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RESTORATIVE DENTAL MATERIALS: SCANNING ELECTRON MICROSCOPY AND X-RAY MICROANALYSIS

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Abstract

Restorative dental materials include the materials used to repair damaged teeth and/or replace missing teeth. The definition could be extended to include a much broader group of dental materials, but this paper concentrates only on those materials used to restore the crown portion of damaged teeth. Auxiliary materials, materials for removable denture prostheses, and root canal materials are excluded. Progress and recent research utilizing SEM (Scanning Electron Microscopy), EDS (Energy Dispersive Spectroscopy), and some related methods are presented for the following dental materials: dental amalgam, enamel and dentin bonding agents, dental composites, dental cements, casting alloys for crowns and bridges, and ceramic-metal and ceramic restorative materials. In addition to the basic characterization of these materials by SEM/EDS techniques, examples of replication methods for SEM study of restorative materials in situ are discussed. Some examples are also presented in the direct use of SEM/EDS for characterization of changes and degradation of restorative materials which occur during clinical use.

KEY WORDS: dental materials, amalgam, composites, bonding, cements, casting alloys, ceramics, replicas, scanning electron microscopy, energy dispersive spectroscopy.

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Introduction

Restorative dental materials comprise that group of materials utilized to reconstruct damaged teeth or to replace missing teeth. In some instances the scope may also include the materials used to reconstruct the maxillofacial complex. Thus the area is very broad. Excellent texts already are available covering the scientific and technical aspects of these materials (60,182). Furthermore, several leading dental journals review progress in materials and restorative dental research on an annual basis (56,183). A recently published conference proceedings of problems and research on restorative dental materials is also available (189).

It is obviously impossible to review this entire field from a perspective of the use of the SEM and x-ray microanalysis in the limited space available here. Therefore, the present paper is limited to the materials used directly to restore the crown portion of teeth as the result of damage from carious lesions (decay) or mechanical trauma. Excluded from the review are all of the materials used to construct complete dentures, removable prostheses, endodontic root canal fillings, and implants. This review will also ignore those materials used to produce impressions, models, and casts.

There are several approaches to the restoration of damaged teeth. The particular choice depends on the extent of the damage and the requirements for esthetics. In the posterior portion of the mouth, the classical material for single tooth restorations has been dental amalgam (silver filling materials). In the anterior portion of the mouth, dental composites (tooth-colored materials) are generally used. They are attached to dentin and enamel using bonding agents. In recent years, extensive research has been devoted to improving composite materials for use in the posterior portion of the mouth where significantly greater mechanical strength and wear resistance are required.

If damage to the tooth crown is more extensive, it is generally necessary to replace all or most of the outer surface of the crown. A precisely fitting metallic, ceramic, or ceramic bonded to metal crown is fabricated and cemented in place. Recently, castable ceramic materials have become available and are utilized in a similar fashion. In cases where esthetics are not important, metallic crowns are generally used because of their high strength and relatively lower cost. More naturally appearing crowns can be fabricated from ceramic bonded to a thin metal casting. If intraoral mechanical forces are low then completely ceramic restorations can be utilized. These techniques can be extended to replace some missing teeth by larger castings which are cemented to relatively sound teeth at either end of the space to form bridges or fixed denture prostheses.

Direct analysis of restorative dental material samples is the most desirable but is rarely possible. Therefore, clinical changes that are occurring intraorally are monitored using replica techniques. Replication methods have been used for electron microscopy studies for a long time but are relatively new for dental research applications. In most cases the techniques use materials that are already used for clinical procedures. Dental impression materials that were originally developed for producing dental casts are well-suited to make negative replicas from which positive replicas or models can be produced for SEM analyses (14,55,77). Pameijer (180) reviewed these methodologies in 1978. Schoen et al (201) screened a large number of materials to identify the most compatible systems. The most popular combination has been use of polyether or polyvinyl siloxane impression materials and slow curing epoxy materials for positive replicas (137). These techniques are now used to evaluate enamel changes (194) and restoration changes with time (47).

Dental research which has involved SEM and x-ray microanalysis techniques will be reviewed for (a) dental amalgam, (b) bonding, (c) dental composites, (d) cements, (e) casting alloys, and (f) ceramic restorations. In the following sections both direct and indirect analysis techniques will be considered.

Dental Amalgam

Dental amalgam is the most widely used restorative material for the restoration of small to moderate size lesions of posterior teeth. It is composed of a silver based alloy which is mechanically mixed with mercury in approximately equal parts by weight to produce a plastic mix which can be condensed into a prepared cavity of the tooth and which will set to a hard durable material. Greener (89) has reviewed the historical development of alloys for amalgam. Until the 1970's, the major alloy was composed largely of Ag_3Sn with minor amounts of Cu and Zn. The alloy particle shape was either in the form of lathe-cut particles (irregular chips) or spherical particles. SEM and energy dispersive spectrometry (EDS) have been used in conjunction with the electron microprobe (104,226) to characterize the basic setting mechanisms. Sutfin and Ogilvie (217) reported on the examination of the major phases of amalgam with the SEM and confirmed earlier metallographic and x-ray diffraction results. That information established that the setting reaction for conventional dental amalgam involved the reaction of Hg with Ag and Sn to produce a matrix of two new phases. The overall reaction is summarized in Table 1. An example of the set microstructure of these conventional amalgams is shown in Figure 1. Okabe et al (174) used the SEM to directly observe the formation of gamma-1 and gamma-2 crystals by immersion of Ag_3Sn and Sn in Hg. Gamma-1 crystals comprise most of the dental amalgam matrix and are generally equiaxed grains. That morphology is readily apparent in Figure 2 in which several gamma-1 crystals have been selectively grown out of the surface of a conventional amalgam. Gamma-2 crystals, on the other hand, are thin elongated blades that do not occupy much volume but still form a continuous path through the matrix because of their frequent intersections with each other (Figure 3). Unfortunately, during intraoral corrosion the gamma-2 phase is selectively attacked and the continuous path allows the entire amalgam to become undermined.

Amalgam alloys having a higher Cu content were first introduced by Innes and Youdelis (103) and led to a whole new class of amalgam with improved performance in clinical trials (134). The exact mechanisms for the substantial improvement obtained in the high Cu amalgams is still under discussion but all of these amalgams

1. Conventional Dental Amalgam:

   $Ag_3Sn + Hg \text{ --> } Ag_3Sn + Ag_2Hg_3(\text{gamma-1}) + Sn_8Hg(\text{gamma-2})$

2. Blended Amalgam Systems:

   $Ag_3Sn + Ag\text{-}Cu + Hg \text{ --> } Ag_3Sn + Ag\text{-}Cu + Ag_2Hg_3 + Cu_6Sn_5(\text{eta-prime})$

3. Single Composition Amalgam Systems:

   $Ag\text{-}Sn\text{-}Cu + Hg \text{ --> } Ag\text{-}Sn\text{-}Cu + Ag_2Hg_3 + Cu_6Sn_5(\text{eta-prime})$

Table 1. Setting Reactions for Dental Amalgams.

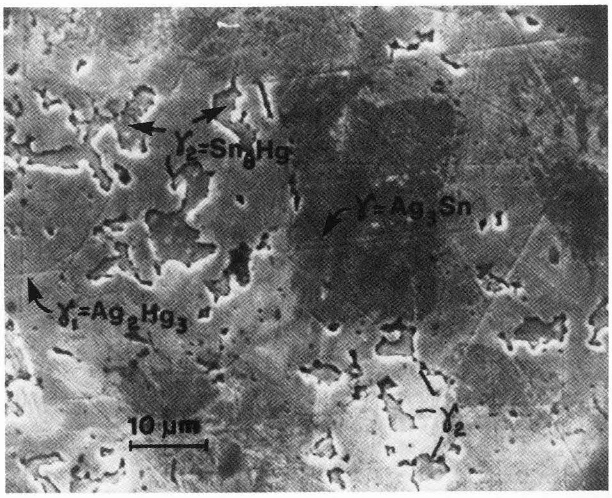

Figure 1. Microstructure of a Conventional Dental Amalgam.

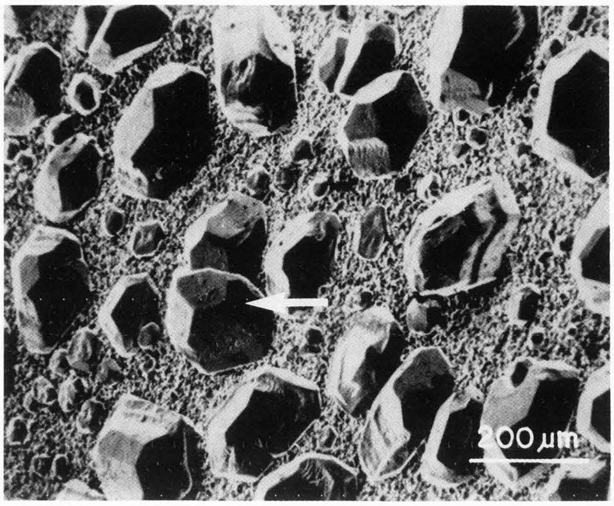

Figure 2. Gamma-1 Crystals Grown Preferentially on the Surface of a Conventional Dental Amalgam.

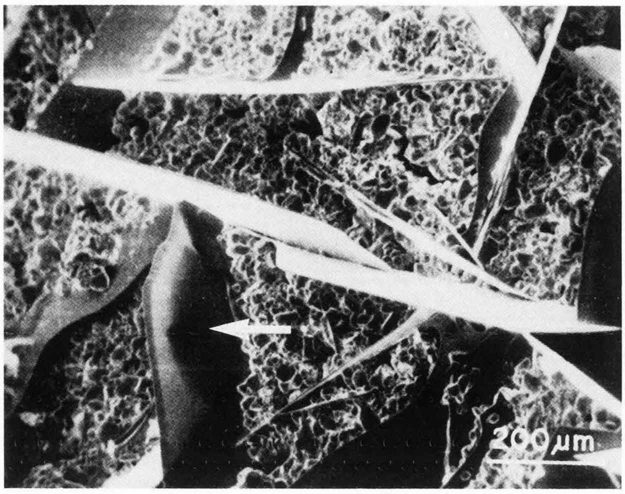

Figure 3. Gamma-2 Crystals Grown Preferentially on the Surface of a Conventional Dental Amalgam.

