



THE METALLOGRAPHY OF
DENTAL AMALGAMS

Presented in Partial Requirement for the
degree of Master of Dental Surgery

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SUMMARY

Porosity in dental amalgam has been investigated by many workers and several explanations of the probable cause of porosity have been documented. Artefact development during preparation of amalgam specimens for metallographic examination has had scant reference in the dental literature, and therefore it is the primary concern of this thesis to elucidate some of the factors which produce porosity as an artefact on polished surfaces of amalgam specimens. The present work has shown that porosity as an artefact can be produced by the removal of phases during the polishing process and by ultrasonic cleaning of specimens between polishing stages.

The ease of manipulation, adequate mechanical properties and low cost has established amalgam as the primary choice material for dental restorations. There have been many publications on amalgam failure and it has been suggested that poor cavity design, faulty amalgam manipulation, marginal failure, creep and corrosion are responsible for defective amalgam restorations. The γ_2 phase is the most reactive phase of dental amalgam and the presence of this phase is believed by some authors to predispose amalgam restorations to marginal breakdown. The present work investigates the γ_2 phase by describing a chemical etch to define this phase, so allowing measurement of the volume fraction of γ_2 phase in a range of amalgam alloys. For in vitro corrosion studies two chemical methods for the dissolution of the γ_2 phase are described.

The thesis also describes an alternative polishing and etching procedure and examines whether vibratory polishing is suitable for final polishing of amalgam specimens.

DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and to the best of my knowledge and belief, contains no material previously published or written by another person, except when due reference is made in the text.

JOHN R. ABBOTT

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CHAPTER 1

INTRODUCTION

1.1 GENERAL

The last two to three years has seen a proliferation in the number of restorative dental amalgams and the practising dentist is required to select the most suitable amalgam for his particular application. A considerable number of properties must be considered in making this selection and many of these properties are related to the microstructure of these materials. To date details of most of these microstructures are not known to be available in either trade or scientific literature and one important aspect of the current work has been to develop metallographic polishing techniques for these recently developed amalgams.

Dental amalgam is produced by trituration of Ag_3Sn with Hg and the resulting amalgam is condensed with hand instruments into cavities prepared in the tooth structure. An amalgam produced from the reaction between Ag_3Sn and Hg consists of three phases, γ (silver-tin), γ_1 (silver-mercury), and γ_2 (tin-mercury), (Fig. 1-1). Such an amalgam can be a difficult material to polish and etch because of the variation in hardness, chemical reactivity, and distribution of mercury between phases. Back and Dietrich (1974) believe that etching procedures are unsatisfactory because mercury ions liberated by the dissolution of the γ_2 phase react with other phases to produce artefacts.



Fig. 1-1. MICROSTRUCTURE OF SILVER-TIN AMALGAM
(Shofu spherical, Wing cyanide etch)

γ = silver-tin phase

γ_1 = silver-mercury phase

γ_2 = tin-mercury phase

(x600 oil immersion)

Although much work has been carried out on the structure of polished and etched amalgams there has been very little reported on possible artefacts which can arise during the metallographic preparation of specimens for optical microscopy.

1.2 SCOPE OF THE PRESENT WORK

The research work involved optical examination of amalgam specimens prepared by metallographic techniques of polishing and etching. The research report is divided into the following sections:

(1) *INVESTIGATION OF THE γ_2 PHASE*

The presence of the highly corrodible γ_2 phase is believed by some authors to be responsible for reduced marginal integrity. Therefore in order to eliminate the γ_2 phase manufacturers of dental amalgam alloys are now producing alloys with a high copper content.

A dispersed phase amalgam consists of γ (silver-tin), γ_1 (silver-mercury), and silver-copper eutectic spheres with surrounding copper-tin reaction rings (Fig. 1-2). A one year clinical evaluation by Duperon, Neville and Kasloff (1971) has suggested that dispersed phase amalgam restorations are more resistant to tarnish and pitting than conventional amalgams. A longer term clinical study by Mahler, Terkla and Van Eysden (1973) indicates that superior marginal integrity is obtained with dispersed phase amalgams. These properties are attributed to absence of the γ_2 phase in the dispersant amalgam. However, controversy still exists among research workers over the γ_2

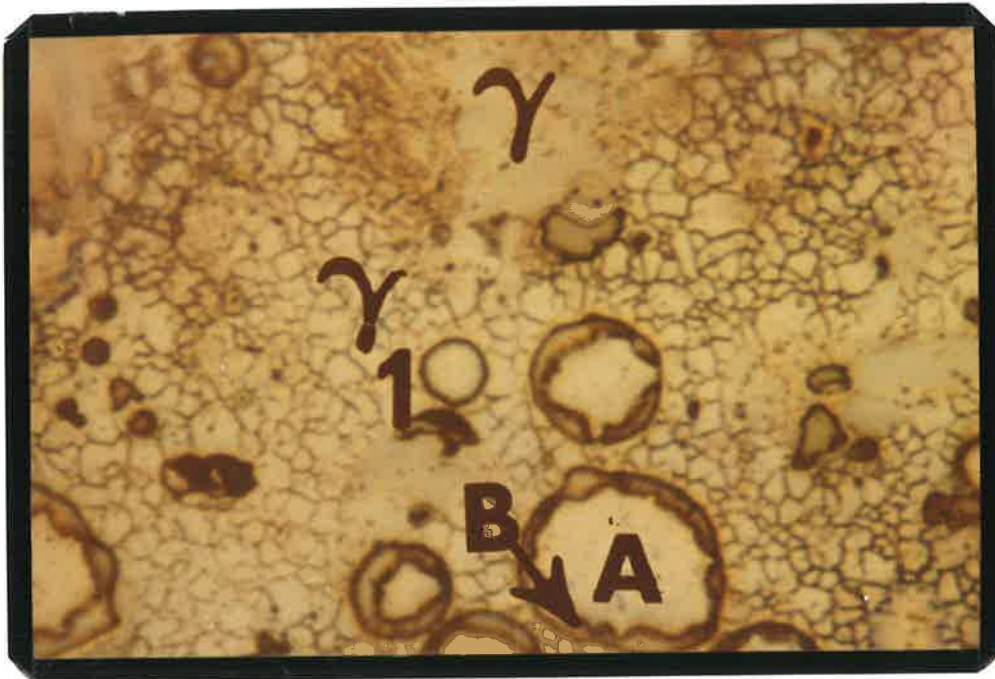


Fig. 1-2. MICROSTRUCTURE OF DISPERSED PHASE AMALGAM
(Luxalloy, vibratory polished)

A = silver-copper eutectic phase

B = copper-tin reaction ring

γ = silver-tin phase

γ_1 = silver-mercury phase

(x240)

content of the copper dispersant amalgams and of the more recent ternary amalgam alloys.

The present investigation is an extension of work undertaken in 1975, which involved specific etchants for the γ_2 phase. Another potential etchant for this phase is described in this research report. These etchants enabled the volume fraction of γ_2 phase to be determined as a function of amalgam brand, type, trituration, temperature and time of storage.

Removal of the γ_2 phase has been achieved with Ringer's solution, 10% sodium citrate, and 1% sodium chloride solution (Sarkar et al (1975), Jorgensen and Saito (1970)). The present study introduces two additional chemical methods which also enable γ_2 dissolution.

(2) POLISHED SURFACE EXAMINATION

a. Porosity from ultrasonic cleaning

Studies of porosity in amalgam have been made as a function of manipulative variables. It is important to establish the bulk porosity of these widely used dental materials.

Ultrasonic cleaning may be used during the preparation of amalgam specimens for metallographic examination. This cleaning method is used to remove abrasive particles remaining after washing which contaminate subsequent polishing stages. This study attempted to demonstrate that some porosity on a

polished amalgam surface could be introduced by ultrasonic cleaning.

b. Phase removal by polishing

Some workers have suggested that removal of the γ_2 phase can occur by polishing or etching procedures. Other workers refute this claim by saying that "proper" metallographic techniques do not produce phase loss. This study involved etching amalgam specimens after each polishing stage and observing whether phase loss had occurred.

c. An alternative polishing method

The present work was concerned with the production of a final polish directly following the abrasive paper stage.

d. An alternative etching method

Before amalgam specimens are etched, it is usual to remove scratches and surface deformation by metallographic polishing procedures using abrasive paper and diamond pastes. The possibility of producing artefacts during the polishing of amalgam specimens prompted an investigation into etching after the abrasive paper stage, rather than after the final polishing stage.

e. Vibratory polishing

After grinding on abrasive papers, mounted amalgam specimens for microscopic examination are polished with diamond or

metal oxide pastes on cloths. The purpose of this study was to examine whether vibratory polishing was suitable as an alternative method of final polishing.

CHAPTER 2

METALLOGRAPHY

The literature survey in this chapter is a summary of a more detailed survey of metallographic theory and practice presented in the 1975 research report. Additions have been made to the skid and vibratory polishing sections.

2.1 GRINDING

The mechanism of metal removal during grinding was demonstrated by Avient, Goddard and Wilman (1960), and by Mulhearn and Samuels (1962). This mechanism involved particles with sharp edges which chipped or displaced surface material laterally resulting in groove formation.

Deformation of the surface layers of a metal specimen can occur during both grinding and polishing operations (Samuels 1955). The superficial layer of a specimen exhibits a severely deformed zone. However, at the polishing stage the strains induced are of a lower magnitude and extend to lower depths compared to those introduced during abrasion (Fig. 2-1). Samuels thus recognized the need for a new approach to metallographic polishing procedures, based on the removal of surface deformation rather than the removal of surface scratches.

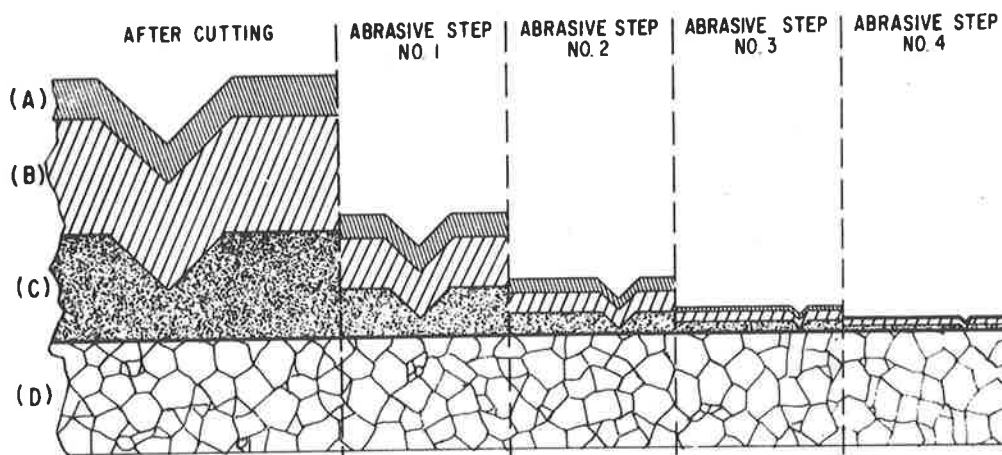


Fig. 2-1.

The effect of the grinding with successively finer grit abrasives on the severely deformed material, (A); the heavily deformed layer, (B); the lightly deformed layer (C) and the undisturbed material (D). (from Richardson 1971)

Abrasion artefacts can arise from inclusions in the specimen (Samuels and Craig 1965). Brittle inclusions can fracture during abrasion resulting in parts of the inclusion falling out of the surface. However, plastic inclusions will tend to elongate in the direction of abrasion.

Bowden and Tabor (1949) showed that when two solids slide over each other, extremely high surface temperatures may be developed even under moderate conditions of load and speed. Samuels and Craig (1965) and Kragelskii (1965) have shown that surface heating during abrasion can cause spontaneous recrystallization of the deformed layer in metals whose recrystallization temperature is below room temperature.

Thus, not only are the artefacts of the damaged layer introduced during grinding but modifications within the damaged layer can produce a distorted impression of the true surface of a specimen.

2.2 ABRASION PROCESS

During the grinding process wear of abrasive paper occurs. This has been described by Mulhearn and Samuels (1962), and Duwell and McDonald (1961). The abrasive particle itself can shear, surrounding particles can fall out by erosion and attrition of the sharp contact points result in a worn paper.

Silicon carbide and emery papers are universally used abrasive papers in metallographic practice. Of the two types of paper, silicon carbide is preferred for the following reasons:

- i. Samuels and Wallwork (1957) noted that the abrasion rates of silicon carbide papers were much higher than the comparable grades of emery paper.
- ii. Samuels and Wallwork (1957) indicated that silicon carbide papers in the range of 220-600 grade were the most satisfactory series because the maximum depth and total depth of deformation decrease in proportion.
- iii. The lubricant used with silicon carbide papers is water, which is much more convenient than the oily fluids used with emery papers.
- iv. There is a risk of clogging with finer abrasive emery papers, even when lubricated, leading to a grossly deformed surface layer.

2.3 PRACTICAL ABRASION METHODS

A simple apparatus is involved for manual silicon carbide abrasion. The apparatus usually consists of a glass plate which supports the silicon carbide papers. The glass plate is tilted either towards or away from the operator. The abrasive paper is held in position by clips and lubrication is supplied by running water from jets. Unidirectional strokes, and pressure applied only during the away stroke should be used (Samuels 1971).

Mechanical devices using continuous belts, rotating wheels or laps are also available for the abrasion process.

2.4 PRINCIPLES OF MECHANICAL POLISHING

Beilby (1921) suggested that polishing was a result of surface flow. Material was smeared over the surface and filled in pre-existing depressions. Thus, the surface of the specimen would eventually be covered by a smooth layer, which he thought was amorphous. However, Beilby did not propose a mechanism for the smearing process.

Bowden and Hughes (1937) suggested that polishing was a thermally activated process and that during polishing heated material is transferred to depressions in the surface of the specimen. Rapid cooling of the surface resulted in the transferred material solidifying in an amorphous-like condition, thus producing the Beilby layer (Fig. 2-2).

Samuels (1971) criticized the Beilby theory as microscopical techniques in Beilby's day were insensitive to minor surface changes so that no structure could be observed on polished surfaces. Thus, the surface appeared to be amorphous. Modern microscopical techniques can demonstrate that polished surfaces consist of a series of fine scratches. Furthermore, the method of polishing in Beilby's day could be best described as burnishing. This method of polishing is completely removed from modern techniques.

2.5 METHOD OF MECHANICAL POLISHING

Samuels (1971) suggests that two distinct stages are required for polishing:

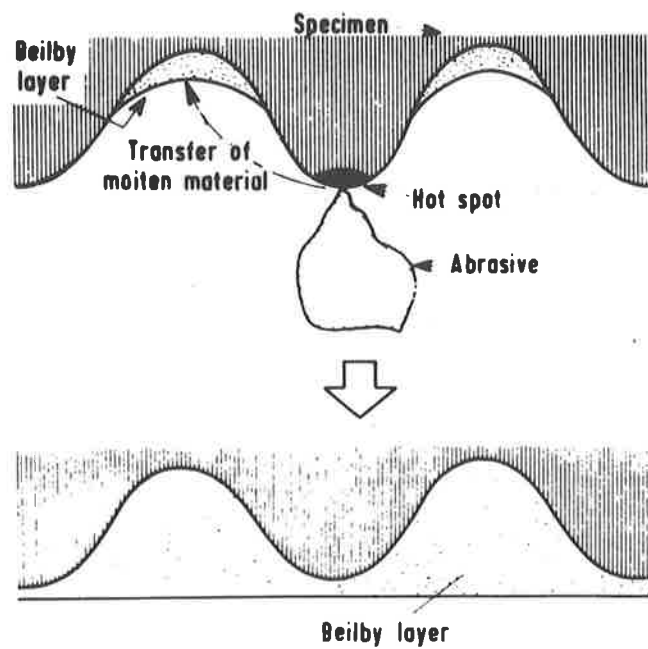


Fig. 2-2. Diagrammatic illustration of the Beilby mechanism of polishing as proposed by Bowden and Hughes. (from Samuels 1971)

- i. Rough : to remove abrasion damage.
- ii. Fine : to produce a "final surface" in which the polishing damage is reduced as low as possible. The rough polishing surface damage must also be removed at this stage.

A system for polishing on diamond abrasive pads has been outlined by Samuels (1952).

- i. A napped cloth is impregnated with diamond paste.
- ii. Kerosene is used as a lubricant.
- iii. a. 4-8 μ m grade diamond paste for the rough stage of polishing.
b. <1 μ m grade diamond paste for the finishing stage.

