12 Mg 24.305 MAGNESIUM																
4		19 K 39.098 POTASSIUM	20 Ca 40.078 CALCIUM	21 Sc 44.956 SCANDIUM	22 Ti 47.867 TITANIUM	23 V 50.942 VANADIUM	24 Cr 51.996 CHROMIUM	25 Mn 54.938 MANGANESE	26 Fe 55.845 IRON	27 Co 58.933 COBALT	28 Ni 58.693 NICKEL	29 Cu 63.546 COPPER	30 Zn 65.38 ZINC	31 Ga 69.723 GALLIUM	32 Ge 72.64 GERMANIUM	33 As 74.922 ARSENIC	34 Se 78.96 SELENIUM	35 Br 79.904 BROMINE	36 Kr 83.798 KRYPTON
5		37 Rb 85.468 RUBIDIUM	38 Sr 87.62 STRONTIUM	39 Y 88.906 YTRIUM	40 Zr 91.224 ZIRCONIUM	41 Nb 92.906 NIObIUM	42 Mo 95.96 MOLYBDENUM	43 Tc (98) TECHNETIUM	44 Ru 101.07 RUTHENIUM	45 Rh 102.91 RHODIUM	46 Pd 106.42 PALLADIUM	47 Ag 107.87 SILVER	48 Cd 112.41 CADMIUM	49 In 114.82 INDIUM	50 Sn 118.71 TIN	51 Sb 121.76 ANTIMONY	52 Te 127.60 TELLURIUM	53 I 126.90 IODINE	54 Xe 131.29 XENON
6		55 Cs 132.91 CAESIUM	56 Ba 137.33 BARIUM	57-71 La-Lu Lanthanide	72 Hf 178.49 HAFNIUM	73 Ta 180.95 TANTALUM	74 W 183.84 TUNGSTEN	75 Re 186.21 RHENIUM	76 Os 190.23 OSMIUM	77 Ir 192.22 IRIDIUM	78 Pt 195.08 PLATINUM	79 Au 196.97 GOLD	80 Hg 200.59 MERCURY	81 Tl 204.38 THALLIUM	82 Pb 207.2 LEAD	83 Bi 208.98 BISMUTH	84 Po (209) POLONIUM	85 At (210) ASTATINE	86 Rn (222) RADON
7		87 Fr (223) FRANCIUM	88 Ra (226) RADIUM	89-103 Ac-Lr Actinide	104 Rf (261) RUTHERFORDIUM	105 Db (268) DUBNIUM	106 Sg (271) SEABORGIUM	107 Bh (272) BOHRNIUM	108 Hs (277) HASSIUM	109 Mt (276) MEITNERIUM	110 Ds (281) DARMSTADIUM	111 Rg (280) ROENTGENIUM	112 Cn (285) COPERNICIUM	113 Uut (...) UNUNTRIUM	114 Fl (287) FLEROVIUM	115 Uup (...) UNUNPENTIUM	116 Lv (291) LIVERMORIUM	117 Uus (...) UNUNSEPTIUM	118 Uuo (...) UNUNOCTIUM

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(1) Pure Appl. Chem., 81, No. 11, 2131-2156 (2009)

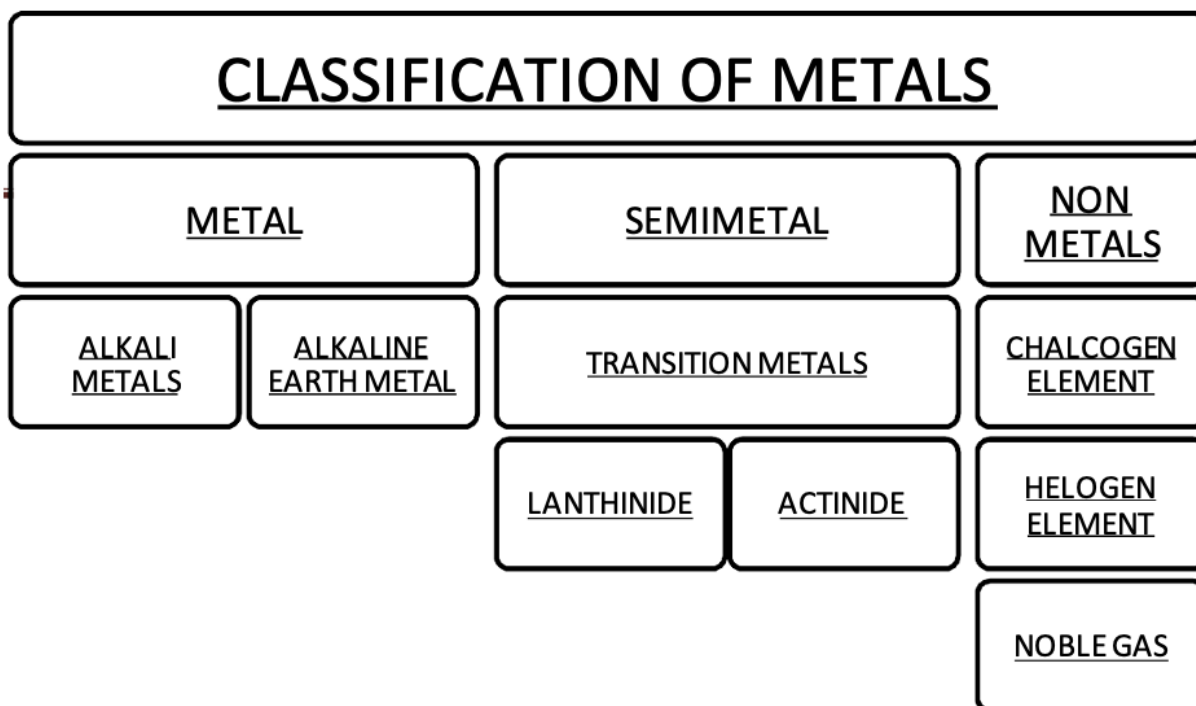
Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element. However three such elements (Th, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

## LANTHANIDE

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
138.91	140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05	174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERIUM	LUTETIUM

## ACTINIDE

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
(227)	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM



Several metals importance for dental alloys are *transition elements*, in which the outermost electron sub shells are occupied before the interior sub shells are completely filled.

### **TYPES OF DENTAL ALLOYS**

Casting alloys are categorized several ways, but the classification system most used by dental practitioners is the American Dental Association (ADA) compositional classification system. The ADA system divides casting alloys into three groups on the basis of wt% composition. The high-noble alloys are those with noble metal content (sum of gold, palladium, and platinum) of at least 60 wt% and a gold content of at least 40 wt %. Most gold-based alloys before 1975 fell into this category. The noble alloys must contain at least 25 wt% noble metal but have no specific requirement for gold content. Finally, the predominantly base- metal alloys contain less than 25 wt% noble metal, with no other specification on composition. The ADA has adopted symbols for each of these classes of alloys to aid the practitioner in knowing to which category a given alloy belongs. This classification system is more encompassing than the previous classification system it replaced in 1984, which focused primarily on gold-based alloys.<sup>2</sup>



*Fig.1 Symbols adopted by the ADA for its three major classifications of alloys based on composition*

The ADA also classifies alloys on physical properties of yield strength and elongation. Four categories of alloys are defined in this scheme. Soft alloys are defined for use in low-stress conditions under which the restoration bears no significant occlusion. Medium alloys are recommended for conditions of moderate stress and light occlusal stress. Hard alloys are recommended for full occlusal loads with single units or short span fixed partial dentures, and very hard alloys are recommended for removable partial dentures and longer-span fixed partial dentures. Each casting alloy is therefore defined by two ADA classification systems—one for composition and one for physical strength.<sup>2</sup>

**Classification of casting alloys by physical properties<sup>2/</sup>**

ADA designation	Yield strength (MPa, in tension)	Elongation (%)
Type 1 Soft	<140	18
Type 2 Medium	140–200	18
Type 3 Hard	201–340	12
Type 4 Extra-hard	>340	10

**Classification on the basis of application and general chemical composition<sup>3</sup>****Noble Alloys***Noble/Gold based Alloys*

Noble/gold-based alloys have the longest history of use in dentistry and are "the standard" with which other alloys are usually compared. They are used for fabrication of inlays, crowns, fixed partial dentures, and metal ceramic restorations

(PFM). Gold adds high corrosion resistance, good castability, good ductility, and the distinctive yellow gold color. Silver reduces density, slowly whitens the alloy color when added in increasing amounts, and counteracts the redness of copper. In PFM alloys, silver may discolor porcelain veneers. Copper strengthens gold-based alloys (AuCu<sub>3</sub>). Both palladium and platinum increase casting temperature, strength, and corrosion resistance of the alloy (Tuccillo and Nielson, 1971). Palladium lowers cost and improves rigidity and sag resistance of PFM alloys (Moffa, 1983). Zinc (traces) increases castability (Raub and Ott, 1983) and forms intermetallic (gold) compounds to harden the alloy (Labarage and Treheux, 1979). Iron improves mechanical properties and in PFM alloys, increases sag resistance (Kojima, 1980) and bond strength with porcelain (Espevik and Oilo, 1979). Tin acts as a bonding element in PFM alloys and a hardening agent in palladium-gold alloys (German, 1979). Iridium acts as a grain refiner in gold-based PFM alloys (Raub and Ott, 1983). Indium serves as a bonding agent in PFM alloys (Espevik and Oilo, 1979). Germanium increases the castability of gold-copper alloys (Townsend and Hamilton, 1983).

*Noble/Gold-Based Alloys: "General" Chemical Compositions*

(A) Crowns and fixed partial dentures

(1) Major: gold, silver, copper

(2) Minor: palladium, platinum, zinc, indium, iridium, rhenium, germanium

(B) Metal ceramic (PFM)

(1) Major: gold, platinum, palladium

Minor: rhodium, silver, indium, tin, iron, iridium, rhenium, copper

*Noble/ Palladium based Alloys*

Noble/palladium based alloys with silver have been available since 1974 (Tuccillo, 1977). In the early 1980's, there was an increase in palladium-based formulations with reduced amounts of

silver. They are used primarily for the fabrication of PFM restorations. However, a variety of type IV, extra-hard alloys exists that can be used to cast inlays, crowns, fixed partial dentures, and removable partial dentures (RPD). Palladium reduces the cost of the alloy while increasing strength, rigidity, and sag resistance (Moffa, 1983). The coefficient of thermal expansion is increased with the addition of silver (Kollmannsperger and Helfmeier, 1983). Indium and/ or tin can be added to improve bonding with the porcelain veneer. Gallium contributes to a homogeneous microstructure. Ruthenium is used primarily as a grain refiner. Palladium based alloys absorb small amounts of carbon that increase brittleness of the alloy (Eichner, 1983). Gas porosities (CO gas) may occur after the alloy is cooled. The palladium-silver alloys are somewhat more difficult to cast (McLean, 1983).

Noble/Palladium-Based Alloys: "General" Chemical Compositions

- (a) Crowns and fixed partial dentures
  - (1) Major: palladium, silver, copper, gold
  - (2) Minor: zinc, indium, iridium
- (B) Metal ceramic (PFM)
  - (1) Major: palladium, silver, gold, copper, cobalt
  - Minor: gold, platinum, indium, tin, gallium, ruthenium, rhenium

### Base Metal Alloys

Base metal alloys were first introduced to dentistry for the fabrication of RPD's in the early 1930's. Subsequently, they have largely replaced the noble-based alloys for RPD's. The most successful RPD alloys are cobalt-chromium based and nickel-chromium-based. There has also been an increase in the use of similar "base metal" alloys for less costly crowns, fixed partial dentures, and PFM restorations due to the dramatic increase in price of gold bullion and gold-containing dental casting alloys in the 1970's.

*Base Metal/Cobalt-based Alloys*

Base metal/cobalt-based alloys are used primarily in the fabrication of RPD's. Several manufacturers (*e.g.*, J.F. Jelenko, Dentsply) market cobalt-based alloys for PFM restorations. Cobalt provides strength, hardness, and corrosion resistance. Chromium provides hardness and resilience and increases corrosion resistance when present in at least 16 wt%. Nickel increases ductility (Asgar and Peyton, 1961) while lowering melting temperature and hardness (Asgar and Allan, 1968). The carbon content of these alloys is critical. It is only slightly soluble in cobalt-chromium solid solution and is present mainly as dispersed carbides of chromium, cobalt, or molybdenum, increasing the strength and hardness of the alloy (Tesk and Waterstrat, 1985). Manganese is a de-oxidizer. Tungsten helps reduce formation of chromium-depleted zones.

*Base Metal/Cobalt-Based Alloys: "General" Chemical Compositions*

- (A) Metal ceramic (PFM)
  - (1) Major: cobalt, chromium, tungsten, molybdenum
  - (2) Minor: copper, silicon, gallium, aluminum, nickel, tantalum, ruthenium
- (B) Removable partial dentures
  - (1) Major: cobalt, chromium, nickel
  - Minor: molybdenum, tantalum, manganese, gallium, silicon, carbon, tungsten

### Base Metal/ Nickel based Alloys

Base metal/nickel-based alloys are used primarily for RPD's and PFM restorations. Nickel yields a softer alloy and lowers the melting temperature. Aluminum (Ni3Al) increases strength and hardness. Carbon may be added to increase strength but increases brittleness as well. Beryllium decreases melting temperature and corrosion resistance (Lee *et al.*, 1985) while improving castability and bonding. Lower melting temperatures also provide a smoother casting surface that requires less finishing. Boron decreases alloy melting temperature (Haudin and Perrin, 1981). Titanium and manganese increase corrosion resistance (Meyer, 1977) and serve as bonding agents (Espevik and Oilo, 1979). Iron increases strength (Meyer *et al.*, 1979). Cobalt increases hardness. Copper increases corrosion resistance (Bui and Dabosi, 1981). Gallium improves castability (Kollmannsperger and Helfmeier, 1983). Yttrium aids in the adherence of oxide layers (Townsend and Hamilton, 1983). Molybdenum increases corrosion resistance (Lee *et al.*, 1985). Tin increases strength and hardness (Ando and Nakayama, 1983).