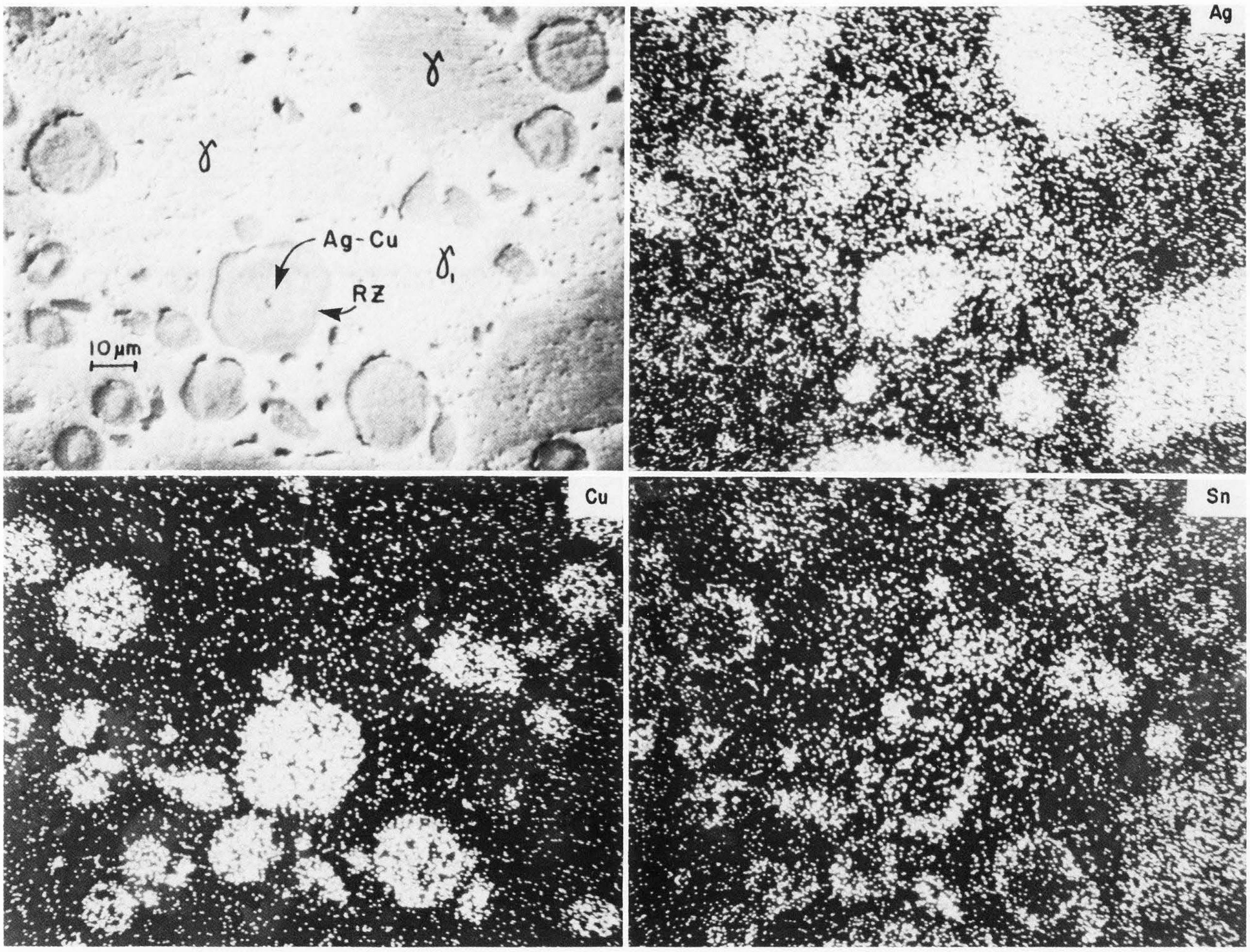

Figure 4. Microstructure of a Blended Particle High Copper Dental Amalgam and X-Ray Distribution Maps for Ag, Cu, and Sn (γ= Ag-Sn Particle, Ag-Cu= Copper Containing Particle, RZ= Reaction Zone, γ_1= Matrix).

display a decreased amount of intraoral corrosion. A combination of SEM, EDS and electron microprobe studies have been used to characterize the microstructure of high Cu amalgams (62,133,135, 138,139,141,175-178). There are two fundamental groups of high Cu amalgams, the blended systems in which irregular Ag_3Sn particles are combined with spherical high Cu particles as shown in Figure 4 and single composition systems in which the Ag-Cu-Sn are contained in a generally spherical particle as seen in Figure 5. The setting reactions are summarized in Table 1. The most notable alteration in these systems is the formation of Cu_6Sn_5 (eta-prime) as a phase instead of the Sn_8Hg (gamma-2) phase found in the older systems. This alteration has significant effects on both the corrosion characteristics and mechanical properties as recently summarized by Marshall and Marshall (140).

Amalgam is the most corrosion prone material used for permanent dental restorations. In conventional dental amalgam, it has been demonstrated that the gamma-2 phase is selectively attacked (106). Holland and Asgar (100) and Sarkar et al (200) demonstrated that the major corrosion products within amalgam contained Sn or Sn-Cl and were similar to products formed by laboratory corrosion. Marshall et al (144) demonstrated that these products also contained oxygen and had characteristic morphologies as seen in Figure 6.

Laboratory corrosion studies demonstrated that the corrosion resistance of the newer high Cu amalgams was much higher than those containing the gamma-2 phase. Marshall et al (136) used the SEM to study both types of amalgam restorations and found less apparent corrosion in high Cu systems, but the products were essentially the same. These products have been found in various other studies (149,153) and have been identified by SEM/EDS and x-ray diffraction as $Sn_4(OH)_6Cl_2$ and SnO (146). Additional products on amalgam surfaces after in vitro corrosion have been identified by SEM/EDS and x-ray diffraction and include Cu_2O, $CuCl_2 \cdot 3Cu(OH)_2$, $ZnSn(OH)_6$, and $CuSn(OH)_6$ but are usually not the main products found in the

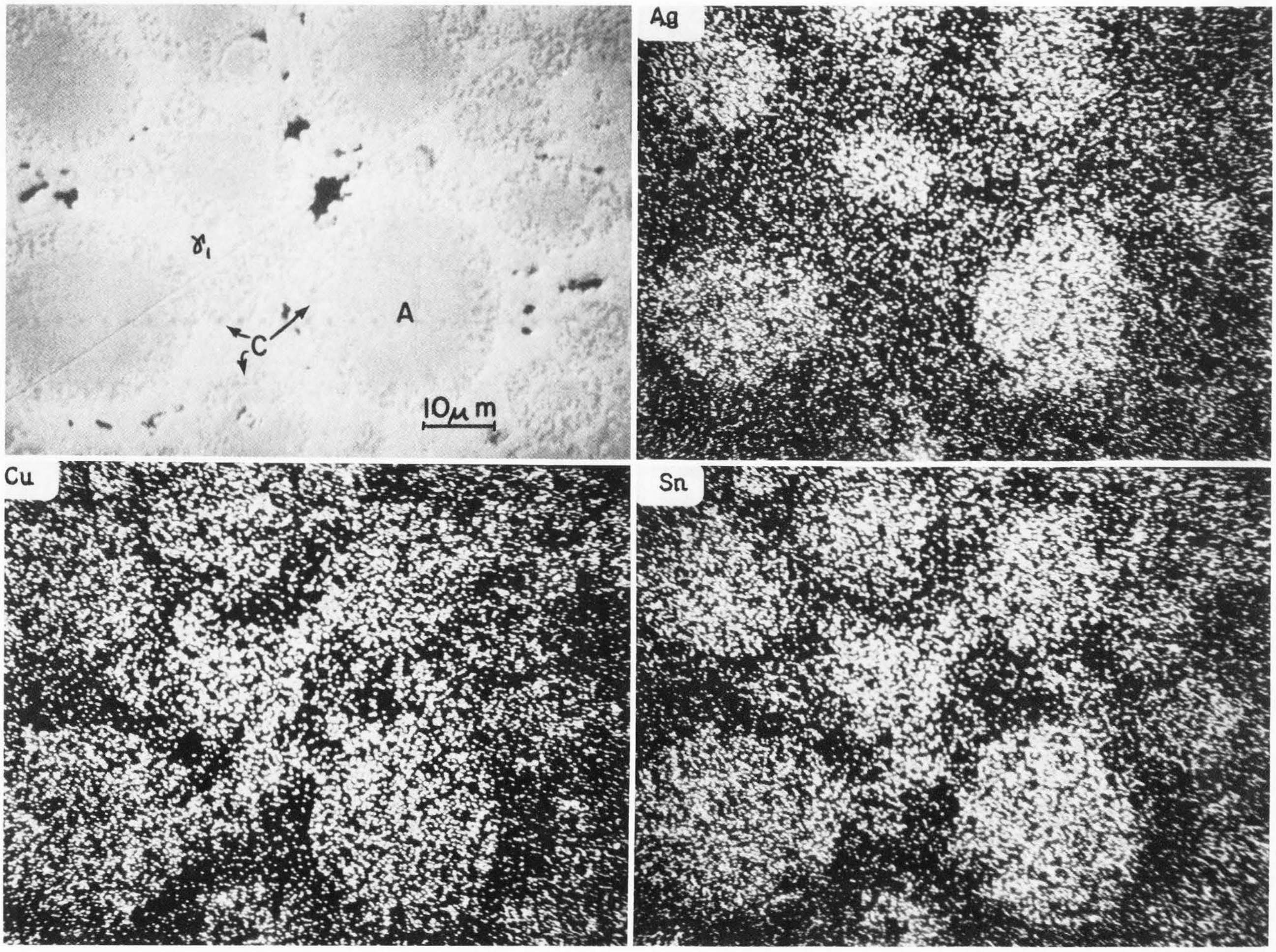

Figure 5. Microstructure of a Single Particle High Copper Dental Amalgam and X-Ray Distribution Maps for Ag, Cu, and Sn (A= Alloy Particle, C= Cu_6Sn_5 Crystals, γ_1= Matrix).