2.5.1 SKID POLISHING

A superior technique of final polishing based on magnesium oxide abrasive has been developed by Samuels (1952). In this technique, a high-quality grade magnesium oxide is mixed to a thick paste with water and forced through a 200-mesh sieve on to a polishing wheel covered with a long napped cloth. The paste is worked into the nap of the cloth and the specimen is allowed to skid on a bed of paste. The polishing rate is low and periods of 5 minutes or more may be necessary. However, there is a danger of scratching the specimen from the carbonation of the magnesium oxide within the five minute polishing period.

2.5.2 VIBRATORY POLISHING

This technique was first introduced by Krill in 1956. The polishing pad is a portion of a torsional pendulum driven by an electromagnet connected to an alternating current supply. As the bowl vibrates, the specimen moves around the periphery of the bowl so that the effects of directional polishing are minimal. The final polished surface is scratch and damage free.

The polishing time, the weight applied to the specimen, and the nature of the liquid in which the abrasive is suspended are important parameters which govern the surface finish (Samuels 1971). An extensive study by Hopkins and Peterson (1963) recommended a total weight of specimen plus holder in the range of 375-600 grams. An abrasive sequence they found useful consisted of 15 μ m alumina followed by a final polishing step using 0.3 μ m alumina.

Samuels (1971) notes that vibratory polishing can produce etch attack, as grain boundaries become visible.

Because of the large number of variables in vibratory polishing, Samuels (1967) was prompted to write:

"The best results clearly will not be obtained with vibratory polishing unless some intelligent experiments are carried out to select the optimum conditions from amongst the possible variables. Once optimum conditions have been established, however, the art will have been removed from final polishing."

2.6 ULTRASONIC CLEANING

During mechanical polishing, cleaning of the specimen and operator's hands is extremely important to prevent abrasive carryover between stages. Samuels (1971) recommends ultrasonic cleaning methods as being more effective than washing specimens with soap or detergent in a stream of water.

Samuels (1971) also believes other useful features of the ultrasonic cleaner are:

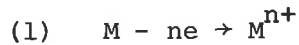
- i. that more efficient cleaning of specimen cracks and fissures occurs,
- ii. some specimen stains may be removed,
- iii. microscope immersion oil can be removed without damage to the specimen surface.

2.7 THE THEORY OF SOLUTION ETCHING

The dissolution of most metals involves the loss of electrons from atoms of the metal, forming positive ions. Oxidation can occur in the presence of an oxidizing solution or by making the metal an anode as in an electrolytic cell. Gifkins (1970) suggested that etching resulted from the use of strong oxidizing agents such as acid which produced differential dissolution of the specimen surface.

2.7.1 CHEMICAL MECHANISM AND THE RATE-DETERMINING STEP

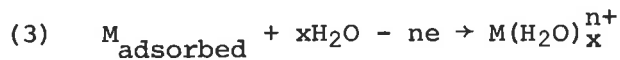
i. Oxidation of the metal



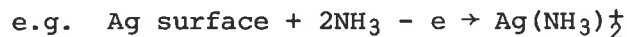
This equation describes the oxidation of a metal atom to form ions. According to Cuming and Moore (1958) this process can occur in two stages.



Equation (2) describes repositioning of an atom from a position in the surface of the lattice to a more exposed position, (e.g. in a step, or on the surface of a metal). Cuming and Moore describe this reaction as "surface migration".



Equation (3) represents the solution process from an exposed portion on the surface. The atom loses electrons and passes into solution. Depending on the etchant used the water molecules of equation (3) will be replaced by some other molecules or ions.

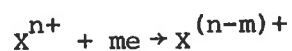


This process is called "ionization".

Stages (2) and (3) co-exist with another stage, the diffusion stage, which occurs when dissolved metal ions go into solution as they accumulate near the surface. Cuming and Moore suggest that any one of these 3 stages may be rate determining.

ii. Reduction of the Oxidant

Such a reaction can be written:

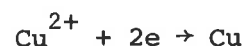


Cuming and Moore divide the oxidants used in etching into 3 types:

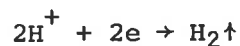
- (1) Oxidants which are reduced to a soluble species, e.g.



- (2) Oxidants which are reduced to an insoluble species which may deposit on the specimen, e.g.



- (3) Hydrogen ion, which is reduced to gaseous hydrogen,



2.7.2 THE COMPONENTS OF AN ETCHANT

A simple classification for the component substances of an etchant is difficult to devise. However, Cuming and Moore believe that the following points are important:

- i. Primarily, an oxidizing system is required to supply a thermodynamic "driving force" to dissolve the metal. The oxidation potential measures the driving force. This can be controlled by the choice and concentration of the oxidant and the concentrations of additional reagents such as acids.

- ii. Various factors may influence the effect of the driving force on different regions of the surface by controlling the activation energy for dissolution.

CHAPTER 3

LITERATURE REVIEW

3.1 METALLOGRAPHIC POLISHING OF DENTAL AMALGAM

Wing (1965) abraded amalgam specimens on three grades of silicon carbide paper (220, 400, 600) followed by alumina wax laps. According to Wing, the wax laps helped to produce a flat specimen surface and reduced the time necessary for final polishing with diamond paste. Two grades of diamond paste, 4-8 μ m and 1 μ m particle size, were used on a short napped cloth on a slowly rotating wheel. Final polishing was achieved by magnesium oxide skid polishing.

Allan, Asgar and Peyton (1965) used 3, 2, 1, 1/0, 2/0, 3/0, 4/0 grades of emery paper for rough polishing. These workers believed that the use of the 4/0 emery paper produced better retention of the γ_2 phase. Intermediate polishing stages were employed with different grades of alumina powder while final polishing was performed with chromium oxide.

3.2 ETCHING TECHNIQUES

Wing's (1965) technique consists of two solutions. The first solution is 8% potassium cyanide with 4% iodine. This is swabbed over the specimen. The second solution consists of equal quantities of 10% ammonium hydroxide and 10% potassium ferricyanide. The specimen is immersed in this solution.

However, Allan, Asgar, and Peyton (1965) believed that the Wing etch did not produce good "phase contrast" and therefore developed an alternative system of etching using potassium dichromate and tincture of iodine. However, the present author (1975) has demonstrated that:

- i. the etchant does not satisfactorily etch the γ_1 phase,
- ii. the γ_2 phase is etched blue-black making it almost impossible to distinguish from porosity in photomicrographs.

In considering the Wing etch the author believes that:

- i. it is a complex two stage procedure,
- ii. ventilation is required as hazardous chemicals are used,
- iii. results are not always consistent,
- iv. the γ_2 phase can easily be over-etched.

It should be noted that the Wing etch is almost universally accepted as the standard etchant for observing microstructure in silver-tin amalgam.

3.3 γ_2 DISCRIMINATION

Neither of the above etchants show the γ_2 phase in isolation at any stage but differentiate the three phases simultaneously. There have been attempts to selectively show the γ_2 phase by an etching and repolishing procedure (Mateer and Reitz 1971), and by using a soft final polishing material, diatomaceous earth (Jorgensen 1966).

3.4 γ_2 DETERMINATION

From the research work of Jorgensen and Otani (1967), and Mateer and Reitz (1971), there is no doubt that conventional silver tin amalgams contain γ_2 phase. In contrast, Sarkar and Greener (1972a) using X-ray diffraction had difficulty in detecting γ_2 phase in the dispersed phase amalgam, Dispersalloy, either because of the absence of this phase or because of superimposition of peaks from other phases making accurate readings difficult to obtain. In a later investigation (1972b), using potentiostatic polarization measurements they claimed Dispersalloy contained 0.3% γ_2 . Wing (1975) believed this evidence was not conclusive unless other factors for the interpretation of polarization curves are explained.

Louka and Rummery (1975) examined polished and etched specimens of Dispersalloy by SEM and X-ray spectrometry and found no γ_2 phase. Similarly the investigation of ternary alloy amalgams with the microprobe by Marshall, Finkelstein, and Greener (1975) and Mahler, Adey and Van Eysden (1976), demonstrated no γ_2 phase.

Bryant (1976) found that the electron microprobe X-ray analyser was only of "some assistance" in determining the γ_2 content of conventional amalgam. Prior to Bryant's (1976) work, Wing and Bryant (1975, 1976), performed electron microprobe analysis on the dispersed phase amalgams of Luxalloy, Dispersalloy and Spheriphase and claimed absence of γ_2 phase.

It appears that most workers agree that the dispersed phase amalgams contain little or no γ_2 phase. When it is considered that X-ray or microprobe analysis has been acknowledged by some of these investigators to be inadequate for γ_2 detection, it would seem desirable to develop a more accurate technique of quantifying γ_2 phase.

3.5 ELIMINATION OF THE γ_2 PHASE WITH TIME

Asgar (1971) hypothesized that during trituration of a dispersed phase alloy, mercury comes into contact with silver-tin and silver-copper particles. The mercury reacts with the silver-tin phase forming silver-mercury and releasing tin. γ_2 may form, but tin and mercury can diffuse into silver-copper particles. The mercury reacts with the silver of the silver-copper phase, then tin and copper react to form the copper-tin phase. Asgar (1974) and Mahler et al (1975) proposed that amalgams incorporating Ag-Cu eutectic particles would eliminate the γ_2 phase within 1 week at body temperature via a solid state diffusion process in which γ_2 reacts with copper to form Cu_6Sn_5 .

3.6 THEORIES AND EXPERIMENTS RELATED TO POROSITY FORMATION

Allan, Asgar and Peyton (1965) observed γ_2 phase associated with porosity which led them to conclude that polishing of dental amalgam produced porosity by loss of γ_2 phase. This theory was not acceptable to Wing (1966) as he was able to polish amalgam containing pure tin-mercury or mixtures of tin-mercury,

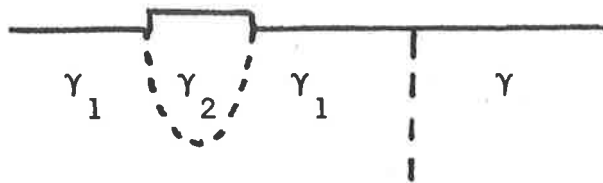
silver-mercury, and silver-tin, without producing voids. According to Wing (1971) voids surrounding particles were due to lack of amalgamation of the γ particle with mercury. However, Mateer and Reitz (1971) believed that fine polishing for prolonged periods would accentuate the discrimination of the γ_2 phase, but eventually the particle would be dislodged, leaving porosity.

Grant, Meshii, Yang and Greener (1966) suggested that the γ_2 phase and voids were difficult to distinguish from each other in optical photomicrographs as both appeared as dark regions within the γ_1 phase. By comparing TEM and optical photomicrographs, Grant et al proposed that:

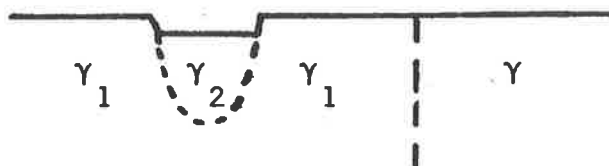
- i. a coarse final polishing powder would raise the γ_2 above the rest of the polished surface;
 - ii. a fine final polishing powder would remove the γ_2 phase, producing a depressed area;
 - iii. the cyanide etch of Wing lightly etched the γ_2 phase,
- while the Allan, Asgar, and Peyton iodine etch deeply etched the γ_2 phase (Fig. 3-2). Grant et al thought that the distribution of porosity in dental amalgam would vary from specimen to specimen according to the finishing procedure.

Bergendal (1968) attempted to reduce porosity by developing a method for reducing air entrapped in the amalgam mix and examined the specimens using optical microscopy techniques. He claimed that amalgams triturated under vacuum had less porosity than those mixed

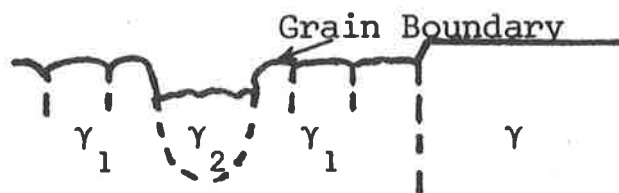
A. ROUGH POLISH



B. FINE POLISH



C. CYANIDE ETCHED



D. IODINE ETCHED

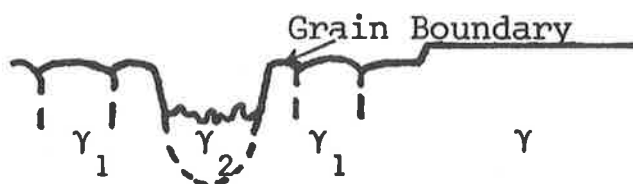


Fig. 3-2. Polishing and etching characteristics of dental amalgam.

(from Grant et al 1966)

with mortar and pestle. Johnson (1970, 1972), Wawner (1970), Wawner and Lawless (1972), claimed porosity formation in dental amalgam was a function of the tin content of the original alloy, whereas Taylor (1972) used metallographic techniques to show that porosity size depended upon the γ particle size.

In each of the above references to porosity, the amalgams were sectioned, ground, polished and cleaned between polishing stages. In one case specimens were etched and then repolished (Mateer and Reitz 1971). The possibility of artefact development during specimen preparation has had scant attention, yet several workers have noted porosity on polished surfaces without considering whether metallographic procedures themselves result in some porosity formation.

CHAPTER 4

AIMS OF THE EXPERIMENTAL INVESTIGATION

4.1 INVESTIGATION OF THE γ_2 PHASE

The aims of this investigation were:

- i. to selectively etch the γ_2 phase with polyvinylpyrrolidone and hence allow a determination of the volume fraction of this phase;
- ii. to assess the potential of both iodine vapor and 10% nitric acid for in vitro corrosion studies of dental amalgam;
- iii. to determine the volume fraction of the γ_2 phase as a function of amalgam type, brand, mode of trituration, time of storage, and temperature of storage.

4.2 POLISHED SURFACE EXAMINATION

The aims of this study were:

- i. to produce a method for polishing dental amalgam following the silicon carbide abrasive paper stage;
- ii. to examine whether dental amalgam can be etched with the Wing cyanide technique directly following silicon carbide abrasion;

- iii. to investigate whether some portion of the porosity observed on metallographically polished amalgam was an artefact from the techniques employed in specimen preparation;
- iv. to optimise conditions for vibratory polishing of dental amalgam.

CHAPTER 5

MATERIALS, EXPERIMENTAL METHODS AND RESULTS

5.1 MATERIAL - AMALGAM ALLOYS

Four conventional silver-tin alloys, four dispersed phase and two ternary alloys were used in this study. Appendix I lists the amalgam alloys, the mercury alloy ratio, time of trituration, batch numbers and manufacturer.

The Silamat¹ and Wig-L-Bug² (Model 5A) were used to triturate the alloy and mercury. Specimens were prepared by hand condensing the non-squeezed amalgam into holes (diameter 3mm and depth 6mm) drilled into Perspex blocks.

New True Dentalloy, 20th Century Micro, Spheriphase (lathe cut), Luxalloy and Dispersalloy were condensed with a 1.5mm diameter amalgam plugger. The remaining amalgams were condensed with a 2.5mm diameter plugger.

5.2 POLISHING MATERIALS AND SEQUENCE

After 24 hours the amalgam surfaces were ground on a series of abrasive papers of grades 320³ to 1000⁴. Polishing was performed sequentially with 7 μ m and A and B grades Struers⁵ diamond pastes on

-
1. H.D. Justi Company, Philadelphia, U.S.A.
 2. Crescent Dental Mfg. Co., Chicago, Illinois, U.S.A.
 3. Universal Carborundum Aust. Pty. Ltd., Victoria, Australia 3074.
 4. Fuji Star/Sankyo Rikagaku, Japan.
 5. Struers Scientific Instruments, Copenhagen, Denmark.

Struers Dur, Mol and Nap cloths. Struers DP liquid was used as the lubricant. In some cases a final polish was achieved with Magomet⁶ (magnesium oxide) on Microcloth⁷.

5.3 SPECIMEN CLEANING

Ultrasonic cleaning is a widely used technique for cleaning polished surfaces of dental amalgam to avoid contamination of polishing pads and to produce a clean surface for microscopic examination. Specimens were placed in a beaker containing 50% distilled water and 50% alcohol, which was partially immersed in the bath of a L & R 'Maxomatic'⁸ ultrasonic cleaner for 30 seconds.

5.4 ETCHANTS

5.4.1 THE WING ETCH (1965)

Wing's technique involves two solutions:

- i. 8% potassium cyanide with 4% iodine, which is swabbed over the specimen;
- ii. 10% ammonium hydroxide and 10% potassium ferricyanide, in which the specimen is immersed.

5.4.2 SPECIFIC ETCHES FOR THE γ_2 PHASE

Table 5-1 lists the etchants and remarks regarding their use. Etchants (i) and (ii) have been shown by the author (1975) to differentiate the γ_2 phase.

6. 7. Buehler Ltd., Evanston, Illinois, U.S.A. 60204.