### Base Metal/Nickel-Based Alloys: "General" Chemical Compositions

#### (A) Crowns and fixed partial dentures

- (1) Major: nickel, chromium, iron
- (2) Minor: molybdenum, silicon, manganese, boron, copper

#### (B) Metal ceramic (PFM)

- (1) Major: nickel, chromium
- (2) Minor: molybdenum, iron, silicon, manganese, beryllium, boron, aluminum, yttrium, tin

#### (C) Removable partial dentures

- (1) Major: nickel, chromium
- Minor: molybdenum, iron, silicon, manganese, beryllium, boron, aluminum, carbon, cobalt, gallium, tin

### Alloys for Implants<sup>1</sup>

- i) Cp Titanium  
Grade I, II, III and IV
- ii) Titanium  
Alloys Ti-6Al-4V alloy  
Ti-6AL – 4V ELI alloy
- iii) Cobalt – Chromium – molybdenum
- iv) Stainless steel (316 L)

## **SOIDIFICATION AND MICROSTRUCTURE OF METALS<sup>10</sup>**

A wide variety of metals is used in dentistry. Each has a melting or solidification temperature that is characteristic of that element. When elements are alloyed together to change their properties, this single melting temperature is changed to a range of temperatures over which the liquid is in equilibrium with solid crystals nucleated in the liquid metal.

The upper temperature for the liquid-solid alloy range is called the liquidus temperature, and the lower temperature limit is called the solidus temperature. When a liquid alloy melt is being

cooled, the liquidus temperature is the temperature at which solid crystals start to nucleate. When a mixture of an alloy liquid and crystals is being heated, the liquidus temperature is the temperature at which the crystals dissolve into liquid. The solidus temperature is the temperature at which the last liquid solidifies on cooling or the first liquid is formed on heating.

Complete melting is needed for casting and soldering and at least an additional 100 °C superheat is needed for a fluid melt to cast. Note that a gas/air torch cannot be used to cast a metal with a liquidus temperature above 1,000 °C because the flame does not get hot enough. Also, a reducing flame rich in gas should be used for casting or soldering, otherwise the liquid metal will be oxidized by the oxygen in air. Oxidation keeps the solder from wetting the surface and flowing. To provide a margin of safety against melting the castings in a fixed partial denture, the liquidus temperature of the solder should be at least 50 °C lower than the solidus temperature of the casting alloy being soldered.

### Unit Cells of Crystal Lattices

Liquid metals nucleate **crystals** upon cooling. The atoms joining the crystals form a unique packing arrangement in space that is characteristic of that metal or alloy at equilibrium. The smallest division of the crystalline metal that defines the unique packing is called the **unit cell**. When the unit cell is repeated in space, the repeating atomic positions form the **crystal lattice** structure of a crystalline solid.

The atoms at the corners of the unit cell are shared among the adjacent eight unit cells, as shown for the body-centered unit cell. Therefore, one eighth of the corner atom is associated with the cell; there are eight corner atoms, so they each contribute one atom to the unit cell. The body-centered atom is totally inside the unit cell and is not shared, so it contributes the second atom to the unit cell mass. Using the **lattice parameters** to calculate the volume of the cubic cell, the density of the metal can be calculated by dividing the mass of atoms in the unit cell by its volume. The lattice parameters for metals and alloys range between 2 Å and 10 Å for the different unit cells formed.

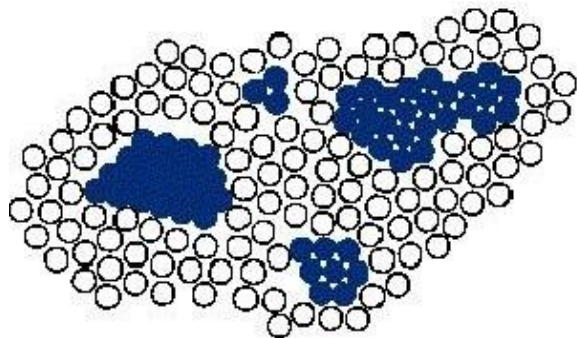


Fig.2 Formation of crystal nuclei in liquid metal

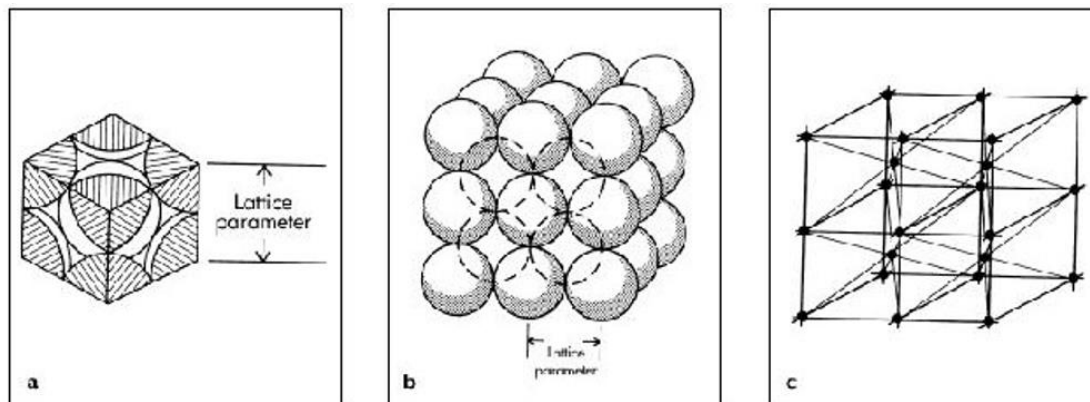


Fig.3 (a) The body-centered cubic unit cell is typical of the crystal lattice of pure iron at room temperature. The lattice parameter for iron is 2.87 Å. (b) A part of a body-centered cubic crystal lattice. It could extend in all directions. In this "hard sphere model," the atoms are visualized as hard spheres of a definite radius in contact. (c) The body-centered cubic space lattice can be visualized as a "point skeleton" of the body-centered cubic crystal lattice.

It has been observed that the position of the neighboring atoms surrounding every atom of a crystal lattice is identical in a pure crystalline metal. When the property of identical periodic points in space was explored mathematically, it was discovered that there are 14 unique ways to arrange points in space.

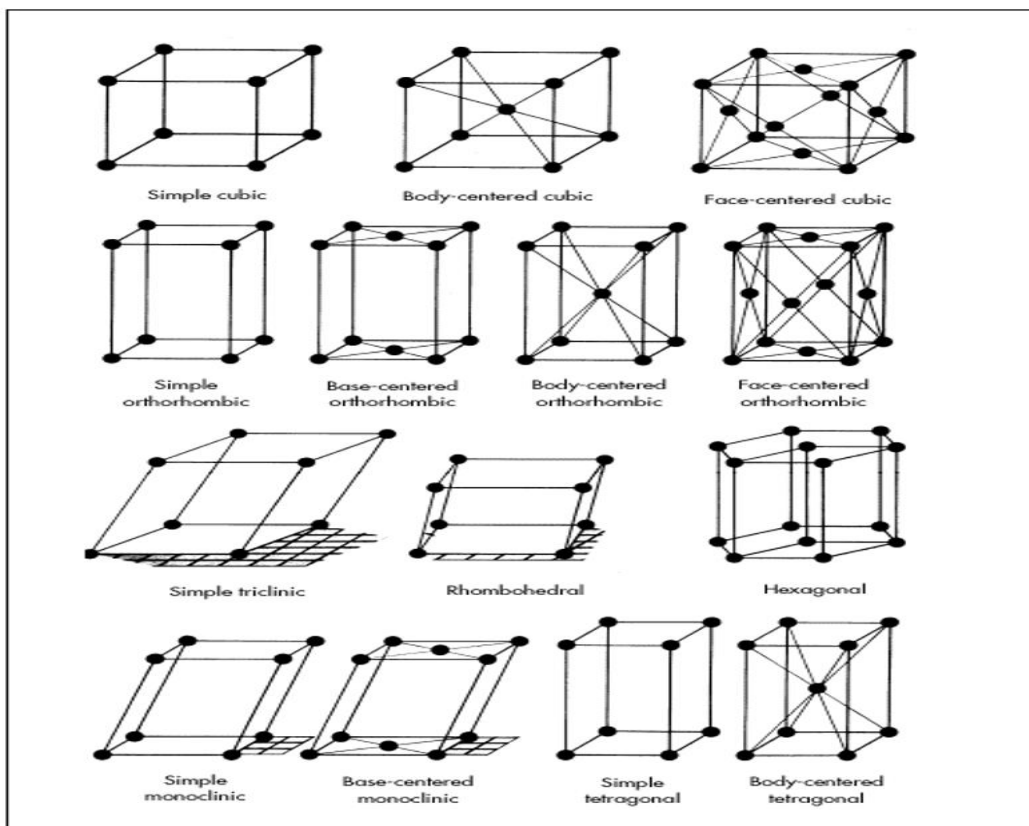




Fig. 4 Unit cells of the 14 space lattice contain atoms arranged so that each one has identical surroundings. (From Mott, 1967. Reprinted from Scientific American.)

These are called **space lattices**. A pure metal crystal lattice is similar to one of the space lattices except that each mathematical point is the site of an atom. Complex crystal lattices like amalgam alloy and enamel have the points of their space lattices replaced by the different atoms of the material or by groups of atoms. The unit cell of each crystalline material, no matter how complex, corresponds with one of these 14 space lattice unit cells.

### **Nucleation And Polycrystalline Grain Structure Introduction**

As the melt of metal is cooled, clusters of atoms come together from the liquid to form solid crystal **nuclei**. These nuclei will be stable and grow into **crystallites** or **grains** if the energy of the system is favorable, that is, the energy is lowered by the process. The energy is lowered by an atom bonding to the solid nuclei, thereby giving up its liquid-state kinetic energy of motion. However, when an atom bonds to the nuclei, the energy can also be raised by the creation of more interfacial surface energy as a result of the increased surface area of the nuclei in contact with the liquid. The energy of the system is favorable for stable nuclei and growth when more energy is lost by bonding than is gained by increasing the interfacial surface area (i.e., energy). Nucleation can occur by two processes. The first, called **homogeneous** nucleation, is enhanced by rapid cooling so the nuclei are super cooled. The result for the system is that more energy is lost when an atom of the liquid bonds to the solid. With rapid cooling (quenching in water) more nuclei are formed per unit volume. These nuclei grow together to form the irregular **polycrystalline** grains or crystallites that fit together like a three-dimensional puzzle to form the bulk of the metal shape.

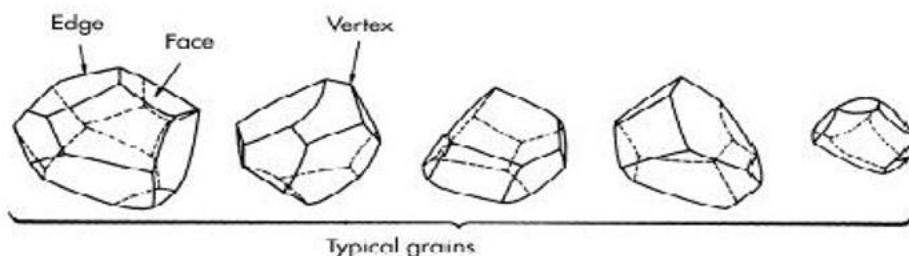
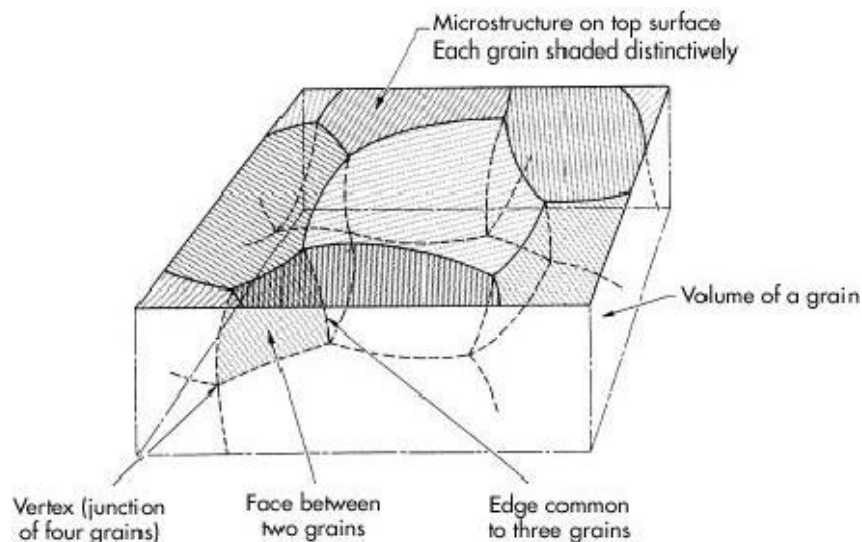


Fig. 5 Irregular polygons called grains or crystallites. An average distance measured across the faces of the crystal grains is called the grain size. It may be less than 1,000 Å or more than 1 cm, depending on the number of nuclei present during solidification. (From Guy et al, 1971. Reprinted with permission.)



*Fig. 6 The grain structure of a metal is revealed by polishing the surface to a mirror finish and etching lightly in acid. To study the grain structure of metals used for dental appliances, a light or scanning electron microscope is needed for magnification because of the small grain sizes. (From Guy et al, 1971. Reprinted with permission.)*

The more nuclei that are formed by rapid cooling, the smaller the grain size or crystallite dimensions. Another means of decreasing the grain size (grain refining) is by adding to the melt a foreign solid particle or surface to which the atoms are attracted, such as a very fine high-melting metal or oxide powder. This process of seeding the nuclei is called heterogeneous nucleation.

### **Grain Size And Properties**

Decreasing the grain size can have a number of beneficial effects on the cast alloy structure of a crown or removable partial denture. The finer grain size can raise the yield stress, increase the ductility (percent elongation), and raise the **ultimate strength**. The change in these properties with grain size is related to the processes of plastic **deformation** and fracture, and to how the boundaries between grains relate to these processes. The size of metal grains in different metals may range from less than 1,000 Å to more than 1 cm. The lattices of the grains are formed in random directions when they grow from the melt. A boundary is formed where the grains grow into contact, because the atoms in one grain's crystal lattice are not in position to mesh with the repeating atoms in the crystal lattices of adjacent grains.

These **grain boundaries** are layers several atoms thick that are distorted from normal atomic positions in order to bridge the mismatch in the lattice orientations of adjacent grains. Only metals with simple body-centered or face-centered cubic unit cells have enough densely packed planes of atoms in their lattices to allow plastic deformation at **yield stress**. These lattice types permit shearing of the densely packed planes of atoms like cards of a microscopic deck sliding over each other. However, the lattice of adjacent grain can be viewed as a second microscopic card deck at a different angle. To get the metal to deform, it is necessary to force the cards of one deck into other decks at an angle. But the more grains per unit volume, the more difficult it is to get the planes (cards) to slide because the dislocated slipping planes run against the grain boundaries sooner. Thus, a greater resistance to slippage is created by more grain boundaries, and higher yield stress results.

