DENSIFICATION AND METALLURGICAL BONDING IN COPPER POWDER COMPACT
DURING ULTRASONIC POWDER CONSOLIDATION

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ABSTRACT

Ultrasonic powder consolidation (UPC) is a novel, low-temperature, rapid powder consolidation process being investigated at the Advanced Materials Processing Laboratory (AMPL), in which a powder compact to be consolidated is pressed under a uniaxial force, heated to a moderately low temperature (normally, < 0.5 T_m), and subjected to ultrasonic vibration for only a few seconds to create full-density, metallurgical bonded bulk materials. In the present study, UPC experiments were performed with a water-atomized copper powder to investigate the progress of powder compact densification and metallurgical bonding under systematically varied consolidation parameters: temperature and time. The extent of powder compact densification was determined on as-polished cross sections of consolidated specimens. The metallurgical bonding in the powder compacts was assessed on polished specimen surfaces subjected to an ultrasonic washing test, also developed at AMPL, in which a polished specimen surface is subjected to ultrasonic waves in water to remove powder particles that are not bonded well.

Image analysis on photomicrographs of as-polished and ultrasonically washed powder compacts showed that both compact densification and particle bonding increased with increasing consolidation temperature and time and that the metallurgical bonding lagged behind the compact densification. At a nominal consolidation temperature of 500 °C, full densification was achieved in 3 s, whereas 4 s were needed to achieve good metallurgical bonding. Delays of metallurgical bonding to similar degrees were observed at the consolidation temperatures of 300 - 600 °C that were investigated, suggesting that UPC is a 2-step process of compact densification followed by metallurgical bonding.

Compact densification progressed as the inter-particle regions were filled with ‘debris’ from
parent particles that rubbed against each other under the applied ultrasonic vibration. Energy-dispersive X-ray spectroscopy (EDS) revealed that the debris-filled inter-particle regions consisted of copper and a very small amount of oxygen, indicating that the debris did come from the parent copper particles. The debris had ragged interfaces with their parent particles and contained nano-sized voids. Local melting at the particle surface, possibly by strain-induced melting point depression, might produce bits of liquid that solidified into the debris.

The debris-filled inter-particle regions decreased with increasing consolidation temperature and/or time as they became integral parts of the consolidated material. Full metallurgical bonding was attained when the debris-filled inter-particle regions were completely transformed to well-defined grains by recrystallization and coarsening under imposed ultrasonic vibration. The extra time required for the transformation of the inter-particle debris to the well-defined grains accounts for the lag of the metallurgical bonding behind the compact densification.
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1 INTRODUCTION

1.1 Overview

Ultrasonic welding (USW) is a material joining process in which ultrasonic vibration is applied to materials clamped together under uniaxial pressure at low temperatures, usually at room temperature. Joining normally takes place very rapidly within a second or less. An exceptional feature of USW is its capability for both monometallic and bimetallic joints [1], as well as metal bonding to polymers [1-7] and ceramics such as glass, alumina, silicon, germanium and quartz [8]. Moreover, it is an economical joining process since it requires no protective atmosphere or extensive prior treatment of materials to be joined. It is widely adapted in various sectors of manufacturing industries, such as electronics, automotive and aerospace industries, because of its ability to join materials rapidly and at low cost without exposing the materials to high temperature [9-11].

Despite the wide acceptance in industry, however, there has been no clear fundamental understanding of the mechanisms involved in USW. It is known that USW of metals involves local, high plastic strain at high cyclic rates [12-17]. This localized high-strain rate strains have been shown to create not only dislocations but also large amounts of excess vacancies in the metals by the non-conservative motion of jogs on screw dislocations [18-20]. This promotes phase transformations, e.g., recrystallization, and atomic diffusion across the interface, although no established fundamental understanding of the strain-induced structural changes in USW currently exits.

Vacancy concentrations in deforming metals have been estimated to increase many orders of magnitude above the thermal equilibrium values by transmission electron microscopy [21-23], calorimetry [24], electrical resistivity measurements [24,25], X-ray diffraction (XRD) [24], and
nuclear magnetic resonance (NMR) [26]. Excess vacancies in large amounts can have impact on the substitutional diffusion in the material undergoing high strain rate deformation. The occurrence of excess vacancy-enhanced diffusion was verified by the experiments of ultrasonically joining 1100 aluminum sheet to copper foil at nominal temperatures of 298 K to 413 K (25 °C to 140 °C) [27] in which EDS revealed significant interdiffusion at the interface that translated into diffusivity values of $1.54 \times 10^{-13}$ to $2.22 \times 10^{-13} \text{m}^2/\text{s}$ that were four orders of magnitude higher than the normal values [27]. Excess vacancies may also affect the thermodynamic stability of the materials that contains the vacancies, possibly causing melting even below the equilibrium melting point [28]. This strain-induced melting point depression effect was first suspected in an ultrasonic welding experiment of aluminum foil and zinc sheet at 513 K (240 °C), which produced an Al-Zn weld indicative of local melting at the interface. Another important phenomenon that might play a role in USW is dynamic softening of the material subjected to ultrasonic deformation termed ultrasonic softening [29]. Although no clear understanding of this phenomenon currently exists, the effect of excess vacancies on dislocation climb is suspected to be responsible [30].