8. L & R Manufacturing Co., New Jersey, U.S.A.

Table 5-1

ETCHING SOLUTIONS FOR THE γ_2 PHASE

	Reagent	Concentration	Time of Application
(i)	Kodak Special Rapid Developer ⁹	Prepared to manufacturer's directions, undiluted	3 min.
(ii)	Sodium Hydroxide	10 wt. % solution	3 min.
(iii)	Polyvinylpyrrolidone (Betadine) ¹⁰	undiluted	1 min.

5.5 METALLOGRAPHIC APPARATUS

In order that the same areas could be identified repeatedly, specimens were marked on a "Miniload Hardness Tester"¹¹. A Wild¹² M20 microscope equipped with x4, x10, x20, x40, x100 (oil immersion) objectives, and bright field, dark field, and polarized illumination was used for optical examination. A x6 Wild photographic lens was incorporated between the microscope and an ASAHI PENTAX ESII¹³ automatic exposure camera.

Photographs were recorded on:

- i. KODAK HIGH SPEED EKTACHROME¹⁴ (tungsten) and developed using KODAK Process E4¹⁵ or UNICHROME Process A¹⁶.

9. Kodak (Aust.) Pty. Ltd., Melbourne, Australia.
 10. F.H. Faulding & Co. Ltd., Adelaide, Australia.
 11. Ernst Leitz GMBH Wetzlar, Germany.
 12. Wild Heerbrugg Ltd., Heerbrugg, Switzerland.
 13. Asahi Optical Co. Ltd., C.P.O. 895, Tokyo 100-91, Japan.
 14. Kodak (Aust.) Pty. Ltd., Victoria, Australia.
 15. Eastman Kodak Co., Rochester, N.Y. 14650, U.S.A.
 16. Uicolor Division, Photosystems Inc., Dexter, Michigan 48103, U.S.A.

- ii. AGFACHROME 50 L Professional¹⁷ (tungsten) developed in AGFACHROME Process 41 or UNICHROME Process B.

For quantitative measurement of porosity and γ_2 phase, a Weibel¹⁸ graticule was inserted into a x10 eyepiece of the Wild microscope. The Weibel graticule has 21 test lines arranged in an hexagonal network, thus giving 42 end points which are used independently from the test lines for point counting techniques.

All measurements were recorded with the x20 objective giving a total magnification x200. Twenty-five fields were counted on each specimen, i.e. 1050 points. Appendix II summarizes the method of calculating volume fractions from the Weibel count.

5.6 INVESTIGATION OF THE γ_2 PHASE

5.6.1 A SPECIFIC ETCH FOR THE γ_2 PHASE

Four specimens of Shofu spherical amalgam were polished to a B paste finish and etched for 1 minute by swabbing with polyvinylpyrrolidone (Betadine). The number of γ_2 particles in twenty areas (x120) was counted.

In order to compare the structure revealed by this etching procedure with that revealed by the Wing method, the specimens were re-etched with Wing's solutions and the number of γ_2 particles in the same area again counted. Table 5-2 shows that after the Wing etch 5% fewer γ_2 grains were noted than with the Betadine etch.

17. Agfa-Gevaert A.G., Leverkusen-Bayerwerk, West Germany.

18. Wild Heerbrugg Ltd., Heerbrugg, Switzerland.

Table 5-2

No. of γ_2 particles observed in specimens (a total of 20 fields from 4 specimens)	
<u>With Betadine</u>	<u>After Wing etch</u>
259	247

Fig. 5-1 depicts the γ_2 phase on the surface of Shofu spherical following the Betadine etch.

5.6.2 REMOVAL OF THE γ_2 PHASE

Two specimens of Shofu spherical, New True Dentalloy, Luxalloy and Dispersalloy were polished and etched for γ_2 phase, followed by either:

- i. immersion in iodine vapor at room temperature in a closed container for periods between a few minutes and three months, or
- ii. swabbing with 10% nitric acid for 30 seconds.

Both treatments removed the γ_2 phase (Fig. 5-2). In the dispersed phase amalgam, treatment with 10% nitric acid produced little reaction after 30 seconds. However, following application for 2 minutes not only was the amalgam surface etched but the reaction ring of the silver-copper eutectic particles was preferentially etched.

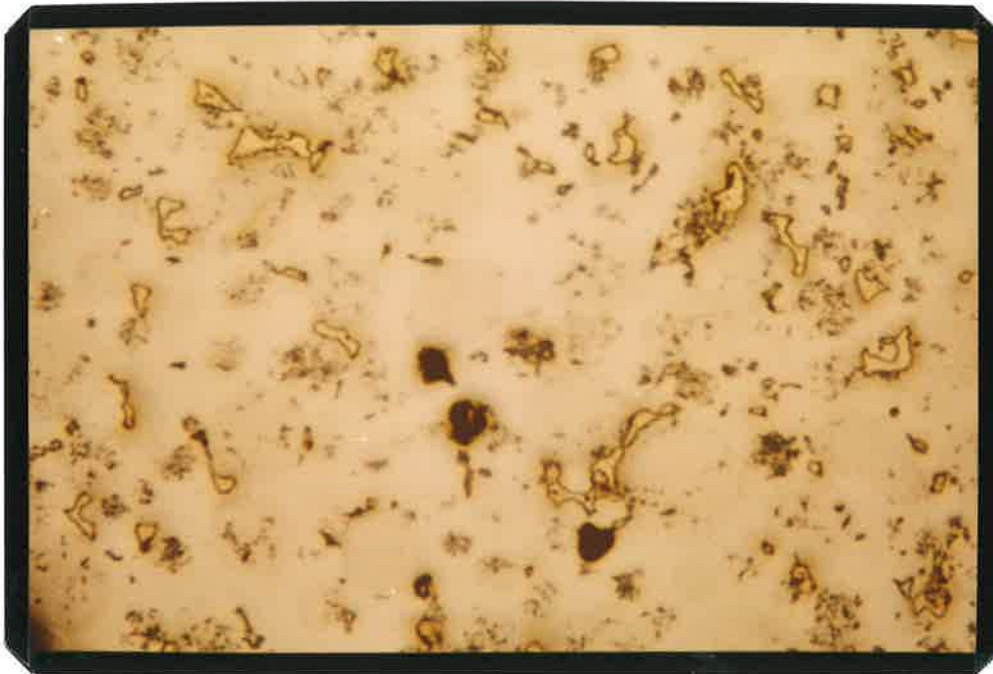


Fig. 5-1. SHOFU SPHERICAL :

*Betadine etch for 1 minute reveals
the γ_2 phase.*

(x120)

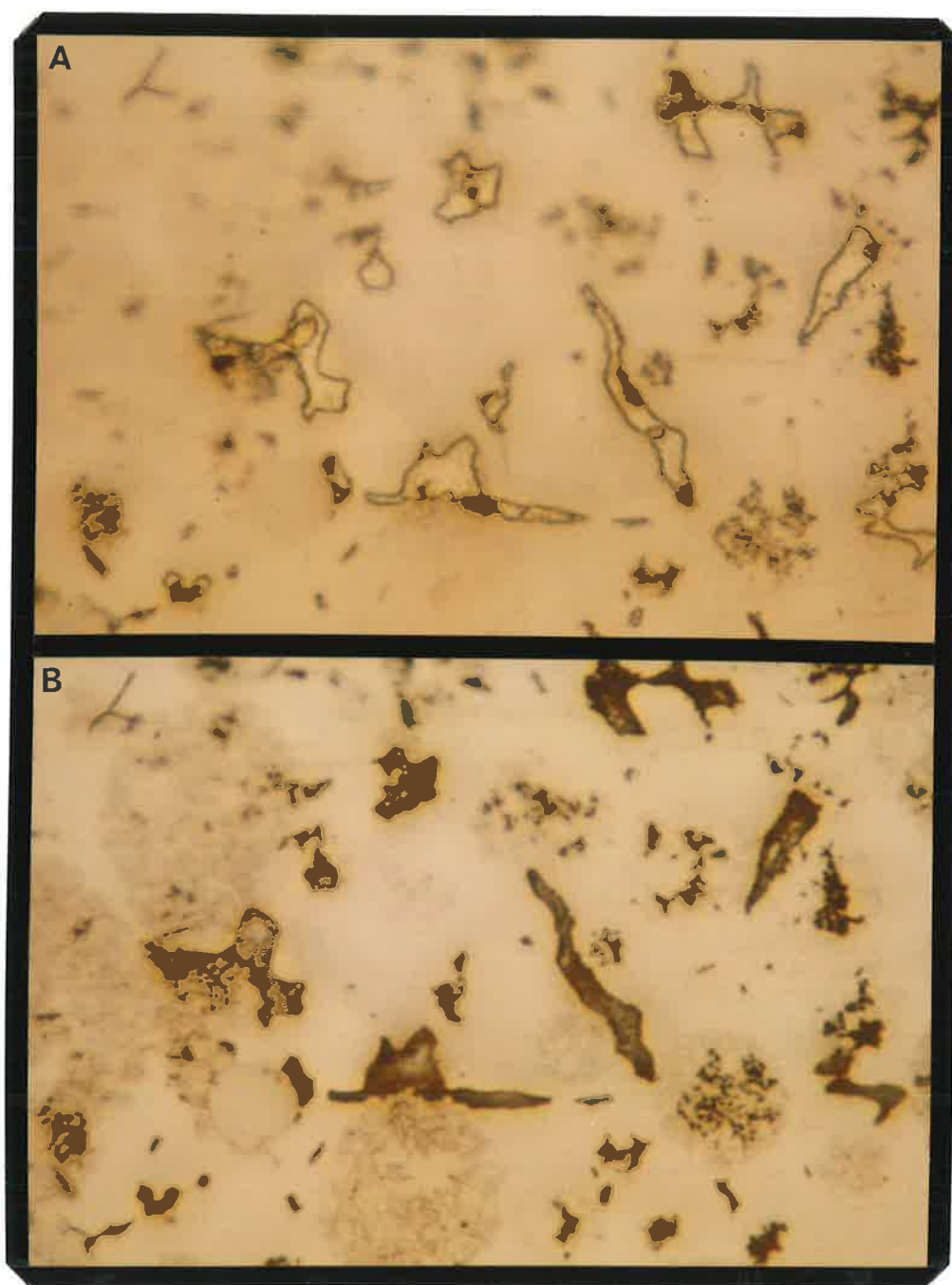


Fig. 5-2. SHOFU SPHERICAL AMALGAM :

A. The γ_2 phase is revealed by application of 10% NaOH for 3 minutes.

B. The γ_2 phase is removed following application of 10% HNO_3 for 30 seconds.

(x240)

Following exposure to iodine vapor for 3 months, the specimen was mounted in self-curing resin and then sectioned perpendicular to the exposed surface and etched. The γ_2 removal was confined to within 50 μm of the exposed amalgam surface. A similar result was obtained in specimens treated with 10% nitric acid for 2 minutes.

Two specimens of Shofu spherical, New True Dentalloy, Luxalloy and Dispersalloy were immersed in 10% nitric acid for 12 hours and then sectioned perpendicular to the exposed surface. In the conventional amalgams, the surface layers exhibited cracks extending through the γ_1 matrix and through γ particles, while γ_2 dissolution had occurred to a maximum depth of at least 400 μm (Fig. 5-3). Preferential dissolution of the copper-tin reaction ring to a depth of 75 μm was observed in the dispersed phase amalgams.

5.6.3 QUANTITATIVE ANALYSIS OF THE γ_2 PHASE

The volume fractions of γ_2 phase in the amalgam alloys listed in Appendix I, triturated by the Wig-L-Bug (low energy) and the Silamat (high energy), were determined after storage under the following conditions:

- i. 24 hours at 25°C (room temperature)
- ii. 24 hours at 37°C
- iii. 6 days at 25°C
- iv. 6 days at 37°C

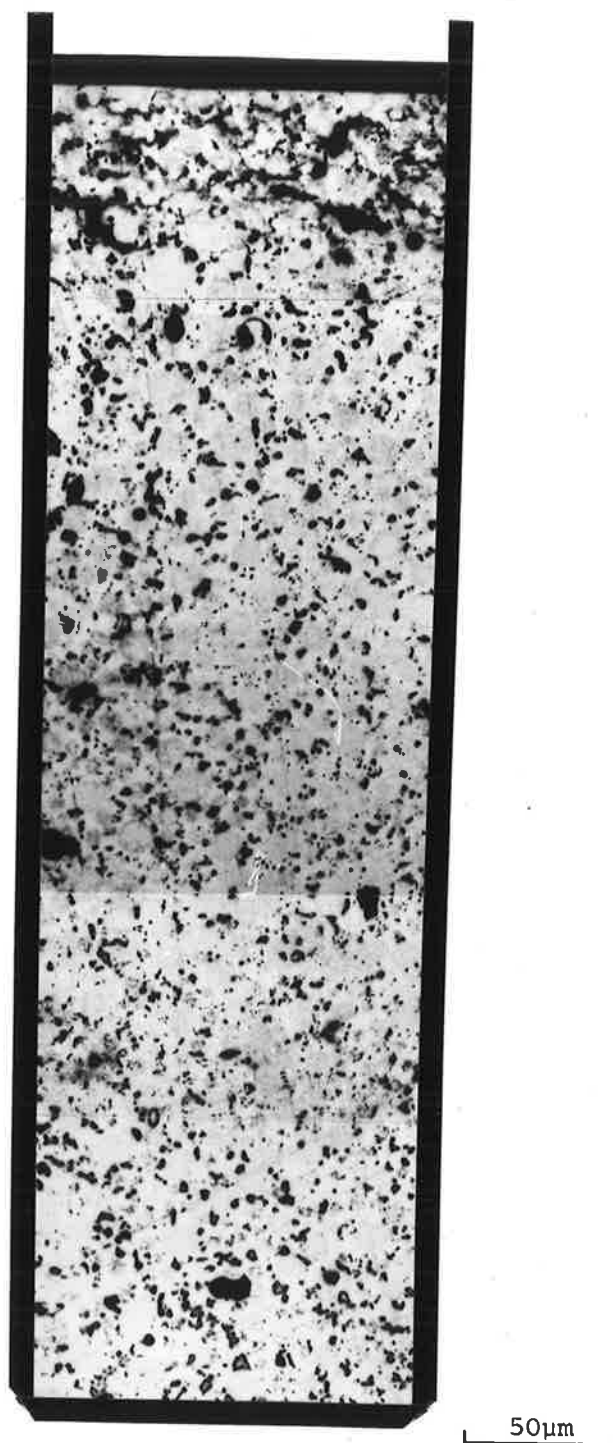


Fig. 5-3. SHOFU SPHERICAL, 10% HNO₃, 12h.

Composite photomicrograph showing γ_2 dissolution to a depth of at least 400 μ m.

Eight specimens of each amalgam were polished to a magnesium oxide finish and then swabbed for 3 minutes with 10% NaOH to reveal all the γ_2 phase (Abbott 1975). Where body temperature was required, the specimens were placed in glass tubes and submerged in a controlled temperature water bath.

The Student's t-test for independent samples was used to compare the mean values of γ_2 volume fractions as a function of storage and trituration variables. The results were tested at the .01 level of confidence. Tables 5-3 and 5-4 list the volume fractions of γ_2 phase. The important results from this analysis are:

- i. Dispersalloy and Luxalloy contain no γ_2 phase after 6 days at 37°C.
- ii. The γ_2 volume fraction of Spheriphase, although initially high, decreases over a period of 6 days at 37°C.
- iii. The ternary amalgam alloys, Tytin and Sybraloy were free of γ_2 .
- iv. High energy trituration (Silamat) produced significantly less γ_2 phase in Spheriphase than did low energy trituration (Wig-L-Bug).
- v. The volume fraction of γ_2 in Shofu, New True Dentalloy and 20th Century Micro did not change over a period of 6 days at 37°C.