On the other hand, a material will fracture because a crack opens up on a grain boundary. This is more likely to occur in large-grain metals, when the planes cannot be slipped into the adjacent grains. Many smaller grains in various orientations can divide the plastic strain among the grains more easily, with more of them oriented for slipping. Large grains must each accommodate a larger strain and will have fewer properly oriented to slip. The result is lower ductility and lower ultimate strength for large-grain metals, which open cracks more readily at grain boundaries because the plastic deformation cannot be accommodated. For these reasons, grain-refined or "micro-grain" alloys produced by heterogeneous nucleation are advantageous for developing fixed partial denture alloys with higher yield stress, better ductility, and improved ultimate strength.

### **Alloy Systems**

Most pure metals are miscible in the liquid state when melted together. When two metals form a solution in the liquid state so their atoms mix randomly on the atomic scale, they are said to form an **alloy**. As the alloy liquid freezes, the atoms may remain randomly distributed on the unit-cell lattice sites in each crystal grain. This random distribution in the solid alloy is called a **solid solution**. But, if like atoms tend to prefer to bond among themselves, then as the nuclei form from the melt, the atoms of different elements may segregate in different grains. The grains of the two different metal elements are mixed together. Different grains may

be practically pure if their elements are insoluble in each other's lattices in the solid state. Or they can have a limited solubility in the other's crystal lattice if the elements exhibit partial solubility in one another.

Metal atoms of two different metal elements are more likely to be soluble in each other's lattices if they (1) have the same atomic lattice type, (2) have similar atomic radii (i.e., a difference of less than 10%), (3) have the same valence number, and (4) form bonds to other atoms with strengths similar to those they form among themselves. On the other hand, if these rules are not followed and the unlike atoms have a strong affinity to each other; grains of an **intermetallic compound** may be formed at definite ratios of the alloying elements (e.g., dental amalgam alloy Ag<sub>3</sub>Sn). The energetically stable (i.e., at equilibrium) crystal lattice structures and their compositions for an alloy that is preferred by "nature" varies with temperature and ratio of the alloying elements that are melted together.

It is not possible to calculate the equilibrium composition and structures and at what temperatures these change. They must be determined experimentally by measuring the temperatures at which the latent heat is liberated when alloy liquid solidifies or solid lattices transform to different crystal lattices. The type of crystal lattice is determined by x-ray diffraction from the crystal atomic planes. The angle and intensity of the x-ray beam reflections (i.e., diffraction) are characteristic of the atomic composition, type of crystal lattice, and position of atoms in their unit cell. Thus, experimental detection of the temperature when heat is liberated indicates when an alloy is changing its structure, and x-ray scattering identifies what lattices are present. This information is portrayed in a **binary phase diagram** of the alloy system. The alloy system represents all possible ratios of the elements.

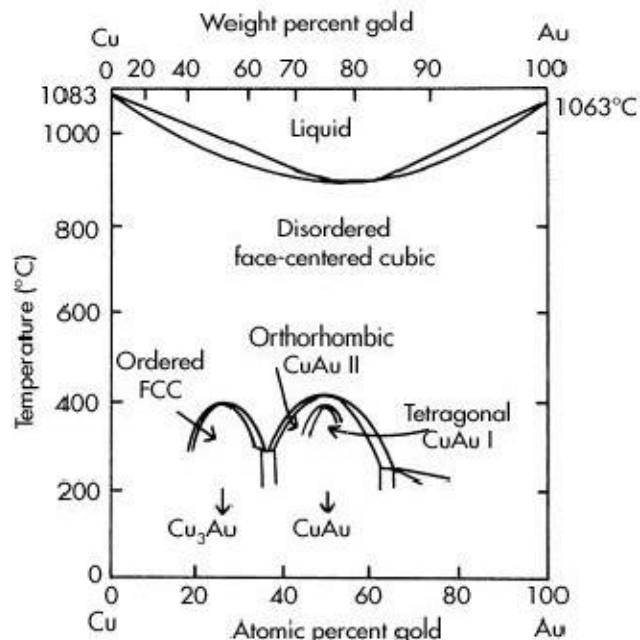
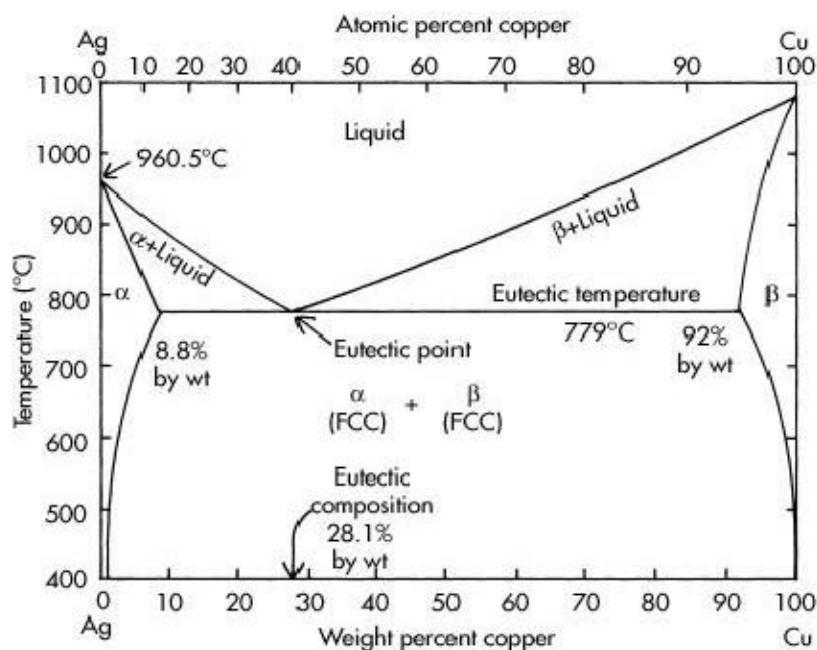


Fig 7 Copper-gold phase diagram. The disordered solid solution (softer) and ordered solid solutions (harder) are produced by heat treatment. FCC = face-centered cubic.

When two elements are alloyed, the system is called a **binary alloy**; when three elements are alloyed, the system is a **ternary alloy**, and so on. An alloy is named by listing its elements in descending order of percent composition. For example, Ag<sub>3</sub>Sn is called silver-tin alloy. If more than two elements are involved, the number of phase changes and their representation becomes complex, but their description follows the same principle.



*Fig 8 Silver-copper phase diagram showing a eutectic (lowest melting) point at 28.1% copper.*

An equilibrium phase is defined as a homogeneous body of matter that is physically distinct and mechanically distinguishable. For a pure material like water, the vapor, liquid, and solid phases are physically distinct because there is a definite boundary between the regions when they exist together. Also, they are mechanically distinguishable in properties like hardness, compressibility, and elastic modulus. However, when the phase definition is applied to an alloy system, it is important to recognize that if two different types of unit cells nucleate from the melt as, for example, at the **eutectic** (lowest melting) point in a two-phase region is formed. The two phases nucleate as separate grains. They are physically distinct, as indicated by grain boundaries that define their limits. Their mechanical properties differ, as can be measured by a micro-hardness tester impinging on individual grains. Note that two-phase alloys are not as corrosion resistant as like single-phase alloys, because microscopic galvanic corrosion cells are set up between the grains of the different phases. Also, porcelain bonding to multiphase alloys is considered potentially weaker because of composition differences of the grains.

### **Deformation in Metals**

There are three types of deformation that can occur in metals, which arise from different mechanisms. The simplest deformation, elastic strain, is the elastic stretching of lattice in which all the atoms are shifted from their equilibrium positions by a fraction of their atomic spacing. The strain is directly proportional to the applied stress (i.e., force/area or force intensity) up to the proportional limit stress. When the stress is removed, the atoms return to equilibrium atomic spacing. Compared with most polymeric materials, metals generally have strong metallic bonds and resist elastic stretching. This stiffness or resistance to elastic strain is indicated by the high elastic modulus of metals. Stiffness is desirable for removable partial dentures, so forces can be transmitted by the framework across an arch to better distribute the load.

It is desirable for the alloy of resin-bonded fixed partial dentures to resist flexing of the bond. Another type of deformation is plastic deformation, a permanent deformation that begins when the elastic limit stress or its approximation, yield stress, is reached. This mode of deformation requires that atoms be shifted to new atomic sites on the lattice. These lattice sites must be identical to the old sites and not far away, so the energy to shift atoms is not too great. Thus, ductility is associated with face-centered and body centered cubic metal lattices, which have more identical sites and more closely packed planes, so atoms do not have to slide far to reach the new lattice sites. Intermetallic compounds are usually brittle because the atomic sites are specific to the different atoms of the compound and not interchangeable. The mechanism of plastic deformation is called **dislocation motion** and produces the slipping of the closely packed planes over each other. A **dislocation** is the line of atoms that denotes the edge of an additional half-plane of atoms that appears to be wedged into the lattice. The lattice is distorted (strained) by the presence of the dislocation line of atoms.

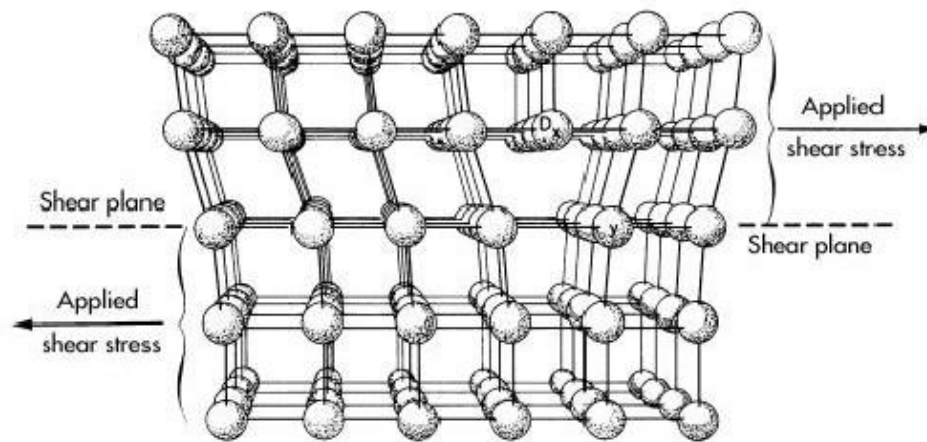


Fig. 9 The distortion (strain) around a dislocation in a simple cubic crystal lattice. The size of the atoms has been reduced so the perspective can be seen. The row of atoms of the dislocation is Dx. (From Ziman, 1967. Reprinted from Scientific American.)

Dislocation motion shifts atoms from one lattice site to the next, rather than moving all the atoms of the plane at one time, which would take much more energy.

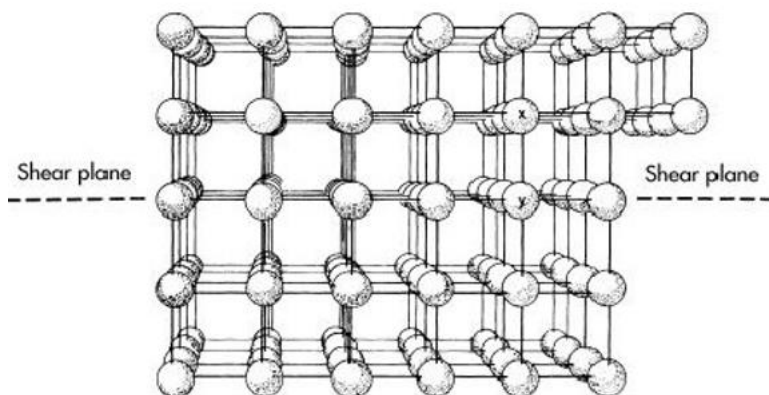


Fig. 10 The crystal lattice as it would appear after the yield stress has been exceeded and the dislocation has moved through the lattice. The solid has been deformed to this new shape. (From Ziman, 1967. Reprinted from Scientific American.)

It is important to understand that any process that impedes dislocation movement tends to harden a metal, raise its yield stress and often lower its ductility. Some processes are reversible, allowing the hardness to be low when making an appliance, for example, after which the metal can be hardened to provide better service if necessary. One process for **hardening** metal is called **cold working**, or work hardening –any plastic deformation of metal by hammering, drawing, cold forging, cold rolling, or bending. These processes produce many dislocations in the metal that cannot slip through each other as easily as the lattice becomes more distorted. The yield stress can be raised more than 100% when a drawn orthodontic wire is compared to the cast metal. In dentistry, cold working occurs when gold foil is compacted, a denture clasp is bent, an

inlay margin is burnished, or a deformed metal layer forms on a crown during finishing and polishing.

A second process for hardening a metal is precipitation hardening. In this process a second phase of finely dispersed clusters of atoms are precipitated from a meta stable supersaturated solid solution by reheating an alloy that was quench-cooled to form the meta stable supersaturated solid. Heat treatment can also be used to harden gold-copper alloys by a slightly different process. In this case, because the gold-copper system forms a complete solid solution at all compositions, the atoms can be interchanged on the lattice sites. However, as the atoms are cooled, the copper and gold atoms tend to separate on alternating planes of the lattice in ordered arrangement. This ordering makes dislocation motion more difficult, raising the yield stress. These alloys are soft if quenched but hard if cooled slowly on the bench top or held in the furnace at the ordering temperature range (350 °C for 30 minutes).

Other heat treatments are used to homogenize the grains of an alloy that have developed composition gradients by rapid cooling and **crystallization** of the melt. When cooled rapidly, the grains of the alloy cannot maintain an equilibrium or uniform composition in the grain. The first part of the grain to cool will be richer than the average composition of the higher-melting-temperature element, and the last part of the grain to solidify is richer in the low-melting alloy component. This inhomogeneity tends to reduce corrosion resistance of the metal because of the galvanic cell created between the center of the grain and the grain boundary. Heating the solid at a temperature and for a duration that allows the atoms to reach equilibrium will improve corrosion resistance.

### **Diffusion In Metals**

Atoms of a crystalline solid vibrate about their fixed lattice positions. As they absorb heat with increasing temperature, they vibrate at greater amplitude. Also, a small fraction of the atom sites are vacant in a metal. As the temperature increases, an atom may momentarily experience an increase in vibration energy, which will be sufficient to permit it to jump from one lattice site to another. As the temperature and time increase, more atoms will be able to jump or diffuse to new lattice sites. This random jumping during heat treatment allows the rearrangement of the crystal lattice.

Atomic diffusion also permits rearrangement of cold-worked metals and permanent deformation of metals at stress levels far below the yield stress if the stress lasts long enough. In general, these rearrangements by diffusion begin to occur at a significant rate as the temperature of metal exceeds one half of its absolute melting temperature. The rate of rearrangement accelerates rapidly as the metal or alloy approaches its solidus temperature.