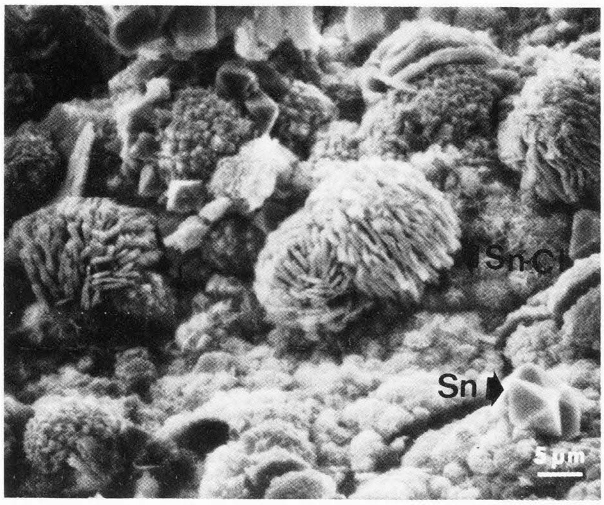

Figure 6. Sn Rich and Sn-Cl Based Corrosion Products from Amalgam. (Sn Rich Products are Polyhedral; Sn-Cl Products are Plates)

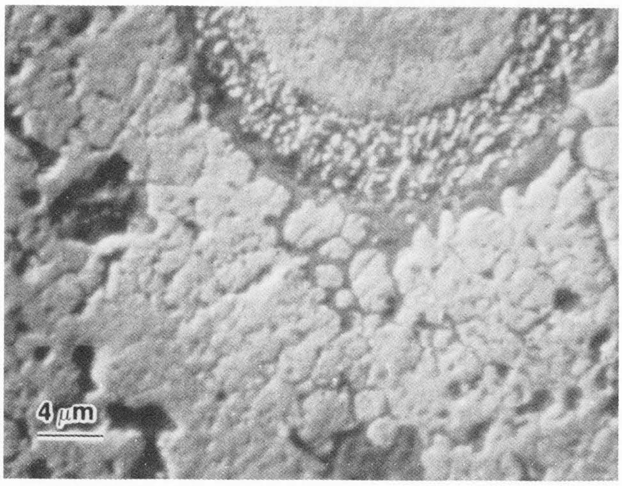

Figure 7. Microstructure of a Corroded High Copper Dental Amalgam. (After Reference 123)

interior of amalgams (122,145).

Several authors have used the SEM to characterize the corrosion attack on the high Cu amalgams (123,124,149,153). It was determined that the Cu_6Sn_5 reaction product was preferentially attacked leaving Sn rich products in the corroded areas. This attack has also been shown to be accompanied by an increase in the gamma-1 (Ag-Hg) to beta-1 (Ag-Hg) phase transformation (123,124). A typical area of corroded amalgam is shown in Figure 7 and the altered microstructure can be compared to Figure 4.

Recently efforts have been made to correlate clinical deterioration events with microstructural variations between different products (142,187). Obvious microstructural changes are apparent when

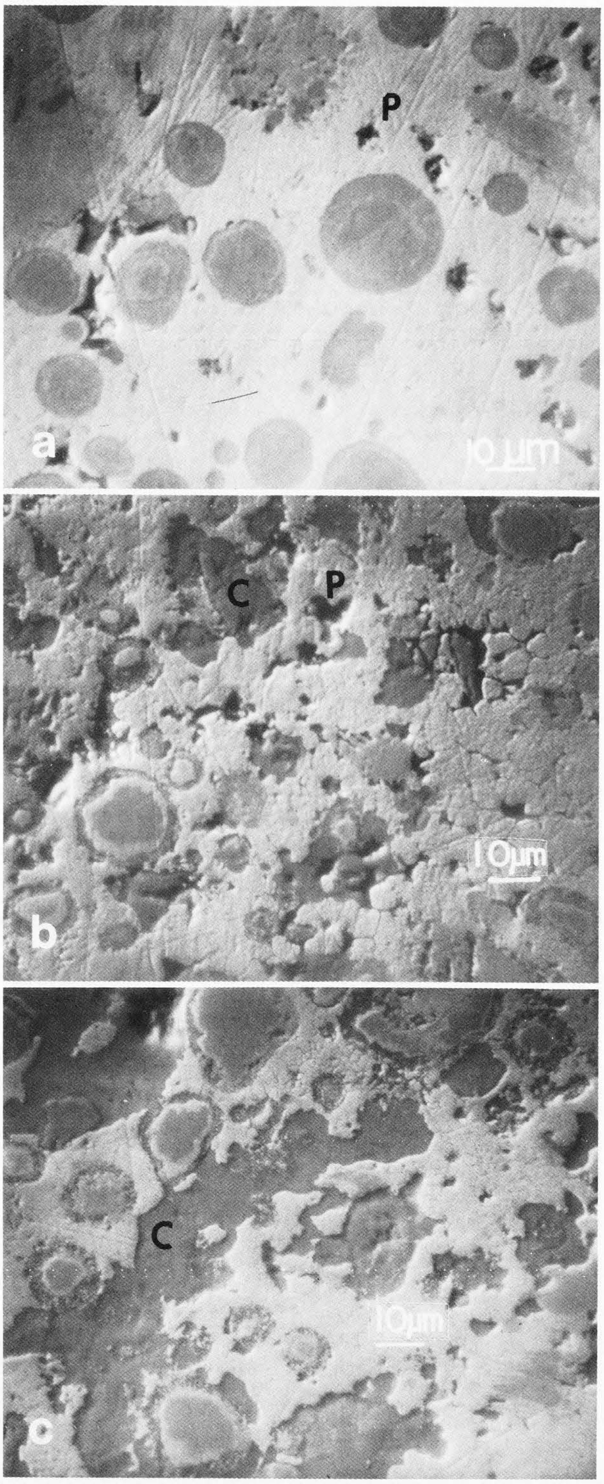

Figure 8. Variations in Corrosion and Porosity in the Microstructure of Retrieved Clinical Dental Amalgam Restorations with the Same Clinical Status. (a) Low Porosity. (b) Moderate Porosity and Corrosion. (c) High Corrosion Product Content. (P= Pore; C= Corrosion Product) (After Reference 142)

comparing restorations which are clinically evaluated as good versus those that are judged as in poor condition. Marked quantities of corrosion products and fractures are typical in the severely deteriorated state, while good restorations exhibited only minor changes in microstructure (187). Efforts to quantify the microstructural characteristics which are unique to a given state of deterioration are more difficult and time consuming. Samples retrieved from controlled clinical trials of the same amalgam and having the same clinical evaluation grade, often show marked variation in corrosion product content and porosity (142) as shown in Figure 8. Berry and Osborne (27) reported on recent clinical trials which have shown that within the class of high Cu amalgams, those materials containing small amounts (1-2%) of Zn appear to be clinically superior to those without Zn. Zn containing high Cu amalgam restorations form a thick Zn rich layer at the tooth-amalgam interface (142) and this may contribute to their apparent clinical superiority.

Bonding

Bonding techniques have revolutionized esthetic dentistry. This technique consists of applying an acid solution to the enamel surface for periods of 1-2 minutes which produces a microscopically rough surface (Figure 9). Columns of packed hydroxyapatite crystals (enamel rods) are partially relieved by acid dissolution. That process generates microscopic irregularities for retention. Resins or composites can be applied to this etched surface and polymerized in situ to form a good mechanical bond between the restoration and the enamel surface. The technique was introduced by Buonacore (46). The SEM has been utilized extensively to characterize the nature of etching and the relationships between etched enamel and the restorative material. Initially it was reported that mineral acids preferentially etched the periphery of enamel rods and yielded the necessary roughness. However, it is now known from SEM studies that the etching pattern of a single tooth exhibits significant variations. The enamel rod cores may be etched preferentially, the enamel rod peripheries may be etched preferentially, or a uniform relatively featureless pattern can occur (143,163,202,203). These patterns have been called types 1, 2, and 3, respectively, and occur for both permanent and primary teeth (39,40). Figure 10 shows a typical example of these patterns.

Most commercial products use phosphoric acids in concentrations from 30-50%. Recent work by Retief et al (191) has shown that pyruvic acid may be a better alternative to phosphoric acid because it produces a rougher surface and higher bond strengths while reducing total mineral loss from the enamel.

Resin which penetrates into etched enamel spaces becomes interlocked with the enamel after it polymerizes. A cross-section of resin interlocked with enamel prisms is shown in Figure 11. The mechanical attachments are called tags. The appearance of the tags is revealed in Figure 12 by decalcification of the enamel. Bayne et al (21) have designated both macrotags and microtags as being involved with bonding.

The acid etch technique is utilized for a variety of procedures including anterior and posterior composite restorations, sealants to prevent pit and fissure caries (169), attachment of orthodontic brackets and devices (155,156), attachment of esthetic veneers to teeth for cosmetic purposes (34,79), and bonding of resin retained bridges (121).

The success of bonding techniques for the enamel surface of the tooth has spurred the search for materials which will bond to dentin, the hard tissue layer below dental enamel. Acid etching can produce surface changes in dentin but the procedure may be irritating to the pulp tissues below the dentin. It also yields very poor mechanical bond strengths between resin and dentin since the fundamental structure of dentin is different than enamel (15,42,92). Most work has been concentrated on efforts to develop materials which will form chemical bonds to the dentin components rather than producing mechanical retention. Dentin bonding agents function as coupling agents. Some part is chemically reactive to tooth structure. Another part is reactive with the overlaid filling materials.