VOLUME FRACTION OF γ_2 PHASE (VOL. %)

24 HOURS at 37°C

6 DAYS at 37°C

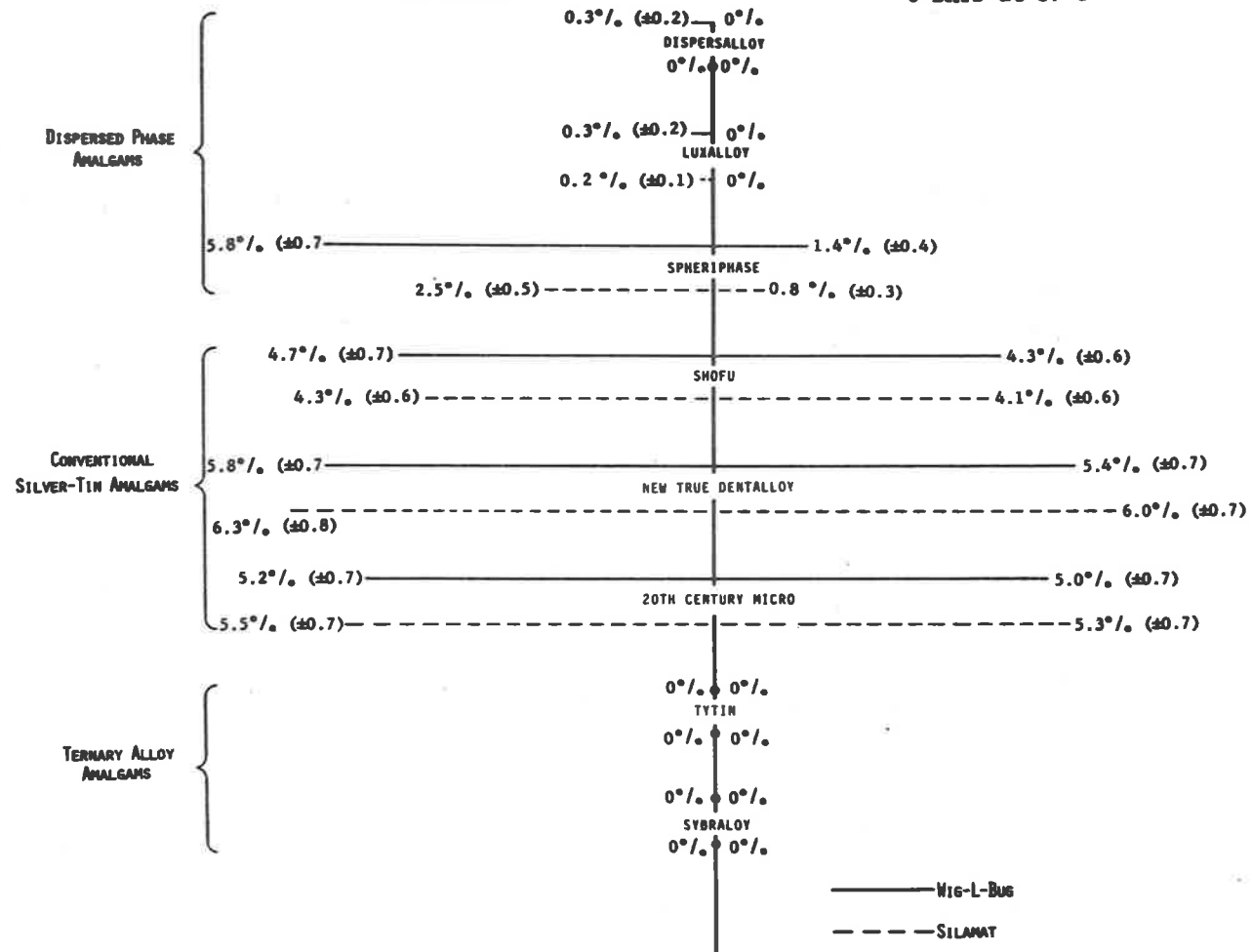


Table 5-4.

- vi. There was significantly less γ_2 at 37°C than at room temperature in Shofu, New True Dentalloy and 20th Century Micro.

Fig. 5-4 depicts the γ_2 phase observed in Dispersalloy, Spheriphase and Shofu.

To study the decrease in γ_2 content with time and temperature, 8 specimens of Spheriphase, Shofu and New True Dentalloy were stored at room temperature for 24 hours, sectioned, etched for γ_2 phase, indented and 20 areas from the specimens were photographed at x120. By incorporating a chromel-alumel thermocouple into an amalgam it was noted that a period of approximately 40 minutes was required for the specimen to equilibrate at 37°C. During this period there was no change in the γ_2 count. The same areas were rephotographed at 24, 72 and 144 hours and the number of γ_2 particles counted.

Fig. 5-5 shows the results of this experiment. The γ_2 count of Shofu and New True Dentalloy did not change over 144 hours, whereas Spheriphase showed a dramatic drop over the same period. The γ_2 particles that were in close proximity to the silver-copper eutectic phase deteriorated over a period of 6 days at 37°C (Fig. 5-6). This deterioration of the γ_2 phase seemed to be associated with the appearance of:

- i. the copper-tin reaction ring around the silver-copper eutectic spheres,
- ii. the development of globules on the silver-copper eutectic particles.

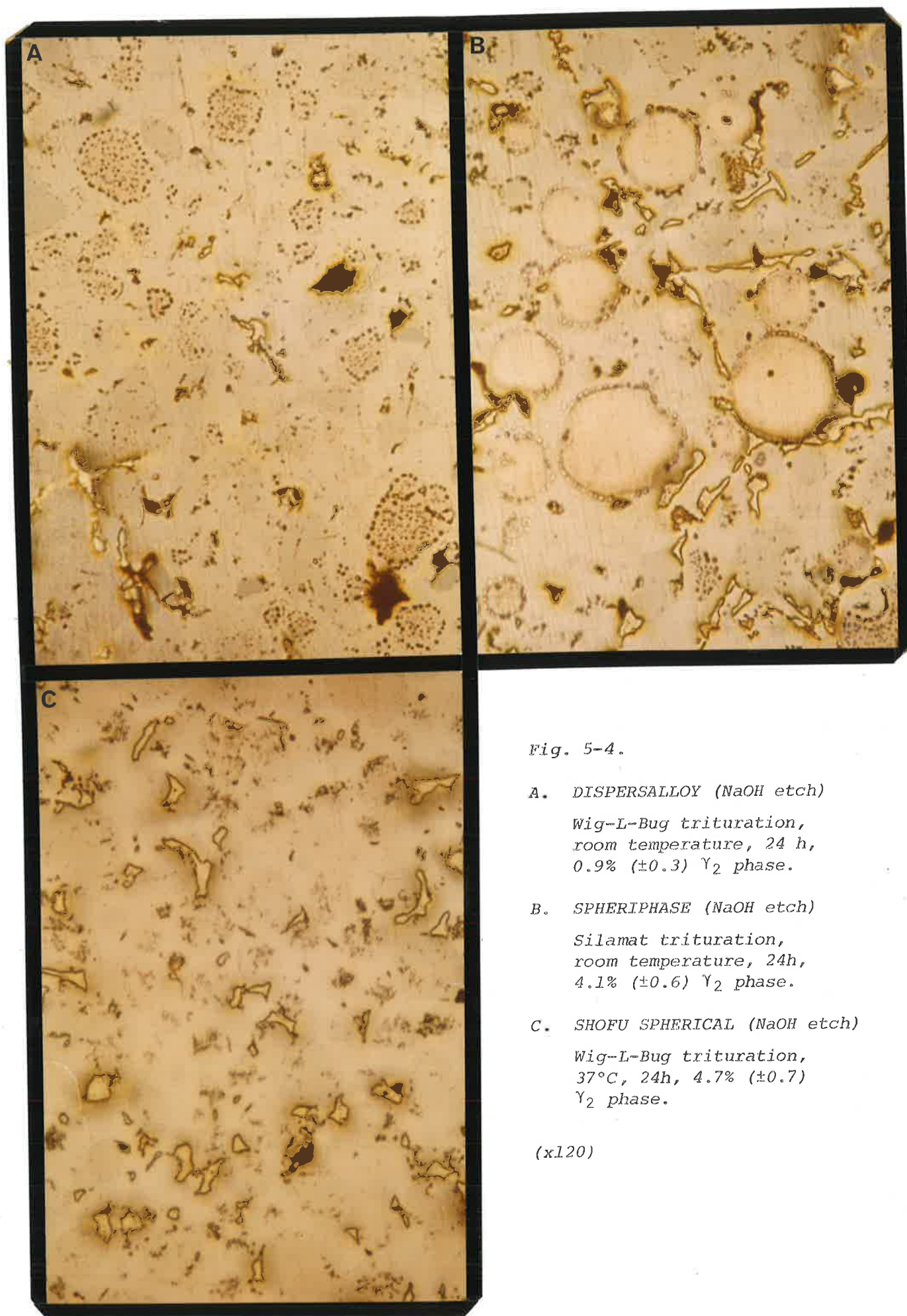


Fig. 5-4.

A. *DISPERSALLOY* (NaOH etch)
 Wig-L-Bug trituration,
 room temperature, 24 h,
 0.9% (± 0.3) γ_2 phase.

B. *SPHERIPHASE* (NaOH etch)
 Silamat trituration,
 room temperature, 24h,
 4.1% (± 0.6) γ_2 phase.

C. *SHOFU SPHERICAL* (NaOH etch)
 Wig-L-Bug trituration,
 37°C, 24h, 4.7% (± 0.7)
 γ_2 phase.

(x120)

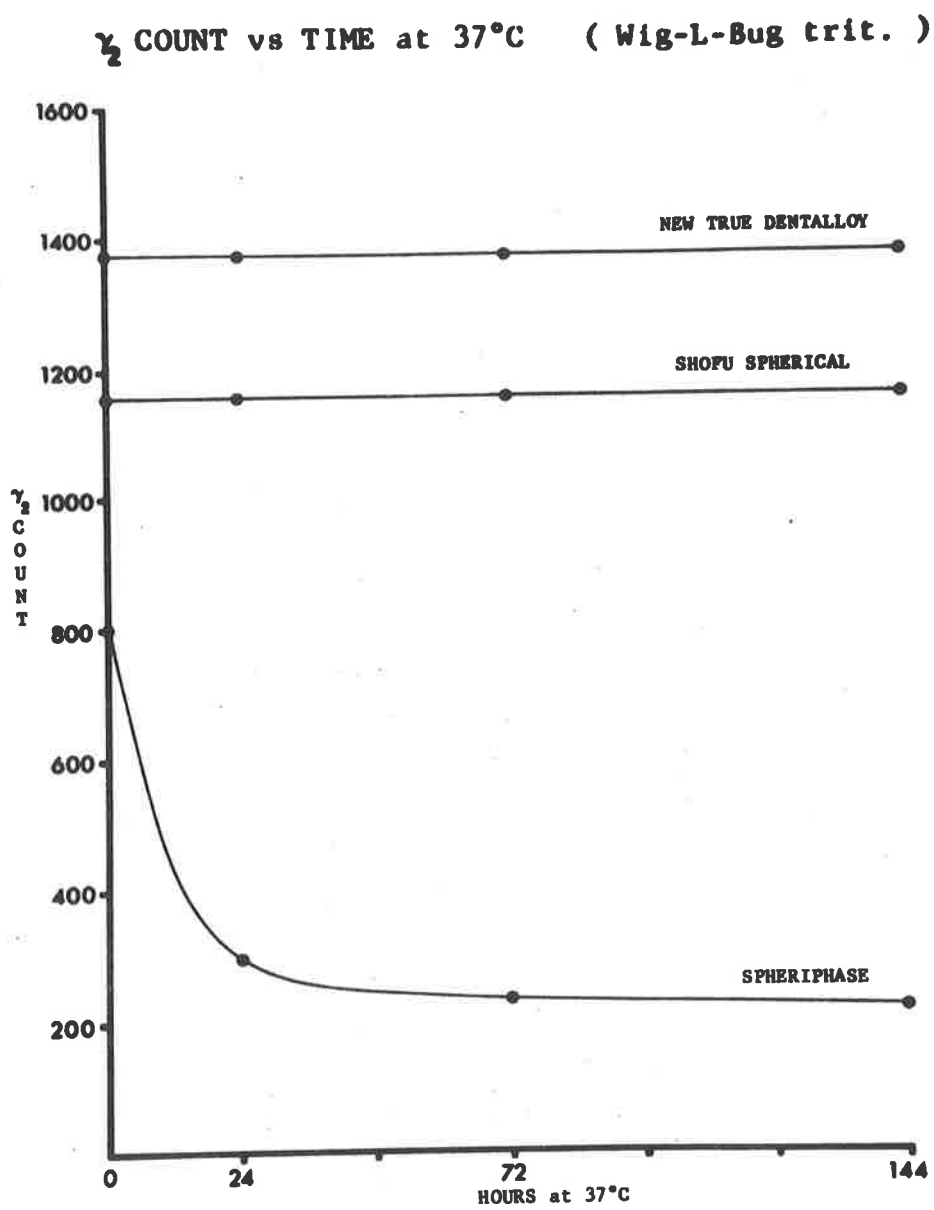


Fig. 5-5.

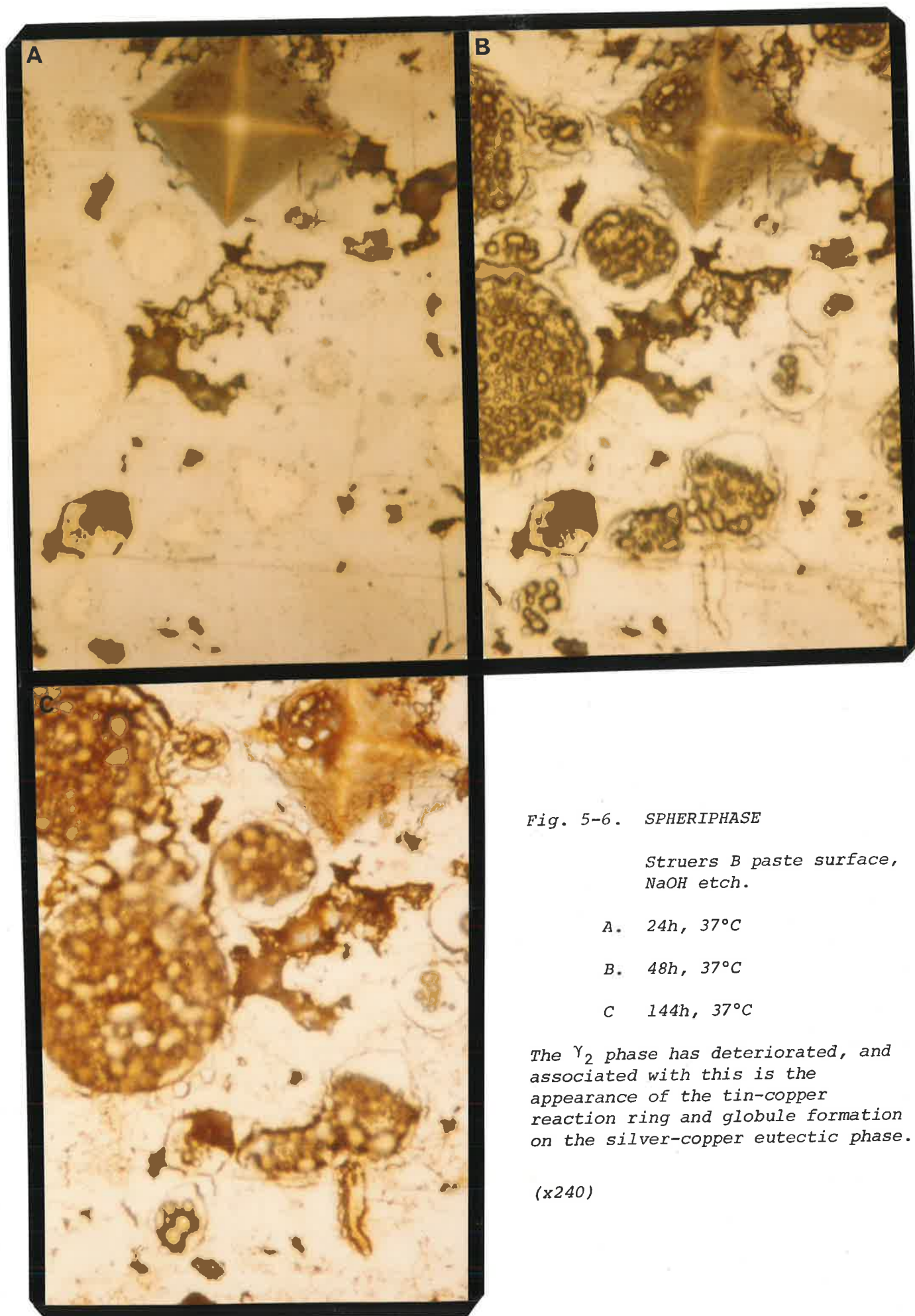


Fig. 5-6. SPHERIPHASE

Struers B paste surface,
NaOH etch.

A. 24h, 37°C

B. 48h, 37°C

C. 144h, 37°C

The γ_2 phase has deteriorated, and associated with this is the appearance of the tin-copper reaction ring and globule formation on the silver-copper eutectic phase.

(x240)

In contrast, the γ_2 phase of the conventional silver-tin amalgams did not deteriorate and no globules were observed. Louka and Rummery (1975) also observed globules on silver-copper eutectic spheres and identified them as mercury.

5.7 POLISHED SURFACE EXAMINATION

5.7.1 AN ALTERNATIVE POLISHING METHOD

Specimens of Shofu spherical amalgam were abraded to 1000 grade silicon carbide paper followed by a magnesium oxide polish (Magomet by Buehler) on a fresh piece of Microcloth using a non-skid polishing technique (Fig. 5-7A and B). It was observed that this method:

- i. produced an almost scratch free surface,
- ii. started to relief polish the γ_2 phase.