There are several heat treatment processes for metals that utilize diffusion among these is an **annealing** heat treatment for release of **residual stress**. It allows the dislocations and atomic vacancies to move and realign to lower the internal residual stress fields in a cold-worked metal at a relatively low temperature and short heating time. If the temperature and heating times are extended for a cold-worked metal, the metal can experience **recrystallization**, in which stress-free grains are crystallized out of the deformed grains. A recrystallization temperature is the temperature at which it would take 1 hour for the cold-worked metal to recrystallize. This temperature is between one third and one half of the absolute melting temperature for most metals. As the temperature and time are further extended, **grain growth** occurs, during which the stress-free grains grow larger at the expense of the disappearing small grains.

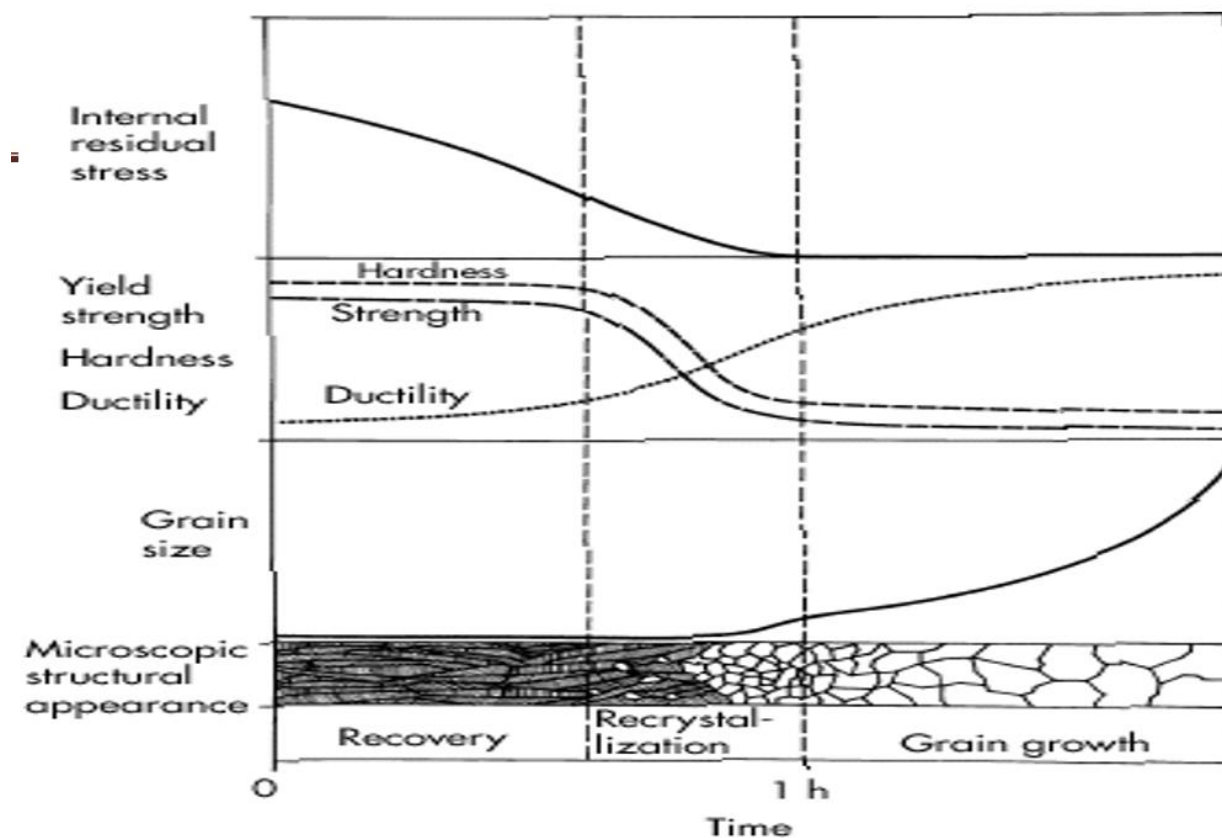
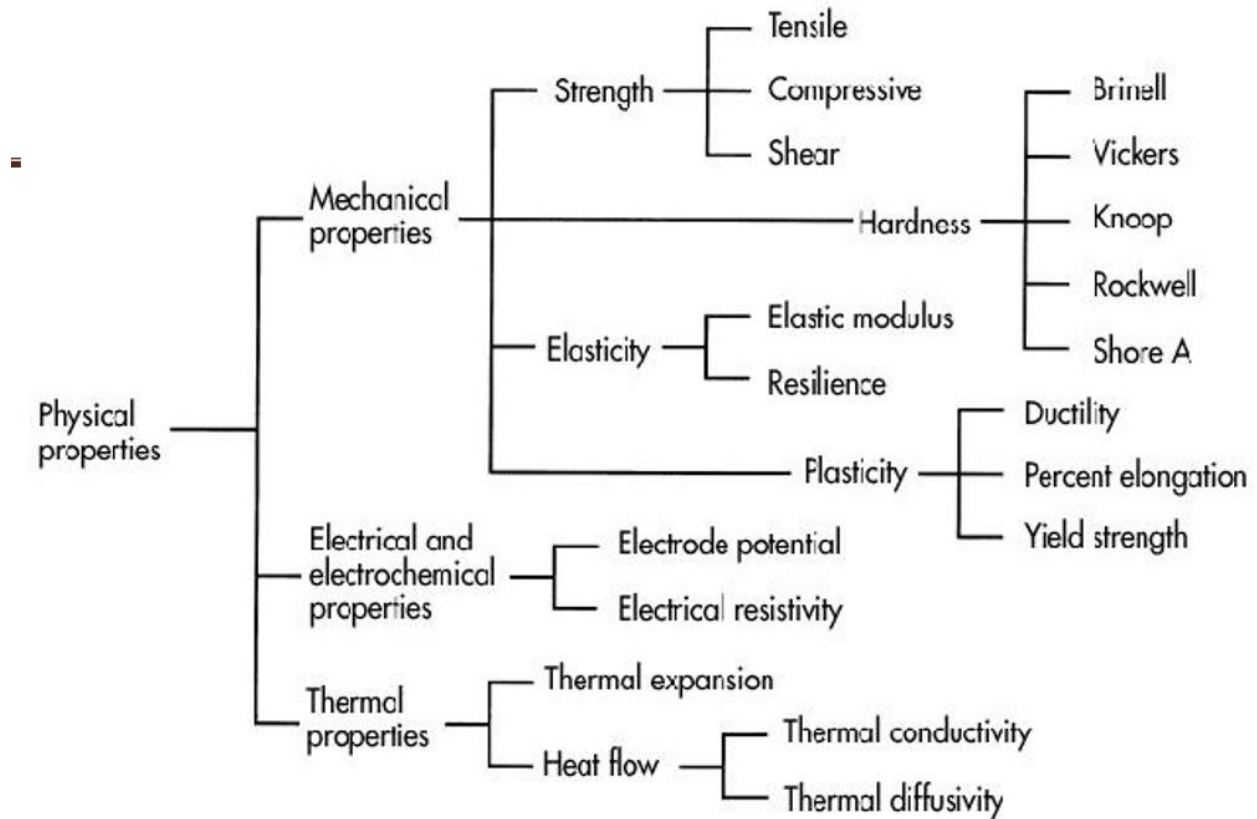


fig 11 A microscopic view of the stages that a cold-worked metal, such as an orthodontic wire, goes through when subjected to prolonged heating. The higher the temperature and the greater the cold working, the more quickly the transitions occur. This figure shows recrystallization being completed in 1 hour, which means the temperature of heating was the recrystallization temperature as per the definition. The changes in properties can be compared with the structural changes. (From Jastrzebski, 1959. Reprinted with permission.)

The residual stress heat treatment relaxes the internal stress, which may cause warpage over time. The chance of corrosion related to residual stress differences on the metal surface are reduced. Recrystallization heat treatment lowers the yield stress and increases the ductility. Grain growth further reduces yield stress and increases ductility. When soldering a cold-worked wire in which a high yield stress is desired (e.g., a partial denture wire clasp or an orthodontic appliance), a low-melting solder and a short soldering time are desirable to minimize recrystallization and grain growth.

## PHYSICAL PROPERTIES OF METALS<sup>10</sup>





### STRESS

Stress is the force ( $F$ ) divided by the cross-sectional area ( $A$ ):

$$\alpha = F/A$$

where  $\alpha$  is the stress  $F$  is the force and  $A$  is the cross sectional area. The basic types of stresses produced in dental structures under a force are **tensile**, **compressive**, and **shear**. All three are present in a beam loaded in the center. If the value of these stresses exceeds the strength of the material, the structure will fail. It is therefore important to know the strength values of materials.

It is rare that an object will be subject to the pure tensile, compressive, or shear stresses experienced by test specimens in a materials testing laboratory.

### STRAIN

When a block of material is subjected to a tensile stress as described in the preceding section, it temporarily becomes longer by a certain amount. This temporary increase in length is called **strain**.

### ELASTICITY

Both stress and strain are directly proportional to the load applied when the cross-sectional area is kept the same. Hence, if the load is doubled, both the stress and the strain likewise will be doubled. It can be seen that the ratio between stress and strain is the same, thus:

$$\alpha/\varepsilon = 2\alpha/2\varepsilon = 3\alpha/3\varepsilon, \text{ where } \alpha \text{ is the stress and } \varepsilon \text{ is the strain}$$

The property of having a constant ratio of stress to strain is called **elasticity**, and the constant that is the ratio of stress to strain is called the **modulus of elasticity**.

The highest stress at which stress is proportional to strain is called the elastic limit, or the **proportional limit**. Because this stress is difficult to determine precisely, as it would entail looking for an infinitely small deviation from proportionality, it is customary to designate a certain permanent deformation or offset (usually 0.002, or 0.2%) and to report the **yield strength** of the material at this strain. Thus the terms "elastic limit" and "proportional limit" are synonymous, whereas "yield strength" has a slightly different meaning. The yield strength of a material is always slightly higher than the elastic limit.

If a material continues to have more and more weight applied to it, it will of course eventually break. If the material is being stretched (tensile loading), the stress at breakage is called the **ultimate tensile strength** (UTS). When many metals are stressed above their proportional limits, they undergo a process called **work hardening**, and actually become stronger and harder. But with the increased strength provided by work hardening comes increased brittleness. It is thus very important to avoid overdoing it when bending a wire or a partial denture clasp—too much bending of the metal back and forth will make it harder and more brittle.

## PLASTICITY

When the elastic or proportional limit is exceeded in a material, it is said to exhibit plastic behavior. (The term "plastic" means "moldable," but the term has come to be associated with polymers.) Materials that experience a large amount of plastic behavior or permanent deformation are said to be **ductile**. Materials that undergo little or no plastic behavior are said to be **brittle**.

The highest stress achieved during this process is called the ultimate tensile strength of the material. The total strain at fracture (elastic strain + plastic strain) is called the **elongation**. Elongation of metals is important in several situations in dentistry. When one is burnishing the margin of a crown, the property that most comes into play is the elongation, although the yield strength is also important. For example, gold alloys are generally easy to burnish because they have lower yield strength. Nickel-chromium and cobalt-chromium alloys may have adequate elongation for burnishing, but their yield strengths are so high that they make burnishing difficult. Another example of the importance of elongation is the bending of a partial denture clasp to adjust the retention.

The entire area under the stress-strain curve is a measure of the energy required to fracture the material, or its **toughness**. The area under only the elastic region of the stress strain curve is a measure of the ability of the material to store elastic energy (the way a compressed spring does). This is called the **resilience** of the material.

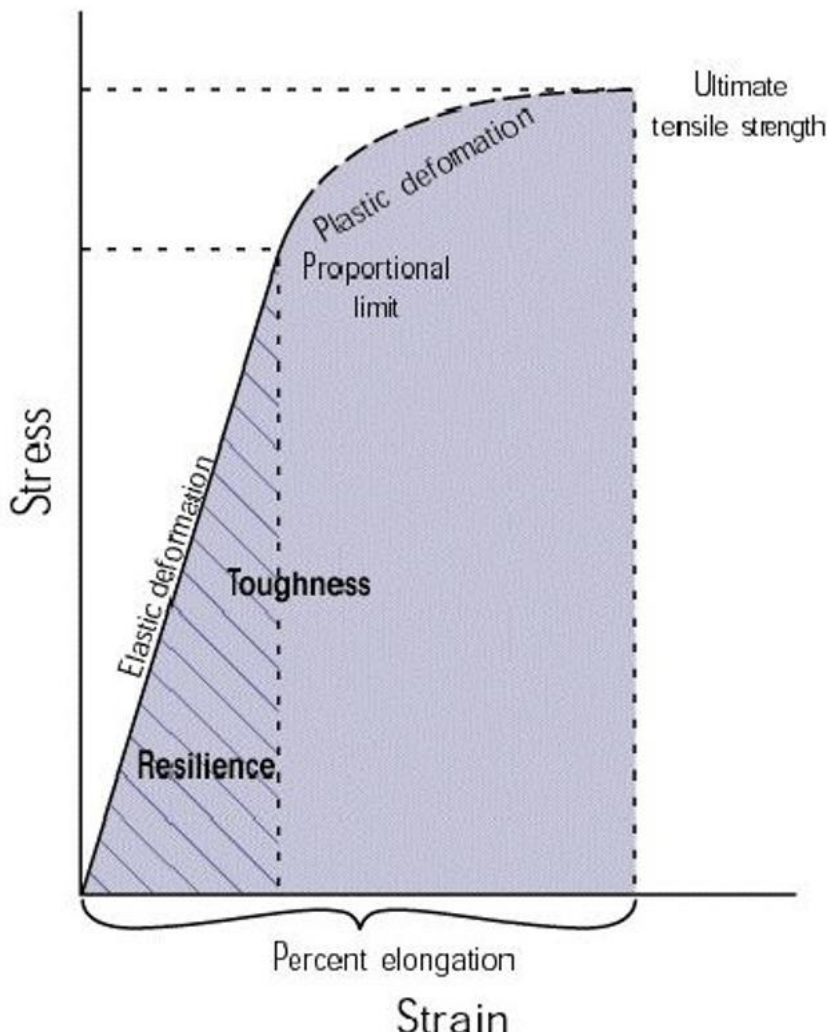


Fig 12 stress – strain curve showing deformation of metals

### FATIGUE

When materials are subjected to cycles of loading and unloading, as during mastication, they may fail due to **fatigue** at stresses below the ultimate tensile strength. Usually, small cracks at the surface or within the material gradually grow larger upon cycling, and eventually the material fails.