Various approaches to the problem have been taken (9,30-32,76,96,159,171,212). Bowen and co-workers (30-32) have introduced a relatively complex (multistep) procedure based on (a) ferric oxalate, (b) NTG-GMA (the adduct of N-p-tolyl glycine and glycidyl methacrylate), and (c) PMDM (reaction product of pyromellitic acid dianhydride and hydroxyethyl methacrylate), or (a) ferric oxalate, (b) NPG-GMA (reaction product of N-phenylglycine and glycidyl methacrylate), and (c) PMDM, which appears to bond to dentin. The adhesive mechanism is still under investigation, but a commercial product based on this system has been introduced. The characteristics of several other commercial products and experimental systems have been studied by Eliades et al (76). Other products are based on polymeric chlorophosphate esters which reportedly bond by forming ionic bonds to the calcium of hydroxyapatite mineral. Polyurethane bonding agents (9) are set in the presence of moisture and can react with carboxyl, hydroxyl and amino groups in the dentin. Munksgaard and Asmussen (159) reported strong bonding to dentin by aqueous mixtures of glutaraldehyde and HEMA (hydroxyethyl methacrylate). That is the basis of a product recently introduced in Europe. It reportedly forms crosslinks with the collagen portion of dentin. Since these and other new dentin bonding materials have significant commercial potential in restorative dentistry, it will take some time to clearly define which systems hold the most long term promise in clinical dentistry. To date the reported results for bond strength are often controversial and widely variable (171).

The SEM has been used extensively in this field to characterize the nature of the dentin surface at various steps in the bonding procedures. One of the first problems which became apparent during these types of investigations was the interference of the smear

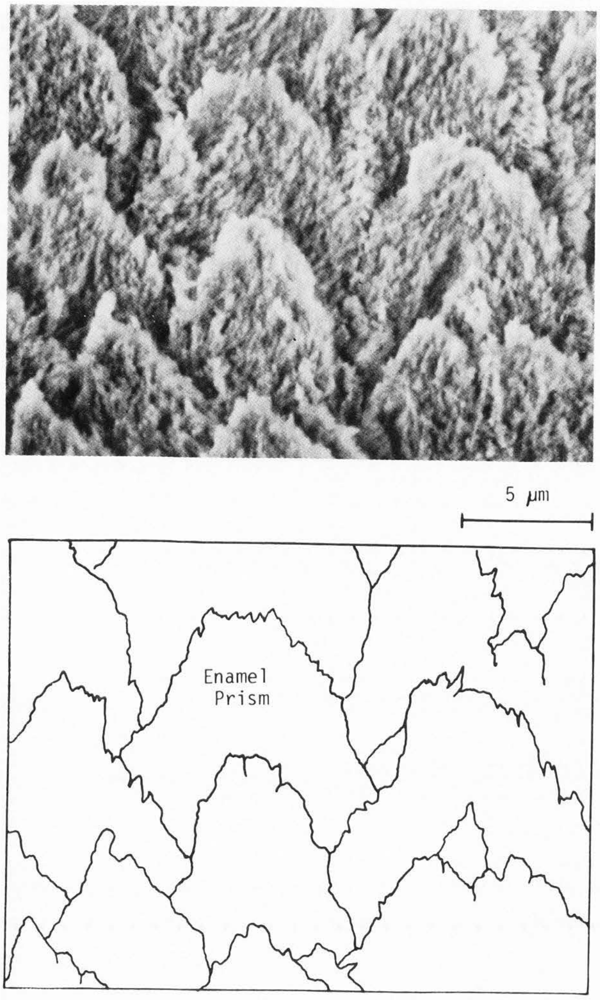

Figure 9. Acid Etched Dental Enamel Rods. (Etching Preferentially of Enamel Rod Peripheries)

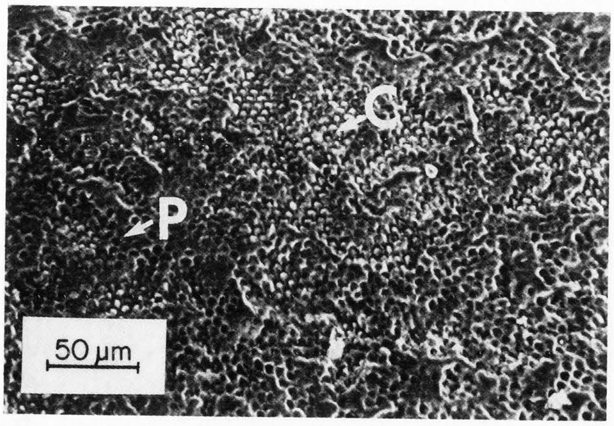

Figure 10. Variations in Etching Pattern of Enamel. (P= Periphery Etching of Rods; C= Core Etching of Rods) (After Reference 143)

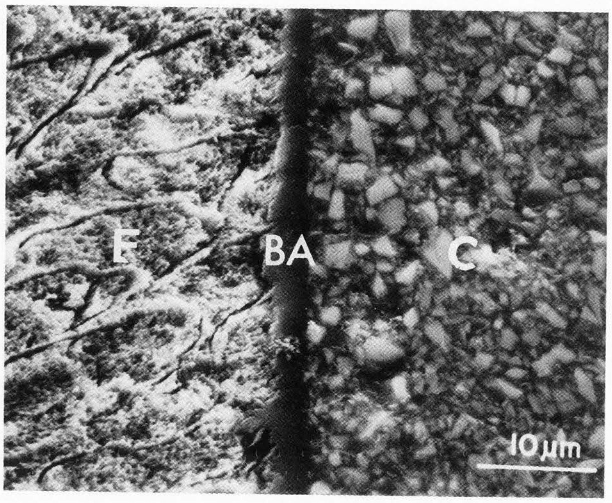

Figure 11. Cross-section of Enamel Rods (E), Bonding Agent (BA), and Composite Resin (C).

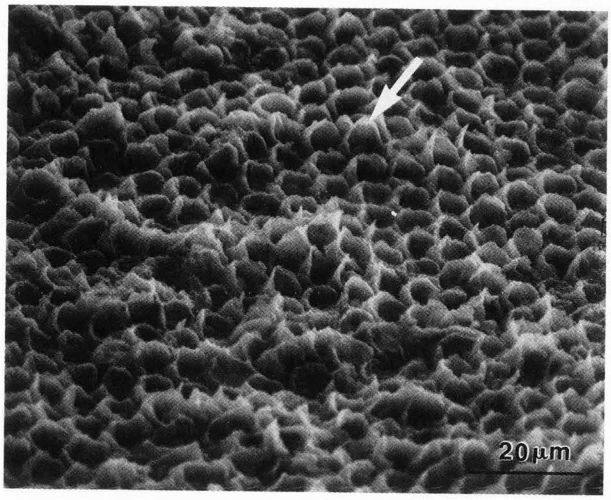

Figure 12. Bonding Agent Tags (Arrow) Exposed by Decalcifying Enamel.

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layer (29,38,72,75). As shown in Figure 13, a layer of compacted debris from cavity preparation is smeared over the surface of both enamel and dentin. The layer on enamel is removed by acid etching of enamel. However, the smear layer normally remains on dentin and interferes with bonding agents unless it is removed by acid etching of the dentin. The layer is only about 5 µm thick but does effectively cover the dentin surface and obscure cut dentinal tubules (Figure 14). Most manufacturers of dentin adhesives recommend the use of cleansing agents to eliminate the smear layer before bonding.

Bonding to dentin on root surfaces is employed to treat root caries and reduce root surface sensitivity. Most root surface sensitivity is attributed to exposed dentinal tubules. Therefore, adhesives have been used to help bond to root surfaces and occlude surfaces of sensitive areas (41).

In cases where bonding agents are applied to dentin prior to acid etching for bonding to enamel, there is still clinical controversy as to whether the dentin adhesives afford protection from the etchant. Eick and Welch (73) have recently examined the nature of some dentin bonding agents after etching.

Certain cementing agents, polycarboxylate and glass ionomer cements, are based on polyacrylic acid which can form primary chemical bonds with the mineral portion of the dentin and enamel. These materials will be discussed in the cements section later. The systems which are being developed for adhesion of polymeric resins to dentin are under very active development.

Dental Composites

During the 1950's, Bowen developed a new monomer system called BIS-GMA (diglycidyl methacrylate adduct of bisphenol-A) which could be polymerized into a crosslinked network that was significantly stronger than polymethyl methacrylate. It was also much less irritating to the pulp. It was compounded with silane coated silica fillers for reinforcement, translucency, and esthetics. This formed the basis of the first dental composites. Since that time, there has been an explosion in commercial products based on modifications involving the types of silicate fillers, particle size of fillers, loading levels of fillers, methods of silanation, modifications of the monomer matrix, and variation in the method of polymerization activation (221). Table 2 describes the current methods of composite classification.

The original composites contained relatively large filler particles that prevented intraoral finishing or polishing to a smooth surface as shown in Figure 15. The large filler then was replaced by a very small particle size filler that was ideal for finishing but which produced such an increase in the surface area of contact of the filler and matrix that the viscosity of the mixture became prohibitively high. Thereafter, a range of compromises developed with either lower filler contents or intermediate sized fillers. Throughout the development of new fillers, the SEM has been used to examine the filler particle size distribution within the matrix and the pattern of fractures through the matrix. During the past few years there has been increasing focus on raising the filler level (61,68,69,97,204,208).

Composite can be formulated to be activated with chemicals, with ultraviolet light, or with visible light. The chemically activated systems are designated as self-curing or auto-curing composites. Generally the visible light-curing systems demonstrate the best resistance to discoloration and they have superseded ultraviolet activated systems and most chemically cured systems. Light cured formulations avoid the need for two component mixing which generates porosity that is clinically detrimental and they eliminate the restraints of fixed working times. The distribution and amount of porosity has been categorized by using SEM analyses of composite cross-sections (80,81,83,87,108,190,204,220,222). Fortunato et al (81) has reported that porosity is caused by mixing and clinical manipulation procedures.

Table 2. Classification Systems for Composite Restorative Materials.