5.7.2 AN ALTERNATIVE ETCHING METHOD

Specimens of Shofu spherical at the 600 grade silicon carbide paper stage (Fig. 5-8A) were treated with a freshly prepared first solution of the Wing etch until the scratches were removed. This involved times of about 5 to 10 seconds. Following application of the second solution the γ (silver-tin) and γ_1 (silver-mercury) phases were clearly defined (Fig. 5-8B). The γ_2 phase (tin-mercury) appeared to be overetched and SEM examination of the specimen in a Siemens Autoscan confirmed this finding (Fig. 5-8C).



Fig. 5-7. SHOFU SPHERICAL :

- A. 1000 grade silicon carbide paper.
- B. Same area as (A) after polishing with magnesium oxide on Buehler Microcloth.

(x60)

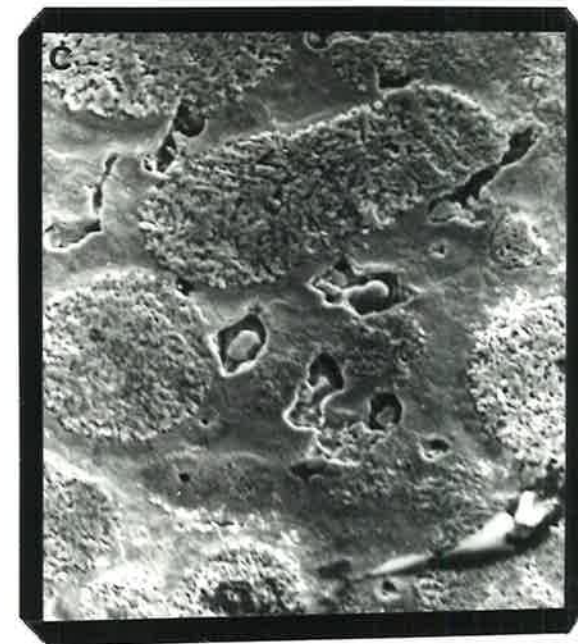
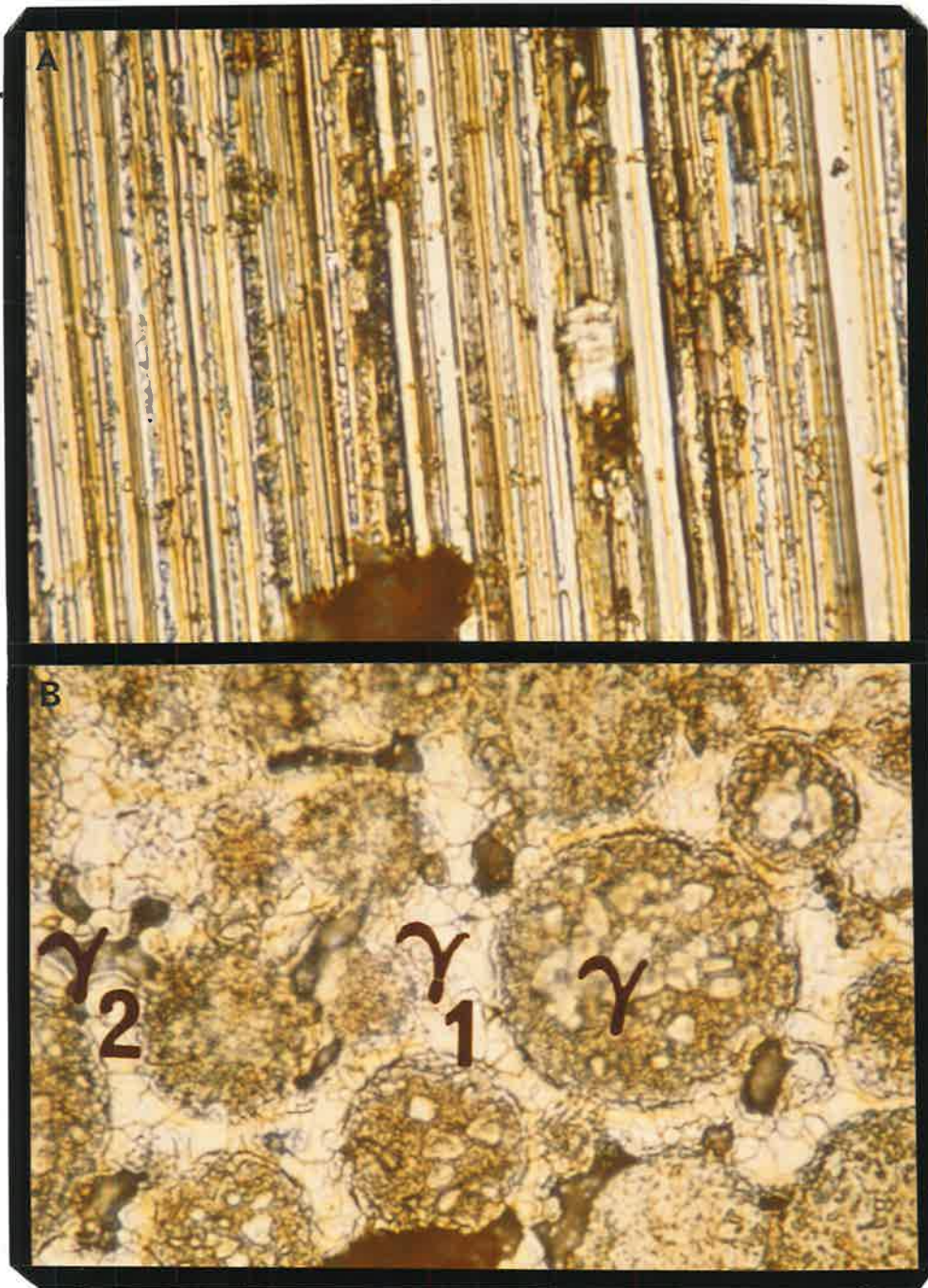


Fig. 5-8. SHOFU SPHERICAL

- A. 600 grade silicon carbide stage.
- B. Same area as (A), following the Wing etch. The γ (Ag-Sn), γ_1 (Ag-Hg) and γ_2 (Sn-Hg) phases are visible. (x240)
- C. SEM of (B) demonstrating the overetched γ_2 phase. (x800)

5.7.3 POROSITY FROM ULTRASONIC CLEANING

Previous unpublished work by Makinson revealed that specimens prepared by diamond polishing and ultrasonic cleaning exhibited porous structures and it was decided to study the influence of ultrasonic cleaning on porosity formation. A G-C Hi-atomic 10 specimen similar in appearance to those published by Taylor (1972) was selected and the following experiments undertaken:

i. Evaluation of porosity

The porosity revealed on the surface of the polished and ultrasonically cleaned specimen was determined by the Weibel method to be 20%. A typical porous area is shown in Fig. 5-9A. Following grinding on 600 grade silicon carbide paper the surface appeared to be free of porous areas (Fig. 5-9B). The specimen was then polished by Struers 7 μ m, A and B pastes on Dur, Mol and Nap cloths respectively. Magnesium oxide on Microcloth was used as the final polishing agent. The porosity of this final polished surface was 5% (Fig. 5-10A). The specimen was then placed in the ultrasonic cleaning bath and a porosity count recorded at one minute intervals for the first 5 minutes. Subsequent measurements were made after 10 and 15 minutes (Fig. 5-10B). It was observed that as the time of ultrasonic cleaning was lengthened, the porosity of the specimen increased (Fig. 5-11).

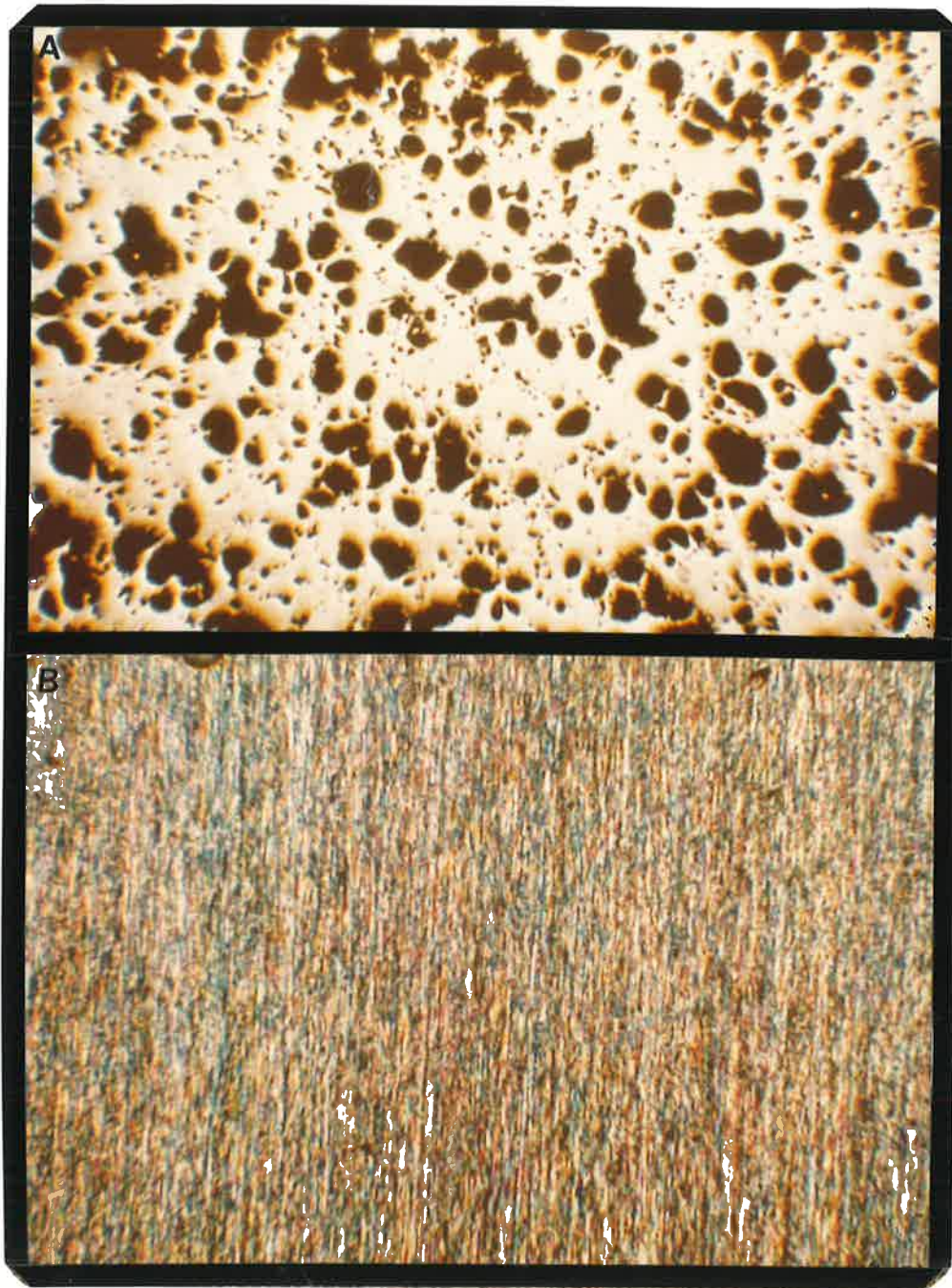


Fig. 5-9. G-C HI-ATOMIC 10 :

- A. The original porous surface.
- B. Following 600 grade silicon carbide paper (dark field). Same area.

(x24)

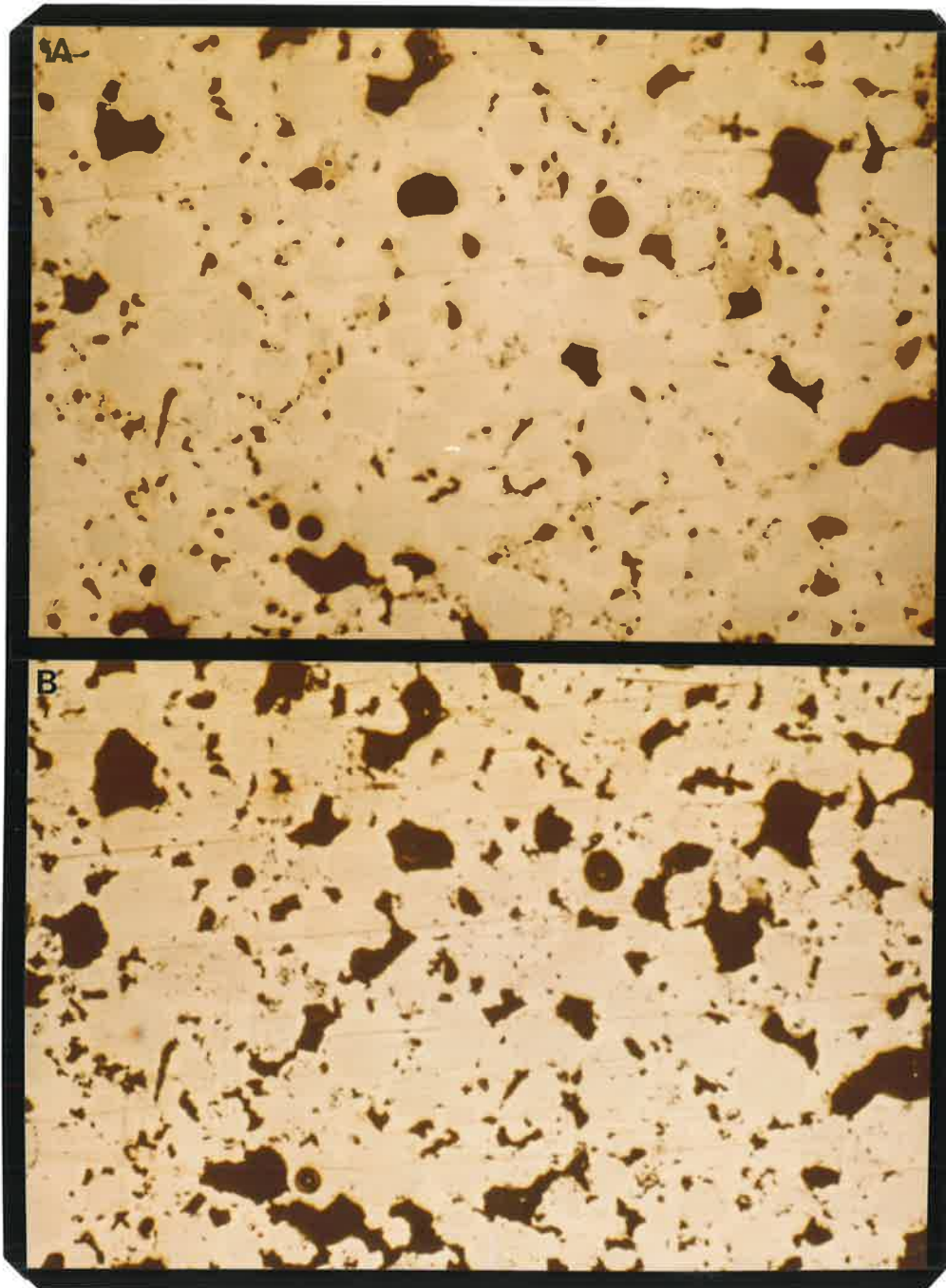


Fig. 5-10. G-C HI-ATOMIC 10 :

A. The final magnesium oxide polished surface.

B. Following a 10 minute ultrasonic clean. Same area.

(x60)