### VISCOUS FLOW

Many dental materials are in a fluid state when they are formed, and **viscous** flow phenomena are important considerations. Our understanding of the behavior of impression materials and amalgam involve **viscoelastic** phenomena. When shear stress strain rate (flow rate) plots are obtained, they enable viscous materials to be classified in several ways. A Newtonian fluid shows a constant viscosity, which is independent of strain rate:

$$\eta = \alpha / \dot{\epsilon}$$

where  $\eta$  is the viscosity in poise,  $\alpha$  is the shear stress acting on the fluid, and  $\dot{\epsilon}$  is the strain, or flow rate.

Actual fluids differ from these in their flow responses to the level of stress applied. Plastic fluids (e.g., putty) don't flow at all until a minimum stress is applied. Pseudo plastic fluids (e.g.,

fluoride gels) show an instantaneous decrease in apparent viscosity or consistency (become more free-flowing) with increasing shear rate. Dilatant fluids (e.g., fluid denture base resins) show an increase in rigidity as more pressure is applied. Thixotropic fluids (e.g., fluoride gels, house paints) flow more freely when vibrated, shaken, or stirred than if allowed to sit undisturbed. Formulation of the various suspensions and gels used in dentistry to impart one or more of these properties can make them easier to handle. For example, impression materials that do not run off impression trays but are less viscous under pressure in a syringe have a definite advantage.

## HARDNESS

The resistance of a material to indentation or penetration is called **hardness**. The technical definition of hardness varies little, if at all, from the familiar definition, with the possible exception that the technical definition carries with it the connotation of a method of measurement. Most of the methods for measuring hardness consist of making a dent in the surface of a material with a specified force in a controlled and reproducible manner and measuring the size of the dent.

### 1. BRINELL HARDNESS NUMBER (BHN)

The indenter for the Brinell hardness test is a small, hardened steel ball, which is forced into the surface of a material under a specified load. This indentation process leaves a round dent in the material, and hardness is determined by measuring the diameter of the dent.

### 2. VICKERS HARDNESS NUMBER (VHN) OR DIAMOND PYRAMID HARDNESS (DPH)

The Vickers hardness indenter is a square, pyramid-shaped diamond, which leaves a square, diamond-shaped indentation in the surface of the material being tested. Hardness is determined by measuring the diagonals of the square and taking the average of the two dimensions. The Vickers hardness test is also called the diamond pyramid hardness test. The Brinell and Vickers hardness tests are both used to measure the hardness of dental alloys, and hardness values on alloy packages are expressed in either Vickers or Brinell hardness numbers. To compare Vickers and Brinell numbers, use the following relationship:

$$\text{VHN} = 1.05 \times \text{BHN}$$

where VHN is the Vickers hardness number and BHN is Brinell hardness number.

### 3. KNOOP HARDNESS (KHN)

The indenter for the Knoop hardness test is also made of a diamond, but its outline is somewhat different from the Vickers indenter; although it is diamond shaped, one diagonal is much longer than the other. Only the long diagonal is measured to determine the Knoop hardness number. The Rockwell hardness test is used primarily for determining the hardness of steels and is the most widely used hardness test in the United States. The Vickers, Brinell, and Knoop hardness tests are more commonly used for dental materials, however. Rockwell uses different hardened steel balls or diamond cones and different loads. Each combination forms a specific Rockwell scale (A, B, and C scales are the most common). The different scales are used for materials of different hardness ranges.

### 4. SHORE A DUROMETER

The Shore A hardness test is used to measure the hardness of rubbers and soft plastics. The Shore

- A scale is between 0 and 100 units, with complete penetration of the material by the indenter

yielding a value of 0, and no penetration yielding a value of 100.

## ELECTRICAL AND ELECTROCHEMICAL PROPERTIES

### ELECTRODE POTENTIALS

An electrochemical series is a listing of elements according to their tendency to gain or lose electrons in solution. The series is referenced versus the potential of a standard hydrogen electrode, which is arbitrarily assigned a value of 0.000 volts. If the elements are listed according to the tendency of their atoms to lose electrons, the potentials are termed oxidation potentials. If they are listed according to the tendency of their ions to gain electrons, the potentials are termed reduction potentials. Reduction potentials at 25<sup>0</sup>C and 1 atmosphere of pressure are termed standard electrode potentials.

Standard electrode potentials

Half-reaction	E <sup>0</sup> (volts)
$\text{Li}^+ + e = \text{Li}$	-3.04
$\text{K}^+ + e = \text{K}$	-2.93
$\text{Ca}^{2+} + 2e = \text{Ca}$	-2.87
$\text{Na}^+ + e = \text{Na}$	-2.71
$\text{Mg}^{2+} + 2e = \text{Mg}$	-2.37

$\text{Al}^{3+} + 3e = \text{Al}$	-1.662
$\text{Zn}^{2+} + 2e = \text{Zn}$	-0.762
$\text{Cr}^{3+} + 3e = \text{Cr}$	-0.744
$\text{Fe}^{2+} + 2e = \text{Fe}$	-0.447
$\text{Ni}^{2+} + 2e = \text{Ni}$	-0.257
$\text{Sn}^{2+} + 2e = \text{Sn}$	-0.1375
$\text{Pb}^{2+} + 2e = \text{Pb}$	-0.1262
$\text{Fe}^{3+} + 3e = \text{Fe}$	-0.037
$\text{H}^+ + e = \text{H}$	0.000 (reference)

$\text{Cu}^{2+} + 2e = \text{Cu}$	+0.342
$\text{Cu}^{+} + e = \text{Cu}$	+0.521
$\text{Ag}^{+} + e = \text{Ag}$	+0.800
$\text{Hg}^{2+} + 2e = \text{Hg}$	+0.851
$\text{Pt}^{2+} + 2e = \text{Pt}$	+1.118
$\text{Au}^{+} + e = \text{Au}$	+1.692

Metals with a large positive electrode potential, such as platinum and gold, are more resistant to oxidation and corrosion in the oral cavity. If there is a large difference between the electrode potentials of two metals in contact with the same solution, such as between gold and aluminum, an electrolytic cell may develop. If this occurs in the mouth, the patient may experience discomfort. The exact nature of tarnish and corrosion of restorative materials *in vivo* is extremely complex and involves much more than electrode potentials of materials. A possible source of the corrosion of gold alloys is accidental contamination of the surface with copper during pickling, and subsequent tarnishing in saliva

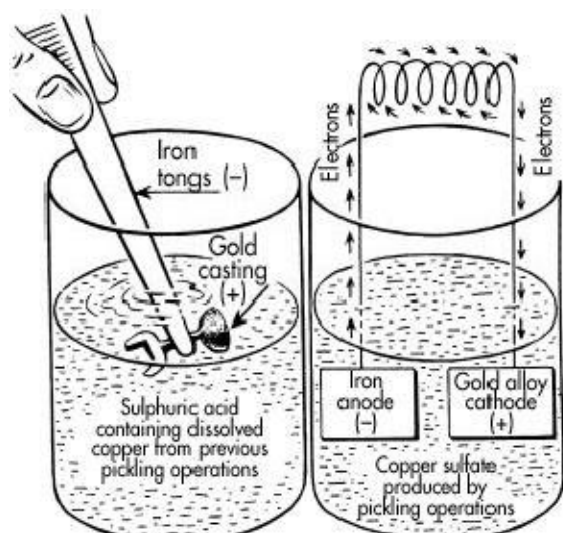


Fig 13 Accidental plating of copper during pickling of gold casting. The model of the cell is formed by iron tongs and gold alloy (right). (From O'Brien, 1962. Reprinted with permission.)

## ELECTRICAL RESISTIVITY

**Electrical resistivity** measures the resistance of a material to the flow of an electrical current. The relationship between the resistance ( $R$ ) in ohms, the resistivity ( $\rho$ ), the length ( $l$ ), and the

cross-sectional area (A) is as follows:

$$R = \rho (l / A)$$

where R is the resistance,  $\rho$  is the resistivity, l is the length and A is the cross-sectional area.

Electrical resistivity of several materials

Material.	Resistivity (ohm-cm)
Copper	$1.7 \times 10^{-6}$
SiO <sub>2</sub> (glass)	$> 10^{14}$
Human enamel	$\sim 4 \times 10^6$
Human dentin	$\sim 3 \times 10^4$
Zinc phosphate	$2 \times 10^5$
Zinc oxide-eugenol	$5 \times 10^9$

The low resistivity of metallic restorative materials is responsible for discomfort to the pulp if dissimilar metals generate a voltage. The insulating properties of cements help to reduce this problem.

## THERMAL PROPERTIES

### Heat flow through a material

Metals tend to be good conductors of heat, and this property must be taken into consideration when placing metallic restorations. Dentin is a thermal insulator (poor conductor of heat); thus, when a sufficient thickness of dentin is present, the patient feels no sensitivity to heat and cold through a metallic restoration. However, when only a thin layer of dentin remains, some thermal protection must be provided for the pulp. A good rule of thumb in determining the thickness of cement base necessary in a given situation is to visualize how much dentin would have to be present in the excavation site so no base would be necessary and then to apply base up to this level. The rate at which heat flows through a material is expressed as **thermal conductivity** or **thermal diffusivity**. The difference between these two terms is described in the following subsections.

### Thermal conductivity

Thermal conductivity ( $k$ ) is a measure of the speed at which heat travels (in calories per second) through a given thickness of material (1 cm), when one side of the material is maintained at a constant temperature that is  $1^{\circ}\text{C}$  higher than the other side. Thermal conductivity is expressed in units of  $\text{cal/cm} \cdot \text{sec} \cdot ^{\circ}\text{C}$ .

### Thermal diffusivity

Whereas thermal conductivity gives an idea of the relative rates at which heat flows through various materials, it fails to take into account the fact that various materials require different amounts of heat (calories) to raise their temperatures an equal amount.

For example, 1 gram of water requires 1.000 calorie to raise its temperature  $1^{\circ}\text{C}$ , whereas 1

gram of dentin requires only 0.28 calorie, and 1 gram of gold requires only 0.031 calorie to produce a 1<sup>0</sup>C temperature increase. Thus, thermal conductivity alone will not tell us, for instance, how rapidly the interior surface under a crown will heat up when the exterior surface is heated. To know how quickly the interior of the crown will approach the temperature of the exterior, we need to know the thermal diffusivity of the alloy. The thermal diffusivity ( $h$ ) of a material (expressed in units of mm<sup>2</sup>/sec) is dependent on its thermal conductivity, heat capacity ( $C_p$ ), and density:

$$h = k / (C_p \times \rho)$$

where  $h$  is the thermal diffusivity  $k$  is the thermal conductivity  $C_p$  is the heat capacity and  $\rho$  is the resistivity

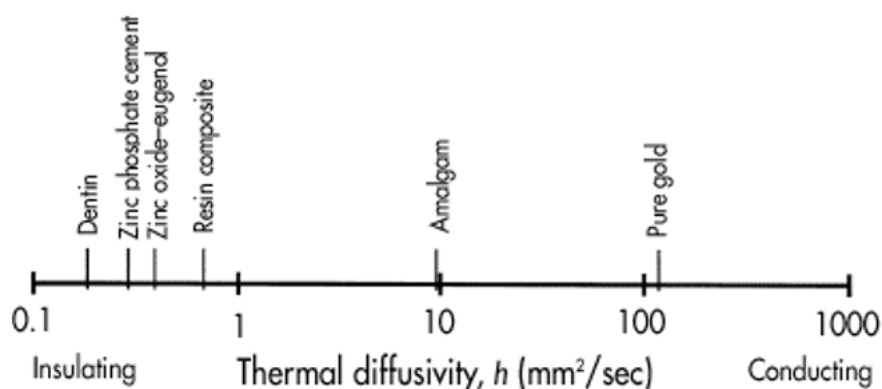


Fig 14 Thermal diffusivities of restorative materials

#### Thermal expansion

There are several situations in dentistry in which the thermal expansion of materials is important. Some restorative materials have coefficients of thermal expansion that are markedly different from tooth structure. In such cases, temperature fluctuations that occur in the mouth can cause **percolation** at the tooth-restoration interface as the restoration contracts and expands. The porcelain and metal in a porcelain-fused-to-metal (PFM) restoration must contract at the same rate upon cooling from the porcelain firing temperature if the buildup of large residual stresses is to be avoided. The cooling of a denture base from the processing temperature to room temperature is primarily responsible for the processing shrinkage that occurs. The thermal expansion behavior of dental wax, gold alloy, investment, and so on is all important in producing properly fitting castings.



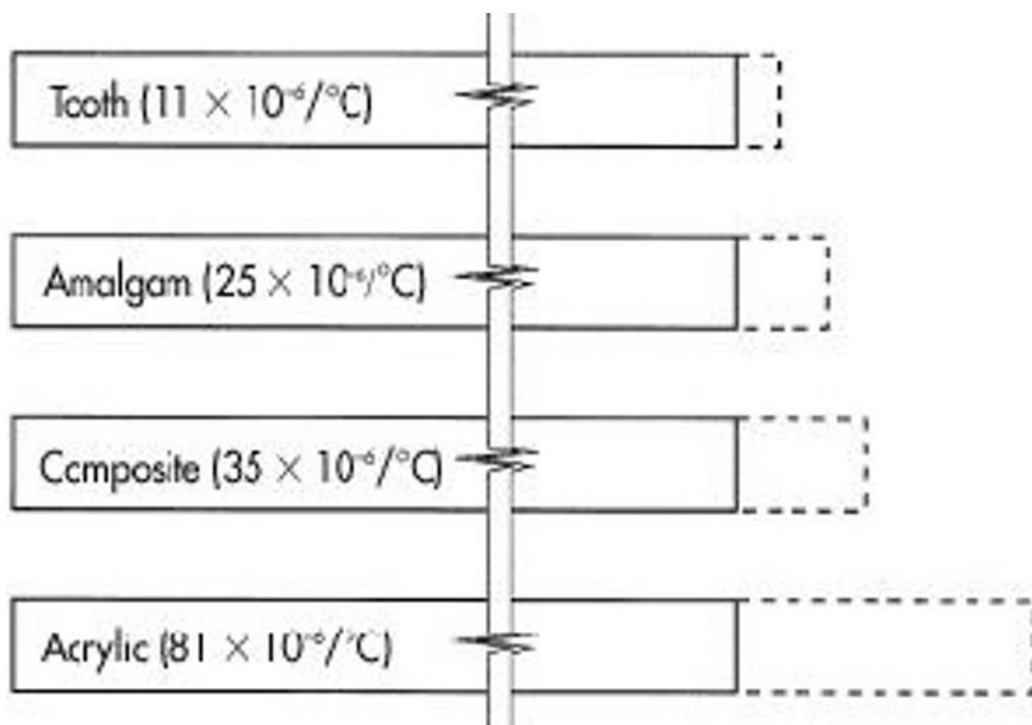


Fig 15 Relative thermal expansions of several restorative materials and tooth structure. The relative amounts the materials expand when heated the same amount are represented by the dashed lines. The amount of expansion is magnified to make it visible for comparison of the materials.