1. Filler Classification Systems:

   a. Amount of Filler:

00 w/o	--- 00 v/o	(Unfilled Resins, P/F Sealants)
	--- 10 v/o	(Lightly Filled Sealants)
	--- 20 v/o	Microfills
50 w/o	--- 30 v/o	
	--- 40 v/o	Hybrids for Anterior Restorations
75 w/o	--- 50 v/o	Macrofills
	--- 60 v/o	Midifills
85 w/o	--- 70 v/o	Hybrids for Posterior Restorations
	--- 80 v/o	(Enamel)
100 w/o	---100 v/o	

   b. Filler Particle Size (or Distribution):

(1)	Macrofill:	Large Particle Size (40 μm)	10-100 μm
(2)	Midifill:	Medium Particle Size (4 μm)	1-10 μm
(3)	Minifill:	Small Particle Size	0.1-1 μm
(4)	Microfill:	Very Small Part Size (0.02 μm)	0.01-0.1 μm
(5)	Hybrid:	Mix of Very Small and Med	

   c. Method of Filler Addition:
      (1) Homogeneous Filler:
         (a) Midifill
         (b) Microfill
         (c) Hybrid
      (2) Heterogeneous Filler:
         (a) Microfill
         (b) Hybrid

2. Matrix Classification Systems:

   a. Matrix Composition:
      (1) BIS-GMA or BIS-GMA Like Monomers
      (2) Urethane Dimethacrylate Monomers

   b. Activation Method for Matrix Polymerization:
      (1) Auto-Cured (Self-Cured)
      (2) Light-Cured (Visible Light Cured)

The bulk properties of composites are the result of contributions of the matrix resin properties, the silane interface, and the reinforcing filler properties. Unfortunately the behaviors of each component are complex and are rarely uniform. The degree of conversion of monomer to polymer in the matrix is only about 55 to 65%. The silanation of different fillers is variable in effectiveness (53). Soderholm has shown that composites with certain types of fillers are more prone to de-silanation in water and these events have been documented with the SEM (207,209,210).

At the intraoral surfaces of composites, there is wear and disintegration that produces a rough surface and also loss of vertical dimension with time (1,113). Figure 16 is a schematic cross-section of a worn composite. Jorgensen has proposed that composite wear occurs when the softer matrix phase is eroded by the abrasive action of the food bolus during mastication (107,109). Gradual loss of the matrix undermines support of the individual filler particles and ultimately particles are exfoliated (170). Wu and others (148,228,229) have also suggested that the resin matrix is weakened by exposure to intraoral fluids causing the surface layers to develop microcracks throughout the resin during occlusal loading. Leinfelder (118) conducted an SEM study which showed that microcracks were present on worn occlusal surfaces.

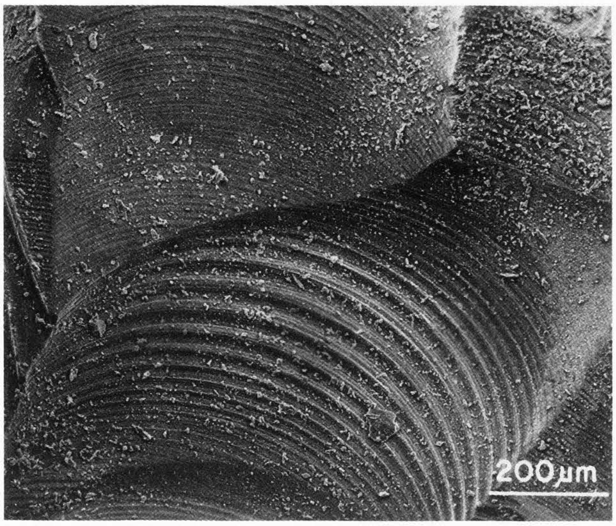

Figure 13. Smear Layer on the Bottom Surface of a Cavity Preparation.

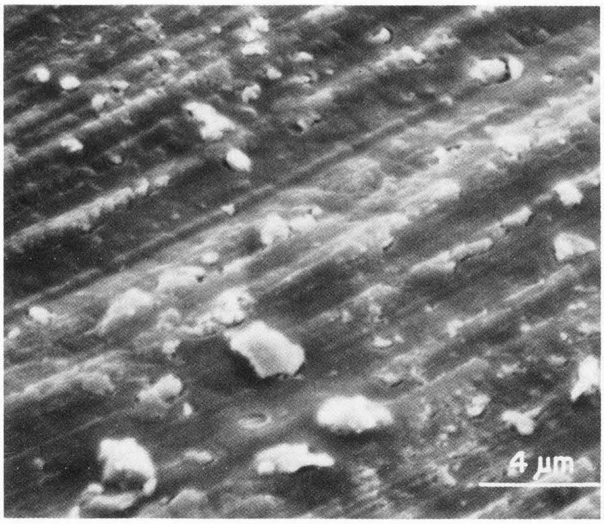

Figure 14. High Magnification View of Dentin Smear Layer.

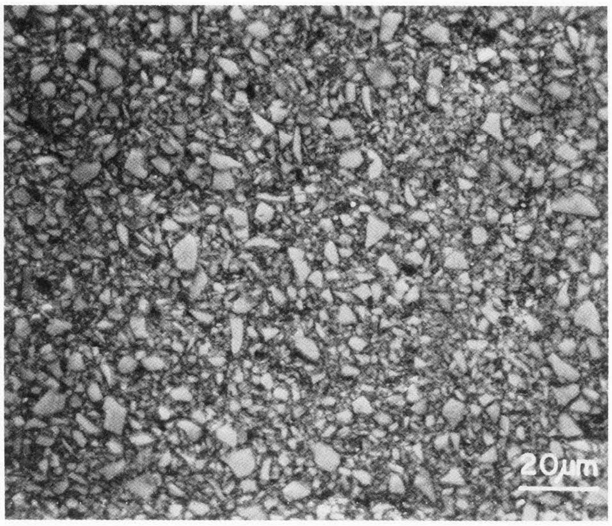

Figure 15. Cross-section of Macrofilled Composite Resin Showing Filler Particles Dispersed in the Polymer Matrix.

Intraoral wear is a combination of processes as demonstrated by Lutz et al (128). Some surfaces are in direct contact with opposing teeth resulting in two body wear. However, wear occurs across all surfaces as a result of food bolus abrasion in three body wear. Wear in contact free areas must be less that 150 µm during the three years after the restoration is inserted in clinical studies for the American Dental Association (ADA) to accept the composite material for use in posterior applications (2). An example of clinical wear of posterior composite is shown in Figure 17 (48). Posterior composite restorations still do not demonstrate adequate wear resistance for many restorative situations (99,102,117,119,128,215,223,230). Clinical investigations employ a combination of direct and indirect macroscopic techniques to estimate the extent of occlusal wear (70,85). Impressions and epoxy replicas (109) are used only when site specific wear information is required. DeLong and Douglas (64,66) have demonstrated a method to digitize the topology of worn composites so that surfaces can be computer analyzed. To some extent that and various other approaches (195) replace the use of the SEM for surface characterization.

With the inevitable accumulation of wear, repair or replacement of composites becomes a key concern. The attachment of new composite to old composite as a repair has been investigated by SEM and mechanical testing techniques to determine rebonding strengths and the effects of mechanical

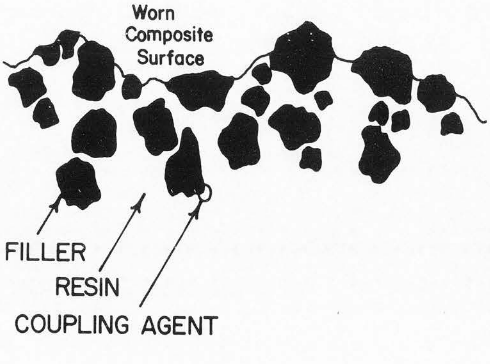

Figure 16. Schematic Cross-section of Worn Composite Resin Demonstrating Exposure of Filler Particles as a Result of Matrix Erosion.

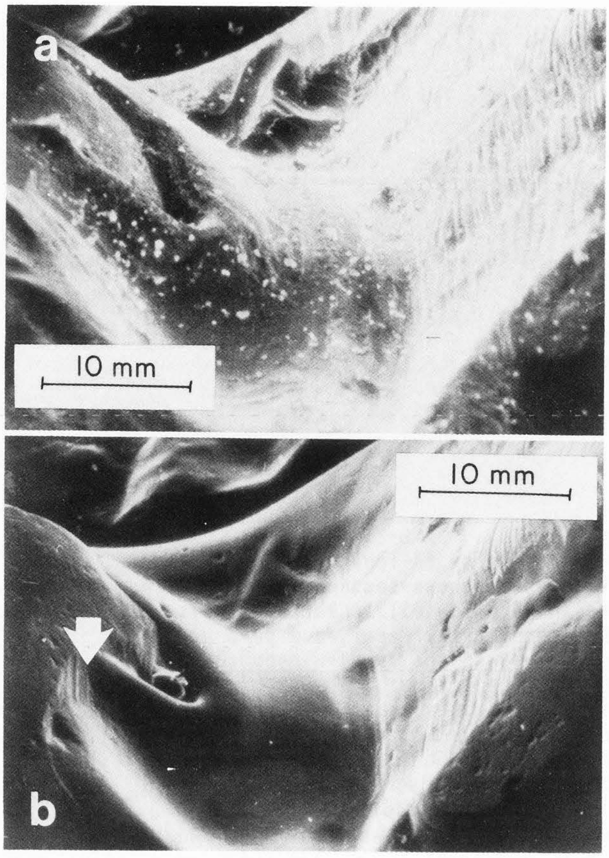

Figure 17. Wear on a Composite Restoration. (a) Replica at Insertion. (b) Replica After 6 Months In Situ. (After Reference 48)

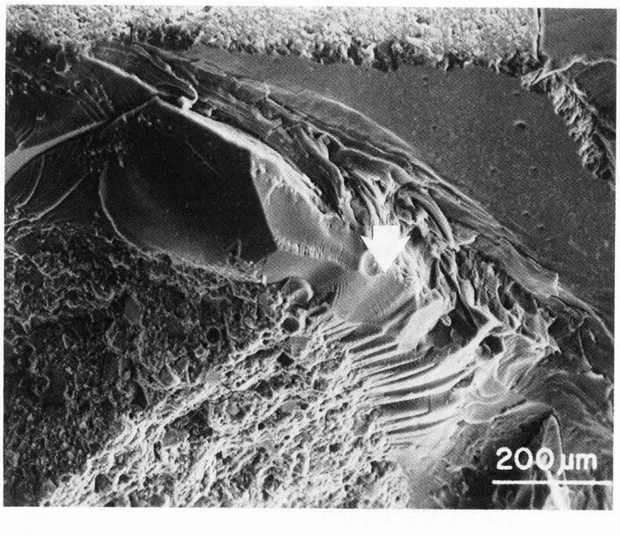

Figure 18. Cross-section Through a Rebonded Composite Resin Showing Concoidal Patterns (Arrow) Associated with Fracture Propagation in the Bonding Agent.

surface preparation techniques (10,35-37,50, 52,86,111,125,126,147,150,162). It has been difficult to use SEM analyses to effectively examine the failed surfaces because the failures generally cross over the repaired boundary. Improved fractographic analyses of the origin and path of cracks during mechanical failures have recently been reported (86). One example is shown in Figure 18.