The motivation of this study on the structural changes in ultrasonic consolidation of copper powder was based on the above phenomena observed in USW. Ultrasonic powder consolidation (UPC), developed in the Advanced Materials Processing Laboratory (AMPL) [8, 31-33], is a USW process in which powder particles, instead of sheets or wires, are ‘joined’ by the application of ultrasonic vibration. In UPC, metallic powders confined in a die under uniaxial pressure is subjected to ultrasonic vibration in much the same way as in sheet joining, although in UPC the material (powder particles) must undergo larger amounts of deformation (compact densification) before the powder becomes a metallurgically bonded bulk material, whereas in
USW much less shape change precedes metallurgical bond formation. Thus, powder particle bonding necessarily lags behind powder compact densification in UPC. This behavior was first noticed by Li in his experiments to optimize UPC conditions for ultrasonic consolidations of copper and aluminum powders at room and moderately elevated nominal temperatures [34].

1.2 Objectives and Approaches

Ultrasonic consolidation of copper spherical powder was performed to fabricate specimens with systematically controlled parameters. Optical microscopy, together with image-analysis carried out on as-polished surfaces of specimens was to investigate densification attained under various UPC conditions, and metallurgical bonding in specimens were examined by a series of ultrasonic washing tests, ultimately yielding the specific UPC conditions necessary for full densification and good metallurgical bonding. Microstructures were studied by performing optical microscopy and SEM on etched and un-etched specimen surfaces.

The work presented in this thesis is aimed to verify and reconfirm the results and conclusions in previous studies, i.e., compact densification preceding metallurgical bonding in the UPC of copper [34] and investigate microstructural changes during the attainment of densification and metallurgical bonding in UPC.
2 LITERATURE SURVEY

2.1 Overview of Powder Metallurgy

Powder Metallurgy (P/M) constitutes an important route for manufacturing because of its ability to mass-produce net-shape parts at high material yield and competitive cost. P/M covers a wide spectrum of product areas ranging from tungsten filaments for light bulbs to dental amalgams, electrical switches, projectiles, rechargeable batteries, bio-implanting materials, aircraft brake pads, oil-less bearings and various automotive parts such as transmission gears [35]. The versatile applications of P/M are reflected by the large metal powder shipments in the United States which exceeded 500,000 metric tons in 2005, of which about 400,000 metric tons were for P/M use. The largest user of P/M parts has been the automotive industry where the use of P/M parts in US automobiles has exceeded 20 kg/car over the years, while somewhat lower but increasing figures are reported for foreign automobiles as well [36].

Another important characteristic of P/M is its ability to control the microstructure of materials, which permits the processing of materials that are otherwise difficult to process, such as high-alloy tool steels and superalloys, and enables the development of advanced materials such as metal-matrix composites (MMC) and various cermets. The ability to control material microstructure is further enhanced when P/M processes are combined with rapid solidification processing (RSP) [37]. A number of advanced RSP alloys have been developed via the latter route over the past two decades [38-42].

The acceptance of P/M in a wide range of manufacturing industry is realized by the development of today’s P/M technology that enables mass-production of dependable high-density P/M parts at competitive cost. However, complete removal of residual porosity is not always achieved, particularly in commercial solid-state pressureless sintering where only weak
capillary forces drive densification while slow diffusion limits the rate. Therefore, an important technical requirement in P/M is to advance full-density consolidation [35] which is defined as the process of converting a powder into a fully densified and metallurgically integrated bulk material. Currently, three fundamental approaches to full-density consolidation are identified: namely (1) sintering-based consolidation, (2) pressure-based consolidation and (3) shock wave consolidation.

In sintering-based consolidation, high density is achieved through improved green compaction, sintering of fine powder or liquid-phase sintering (LPS). The methods for improved green compaction developed to date include axial cold pressing (ACP), cold isostatic pressing (CIP), cold powder extrusion (CPE), roll compaction (RC) and powder forging (PF) [33-49]. While improved green compaction can produce up to 98% dense green compacts [50], complete removal of isolated residual pores during subsequent sintering must necessarily depend on slow diffusional transport, which is rarely practical. Nearly full-density can be achieved by metal powder injection molding (MPIM) [51, 52] with fine (< 10 μm) powders but binder removal and dimensional control are often challenging [35]. LPS, which can be achieved with persistent or transient liquid [53], is a full-densification process. Full-density materials can be produced also by infiltration of a porous P/M compact with a liquid phase. These processes involving liquid, however, suffer from structural degradation that may take place in the presence of the liquid.