## TARNISH AND CORROSION BEHAVIOUR OF DENTAL GOLD ALLOYS

### Tarnish

Tarnish is defined as a surface discoloration or decrease in luster of an alloy restoration which may be due to the formation of a surface product. Long term alloy immersion in a solution which simulates mouth conditions provides the surest *in vitro* procedure to predict clinical behavior of the alloy. However, accelerated immersion tests are preferred by alloy developers and by investigators for testing compliance with specifications, but such tests must be proven to predict long term and ultimately, clinical behavior. Several synthetic saliva solutions, as well as aggressive solutions have been used in attempts to identify in accelerated tests the conditions under which an alloy tarnishes. Since chlorides are present in saliva and certain foods such as fish and eggs have high sulphur content, both chloride and sulphide solutions are commonly chosen as immersion test media.

Dental alloys have thus been subjected to immersion tests in various sulphide, chloride, and artificial saliva solutions. Tarnishing occurs primarily in sulphide solutions and the tarnish has been identified as a sulphide of silver. Ranking of alloys in terms of susceptibility to such tarnishing has been recorded both subjectively, by comparing color changes visually with a pre-established scale of color variation, and quantitatively, using a colorimeter or spectrophotometer.

## Corrosion

Corrosion involves a reaction between a material and its environment, resulting in the deterioration of the former. Dental alloys which are placed in the oral environment may be affected by electrochemical corrosion processes. Thus, *in vitro* corrosion behavior can be predicted from results of electrochemical testing. Potentiodynamic anodic polarization is an electrochemical technique which characterizes corrosion behavior and for low gold content alloys it has been successfully applied to relating resistance to corrosion with composition. In this technique, specimens are scanned through a range of applied potentials, and the current output which is proportional to the extent of corrosion is monitored. During forward scanning in the anodic direction, the samples are oxidized; during reverse scanning, they are reduced.<sup>9</sup>

The current-potential relationship for low gold content alloys has been found to exhibit hysteresis when samples are successively polarized from  $-200$  to  $+400$  mV during forward scanning and from  $+400$  to  $-200$  mV during reverse scanning in a 1 per cent sodium chloride solution as the electrolyte. Although the alloys tested differed in noble metal contents, their corrosion potentials (where the current reverses polarity) and magnitude of current density at any potential, did not differ significantly during forward scanning, that is, their corrosion behavior was indistinguishable. Also, their breakdown potentials (zero current potential during reverse scanning) were similar. However, during reverse scanning, current density peaks were observed around 0 mV. These peaks were interpreted as being due to the reduction of silver, the major corrodible element in these alloys.

A minor contribution to corrosion, stemming from the presence of copper, was recorded. The relative magnitude of these current density peaks, which is proportional to the extent of corrosion, was used to rank the corrosion resistance of the alloys. As the gold + PGM content of dental alloys is decreased, the silver content is normally increased. Corrosion susceptibility, as determined by the relative current density peak magnitudes was found to correlate with the silver content of the alloys studied. Current density peaks of decreasing magnitude were recorded as alloys of decreasing silver content were tested.

A systematic study of binary, ternary and commercial dental gold alloys confirmed that the current density peak at 0 mV during reverse scanning is characteristic of gold alloys containing corrodible silver. Binary gold-silver alloys were studied by an electrochemical hysteresis technique similar to that described above. When the silver content of the alloys was decreased from 65 to 15 atomic per cent, the peak observed in the silver-rich alloys was totally suppressed. For binary gold-copper alloys, a current density peak which occurred at  $-125$  mV during forward scanning was attributed to the formation of cuprous chloride (CuCl). When gold-silver-copper ternary alloys were examined, current density peaks were found at potentials which indicated that both silver and copper were involved in the corrosion process. The corrosion behavior of commercial gold alloys having varying noble metal contents was characterized on the basis of current density peaks associated with reactions involving copper and silver. The extent to which a silver-rich second phase was present in these alloy had a secondary effect on their corrosion resistance.<sup>9</sup>

Corrosion in gold alloys occurs primarily in silver rich regions and secondarily in copper rich regions. galvanic microcells form on two phase alloys, where the more active phase corrodes

with respect to the noble matrix. Consequently, the microstructure of an alloy can have an added influence on its corrosion resistance. In a study to examine the effect of casting investment temperature on the microstructure and corrosion characteristics of low gold content dental alloys the rate of cooling was varied by using moulds at 700°C and 20°C. Even rapid cooling resulted in a two-phase structure, but with a fine grain size and a minor proportion of second phase. Potentiodynamic polarization measurements were made on the resulting castings. The magnitudes of the current density peaks, corresponding to copper and silver corrosion processes, were greater for alloys cast into investment at a higher temperature. Therefore, such alloys corroded to a greater extent. These results are indicative of the importance of the microstructure for the corrosion behavior of an alloy, especially of the detrimental effects of large grain size and of a coarse second phase.<sup>9</sup>

### **BIOCOMPATIBILITY – DEFINITION, TESTING AND STANDARDS**<sup>8</sup>

Besides functional performance and aesthetics, biocompatibility is a third important requirement for dental restorative materials. Where dental restorations are based on the use of different alloys, there is the obvious potential for oral polymetallism. Indeed, two alloys of different composition have different electrochemical potentials, and inevitably induce corrosion, with the subsequent release of metal ions into the tissue. The ion release from metallic prostheses and implants is the main cause of any unwanted primary and secondary reactions in the human body. This phenomenon may lead to the deterioration of dental devices, and in the worst case, may cause prosthesis failure or fracture. For several years, research teams have been attempting to find a correlation between the corrosion behavior 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 response have not yet been clearly established.

Different ions are released at different rates from the alloy: gold, indium and palladium do not dissolve in commonly used cell culture media, whereas silver, copper, gallium, nickel and zinc are dissolved after a defined period under identical experimental conditions. However, gold and platinum show no dissolution in artificial saliva, but other ions especially indium, copper, zinc, gallium, cobalt, and nickel, are detected. The dissolution behavior of alloys can be different under other experimental conditions and it is generally recognized that the nature, rather than the quantity of released corrosion products, is important for cytocompatibility.

To predict the biocompatible properties of a material, it is necessary to obtain information about dissolution behavior, cytotoxicity and, with regard to metals and alloys in the mouth, data about electrochemical potentials. A large number of tests have been developed with this aim in mind and elements of them are defined in standards which must be met in order to conform to the EU Directive 93/42/EEG. Historically, immersion tests have been commonly used to detect the release of metal ions in a solution of artificial saliva. This in vitro test is intended to simulate the type of corrosion occurring in the human mouth. The artificial saliva consists of deionized water containing lactic acid and sodium chloride with a pH of 2.3.

Cast specimens of the alloy to be tested are suspended in glass containers with the artificial saliva. After 7 days the solutions are analyzed for all elements originally contained in the alloy. Discoloration on oral metallic restorations can occur either from inhomogeneous alloys, surface porosities or if different alloys with different electrochemical potentials are joined together.

Less noble alloys work as an anode whereas higher noble alloys are cathodes with the saliva as electrolyte. For instance, the cathode deposit of copper and silver discolors the higher noble alloy as a result of copper and silver sulfide formation.

The immersion test is the mostly commonly used of all standardized and recommended test methods. A total release of metal ions during the 7 days storage in the corrosion medium should not exceed 100  $\mu\text{g}/\text{cm}^2$ , although this limit is not obligatory. It can be seen that high gold alloys show a moderate ion release, except for a palladium-free alloy with a very high release of zinc ions. Research suggests that palladium seems to be necessary in gold alloys in order to prevent corrosion of base metals. This is confirmed by the relatively low ion release from palladium and silver/palladium based alloys.

Generally it is found that copper, zinc and indium ions are passing into solution. High gold alloys have been studied in order to find an alloy resistant to corrosion and it has been found that there are alloys containing 92-93% of gold, 3- 4% of palladium and additional quantities of platinum, silver and tin that has a total ion release of less than 0.1  $\mu\text{g}/\text{cm}^2$  after seven days. In terms of base metal alloys, large differences in metal ion release have been observed. While pure titanium and beryllium-free nickel base alloys show very acceptable results, a considerable release of cobalt ions from cobalt-base alloys is found.

Extremely high corrosion occurs in beryllium containing nickel-based alloys, and much more in copper based alloys, which can never be recommended for use in the oral environment. Discoloration of a dental alloy is not only due to an electrochemical reaction. It can be caused by a chemical reaction on the surface of the alloy, if a surplus of metals reacting with sulphur and oxygen, e.g. silver and copper are present. Discoloration is only minimized if the total quantity of gold and PGM's present in the alloy exceeds 60%.

Metals and alloys in the human mouth possess electrochemical potentials in saliva. Electrochemical tests are carried out by measuring the electrochemical potential of an alloy against a reference electrode of saturated calomel. Electrochemical potentials in the mouth can be measured between two different alloys or between a metallic restoration and a gold cube as a reference electrode placed on the oral mucosa. Low breakdown potentials can lead to corrosion.

Measurements have been performed by anodic polarization in an electrolyte containing 0.9% of sodium chloride at pH 7.4. The higher the potential, the more noble the metal or alloy. It is obvious that the content of gold in an alloy plays the most important role, i.e. the higher the gold content, the higher the breakdown potential. A general guideline is that the breakdown potential should not be less than 600 mV. This can be achieved with gold alloys containing more than 40% of gold. The breakdown potentials of gold/copper alloys are much higher than those of the palladium/copper alloys at the same content of gold and palladium, respectively.

It is clear that the maximum potential of the gold alloys is reached at 40% gold content. Absolute numbers of breakdown potentials vary because of different electrolytes. The breakdown potentials of non-precious alloys are very different,

especially those of nickel based alloys, which show a wide variation. The reason for this is that non-precious alloys need a passivation layer on their surface in order to avoid corrosion. In contrast, gold and high gold alloys do not need any passivation, since they are noble by nature.

To form a passivation layer, non-precious alloys need a very dense oxide layer with strong adherence. For cobalt- and nickel-based alloys, the combined chromium and molybdenum content should be a minimum of 30%. Titanium forms a very strong passivating oxide layer in oxygen-containing atmospheres, leading to its excellent biocompatibility. Cell proliferation tests,

according to the previously described standards, have been carried out on the alloy groups. The percentage of proliferation in a 75% elute concentration is calculated as cell activity. There appears to be a slight correlation to the total release of metal ions, which is more obvious for the nickel- and copper-based alloys.

In terms of the potential of allergic reaction of dental alloys, an epidemiological study has been carried out using patch tests. As a result of these tests a ranking of the estimated “allergenic potential” has been attempted for the alloy groups. No alloy or group of alloys appears to be completely free of “allergenic potential”. Except for the nickel group, however, no statistically significant differences between particular groups have been found. In another series of patch tests, gold alloys with different contents of nickel and palladium were assessed and the results compared with the release of nickel and palladium ions.

A correlation was found between allergic reactions of patients and release of nickel ions. Although no palladium ions have been released in this test, it is considered that there is a cross allergy between nickel and palladium, and that if a patient is allergic to nickel, no palladium containing material should be incorporated. In a recent study, the technical and clinical properties of crown materials were compared. It is clear that electroformed crowns exhibit superior performance over other systems, particularly in terms of biocompatibility and aesthetics, with porcelain veneered cast gold crowns ranked in second place.

### ***Screening test for metal identification in prosthetic dentistry***<sup>5</sup>

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#### **A. Metal identification using the splint-test**

The splint-test consists in two steps; sample taking and EDX analysis. A powdery sample is taken by abrasion of the metallic prosthesis in the patient’s mouth. The metal debris are then collected and sent to a laboratory equipped with an electron microscope for the analysis of

the chemical composition of the clinically used alloys. The splint-test has been routinely and successfully employed by one of the authors (F. Schmidli) for over 15 years.

#### **B. Metal identification using rapid field tests**

In this approach of rapid testing, a powdery sample is taken in the very same way as in the splint-test. Instead of sending the sample to the laboratory for EDX-analysis, however, the metal identification is carried out on the spot using specific chemical reactions. To do so, the collected metal debris first has to be dissolved. For the dissolution, the sample is placed in a test tube (of a volume of about 5 mL). When adding about 1 mL (5 drops) of hydrochloric acid solution (concentration 4M), the debris will dissolve within approximately 15 minutes. The use of specific analytical reactants, each with a high selectivity for either nickel, cobalt, iron or copper, then allow the discrimination between non-precious (NiCr, CoCr) and precious metal alloys.

##### **Nickel test**

Dimethylglyoxime and rubeanic acid tests are employed for the detection of the presence of nickel. The two reactants are well known and have been used for a long time in analytical chemistry. In particular, they are used for the rapid nickel testing of products intended to come into direct and prolonged contact with the skin according to European Directives on Nickel. For the present case, a micro haematocrit tube (Brand GMBH, ISO 12772) is used to take 3 micro

liters of the sample solution and to drop them on an analytical test strip from the “MERCK Nickel Test” (Merck quanta, art. 1.10006.0001). A further drop of ammoniac of concentration 10% is added. A red coloration of the strip indicates the presence of nickel. Now dimethylglyoxime also forms colored complexes with the cations of  $\text{Fe}^{2+}$  (red),  $\text{Pd}^{2+}$  (orange) and  $\text{Pt}^{4+}$  (yellow).

Therefore, a second test with rubeanic (dithio-oxamide) acid is necessary in order to avoid any misinterpretation, Again, drop 3 micro liters of the sample solution on an analytical strip and add this time a drop of saturated ammonium acetate. A dark blue color confirms the presence of nickel since rubeanic acid does not form colored complexes with neither iron nor palladium nor platinum. In consequence, the dental metal is a NiCr alloy if both tests respond with the specific colors. Note that Vademekum 2 - does not list any precious metal alloy containing nickel, chromium or cobalt. Given that the later generations of NiCr alloys often contain significant amounts of iron, the detection of this element might be useful.

#### **Iron test**

Three micro liters of the sample solution are dropped on an analytical test strip from the “MERCK Iron Test” (Merck quanta 1.10004.0001). A red color of the complex formed after the addition of a drop of ammoniac (concentration 10%) indicates the presence of iron. If both the nickel and iron tests were positive, the metal is identified as a NiCrFe alloy.

#### **Cobalt test**

Three micro liters of the sample solution are dropped on a specific analytical test strip from MERCK (Merck quanta 1.10002.0001). A green color indicates the presence of cobalt and the metal is identified as a CoCr alloy. It is worth to note that the identification of chromium is more complicated. Dissolved chromium exists in two oxidation states;  $\text{Cr}^{+3}$  &  $\text{Cr}^{+4}$ . The dissolution of a chromium alloy in hydrochloric acid produces  $\text{Cr}^{+3}$ , for which no selective indicator exists in analytical chemistry.