During curing of composite there is polymerization shrinkage that tends to pull bonding agent away from the walls of the restoration (11,33,63,71,94,95,160). To minimize these stresses, most composites are added and cured in increments of no more than 1.5 mm at a time. Eick and Welch (74) have demonstrated that even with that precaution that there is still some marginal separation. It not only reduces enamel retention, but also permits microleakage (67,91). Recent work by Cox (59) and Bergenholtz et al (26) have shown that the penetration of endotoxins of intraoral bacteria along marginal openings is the primary cause of pulpal irritation leading to clinical changes in pulp vitality.

Dental Cements

In dentistry, dental cements were originally used as insulating bases under other restorations such as dental amalgam or direct gold. Over the past 120 years cements have also been employed as direct filling materials, temporary restorations, root canal filling materials, and as periodontal dressings. The principal requirements for almost all applications are that cements provide some mechanical strength, resist solubility and disintegration, and not cause irritation to tissues during setting (84,182). Of these requirements, the resistance to solubility and disintegration has been the most challenging because the actual chemical reactions of cements have been poorly understood and their in vitro test and in vivo test behaviors have never correlated very strongly. During the past several years there has been increased emphasis on understanding these events.

Dental cements are mixtures of reactive powder particles that chemically act as bases and react with acidic liquids to form a salt as a reaction product. The microstructure of set dental cements is a matrix of reaction products embedded with unreacted powder particles. The particles are less soluble, increase the mechanical strength, and reduce the amount of chemical reaction that might adversely influence the pulp below cemented surfaces (20,60,182).

One of the earliest dental cements was a mixture of zinc oxide and eugenol (ZOE). Wilson et al (225) have reported that the zinc eugenolate reaction product matrix is very weak and is susceptible to hydrolytic disruption. Microscopic techniques such as SEM and EDS have been difficult because of the small grain size of the phases and the inorganic nature of several of the phases. Recently, Bayne et al (17,22-24) have reported the characteristics of the matrix. Zinc eugenolate crystals are shown in Figure 19. Prosser and Wilson (188) have examined the effect of different zinc oxide types. It has been shown that other

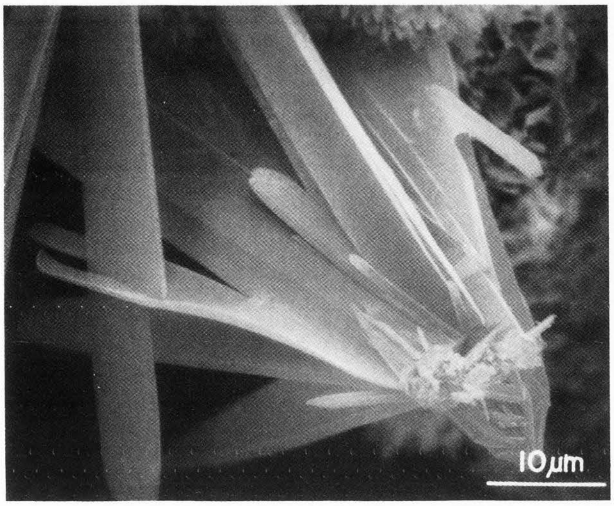

Figure 19. Pure Zinc Eugenolate Crystals.

variables such as temperature and unusual acids also affect solubility (19,25).

To improve the solubility resistance and mechanical strength of these materials it is common to add reinforcing polymer powder beads (Reinforced ZOE). The actual mechanism of reinforcement is unknown but the beads seem to at least partially dissolve in eugenol during mixing. Figure 20 demonstrates the strange sponge-like appearance that some beads may acquire during partial dissolution and entrapment into the matrix.

Despite polymer reinforcement effects, Brauer et al (45) have shown that the best improvements in zinc oxide and eugenol formulations are realized when most of the eugenol is replaced with

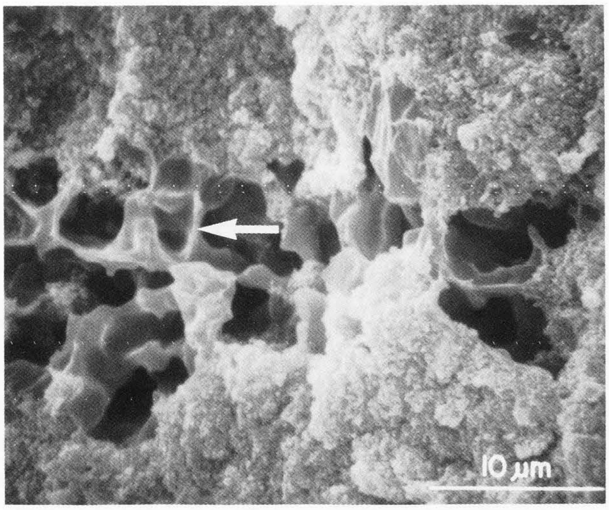

Figure 20. Partially Dissolved Reinforcing Polymer Bead (Arrow) in Reinforced ZOE Cement.

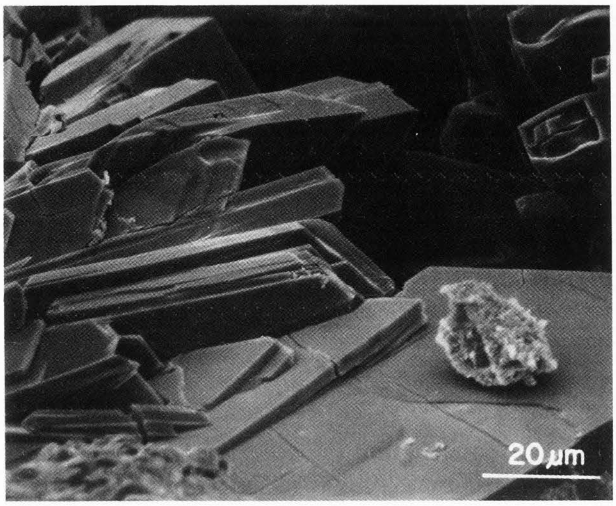

Figure 21. Partially Dissolved ZOE-EBA Cement after 24h Water Immersion.

ethoxybenzoic acid (EBA). Phillips and Love (184) explored the effects of a range of cement modifiers on solubility resistance. These modified cements (ZOE-EBA) appear to form a mixture of both zinc eugenolate, zinc ethoxybenzoate crystals, and some other intermediates (18). Clinical studies indicate that these cements have high solubility during the first few hours (54). That is evidenced by the appearance of dissolved cement specimens as shown in Figure 21. Brauer et al (44) have shown that the strength and solubility resistance are improved by reinforcement with Al_2O_3.

Recently, ZOE-EBA has been modified by replacing the eugenol with hexyl vanillate (43,211). In these new cements (ZOHV-EBA) zinc oxide is reacted with hexyl vanillate (HV) and EBA. These materials are extremely resistant to dissolution and demonstrate much better mechanical strength. Faison and Bayne (78) have analyzed the microstructure of these cements. Both ZOE-EBA and ZOHV-EBA also contain alumina reinforcing powder particles and rosin. The microstructure of ZOHV-EBA is shown in Figure 22.

The classical dental cement for retention (luting) of cast crowns and bridges has been zinc phosphate cement (ZP). It is a mixture of zinc oxide powder with phosphoric acid in water. The setting reactions include several intermediates. It is presumed that the final product is crystalline tertiary zinc phosphate. The matrix has only been superficially studied by replication techniques (88). Jorgensen (105) has suggested that the type of zinc oxide may influence the final matrix as well. The surface of most clinical zinc phosphate cements forms hopeite crystals during exposure to excessive moisture. An example of this side reaction is shown in Figure 23. The principal advantage of ZP cements over others is their relatively high mechanical strength. However, the fact that phosphoric acid is incorporated into the cement requires that

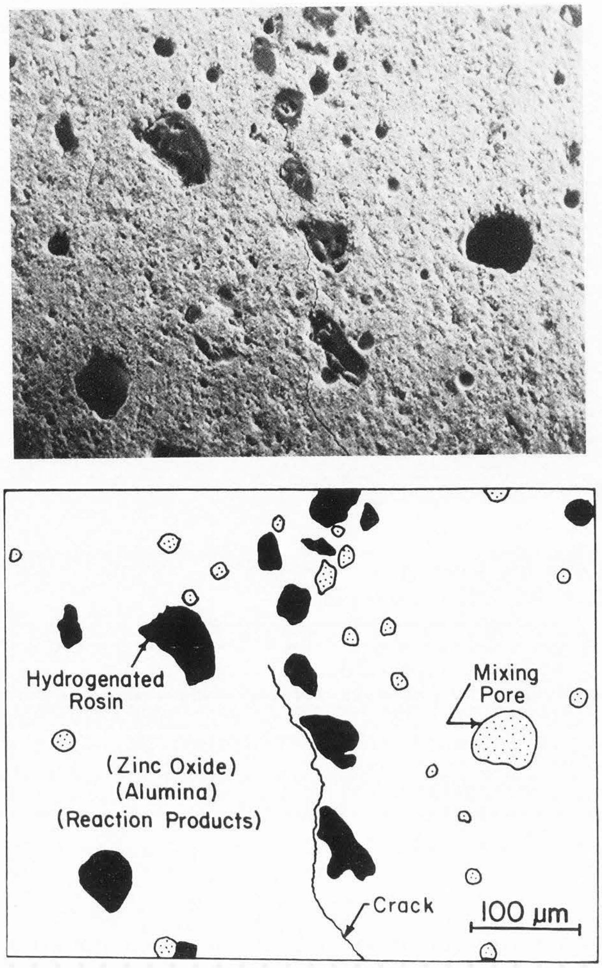

Figure 22. Microstructure of ZOHV-EBA cement. (a) SEM Micrograph. (b) Schematic Diagram Identifying Phases.

special mixing and operative procedures be used to minimize pulpal irritation.