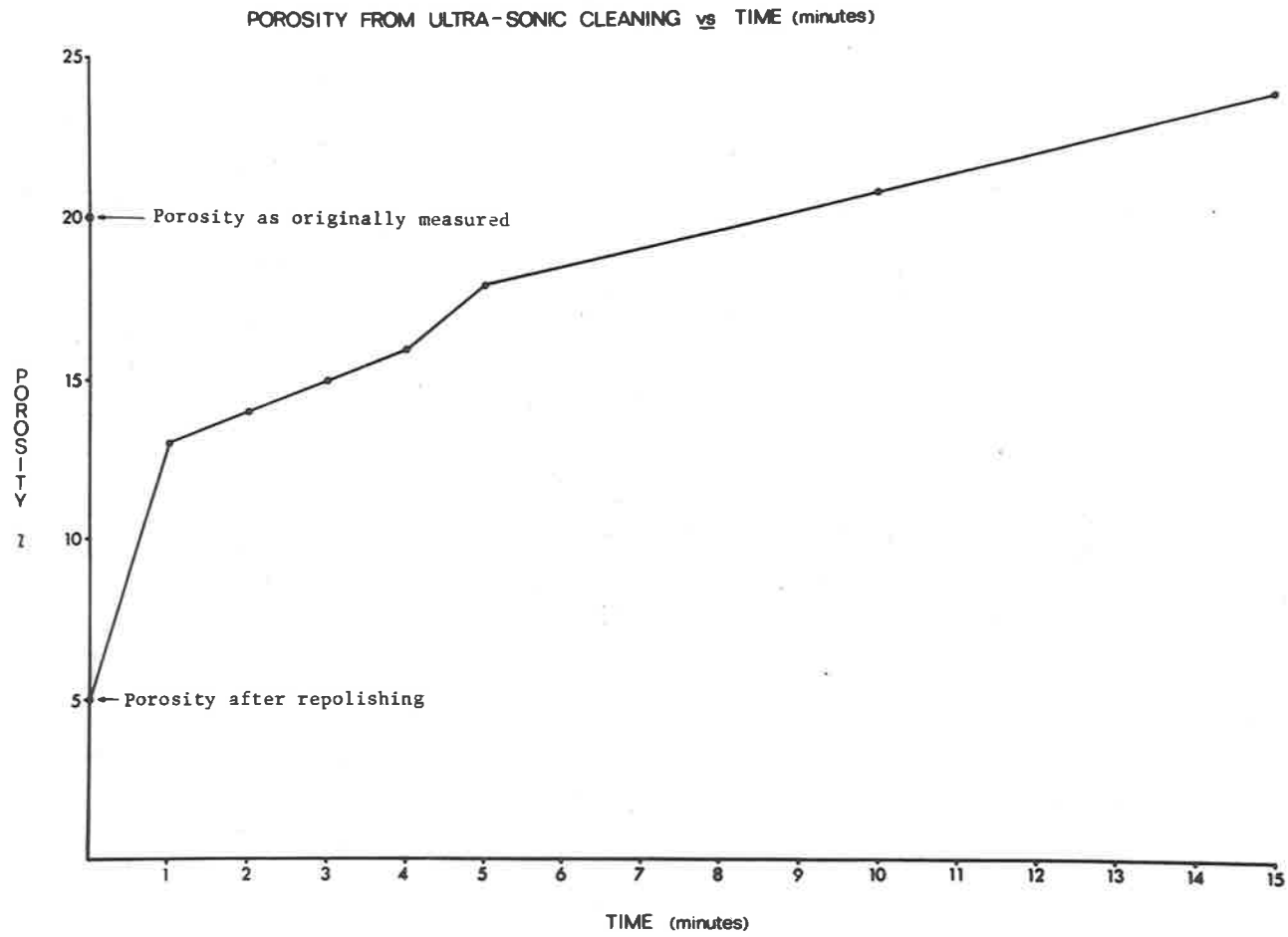


Fig. 5-11.



On repolishing the specimen to a B paste finish and then ultrasonically cleaning the specimen for 30 seconds, a section of amalgam lifted out of the surface with cracks extending around its periphery. Following an additional 30 second ultrasonic clean the area was rendered porous (Fig. 5-12). On specimens etched by the Wing solutions porosity formation was observed to occur by removal of γ and γ_1 phases (Fig. 5-13). In other areas γ_2 loss occurred.

ii. To determine if debris was on the surface

The specimen was ground on 600 grade silicon carbide paper and then immediately etched by the Wing cyanide technique, followed by a 30 second ultrasonic clean (Fig. 5-14). Following the ultrasonic clean what appeared to be debris within a pore was removed. However, the material displaced could not positively be identified as debris. The specimen was then polished by the alternative polishing method (Section 5.7.1) and then etched with the Wing solutions, but once again, a few areas were not fully defined and could have been debris within porosity.

To examine this effect in more detail the magnesium oxide polished surface was repolished using 3M¹⁹ composite resin polishing paste on a Mol cloth with alcohol as a lubricant. The quartz paste is birefringent under polarized light, but

19. Minnesota Mining & Mfg. Co., Minnesota 55101, U.S.A.

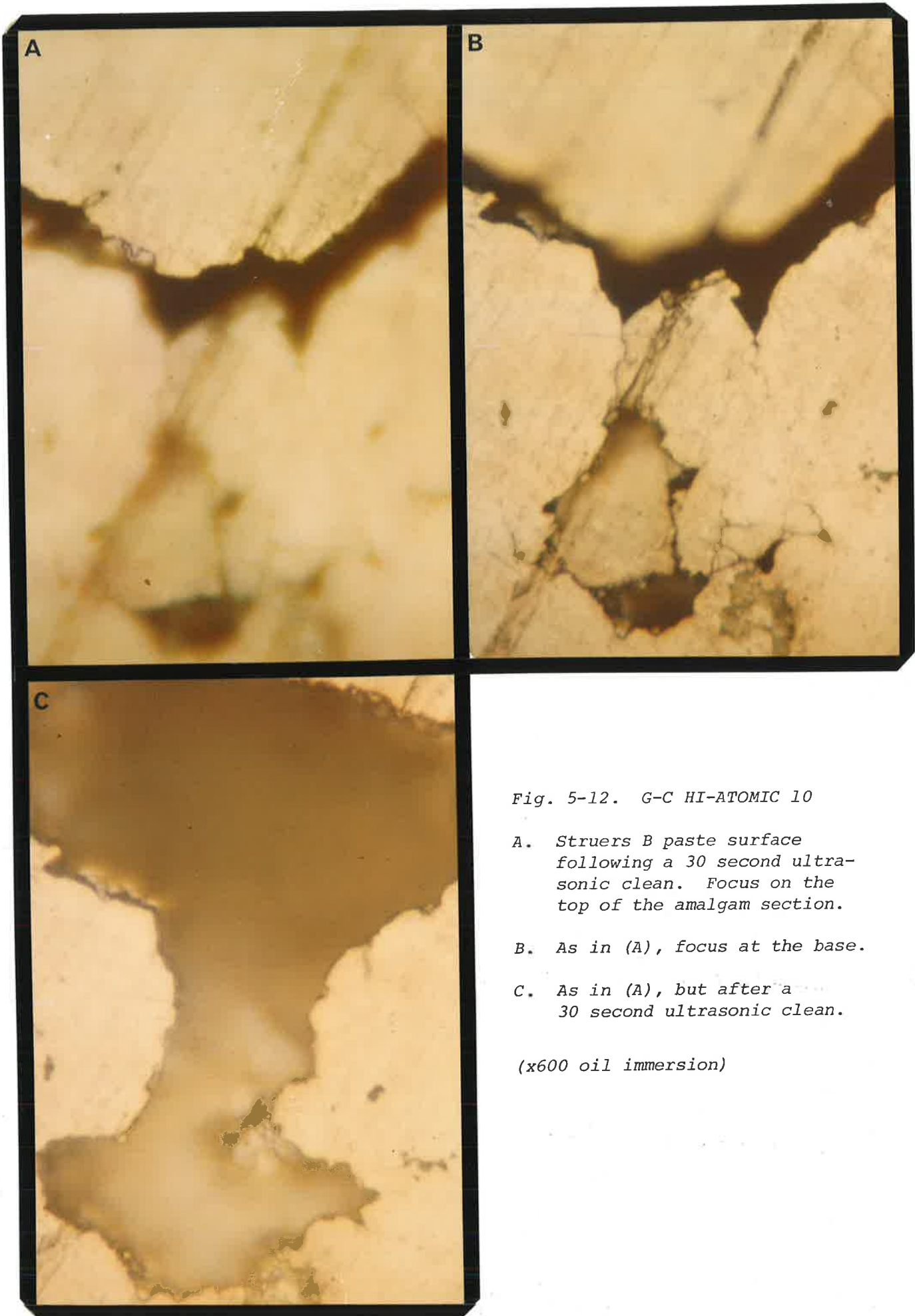


Fig. 5-12. G-C HI-ATOMIC 10

A. Struers B paste surface following a 30 second ultrasonic clean. Focus on the top of the amalgam section.

B. As in (A), focus at the base.

C. As in (A), but after a 30 second ultrasonic clean.

(x600 oil immersion)

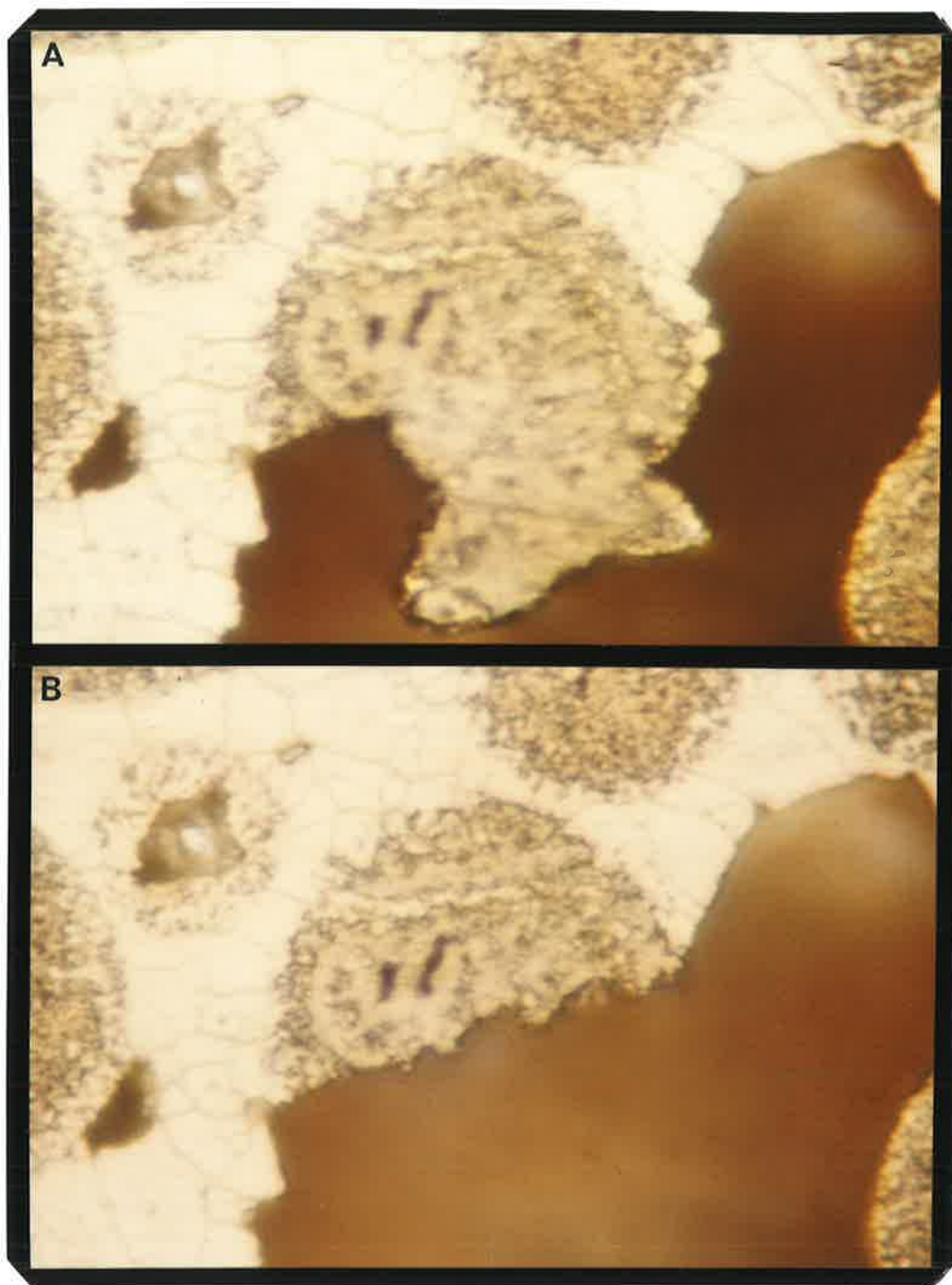


Fig. 5-13. G-C HI-ATOMIC 10 :

A. Magnesium oxide surface etched by the Wing technique.

B. As in (A), but after a 30 second ultrasonic clean.

The γ particle has shattered and some γ_1 loss has occurred.

(x600 oil immersion)

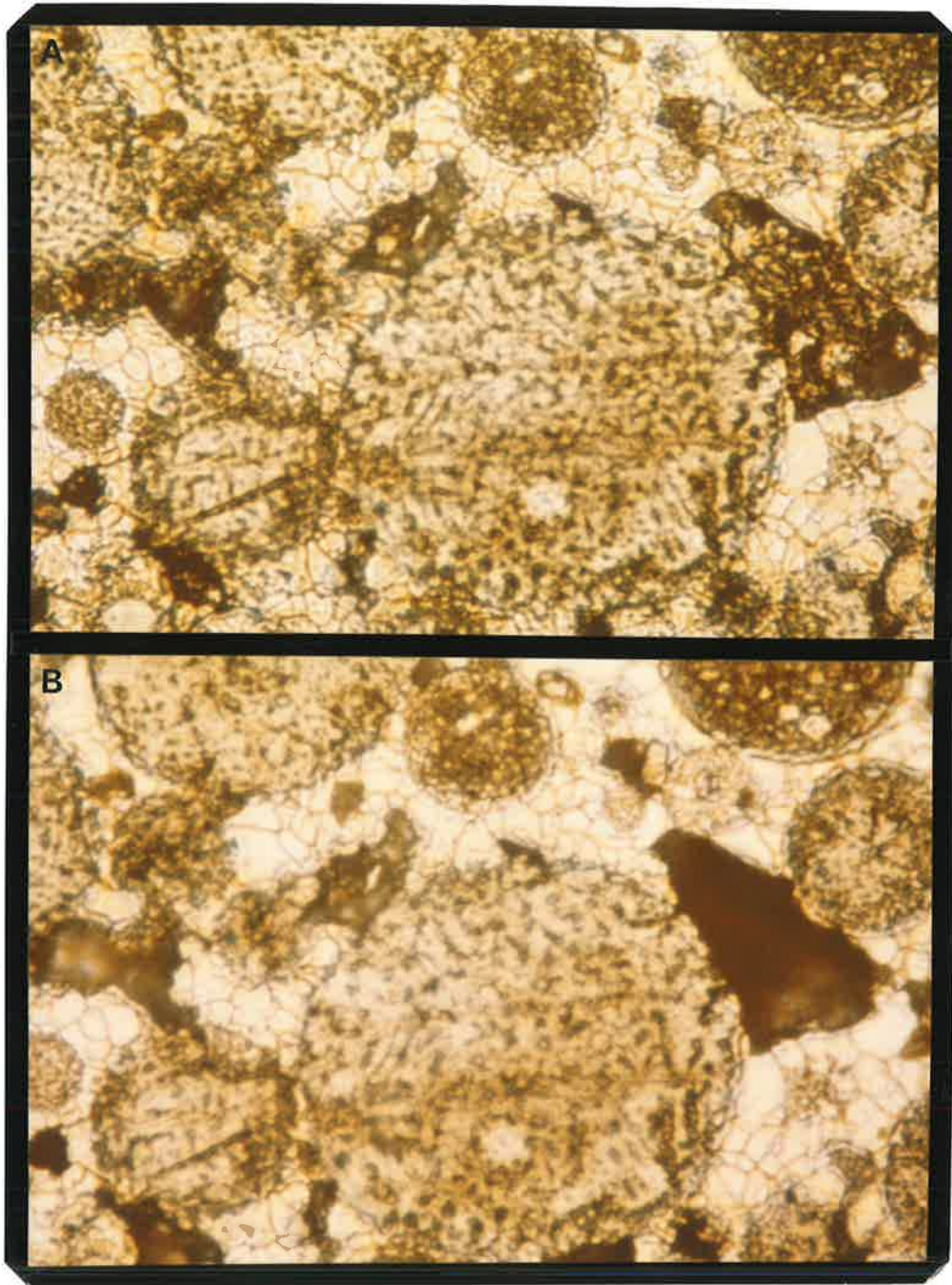


Fig. 5-14. G-C HI-ATOMIC 10 :

- A. The Wing etched 600 silicon carbide stage.*
- B. Same area as (A), but following a 30 second ultrasonic clean.*

(x240)

after washing the specimen surface and re-examining under polarized light no trace of abrasive was detected, suggesting that there were no porous areas filled with polishing paste.

These above experiments suggested that the G-C Hi-atomic specimen was inherently free of porosity but use of ultrasonic cleaning could promote loss of particles and porosity formation.