#### **Copper test**

Three micro liters of the sample solution are dropped on a specific analytical test strip from MERCK (Merck quant® 1.10003.0001). A violet coloration indicates the presence of copper. If nickel is detected together with copper, then the metal is identified as a copper base alloy of the type NPG, Gaudent, Trindium, Orden, Goldent etc. If only copper but no nickel is detected, the alloy is most probably a precious metal containing copper. A further test would then be necessary to confirm the precious nature by testing for gold or platinum.

#### **Gold and platinum test**

The presence of either gold or platinum can be tested by use of stannous chloride. With gold, stannous chloride forms the purple of Cassius, a blood-red complex. Platinum ions form a similar, blazing red complex.

#### **GOLD (AU)<sup>7</sup>**

Pure gold is a soft, malleable, ductile metal that has a rich yellow color with a strong metallic luster. Although pure gold is the most ductile and malleable of all metals, it is relatively low in strength. The density of gold depends somewhat on the condition of the metal, whether it is cast,

rolled, or drawn into wire. Small amounts of impurities have a pronounced effect on the mechanical properties of gold and its alloys. The presence of less than 0.2% lead causes gold to be extremely brittle. Mercury in small quantities also has a harmful effect. Therefore, scrap of other dental alloys, such as technique alloy or other base-metal alloys, including amalgam, should not be mixed with gold used for dental restorations.

Air or water at any temperature does not affect or tarnish gold. Gold is not soluble in sulfuric, nitric, or hydrochloric acids. However, it readily dissolves in combinations of nitric and hydrochloric acids (aqua regia, 18 vol% nitric and 82 vol% hydrochloric acids) to form the trichloride of gold ( $\text{AuCl}_3$ ). It is also dissolved by a few other chemicals, such as potassium cyanide and solutions of bromine or chlorine. Because gold is nearly as soft as lead, it must be alloyed with copper, silver, platinum, and other metals to develop the hardness, durability, and elasticity necessary in dental alloys, coins, and jewelry. Through appropriate refining and purification, gold with an extremely high degree of purity may be produced. Gold can be work hardened to improve its physical properties. Without the improvement, cast gold would lack sufficient strength and hardness.

### **CARAT AND FINENESS OF GOLD-BASED ALLOYS.**<sup>7</sup>

For many years the gold content of gold containing alloys has been described on the basis of the carat, or in terms of fineness, rather than by weight percentage. The term *carat* refers only to the gold content of the alloy; a carat represents a 1/24 part of the whole. Thus 24 carat indicates pure gold. The carat of an alloy is designated by a small letter *k*, for example, 18k or 22k gold. The use of the term *carat* to designate the gold content of dental alloy is less common now. It is not unusual to find the weight percentage of gold listed or to have the alloy described in terms of fineness.

*Fineness* also refers only to the gold content, and represents the number of parts of gold in each 1000 parts of alloy. Thus 24k gold is the same as 100% gold or 1000 fineness (i.e., 1000 fine). The fineness represents a precise measure of the gold content of the alloy and is often the preferred measurement when an exact value is to be listed. An 18k gold would be designated as 750 fine, or, when the decimal system is used, it would be 0.750 fine; this indicates that 750/1000 of the total is gold. Both the whole number and the decimal system are in common use, especially for noble dental solders. The fineness system is somewhat less relevant today because of the introduction of alloys that are not gold-based. It is important to emphasize that the terms *carat* and *fineness* refer only to gold content, not noble-metal content.

### **PLATINUM (Pt)**<sup>7</sup>

Platinum is a bluish white metal; is tough, ductile, and malleable; and can be produced as foil or fine-drawn wire. Platinum has hardness similar to that of copper. Pure platinum has numerous applications in dentistry because of its high fusing point and resistance to oral conditions and elevated temperatures. Platinum increases the hardness and elastic qualities of gold, and some dental casting alloys and wires contain quantities of platinum up to 8% combined with other metals. Platinum tends to lighten the color of yellow gold-based alloys.

Palladium can be combined with gold, silver, copper, cobalt, tin, indium, or gallium for dental

alloys. Alloys are readily formed between gold and palladium, and palladium quantities of as low as 5% by weight have a pronounced effect on whitening yellow gold-based alloys. Palladium-gold alloys with a palladium content of 10% or more by weight are white. Alloys of palladium and the other elements previously mentioned are available as substitutes for yellow-gold alloys, and the mechanical properties of the palladium-based alloys may be as good as or better than many traditional gold-based alloys. Although many of the palladium-based alloys are white, some, such as palladium-indium-silver alloys, are yellow.

### **IRIDIUM (Ir), RUTHENIUM (Ru), AND RHODIUM (Rh)<sup>7</sup>**

Iridium and ruthenium are used in small amounts in dental alloys as grain refiners to keep the grain size small. A small grain size is desirable because it improves the mechanical properties ~~and uniformity of properties~~ within an alloy. As little as 0.005% (50 ppm) of iridium is effective in reducing the grain size. Ruthenium has a similar effect. The grain-refining properties of these elements are largely due to their extremely high melting points. Iridium melts at 2410° C and ruthenium at 2310° C. Thus these elements do not melt during the casting of the alloy and serve as nucleating centers for the melt as it cools, resulting in a fine-grained alloy. Rhodium also has a high melting point (1966° C) and has been used in alloys with platinum to form wire for thermocouples. These thermocouples help measure the temperature in porcelain furnaces used to make dental restorations.

### **SILVER (Ag)<sup>7</sup>**

Silver is a malleable, ductile white metal. It is the best-known conductor of heat and electricity and is stronger and harder than gold but softer than copper. At 961.9° C, the melting point of silver is below the melting points of both copper and gold. It is unaltered in clean, dry air at any temperature, but combines with sulfur, chlorine, phosphorus, and vapors containing these elements or their compounds. Foods containing sulfur compounds cause severe tarnish on silver, and for this reason silver is not considered a noble metal in dentistry.

Pure silver is not used in dental restorations because of the black sulfide that forms on the metal in the mouth. Adding small amounts of palladium to silver-containing alloys prevents the rapid corrosion of such alloys in the oral environment. Silver forms a series of solid solutions with palladium and gold, and is therefore common in gold- and palladium-based dental alloys. In gold-based alloys, silver is effective in neutralizing the reddish color of alloys containing appreciable quantities of copper. Silver also hardens the gold-based alloys via a solid-solution hardening mechanism. In palladium-based alloys, silver is important in developing the white color of the alloy. Although silver is soluble in palladium, the addition of other elements to these alloys, such as copper or indium, may cause the formation of multiple phases and increased corrosion.

### **COPPER (Cu)<sup>7</sup>**

~~Copper is a malleable~~ and ductile metal with high thermal and electrical conductivity and a characteristic red color. Copper forms a series of solid solutions with both gold and palladium and is therefore an important component of noble dental alloys. When added to gold-based alloys, copper imparts a reddish color to the gold and hardens the alloy via a solid-solution or ordered solution mechanism. The presence of copper in gold based alloys in quantities between



approximately 40% and 88% by weight allows the formation of an ordered phase. Copper is also commonly used in palladium-based alloys, where it can be used to reduce the melting point and strengthen the alloy through solid-solution hardening and formation of ordered phases when Cu is between 15 and 55 wt%. The ratio of silver and copper must be carefully balanced in gold- and palladium-based alloys, because silver and copper are not miscible. Copper is also a common component of most hard dental solders.

### **ZINC (Zn)<sup>7</sup>**

~~Zinc is a blue~~-white metal with a tendency to tarnish in moist air. In its pure form, it is a soft, brittle metal with low strength. When heated in air, zinc oxidizes readily to form a white oxide of relatively low density. This oxidizing property is exploited in dental alloys. Although zinc may be present in quantities of only 1% to 2% by weight, it acts as a scavenger of oxygen when the alloy is melted. Thus zinc is referred to as a *deoxidizing agent*. Because of its low density, the resulting zinc oxide lags behind the denser molten mass during casting and is therefore excluded from the casting. If too much zinc is present, it will markedly increase the brittleness of the alloy.

### **INDIUM (In)<sup>7</sup>**

~~Indium is a soft,~~ gray-white metal with a low melting point of 156.6° C. Indium is not tarnished by air or water. It is used in some gold-based alloys as a replacement for zinc and is a common minor component of some noble ceramic dental alloys. Recently, indium has been used in greater amounts (up to 30% by weight) to impart a yellow color to palladium silver alloys.

### **TIN (Sn)<sup>7</sup>**

~~Tin is a lustrous,~~ soft, white metal that is not subject to tarnish in normal air. Some gold-based alloys contain limited quantities of tin, usually less than 5% by weight. Tin is also an ingredient in gold based dental solders. It combines with platinum and palladium to produce a hardening effect, but also increases brittleness.

### **GALLIUM (Ga)<sup>7</sup>**

~~Gallium is a grayish~~ metal that is stable in dry air but tarnishes in moist air. It has a very low melting point of 29.8° C and a density of only 5.91 g/cm<sup>3</sup>. Gallium is not used in its pure form in dentistry, but is used as a component of some gold- and palladium based dental alloys, especially ceramic alloys. The oxides of gallium are important to the bonding of the ceramic to the metal.

### **NICKEL (Ni)<sup>7</sup>**

Nickel has limited application in gold- and palladium-based dental alloys, but is a common component in non noble dental alloys. Nickel has a melting point of 1453°C and a density of 8.91 g/cm<sup>3</sup>. When used in small quantities in gold-based alloys, nickel whitens the alloy and increases its strength and hardness.

## **TITANIUM: A MIRACLE METAL IN DENTISTRY**<sup>6</sup>

The use of titanium and titanium alloys for medical and dental applications has increased dramatically in recent years. Titanium (pronounced /tai' teiniem) was discovered in England by William Gregor in 1791 and named by Martin Heinrich Klaproth for the Titans of Greek mythology. Titanium is a chemical element with the symbol Ti and atomic number 22. Sometimes called the "space age metal". It is a light, strong, lustrous, naturally corrosion-resistant (including to sea water and chlorine) transition metal with a grayish color. This metal has a high melting point at around 1,700 °C; one of the highest melting points of any known metal. Many of titanium's physical and mechanical properties make it desirable as a material for implants and prostheses.

Today, titanium and titanium alloys are used in so many biomedical applications; Cp titanium is used for dental implants, surface coatings, and more recently for crown, partial and complete dentures, and orthodontic wires. Several titanium alloys are also used. Wrought alloys of Ti with Ni and Ti with Molybdenum are used for orthodontic wires. The term titanium is often used to include all types of pure and alloyed titanium.

### **Commercially pure Titanium (Cp Ti)**

Cp Titanium is available in four grades. The main differences among them is the concentration of the oxygen (0.18 to 0.40 wt %) and iron (0.20 to 0.50 wt %). These slight differences in concentration have a substantial effect on physical and mechanical properties.

**Titanium alloys** Pure titanium undergoes a transition from a hexagonal close packed structure (alpha phase) to a body centered cubic structure (beta phase) at 883 °C. It remains in this crystallographic structure until melting at 1672°C. Elements such as Al, Ga, and Sn, with the interstitial elements (C, O, and N) stabilize alpha phase, resulting in alpha titanium alloy. On the other hand, elements such as V, Nb, Ta, and Mo, stabilize the beta phase. Titanium can be alloyed with various elements to change its characteristics, primarily to improve the physical and mechanical properties, such as strength, high temperature performance, creep resistance, weldability, response to ageing heat treatments, and formability.

**Alloying elements can be added to stabilize one or the other of these phases by either raising or lowering the transition temperatures. Alloying elements are added to stabilize either alpha or beta phase, by changing beta transformation temperature. For example, in Ti-6Al-4V, aluminum is as alpha stabilizer, which expands alpha phase field by increasing the (alpha+ beta) to beta -transformation temperature, where as vanadium, as well as copper and palladium, are beta stabilizers, which expand the beta phase by decreasing the (alpha+ beta) to beta- transformation temperature . ASTM International (the American Society for Testing and Materials) recognizes four grades of commercially pure titanium (Cp Ti), or Ti, and three titanium alloys (Ti-6Al-4V, Ti-6Al-4V Extra Low Interstitial [low components] and Ti-Al-Nb). The most widely used titanium alloy is the Ti- 6Al-4V alpha-beta alloy.**

### **Applied Physical Properties**

#### **Biocompatibility & Osseo integration**

Among all the other properties of titanium, the excellent biocompatibility is the most practical aspect for the application in dentistry. This useful biological property of titanium is based on the existence of titanium oxide (TiO<sub>2</sub>) layers, which are naturally formed in oxygen containing environments. It is also possible to be produced with various artificial techniques, e.g., anodizing. This metals forms protective surface layers of semi- or nonconductive oxides.

Because of their isolating effect, these oxides are able to prevent to a great extent a flow of ions. This isolating effect is demonstrated by the dielectric constants  $K$  of the various metal oxides. The isolating effect of an oxide layer with a dielectric constant is similar to that of water; implants of Ti are not recognized by the bone or tissue as foreign body. Because of their large surface, the primary corrosion products are particularly responsible for organic and inorganic reactions. These corrosion products have different thermodynamic stability with only a low reactivity to the proteins of the surrounding tissue.

Biocompatibility depends on mechanical and corrosion/degradation properties of the material, tissue, and host factors. Biomaterial surface chemistry, topography (roughness), and type of tissue integration (osseous, fibrous, and mixed) correlate with host response. Biocompatibility of the implants and its associated structure is important for proper function of the prosthesis in the mouth. Titanium is relatively inert, corrosion resistance metal because of its thin (approximately 4nm) surface oxide layer. Studies have shown that Titanium readily adsorbs protein like albumin, laminin, glycosaminoglycans, collagenase, fibronectins, complement proteins, fibrinogens etc from the biological fluids.

**Osseo integration**” is defined as the apparent direct attachment or connection of osseous tissue to an inert, alloplastic material without intervening connective tissue. Bränemark observed the fusion of bone with titanium chambers when he had placed them into the femurs of rabbits. Surface composition, hydrophilicity and roughness are parameters that may play a role in implant–tissue interaction and osseointegration. Osseo integration firmly anchors the titanium dental or medical implant into place. Titanium is one of the best metals that allows for osseointegration because it is absolutely inert in the human body, immune to attack from body fluids, compatible with the bone growth and strong and flexible. Titanium is the most biocompatible of all metals the osseointegration rate of titanium dental implants is related to their composition and surface roughness or application of osteoconductive coatings. Rough-surfaced implants favor both bone anchoring and biomechanical stability. Surface treatments, such as titanium plasma-spraying, grit-blasting, acid-etching, anodization or calcium phosphate coatings can be used.