During the late 1960's, Smith (151,152,205) created a new and adhesive dental cement based on a mixture of zinc oxide with an aqueous polyacrylic acid solution. The resulting cement is called polycarboxylate cement (PC). Setting occurs when partially dissolved zinc oxide releases zinc ions to crosslink polyacrylic acid chains. Figure 24 shows the zinc polyacrylic matrix after removing embedded zinc oxide particles. At the same time that setting is occurring it is also possible for pendant carboxylic acid groups on the polymer to chelate and bond to calcium ions on the surface of tooth structure (51,206). The actual interactions with tooth structure have been impossible to observe directly with chemical analysis techniques or SEM approaches and understandings of adhesion have been principally based on laboratory bond strength studies.

In the mid 1970's, another variation on the same theme was offered when silicate glass powder was added to aqueous polyacrylic acid solutions. The mixture was designated as glass ionomer (GI) cement. Its advantage over PC cement has been that it provides esthetics (158). Despite widespread trials of GI cement in a range of dental applications, it has not demonstrated superior performance to alternative materials in any single application (182).

All dental cements seem to be porous to some degree and capable of continued reaction with their intraoral environment (25). This makes understanding their behavior very complicated. In addition the reactants and products are both organic and inorganic materials which are not amenable to chemical characterization procedures such as EDS. To date the only reported EDS analyses have been limited to relatively well characterized systems in which standards and optimal analysis conditions have been possible (18).

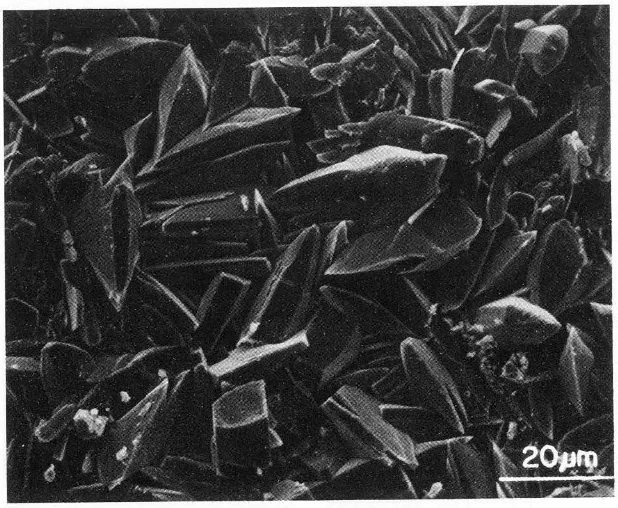

Figure 23. Hopeite Crystals Covering the Surface of Zinc Phosphate Cement.

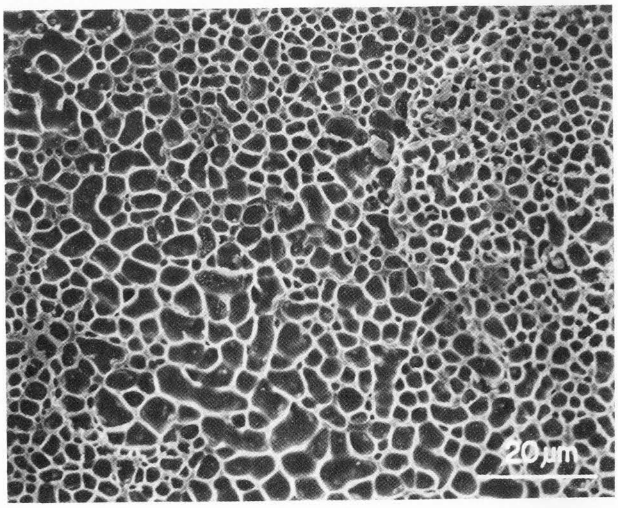

Figure 24. Matrix of Polycarboxylate Cement After Removing Residual Zinc Oxide Particles.

Casting Alloys

Alloys used for casting crowns and bridges can be conveniently divided into two major groups. Alloys intended primarily for use with ceramo-metal restorations will be discussed later. The second major group are alloys developed for all metal restorations and normally have lower melting ranges and can be cast with traditional dental methods.

Gold alloys containing a minimum of 75% Au were the traditional materials of choice for metallic fixed prostheses (3). However after the dramatic increase in the cost of gold, many new and more economical alloy systems have been evaluated. The SEM and/or EDS have been utilized to characterize their compositions and microstructures (116). The more generally successful alternative alloys are the low Au casting alloys (157) and Ag-Pd alloys. The low gold casting alloys generally range from 10-70% Au, with most alloys between 40 and 65% Au, and are often based on Au-Ag-Cu ternary or Au-Pd-Ag-Cu quaternary alloys (197). A recent classification divides all alloys into three groups: high noble alloys with at least 60% noble elements, noble alloys with at least 25% noble elements and predominantly base metal alloys with less than 25% noble element content (4,5). Therefore the low gold alloys would be classified as noble alloys. The second group of widely used alloys are based on Ag-Pd and contain 20-30% Pd and can be classified in either the noble or base metal groups. The mechanical and physical properties of these new alloy groups are comparable to the traditional high noble alloys (28). Perhaps the most significant problem with the alternative alloys is their potential for corrosion and tarnish. The SEM and EDS have been used as an adjunct in a number of studies of the microstructural basis for tarnish and corrosion.

Several alloys of the Au-Cu-Ag system have been shown to form a grain boundary precipitate during hardening treatments (120). Sarkar (196) demonstrated by SEM/EDS methods that such Ag rich precipitates are corroded preferentially and form AgCl in a chloride containing solution such as saliva. Similar results on a broad range of alloys of this family were reported by Gallant and Wright (82). Wright et al (227) also found that in single phase alloys of this group, the corrosion characteristics were controlled by the noble metal content of the alloy. Corso et al (58) found a similar dependence on nobility and demonstrated via the SEM that in low gold alloys that the addition of Cu yielded a two phase structure with a corrosion prone Ag rich phase. Corso et al (57) also reported on the tarnish resistance in artificial saliva and sulfide solutions for the same alloys. They found that tarnish occurred on the Ag rich phase and that heat treatments used to eliminate or minimize two phases had a more pronounced effect on tarnish than it did on corrosion. Hero and Valderhaug (98) also found that as cast two phase alloys tarnished more than heat treated alloys, but found that tarnish occurred predominantly in Cu rich areas rather than Ag rich areas. They attributed this to very fine alternation of Ag and Cu rich lamellae in the Cu rich areas which act as microgalvanic cells. Holland et al (101) evaluated the same alloy for corrosion in various structural states and found that the single phase structure was most corrosion prone, while the multiphase structures were more tarnish prone.

Binary alloys of Ag and Pd form a continuous solid solution and therefore alloys of this family are single phase when homogenized. Most commercial alloys for completely metal crowns have 60-70% Ag and approximately 25% Pd. The remaining alloying elements are usually Au, Cu, Zn and In. Many of these alloys are classified as noble alloys based on the combined Au and Pd contents.

Vaidyanathan and Prasad (218,219) evaluated the tarnish and corrosion of alloys over the entire range of the Ag-Pd binary system. They found that Pd reduces both corrosion and tarnish of Ag and that both tarnish and corrosion are initiated at grain boundaries in the single phase system. Sarkar et al (198) studied the corrosion in chloride solutions of five commercial Ag-Pd alloys in the as cast state. These alloys contained varying amounts of Au, Cu, In and Zn. The microstructures consisted of a dendritic phase and a matrix phase in which both phases consisted of Ag-Pd solid solutions. The matrix phase contained more Ag and was the site of corrosion attack. Au additions improved corrosion resistance and Cu additions adversely affected corrosion resistance.

Significant additions of Cu to the Ag-Pd alloys result in formation of additional phases which decrease corrosion and tarnish resistance. Niemi and Hero (164,165) and Niemi and Holland (166) studied the relationships of microstructure and corrosion and tarnish resistance in commercial and experimental alloys of the Ag-Pd-Cu-Au system. They identified a variety of phases by means of SEM, microprobe, and x-ray diffraction including Pd-Cu and Pd-Cu-Zn phases. Microgalvanic cells were active in these materials and resulted in decreased corrosion and tarnish resistance.

Dental Ceramic Restorations

Ceramic dental restorations are esthetic alternatives to metallic restorations. Completely ceramic and ceramic bonded to metal restorations both are used in dentistry today. Completely ceramic restorations have two major shortcomings. Their high hardness results in the wear of opposing teeth. Their inherent brittleness leads to clinical fractures. Both problems are reduced by fusing a ceramic layer onto a metal substructure. SEM/EDS analyses have been used to examine both types of ceramic restorations.

In ceramic bonded to metal restorations the critical feature is the bond between the ceramic and metal (181). An appropriate bond involves an electronic structure including metallic bonds in the metal, oxidation of the metal surface, and ionic bonding of the metal oxides to the oxides in the ceramic layer. SEM/EDS analysis of the interface has been the primary source of identification of the elements participating in the bonds. When this type of restoration first became popular, the most common substrate alloy contained 80 to 88% Au, with Pt and Pd making up a total of approximately 97% noble metals. Sn and In were added to promote the formation of oxides which would bond with the ceramic. When the cost of noble metals increased dramatically in the 1970's a variety of alternative alloys was introduced. Many contained the noble metals Au and/or Pd but had significant non-noble metal contents. Others were entirely base metals, predominantly Ni-Cr alloys. All these alloys contain elements which should preferentially oxidize and form bonds to the ceramic. However, their interfaces are inherently difficult to study and offer a major analytical challenge. Often in investigations of metal-ceramic interfaces, insufficient attention has been directed to the problems associated with beam spreading and characterization of excitation volumes at the interface. Although SEM/EDS techniques have been extremely useful in identifying concentration gradients and oxide formations at or near the interface, the details of the interface are still not well understood.