5.7.4 PHASE REMOVAL BY POLISHING

Specimens of Shofu spherical amalgam were ground on 600 grade silicon carbide paper and etched with Kodak Special Rapid Developer for 3 minutes (Abbott 1975). This procedure was repeated for 1000 grade silicon carbide paper, 7 μ m, A and B diamond pastes. Figure 5-15 shows that the γ_2 phase was removed at the A paste stage. In other cases γ_2 loss occurred at the B paste stage. The experiment was repeated but with no etching between polishing stages. In this case, no γ_2 loss was observed. However, if polishing steps were repeated, from B paste back to A paste, the γ_2 phase was removed. It was noted that if polishing steps were repeated, the direction of polishing on the Mol cloth with A paste was important, if the γ_2 phase was to be preserved (Fig. 5-16). Polishing with the "grain" of the cloth (Fig. 5-17) resulted in only slight removal of the γ_2 phase, while polishing against the "grain" of the cloth produced complete γ_2 removal. Prolonged polishing at either the A or B paste stages also resulted in γ_2 removal.



Fig. 5-15. SHOFU SPHERICAL

A. 1000 silicon carbide stage etched with photographic developer.

B. 7µm diamond paste stage etched with photographic developer.

C. A diamond paste stage showing loss of γ_2 .

Same area.

(x600 oil immersion)



Fig. 5-16. SHOFU SPHERICAL

- A. Struers B paste surface.
- B. Repeat Struers A paste by polishing with the 'grain' of the Mol cloth. Some γ_2 removal has occurred.
- C. Polish against the 'grain' of the Mol cloth. Further removal of the γ_2 phase has occurred.

(x600 oil immersion)

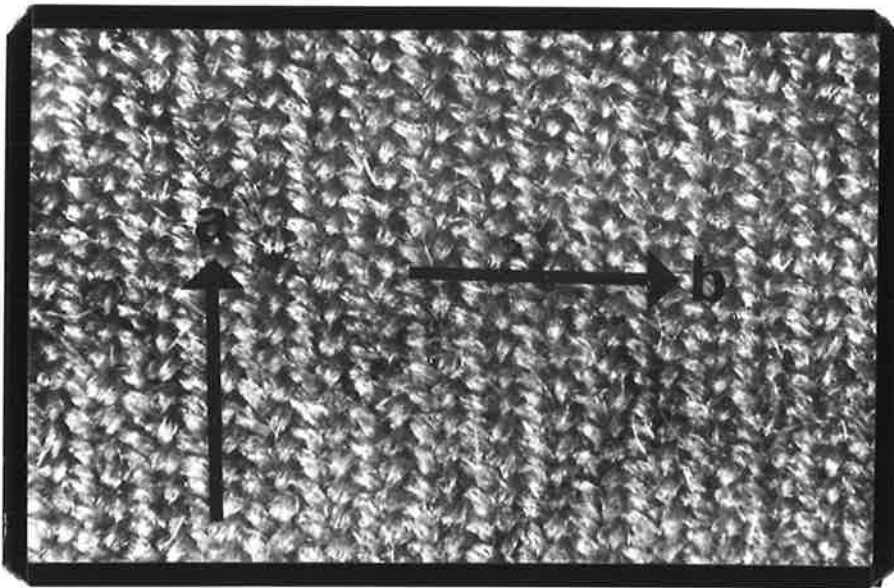


Fig. 5-17. STRUERS MOL CLOTH :

- a. Polish with 'grain'.*
- b. Polish against 'grain'.*



Fig. 5-18. SHOFU SPHERICAL :

- A. Worn 600 grade silicon carbide paper.
- B. Fresh 600 grade silicon carbide paper.

An increase in porosity has occurred from (A) to (B). Same area.

(x24)

An additional experiment involving grinding the specimen with worn 600 grade silicon carbide paper followed by fresh 600 grade paper resulted in an increase in specimen porosity, as shown in Fig. 5-18. When the experiment was repeated with worn and fresh 320 grade and 400 grade silicon carbide papers the same effect was observed.

5.7.5 VIBRATORY POLISHING

Specimens of Shofu spherical, 20th Century Micro, Luxalloy, Dispersalloy, Spheriphase, Tytin and Sybraloy were polished to a Struers B diamond paste finish.

A Buehler Vibromet vibratory polishing machine was used with 30cm diameter adhesive backed Microcloth. The specimen holders weighed 330g. The machine had 7 speed settings and for this study was run on a low speed (1.5-2 arbitrary scale).

The polishing materials used were:

600 grade aluminium oxide²⁰

0.05 μ m aluminium oxide²¹

α aluminium oxide²²

γ aluminium oxide²³

levigated aluminium oxide

cerium oxide I, II

tin oxide

20. 21. Buehler Ltd., Evanston, Illinois, U.S.A. 60204

22. 23. Reliant Works, Betchworth, Surrey

whiting

rouge

magnesium oxide²⁴

zircate²⁵

toothpaste, a. Fluoriguard²⁶, b. Sensodyne²⁷

These polishing materials were tested with the 344g load or by the weight of the specimen itself (14g). Polishing times varied from 3 minutes to 48 hours.

Surface scratches and porosity formation were a common finding amongst 600, levigated, γ and α aluminium oxide, tin oxide, whiting, zircate and Sensodyne. With all fine polishing materials, the γ_2 phase of Shofu, 20th Century Micro, and Spheriphase becomes visible after 3 minutes of vibratory polishing (Fig. 5-19A). γ_2 phase removal occurred within 15 minutes with all abrasives (Fig. 5-19B) and was complete after 2 to 5 hours, irrespective of the load applied.

The materials, load and time which revealed γ_1 grain boundaries in Sybraloy and Tytin are shown in Table 5-5, while Fig. 5-20 demonstrates the detail seen in these recently developed amalgam alloys. Only with magnesium oxide for 10 hours (344g) did Shofu and 20th Century Micro reveal γ_1 grain boundaries.

24. Buehler Ltd., Evanston, Illinois, U.S.A. 60204

25. L.D. Caulk Co., Div. D.S. Co., Milford, Del. Toronto, Ont.

26. Colgate-Palmolive Pty. Ltd., Sydney, Australia.

27. Stafford-Miller Ltd., Sydney, Australia.

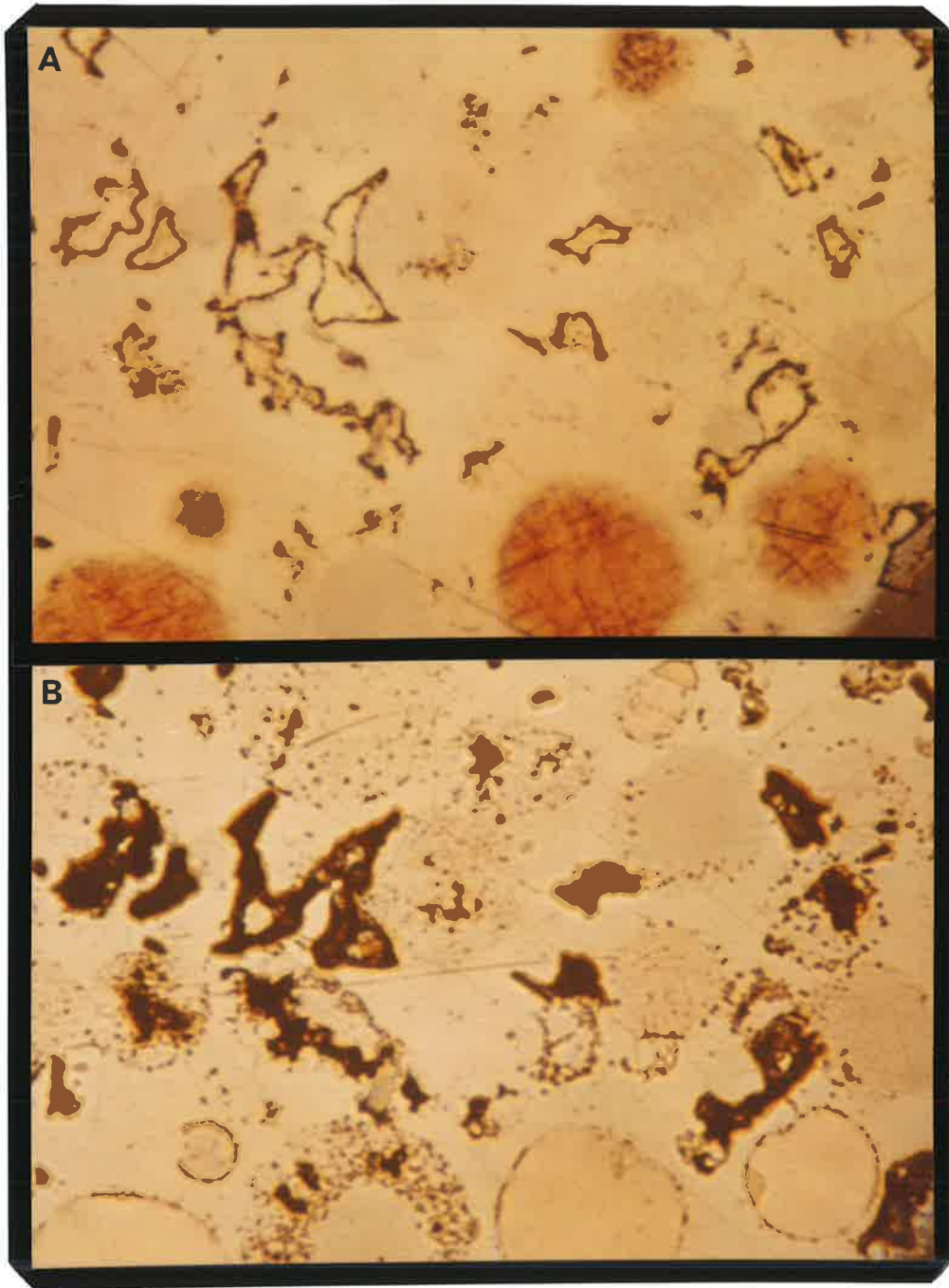


Fig. 5-19. SPHERIPHASE :

- A. 3 minute vibratory polish with magnesium oxide under a 14g load.*
- B. Same area as (A), but after a 15 minute vibratory polish.*

(x240)

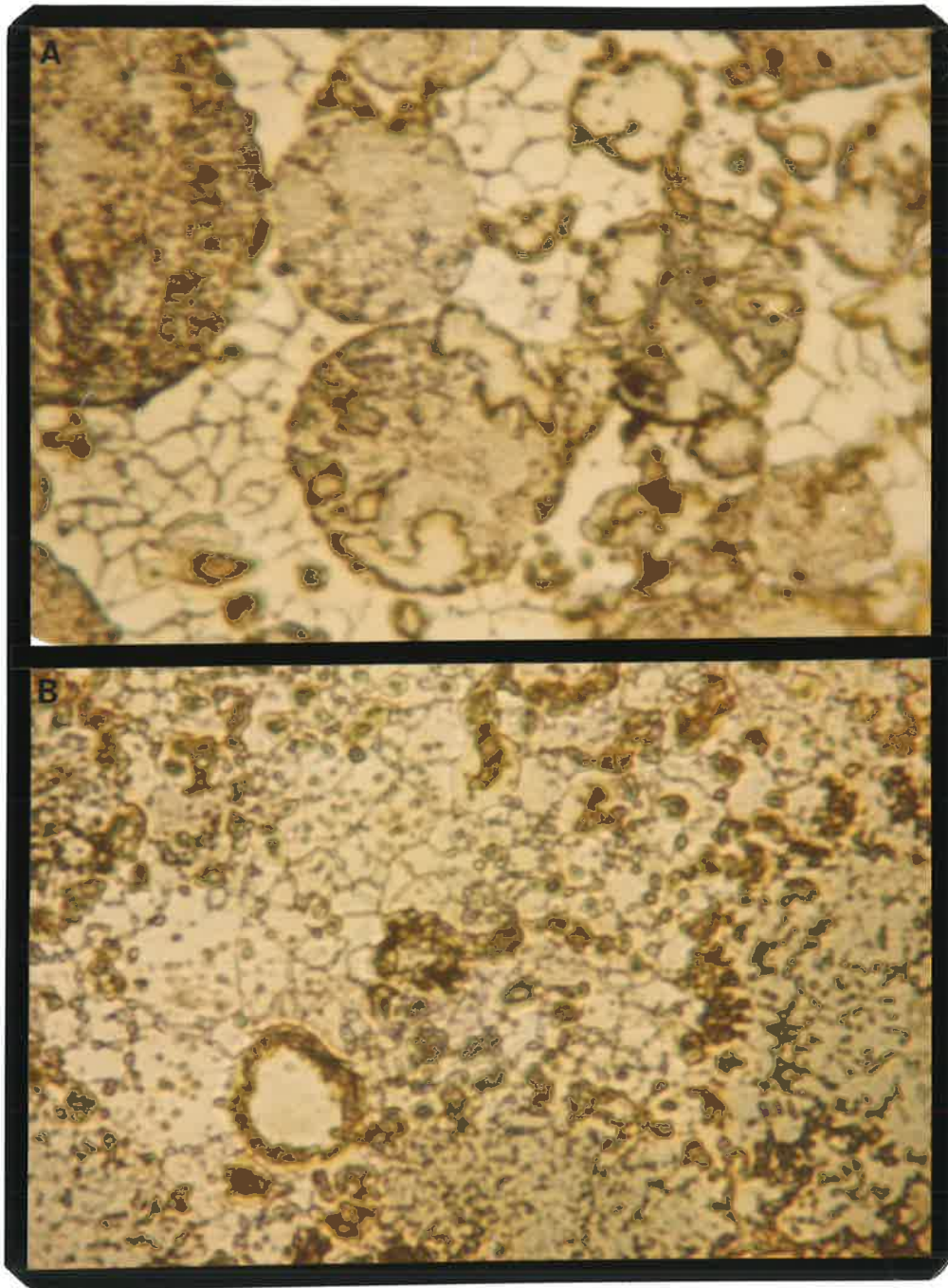


Fig. 5-20. A. SYBRALLOY: vibratory polished for 12 hours, with a 14g load. (rouge)

B. TYTIN: vibratory polished for 24 hours with a 14g load. (magnesium oxide)

(x600 oil immersion)

Table 5-5

OPTIMUM CONDITIONS FOR VIBRATORY POLISHING TERNARY AMALGAM ALLOYS

Polishing Agent	Load (g)	Time (h)
Magnesium oxide	344	10
Magnesium oxide	14	24
Cerium oxide I	14	24
Fluoriguard	14	36
Rouge	14	12

The conditions necessary to show γ , γ_1 and the silver-copper eutectic with reaction ring in the dispersed phase amalgams are listed in Table 5-6. Fig. 1-2 depicts the surface produced by cerium oxide on the Luxalloy specimen.

Table 5-6

OPTIMUM CONDITIONS FOR VIBRATORY POLISHING DISPERSED PHASE AMALGAM

Polishing Agent	Load (g)	Time (h)
Magnesium oxide	344	24
Cerium oxide I	14	48

0.05 μ m aluminium oxide after 5 hours with a 344g load revealed the structure of the silver-copper eutectic reaction ring plus the lathe cut γ particles in Dispersalloy and Luxalloy (Fig. 5-21A). In Sybralloy the γ ternary alloy particles and possibly a second phase were revealed (Fig. 5-21B).