### **Toxicity**

Pure titanium and Ti–6Al–4V alloy have been mainly used as implant materials. V- free titanium alloys like Ti–6Al– 7Nb and Ti–5Al–2.5Fe have been then developed because toxicity of V has been pointed out. Al- and V-free titanium alloys as implant materials have been developed. Most of them are, however,  $\alpha+\beta$  type alloys.  $\beta$  type titanium alloys composed of non-toxic elements like Nb, Ta, Zr, Mo or Sn with lower moduli of elasticity and greater strength has been developed recently.

### **Chemical Properties**

The oral cavity is subjected to wide changes in the pH and fluctuation in the temperature. The disintegration of the metal may occur through the action of moisture, atmospheric acid and alkaline other chemical agents.

Further it has been reported that water, oxygen, chloride, sulphur corrodes various metal present in the dental alloys. Corrosion can severely limit the fatigue life and ultimate strength of the material leading to mechanical failure of the dental materials.

Titanium has excellent corrosion resistance and biocompatibility in biological fluids. The influence of contaminants and surface treatments of titanium implants (like alumina-blasting, acid etching, anodization, hydroxyapatite coating,) on osseous integration has been extensively studied. Many authors have studied the corrosion behavior of commercially pure titanium in artificial saliva.

All the studies concluded that the titanium corrosion resistance in these media is due to the formation of an adherent and highly protective oxide film on its surface which is mainly formed of TiO<sub>2</sub>. Titanium is a thermodynamically reactive metal as suggested by its relatively negative reversible potential in the electrochemical series. It gets readily oxidized during exposure to air and electrolytes to form oxides, hydrated complexes, and aqueous cationic species. The oxides and hydrated complexes act as barrier layers between the titanium surface and the surrounding environment and suppress the subsequent oxidation of titanium across the metal/barrier layer/solution interface. Even if the barrier layer gets disrupted, it can get reformed very easily, leading to spontaneous re-passivation.

### **Clinical significance of corrosion**

Resistance to corrosion is critical important for a dental material because corrosion can lead to roughening of surface, weakening of the restoration and liberation of element from the dental alloy. Liberation of elements can produce discoloration of adjacent soft tissue and allergic reactions in susceptible patients. The long term presence of corrosion reaction products and ongoing corrosion lead to fractures of the alloy-abutment interface, abutment, or implant body.

### **Strength**

Many of titanium's physical and mechanical properties make it desirable as a material for implants and prostheses. Certainly, an implant should be designed to be as strong as possible. Even in everyday activities, you will place high levels of mechanical stress on your bones and joints. The ideal implant should be able to withstand these stresses day to day for years without breaking or permanently changing shape.

An implant should also be designed to withstand the fatigue effect of the accumulation of these repeating stress cycles for an acceptable period of time (service life). The strength and rigidity of titanium are comparable to those of other noble or high noble alloys commonly used in dentistry. Titanium also can be alloyed with other metals, such as aluminum, vanadium or iron, to modify its mechanical properties. The Cp-titanium grades are nominally all alpha phase in structure, whereas many of the titanium alloys have a two phase alpha + beta structure.

There are also titanium alloys with high alloying additions having an entire beta phase structure, while alpha alloys cannot be heat treated to increase strength. The mechanical properties of

(alpha+ beta) titanium alloys are dictated by the amount, size, shape, and morphology of alpha phase and density of alpha/beta interfaces. Microstructures with a small ( $< 20\mu\text{m}$ ) alpha grain size, a well dispersed beta phase, and a small alpha /beta interface area such as in equiaxed microstructures, resist fatigue crack initiation best and have the best high - cycle fatigue strength (approximately 500 - 700 MPa). Lamellar microstructures have greater alpha/beta surface area and more oriented colonies; have lower fatigue strengths (approximately 300 – 500 MPa) than do equiaxed microstructures.

**Greger et al** in the year **2010** have studied the **mechanical properties of ultra-fine grain titanium** and concluded that the strength properties of commercially pure titanium increased significantly as a result of grain refinement. Ultra-fine grain has higher specific strength properties than ordinary titanium. Strength of ultra-finegrain varies around 1250 MPa, grain size around 300 nm. Another important characteristic of titanium- base materials is the reversible transformation of the crystal structure from alpha (hexagonal close-packed) structure to beta (body- centered cubic) structure when the temperatures exceed certain level. This allotropic behavior, which depends on the type and amount of alloy contents, allows complex variations in microstructure and more diverse strengthening opportunities than those of other nonferrous alloys such as copper or aluminum.

Titanium has a relatively high tensile strength; it takes quite a bit of pressure to pull titanium apart. According to Key to Metals, titanium has a tensile strength of between 30,000 and 200,000 lbs. per square inch. Titanium alloy contains roughly six weight percent of aluminum and four weight percent of vanadium, which doubles its tensile strength relative to commercially-pure titanium, but reduces its ductility. The yield strength (170 – 480 MPa) and ultimate strength (240 – 550 MPa) varies depending on the grade of titanium.

### **Shape memory**

In the early 1960s, William Buehler along with Frederick Wang at the U.S Naval Ordnance Laboratory discovered the shape memory effect alloy of nickel and titanium, which can be considered a breakthrough in the field of shape memory (Buehler et al. 1967). This alloy was named Nitinol (Nickel-Titanium Naval Ordnance Laboratory) .The first efforts to exploit the potential of NiTi as an implant material were made by Johnson and Alicandri in 1968 (Castleman *et al.* 1976).

The use of NiTi for medical applications was first reported in the 1970s [36]. Nitinol [also known as a **shape memory alloy** (SMA), smart alloy, memory metal, or musclewire] is an alloy that “remembers” its shape. Nitinol possess a unique combination of properties, including super elasticity or pseudo elasticity and shape memory, which are very attractive for biomedical applications. NiTi has been used *in* orthopedic and orthodontic implants. Their ability to recover large strains and dissipate mechanical work without macroscopic permanent deformation has generated significant interest in various field ology.

Among all SMA, titanium nickel (TiNi) is the most important alloy. The unusual properties of this smart material are derived from the two crystal structures that can be inter-converted by changes in temperature or pressure. At temperatures between about 0 and 100°C, there are two important phases or crystal structures of NiTi that can be referred to as the high temperature and low temperature phase, or as austenite and martensite, respectively. The austenite phase has the symmetry of a cube and is characterized by hardness and rigidity. The wire sample of NiTi can be bent at room temperature, but will return to its linear shape when heated by hot air or water as its atoms move in a kind of “atomic ballet.”

Moreover, the wire can be heated to the much higher temperature (approximately 500°C), where it can be trained to “remember” a new shape. Subsequently, when the wire is distorted at room temperature and heated by hot air or water, it will return to this new shape. In dentistry, the material is used in orthodontics for brackets and wires connecting the teeth. Once the SMA is placed in the mouth its temperature raises to ambient body temperature. This causes the Nitinol to contract back to its original shape applying a constant force to move the teeth. These SMA wires don't need to be retightened as often as they can contract as the teeth move unlike conventional stainless steel wires. Additionally, Nitinol can be used in endodontic, where Nitinol files are used to clean and shape the root canals during the root canal procedure.

### **Flexibility**

While strength characteristics of implants are important, they must also be somewhat flexible to avoid shielding of bones from stress (“stress shielding”). When stress is applied to a stiff dental/orthopedic implant, the implant will carry most of the stress and the bone may start to resorb and may become less dense and weak. On the other hand if stress is applied to a less stiff or more flexible implant, some of the stress can be shared with the surrounding bone. This will help to keep the bone active and strong.

Flexibility and elasticity are rivals that of human bone. Titanium's modulus of elasticity and coefficient of thermal expansion matches those of human bone, reducing the potential for implant failure. When beta alloyed (as with niobium and zirconium); titanium is used for low modulus application. When alpha beta alloyed (as with titanium) is used for applications requiring greater modulus, such as bone plates. The modulus (100 GPa) is also about half the value of other metals. Retention of a partial denture depends on the amount of undercut engaged on an abutment tooth and the flexibility of the clasp. Flexibility is influenced by clasp length and the denture base material. Titanium clasps are purported to have greater flexibility than cobalt-chromium cast clasps which should enable them to engage deeper undercuts or be used where shorter clasp arms are needed such as on premolar teeth.

### **Density**

The density of Cp Ti (4.5 g/cm<sup>3</sup>) is about half of the value of many of other base metals. Titanium is lighter than the stainless steel (approximately 56% as dense) yet has a yield strength twice and ultimate tensile strength almost 25% higher. This gives it a highest strength –to – weight ratio of any metal suited to medical use.

### **Non-magnetic**

Commercially pure titanium and all the titanium alloys are non magnetic. The physical difference between ferromagnetic and non-ferromagnetic materials lies in the degree of magnetization. Titanium is not susceptible to outside interference and won't trigger metal detector. Another benefit to titanium for use in medicine is its non-ferromagnetic property, patients with titanium implants can be safely examined with magnetic resonance imaging (convenient for long-term implants).

## **SUMMARY**

Metals are used in almost all aspects of dental practice, including the dental laboratory, direct

and indirect dental restorations, implants, and instruments used to prepare teeth. Metals have optical, physical, chemical, thermal, and electrical properties that are unique among the basic types of materials and suitable for many dental applications. Although tooth-colored materials are often desired for restorations, metals provide strength, stiffness, and longevity for long-term dental applications that are often not achievable with other classes of materials. Evidence in the scientific literature of clinical performance is the most extensive for this material class.<sup>7</sup>

Metals are ductile and malleable and therefore exhibit elastic and plastic behavior; they are good electrical and thermal conductors, higher in density than other classes, exhibit good toughness, are opaque, and can be polished to a luster. Metals may be cast, drawn, or machined to create dental restorations and instruments.<sup>7</sup>

The twentieth century generated substantially new changes to dental prosthetic materials. The major factors that are driving new developments are

(1) **Economy**-the new material performs the same function as the old material but at a lower cost;

**Performance** the new material performs better than the old product in some desirable way, such as ease of processing, improved handling characteristics, or increased fracture resistance; and

(3) **Aesthetics**-the new material provides a more aesthetic result, such as increased translucency. The metals in dental casting alloy classification is useful for estimating the relative cost of alloy, because the cost is dependent on the noble metal content as well as on the alloy density. It is also useful for identification of the billing code that is used for insurance reimbursement. Because insurance companies may pay more for high noble than for noble alloys or predominantly base metal alloys, it is important for dentists to correctly identify the noble metal category of the alloy they are using.<sup>1</sup>

The production of dental prostheses made with a core or framework of metal usually involves the casting of a molten pure metal or an alloy into a refractory mold. The mold is formed around a wax or plastic pattern of the prosthesis that will be produced from the cast metal. The wax or plastic is subsequently eliminated at an elevated burnout temperature, and the molten metal is cast into the mold under centrifugal force.<sup>1</sup>

Most alloys solidify over a range of temperatures in which solid and liquid phases coexist, rather than at a single temperature as does a pure metal. The presence of atoms of more than one metal may also cause certain reactions in the solid state that can not occur with a pure metal; these reactions directly affect the properties of the alloy. When observed with the optical microscope, the grains of such alloys may resemble those of pure metals.<sup>1</sup>

Physical properties are based on the laws of mechanics, acoustics, optics, thermodynamics, electricity, magnetism, radiation, atomic structure, or nuclear phenomena. **Hue, value, and chroma** are physical properties that are based on the laws of optics, which is the science that deals with phenomena of light, vision, and sight. **Thermal conductivity** and **coefficient of thermal expansion** are physical properties that are based on the laws of thermodynamics.<sup>1</sup>

In most cases corrosion is undesirable. However, in dental practice, a limited amount of corrosion around the margins of dental amalgam restorations may be beneficial, since the corrosion products tend to seal the marginal gap and inhibit the ingress of oral fluids and bacteria. Some metals and alloys are resistant to corrosion because of inherent nobility or the formation of a protective surface layer.<sup>1</sup>

For dental restorations, various elements are combined to produce alloys with adequate properties for dental applications because none of the elements by themselves have properties that are fully suitable. These alloys may be used for dental restorations as cast alloys or may be manipulated into wire or other wrought forms.<sup>7</sup>

The selection of a metal for a cast restoration is ultimately the legal and ethical responsibility of the practitioner, but this decision often is made by the dental laboratory. Given the complexities of the decision, its abrogation to the dental laboratory is not surprising. However, given the long-term consequences of this decision on the oral health of the patient, selection of casting alloys should be made primarily by the practitioner with consultation from the dental laboratory.<sup>2</sup>

The practitioner often focuses on the cost and color of the alloy as major factors in this decision, but cost and color are the least important factors in selecting a material for a successful prosthesis. Furthermore, the initial cost of the alloy is often a poor indicator of the overall long-term cost of the restoration. If the restoration fails because of poor clinical performance and must be replaced

prematurely, the costs of these repairs (in patient discomfort, time, and money) will far exceed the initial savings of using an inferior alloy.<sup>2</sup>

The selection of a metal in casting alloy is best customized for a particular clinical situation. The systemic health of the patient should be the first consideration, and the practitioner should avoid alloys that contain elements to which the patient is hypersensitive. These elements are most commonly nickel and cobalt, although allergies to palladium and gold have also been reported. The complete composition of the alloys therefore must be considered by the practitioner in this regard because even trace elements can elicit reactions through disproportional corrosion from grain boundaries or secondary phases. The physical requirements of the alloy are also a primary consideration. For example, if the restoration involves long spans, then an alloy with the highest modulus of elasticity is advisable, particularly if the prosthesis is porcelain–metal.<sup>2</sup>

The fit of the restoration depends to a large extent on the ability of the laboratory to manage casting shrinkage. This issue is most difficult with high-melting alloys. The tensile strength is important if the restoration involves connectors between multiple units and if these connectors are narrow gingivo-occlusally because of short clinical crowns, periodontal considerations, or esthetic requirements. The color of the alloy's oxide may be important in porcelain–metal restorations.<sup>2</sup>

Finally, practitioners should maintain records of the materials that they use for cast restorations and should give patients this information. The Identalloy system is a convenient means to maintain good dental records and inform patients. Most manufacturers supply laboratories with stickers that contain the name and composition of their alloys, and most good laboratories supply these stickers to the practitioner upon request. Practitioners should use this, or other means, to maintain records of the materials used. These records are important to help diagnose future



problems that might occur (biologic reactions or mechanical failures) and are important legal resources to defend the practitioner in the event of litigation.<sup>2</sup>

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