The change in concentration of major alloying elements as well as the minor elements expected to form in the oxide layer have been studied by x-ray line scans across polished interfaces in gold based alloys (6,115). Lautenschlager et al (115) found sharp changes in Au, Pt, Ag, Si, and O concentrations near the metal-ceramic interface and gradual increases in Fe and Sn within a few micrometers of the interface. Anusavice et al (6) found a Sn rich layer in the interface with Sn depletion on the ceramic side only, showing that the Sn in the interface was from the ceramic. Elemental distribution x-ray maps have been used to show concentrations of major and minor alloying elements near the metal-ceramic interfaces (114,172,173,214). An example of such maps is shown in Figure 25. Ohno, et al (173) found internal and/or external oxide layers, depending upon the base metals present in the Au alloys.

The substantial use of Ni-Cr alloys as economical alternatives to Au alloys resulted in a need to understand microstructural changes and the oxides which formed near the metal-ceramic interface of these alloys. Compositional

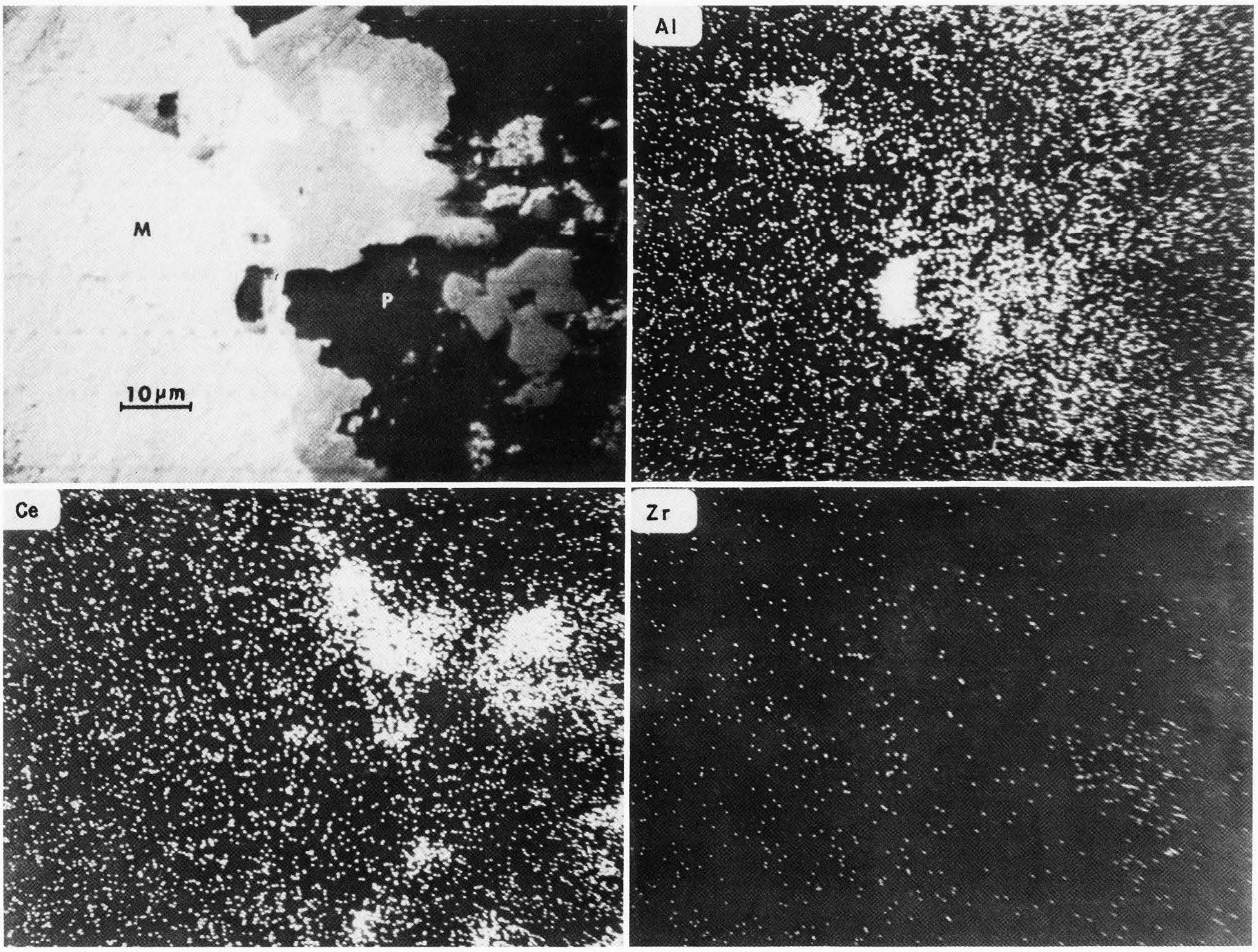

Figure 25. SEM Micrograph and Elemental X-Ray Maps of Al, Ce, Zr Elements Near the Interface of a Ceramic-Metal Restoration (P= Porcelain, M= Metal). (After Reference 114)

variations across the interfaces have been studied in terms of oxide phases presumed to form on the metal (7,8,131,224) and the microstructural features in the metal near the interface (12,131, 192,224). Williams, et al (224), Baran (12), and Ringle et al (192) identified thin zones in the metal near the metal-ceramic interface which were distinctly different in composition from the bulk metal. Mackert, et al (130,131) characterized Ni and Cr rich oxides in Ni-Cr and Co-Cr alloys which had both adherent and non-adherent oxides and concluded that minor alloying elements had a role in controlling adherence of the oxides by affecting the growth mechanism. In alloys with strongly adherent oxide layers, those investigators found large oxide extensions in the NiBe intermetallic phase (macropegs) and small oxide extensions into areas where Be was in solid solution (micropegs). They concluded that Be was the oxide active element responsible for adherence (131) in those systems.

Mackert et al (132) also used SEM and EDS analyses to show that adherence between metal and ceramic is dependent on mechanical locking in Ag-Pd alloys. They identified Ag rich nodules on the surface of a Ag-Pd alloy which formed as a result of internal oxidation of Sn and In. No oxides were found on the surface so it was concluded that the metal-ceramic bond was mechanical in this case.

In addition, the SEM has been used to study surface texture and its effect on the bond strength of ceramic to metal for several alloys ranging from high gold to base metal (49,127). Carpenter and Goodkind (49) showed that a smooth metal surface (0.05 μm Al_2O_3 polish) resulted in interfacial failure whereas rougher surfaces (50 μm or 280 μm) resulted in failure within the porcelain. Qualitative SEM observations of texture confirmed profilometer measurements. They also observed that more voids were present in the interface between base metal and porcelain than in the interface between gold alloy and porcelain.

The SEM has also been used to study the adherent porcelain remaining on the metallic substrate after bond strength tests (179). The extent of coverage has been measured by using EDS to measure the Si counts coming from the remaining ceramic (193) where it can be assumed the Si content of the alloy was negligible. Marginal openings of ceramic-metal restorations have been studied in the SEM as a function of margin design at various stages of the porcelain application (231). No clinically significant changes were found in these evaluations.

The SEM has been widely used to study microstructures (93,129,168,185), defects (65,154, 161,186), and roughness (13,16,112,167,216) of completely ceramic restorations. The presence of the crystalline phase, leucite, has been confirmed with the SEM (129) as well as the determination of its volume percent (93). Small compositional fluctuations have been characterized by back scattered images (185). A Robinson backscatter detector was used to detect small compositional fluctuations, 0.2 atomic number units, to show the difference between leucite ($KAlSi_2O_6$, Z=10.8) and potash feldspar ($KAlSi_3O_8$, Z=10.6) (110).

Porosity measurements have been correlated with strength (161,185) and type of foil used to support the porcelain during the firing stages (161,186). Delong et al (65) used the SEM to study wear facets and porosity during abrasion of porcelain in an artificial mouth. Morena et al (154) showed that cracks in feldspathic porcelain are formed between the leucite crystals but cracks in aluminous porcelains penetrated the Al_2O_3 crystals. Surface roughness has been qualitatively judged in the SEM as a function of dissolution and abrasion (16,167) and as a function of polishing techniques (13,112,216).

Sarkar and Jeansonne (199) used SEM and EDS to study the morphology and chemistry of Sn plated Pt foil versus unplated Pt foil during ceramic firing procedures for completely ceramic crowns. They found the Sn plated Pt foil formed a superior bond because of the rougher interface and because failures occurred cohesively within the ceramic for Sn plated Pt foil. The Sn appeared to penetrate into the porcelain and Sn oxide crystals were identified.

Two new types of completely ceramic restorations, molded (213) and cast (90) systems, have been characterized using SEM analyses. In cast ceramics, Grossman (90) has shown the growth of mica crystals as a function of heat treatment and the interlocking of the mica crystals. The mica crystals can be seen in Figure 26. The formation of the mica crystals is important in providing a translucent restoration as well as modifying the physical and mechanical properties of the restoration.

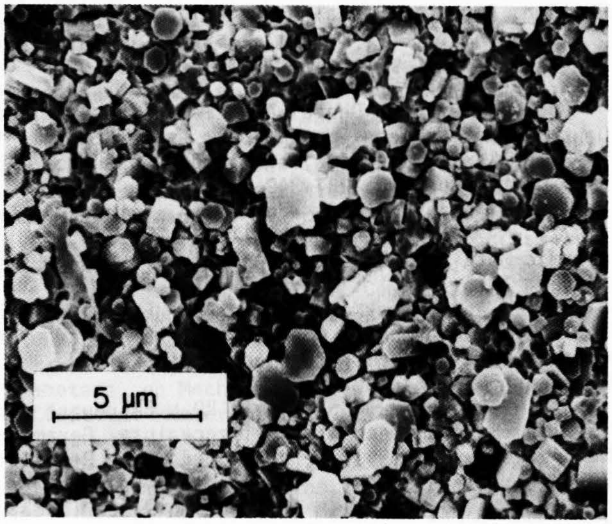

Figure 26. Mica Crystals in Cast Ceramic Restorations.

Summary

SEM, EDS, and microprobe analyses of dental restorative materials have substantially increased understandings of their microstructures and microstructural changes that seem to be occurring intraorally. However, many important events involve phases or zones that are at or just below the resolution limits of most SEM instruments. Also, many of the phases involve oxygen or other light elements that are difficult to detect quantitatively with EDS techniques. Therefore, additional work and improved techniques are needed to distinguish important events that are taking place in restorative dental materials.

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Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.