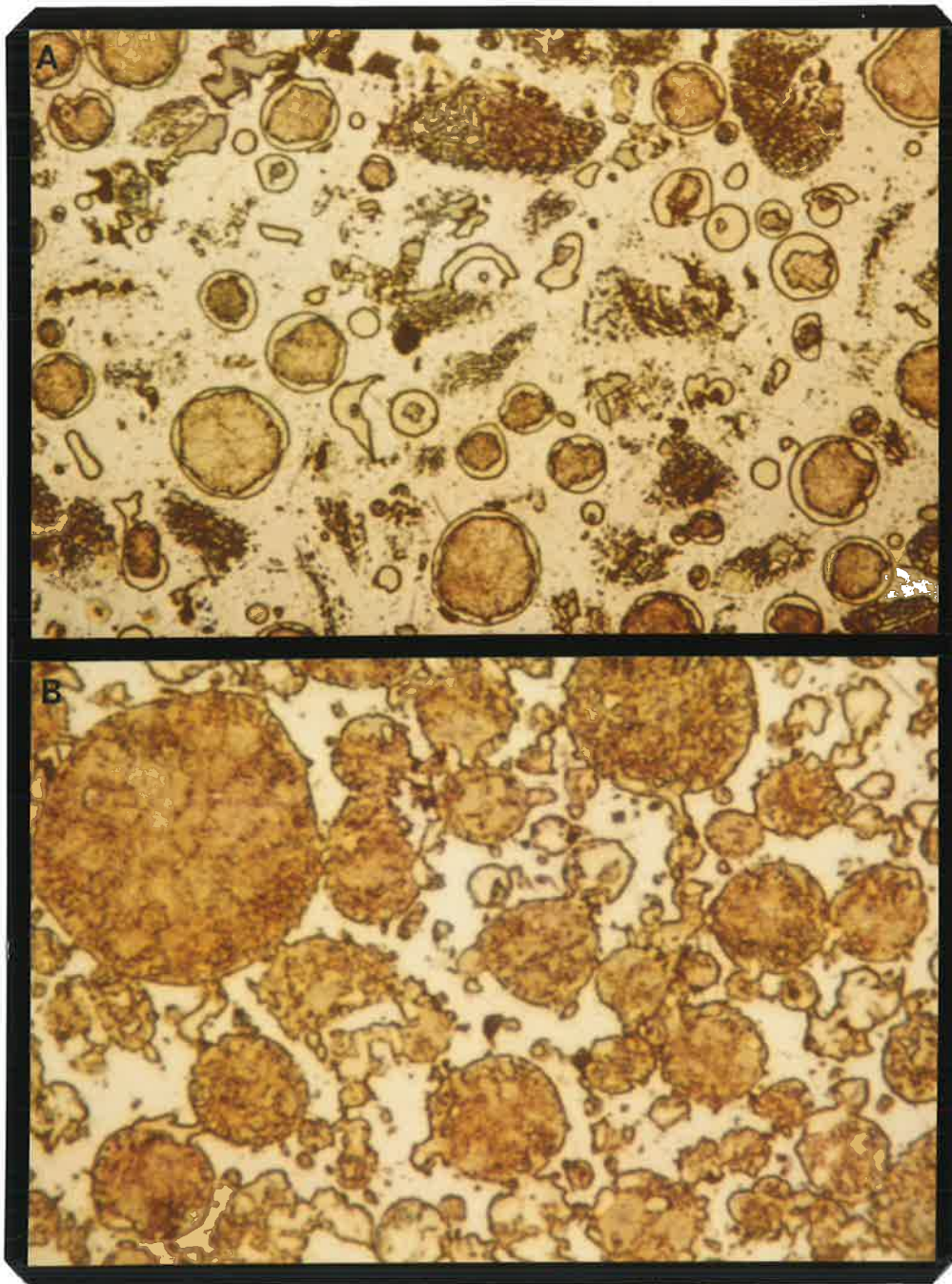


Fig. 5-21. A. LUXALLOY. (x120)

B. SYBRALLOY. (x240)

Vibratory polished for 5 hours with a
344g load using 0.05 μ m Aluminium oxide.

CHAPTER 6

DISCUSSION

6.1 INVESTIGATION OF THE γ_2 PHASE6.1.1 A SPECIFIC ETCH FOR THE γ_2 PHASE

The 1% available iodine in Betadine is believed to account for its etching ability on dental amalgam. After swabbing with Betadine and re-etching with the Wing solutions, some of the γ_2 particles became heavily etched at their grain boundaries, which may explain the γ_2 particle count difference between Betadine and the Wing etch. Within the limit of the optical microscope (0.5 μ m) Betadine revealed all the γ_2 phase and hence is comparable with the four etchants presented in the 1975 research report. The Betadine etch provides a convenient method of selectively identifying the γ_2 phase for volume fraction determination. It makes point-counting techniques easier and more accurate than the Wing etch. This is likely to be of considerable benefit with electron probe and X-ray analysis techniques and with image analysing computers such as the Quantimet.²⁸

6.1.2 REMOVAL OF THE γ_2 PHASE

Either iodine vapor or 10% nitric acid are effective agents:

- i. to chemically remove the γ_2 phase of conventional silver-tin amalgams,

28. Metals Research Ltd., England

- ii. to preferentially etch the reaction ring of the silver-copper eutectic spheres in the dispersed phase amalgams.

There is controversy over the depth of γ_2 dissolution in dental amalgam. Part of this controversy may be related to the chemical compositions of the corrosive solution. Stevenson and Wing (1976) demonstrated by in vitro experiments using sodium citrate solution that γ_2 removal occurred to a depth of 500 μm . However, the work of Jorgensen and Saito (1970), Holland and Asgar (1974) and Mateer and Reitz (1972) has suggested dissolution of the γ_2 phase occurs throughout an entire amalgam. The present study has shown that γ_2 dissolution can occur to a depth of 400 μm . Possibly this depth would have been greater if longer times of immersion were used.

Jorgensen and Saito (1970) published photomicrographs of amalgam specimens with an abnormally high γ_2 content and claimed that a continuous network of γ_2 phase exists so that γ_2 dissolution can occur throughout an entire amalgam. However, it is generally believed that the γ_2 phase does not form a continuous network. Clearly further work is required to study the mechanism by which dissolution of a discontinuous γ_2 phase could occur.

6.1.3 QUANTITATIVE ANALYSIS OF THE γ_2 PHASE

The 0.3% (± 0.2) volume fraction of γ_2 in Dispersalloy obtained from Wig-L-Bug trituration and storage at 37°C for 24 hours is in agreement with the result of Sarkar and Greener (1975) who used

potentiostatic polarization measurements. However, a further reading at 6 days produced no γ_2 phase. The results are then in agreement with Wing (1975), Wing and Bryant (1975, 1976), Marshall et al (1975), Mahler et al (1976).

The γ_2 content of the dispersed phase amalgams stored at room temperature did not change significantly over 6 days whereas at 37°C a significant change occurred. Thus, the volume fraction of the γ_2 phase in dispersed amalgams does depend on storage temperature. Confirmation of the results obtained by Asgar (1974) and Mahler et al (1975) that γ_2 phase elimination in dispersed phase amalgams occurs over 1 week at body temperature has been obtained. Evidence to support Asgar's (1974) theory of the continuing reaction of γ_2 particles with the silver-copper eutectic phase has also been obtained.

The claim of Wing and Bryant (1975, 1976) that Spheriphase contains no γ_2 phase is in disagreement with results of the present study. However, these workers do not state the temperature and time of storage of their specimens. The γ_2 phase in this amalgam was not eliminated after 6 days at 37°C, while after storage at room temperature for 6 days 10.3% (± 0.9) γ_2 phase was present. These workers also used the electron microprobe for γ_2 analysis, which Bryant (1976) acknowledged as having limited use in measurements of the volume fraction of the γ_2 phase.

No γ_2 phase could be detected in the ternary alloy amalgams, Tytin and Sybraloy, and this result supports the work of Marshall et al (1975) and Mahler et al (1976).

The results of the γ_2 analysis in conventional amalgams indicate that temperature was a significant variable, while in dispersed phase amalgams, trituration, temperature and time of storage should be recognized as variables which can affect the volume fraction of this phase. These variables did not have any effect on the γ_2 content in the ternary amalgam alloys.

6.2 POLISHED SURFACE EXAMINATION

6.2.1 AN ALTERNATIVE POLISHING METHOD

By utilizing the alternative polishing method involving final polishing immediately after 1000 grade silicon carbide paper, the 7 μ m, A and B diamond pastes can be eliminated. To produce a satisfactory polish it is necessary to use,

- i. a fresh piece of Microcloth,
- ii. freshly prepared magnesium oxide mixed to a slurry with alcohol.

Although Microcloth can be washed, a fresh piece of cloth is desirable because of the possibility of magnesium carbonate crystals remaining in the cloth and scratching specimens. It is not necessary to have a large piece of polishing cloth for this technique, and for economic reasons, adhesive backed Microcloth can be cut into several small pieces. Generally specimens take 2-3 minutes to be adequately polished by this new method.

6.2.2 AN ALTERNATIVE ETCHING METHOD

The results have shown that the Wing etch was highly reactive since it was possible to etch immediately following the silicon carbide stage to satisfactorily reveal the microstructure. The advantage of this technique is that it avoids 4 or 5 additional polishing steps during which artefacts may be introduced.

6.2.3 POROSITY FROM ULTRASONIC CLEANING

Bergendal (1968), Johnson (1972), Wawner (1970), Wawner and Lawless (1972), and Taylor (1972), based on observations of polished surfaces, have proposed mechanisms for porosity formation in amalgam caused by air entrapment and by variations in silver-tin content and γ particle size. However, the validity of these mechanisms is questionable since the present work has demonstrated that ultrasonic cleaning produces some of the porosity seen in polished dental amalgam by loss of γ , γ_1 and γ_2 phases. It was also observed that γ particles which extend into porous regions are more prone to loss during ultrasonic cleaning and are gradually removed as fragments of the γ particle fracture.

6.2.4 PHASE REMOVAL BY POLISHING

The γ_2 phase is the softest phase in dental amalgam and once it has been delineated by etching or polishing, it can be removed at the A or B diamond paste stage. It must be established that polishing procedures which do not result in γ_2 removal are used for

quantitative measurements of γ_2 phase. To minimize γ_2 removal during polishing the following precautions should be taken:

- i. use worn silicon carbide papers,
- ii. avoid etching between stages,
- iii. avoid repeating polishing steps,
- iv. polish with the "grain" of the Mol cloth,
- v. minimize the polishing time at the A and B diamond paste stages.

These conditions infer that scratches on amalgam specimens may have to be tolerated if the γ_2 phase is to be retained.

6.2.5 VIBRATORY POLISHING

Vibratory polishing of amalgam specimens produced definition of grain boundaries within a few minutes to several hours, depending upon the amalgam type, polishing agent and load applied, and as such would be an alternative to etching procedures.

The removal of the γ_2 phase within 15 minutes raises an interesting speculation. Jorgensen and Saito (1970) used vibratory polishing in their study of the structure and corrosion characteristics of dental amalgam. Amalgam specimens were stored in a 10% sodium citrate solution from 2 to 32 weeks at 37°C and were then sectioned and vibratory polished with diatomaceous earth. Upon microscopic examination, the γ_2 phase was found to be removed over the entire section. Jorgensen and Saito claimed that the 10%

sodium citrate solution corroded the γ_2 phase and because all the γ_2 had been removed, the γ_2 particles must form a continuous network. However, the possibility arises that vibratory polishing and not the citrate solution removes the γ_2 phase so that Jorgensen and Saito may have been interpreting a polishing artefact.

CHAPTER 7

CONCLUSIONS

7.1 γ_2 PHASE EXAMINATION7.1.1 A SPECIFIC ETCH FOR THE γ_2 PHASE

Betadine selectively etches the γ_2 phase on a polished surface and allows easier and more accurate quantitative analysis of this phase than the Wing etch.

7.1.2 REMOVAL OF THE γ_2 PHASE

Either 10% nitric acid or iodine vapor remove the γ_2 phase. Specimens treated with 10% nitric acid show γ_2 removal to a depth of at least 400 μ m.

7.1.3 QUANTITATIVE ANALYSIS OF THE γ_2 PHASE

- i. The number of γ_2 particles and the volume fraction of γ_2 phase in dispersed phase amalgams decreases over a period of 144 hours at body temperature.
- ii. The number of γ_2 particles and the volume fraction of γ_2 phase in conventional silver-tin amalgams do not change significantly over a period of 6 days at body temperature.

- iii. Ternary alloys do not contain amounts of γ_2 phase detectable by conventional optical microscopy techniques.
- iv. Significantly less amounts of γ_2 phase are observed in Spheriphase when triturerated by the Silamat than by the Wig-L-Bug.

7.2 POLISHED SURFACE EXAMINATION

7.2.1 AN ALTERNATIVE POLISHING METHOD

A final polish can be obtained directly following the 1000 silicon carbide stage, thereby eliminating diamond paste stages.

7.2.2 AN ALTERNATIVE ETCHING METHOD

By applying the Wing etch at the 600 silicon carbide stage, it is possible to obtain structural details of the γ , γ_1 and γ_2 phases without completing the normal polishing sequence and then etching.

7.2.3 POROSITY FROM ULTRASONIC CLEANING

Ultrasonic cleaning can result in porosity as an artefact on polished dental amalgam by causing loss of γ , γ_1 and γ_2 phases.

7.2.4 PHASE REMOVAL BY POLISHING

- i. Specimens etched to define the γ_2 phase are predisposed to γ_2 loss at the next polishing stage.

- ii. Repolishing of amalgam specimens to remove scratches can result in γ_2 removal.
- iii. In order to preserve the γ_2 phase when polishing steps are repeated, it is advisable to polish the specimen with the "grain" of the Mol cloth.
- iv. Once the γ_2 phase has been defined by the finest polishing materials, it may be removed by further polishing. Therefore prolonged polishing at the final polishing stages should be minimized.
- v. Fresh silicon carbide papers can result in increased porosity. To minimize this effect the use of worn abrasive papers is advocated.

7.2.5 VIBRATORY POLISHING

Although polishing times are long, vibratory polishing offers an alternative method to etching for obtaining structural details of dental amalgam. However, this method of polishing can result in surface artefact by removal of the γ_2 phase.

CHAPTER 8

SUGGESTIONS FOR FUTURE INVESTIGATION

The oral environment is extremely corrosive. Amalgam restorations are continually bathed in saliva which fluctuates in temperature and pH from the ingestion of foods and liquids. Even polished amalgam margins exhibit surface roughness and allow the tenacious adhesion of food and bacteria. Acid is produced by bacteria breaking down sugar, thus producing a very conductive and localized reaction on the metallic restoration. These environmental factors contribute to corrosion and in turn alter the physical and mechanical properties of the amalgam. Tarnish of amalgam results in loss of aesthetic qualities because the surface of the filling discolours. According to Phillips (1973), tarnish is the forerunner of corrosion and the ingestion of foods containing significant amounts of sulphur form the tarnish film which may in time chemically attack the metallic surface.

The release of mercury from the corrosion of the γ_2 phase in conventional silver-tin amalgam is believed by Jorgensen (1965) to promote failed amalgam margins. The corrosion of conventional silver-tin amalgams warrants further investigation to determine the mechanism by which dissolution of a discontinuous γ_2 phase occurs.

The present study has shown that the high copper (30%), low silver (40%), ternary amalgam alloys (e.g. Sybraloy), contain no detectable γ_2 phase. A preliminary in vitro study of Sybraloy by Marek and Hochman (1976) demonstrated that unlike conventional amalgam where corrosion is localised on the γ_2 phase, the corrosion of Sybraloy was uniform. Sarkar and Fuys (1976) tarnished high copper amalgam specimens by immersion in 0.1% Na_2S solution and observed that the tarnish resistance was adversely affected by the presence of large amounts of copper.

At the present time some dental practitioners are changing over to these new amalgam alloys. As there will not be any clinically significant surveys completed before 5 to 10 years the public will be the testing ground for these materials. The present investigation has established satisfactory procedures for the metallographic examination of dental amalgam and it would seem appropriate to use these procedures in an investigation of the tarnish and corrosion characteristics and the fracture mechanisms of the high copper amalgams. Indeed, all the relevant properties (e.g. compressive strength, static creep, dimensional stability, ease of manipulation) of these amalgams should be appraised and compared to the conventional silver-tin amalgams. In this way, it may be possible to determine if the high copper amalgam alloys are a clinical improvement on the conventional silver-tin amalgam formulated by G.V. Black in 1895.

APPENDIX I

ALLOY BRAND	HG:ALLOY	SILAMAT	WIG-L-BUG	BATCH NO.
New True Dentalloy ¹	8:7	10 sec	20 sec	277231
Shofu Spherical ²	6:7	10 sec	20 sec	037571
20th Century Micro ³	8:6	10 sec	20 sec	-
Hi-Atomic 10 ⁴	13:15	-	15 sec	-
Spheriphase (lathe) ⁵	10:10	7 sec	20 sec	50723
Spheriphase (spherical) ⁶	10:10	7 sec	20 sec	70211
Luxalloy ⁷	1.2:1	5 sec	25 sec	-
Dispersalloy ⁸	7:7	5 sec	20 sec	5A007
Tytin ⁹	6:7	5 sec	25 sec	-
Sybraloy ¹⁰	5:6	8 sec	-	0112761357

1. 9. S.S. White, Dental Products International, Philadelphia, U.S.A.
2. Shofu Manufacturing Co. Ltd., Kyoto, Japan.
3. L.D. Caulk Co., Div. D.S. Co., Milford, Del. Toronto, Ont.
4. G-C Chemical Mfg. Co. Ltd., Japan.
5. 6. Southern Dental Industries, Melbourne, Australia.
7. Vivadent Schaan/Liechtenstein.
8. Johnson & Johnson Dental Products Co., East Windsor, N.J.
10. Kerr Sybron Corporation, Romulus, Michigan.

APPENDIX II

ILLUSTRATION OF THE WEIBEL METHOD to determine the volume fraction of γ_2 phase in dental amalgam.

Shofu spherical specimen etched with 10% NaOH.

Optics combination: Objective 10x/0.45, eyepiece 10x

Fields counted: 25

Total number of points counted (P): 1050

Points corresponding to γ_2 : $P_{\gamma_2} = 56$

Points corresponding to voids: $P_v = 4$

Fraction of γ_2 : $\frac{56 \times 100}{1050} = \underline{5.3\%}$

Fraction of voids: $\frac{4 \times 100}{1050} = 0.4\%$

Remaining volume: = 94.3%

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