Pressure-based consolidation takes various forms such as uniaxial hot pressing, hot isostatic pressing (HIP), extrusion, forging and rolling [35, 50, 54-59]. Full-density consolidation is achieved in the absence of liquid, but the consolidation temperature and applied stress need to be high enough to facilitate powder deformation [54]. High temperature is required also to assure metallurgical bonding of the powder particles. Full-density consolidation of powders produced
by rapid solidification processing (RSP) normally requires a pressure-based consolidation process. Due to the exposure to high temperature, however, the novel rapid solidification microstructures of the powder are largely lost in the consolidated bulk material.

Shock wave consolidation is performed via propagating a shock wave through the powder to cause the powder particles to weld rapidly as the shock wave passes by. The shock wave may be generated by using an accelerated mass that strikes the powder at a high velocity (cold dynamic compaction) or by detonating a shaped explosive charge placed around the powder (explosive compaction). The high-strain rate and momentary heating produced by the shock wave cause local melting of the interparticle contacts [35], which may permit rapid full-density consolidation. Since no powder preheating is required in this process, the consolidated material may suffer minimum structural changes if parameters are adjusted properly. This permits consolidation of RSP powders with novel metastable structures into a high-performance material. However, the use of an explosive or high-velocity mass to generate a shock wave limits the applicability of this approach to materials with small volumes and simple geometries. In addition, safety issues, high equipment cost and low productivity, all inherent in shock wave consolidation, limit the industrial viability of this approach.

Full-density consolidation requires both physical densification of the powder compact and metallurgical joining of the powder particles. In sintering-based consolidation, densification is driven by capillary forces and is kinetically limited by diffusional mass transport [60-65]. In pressure-based consolidation and shock wave consolidation, densification, driven by applied forces, proceeds faster and more thoroughly as the rate is limited by plastic flow. In any consolidation route, powder joining necessarily requires sufficient diffusional mass transport. This normally translates into use of a high consolidation temperature, which deleteriously affects
the microstructure of the consolidated material. Virtually all of the high-performance materials produced by P/M routes today, e.g., RSP alloys and metal-matrix composites (MMC), suffer, to some extent, from the structural degradation caused by the excessive but necessary exposure to high temperature during consolidation [57].

An ideal full-density consolidation process may be defined as one in which both full densification and metallurgical particle joining are achieved rapidly, economically and without affecting the microstructure of the starting powder. None of current full-density consolidation processes satisfies all of these criteria.
2.2 Ultrasonic Welding and Powder Consolidation

Ultrasonic welding (USW) is a solid-state joining process, producing metallurgical bonded joints from sheets, foils or wires by local high-frequency vibration, combined with normal compression of the parts [66]. Parts to be bonded are placed on a stationary base (anvil) and compressed under a controlled normal force by an ultrasonic probe (sonotrode). In metal USW the sonotrode is vibrated at a desired amplitude and a frequency between about 20 and 100 kHz in a direction parallel to the joint plane. Polymer USW uses vibrations normal to the joint plane. Highly localized initial interfacial slip causes disruption and dispersion of surface films (oxides, adsorbed impurities, moisture, etc.), breakdown of asperities and interpenetration of the two part geometries in some instances by plastic instability, permitting fresh metallic contact and formation of microwelds. Further processing results in an increase in bonded area and cyclic high strain-rate plastic deformation in the foils as well as elastic deformation hysteresis, generating modest heating. These highly localized high-strain rate shear strains have been shown to create large concentrations of excess vacancies in the parent metals [28]. This promotes recrystallization and other phase transformations (but without formation of brittle intermetallic compounds [67]) and atomic diffusion across the weld interface, although no established fundamental understanding of the strain-induced structural changes in USW currently exits.

An exceptional feature of USW is its capability for both monometallic and bimetallic joints [1], as well as metal bonding to polymers [1-7] and ceramics such as glass, alumina, silicon, germanium and quartz [68]. In particular, most metals and many of their alloys can be readily welded to themselves and to other metals [66]. Thermoplastics can also be welded to other polymers (polyethylene, ABS, PVC etc) [69]. Other advantages of USW include its short welding time and limited pressure and heat, preventing damage to plastics and semiconductors,
as well as joint deformation and residual stresses. Properly made ultrasonic bonds exhibit shear strength, hardness, high temperature behavior and corrosion resistance comparable to the base material [66]. In addition, USW is not sensitive to surface oxide films, coatings and insulations, and usually requires no protective atmosphere. There is no need for special health and safety precautions, and no environmental hazards [67]. Finally, the USW process has an excellent energy efficiency (80-90% of electrical power is delivered into the weld zone).

Ultrasonic powder consolidation (UPC), being developed in the Advanced Materials Processing Laboratory (AMPL) [17, 25, 31, 34], is a variation of USW in which application of ultrasonic vibration to powder effects consolidation of the powder into metallurgically bonded bulk materials at room and moderately elevated temperatures. The UPC process was initially investigated by Gunduz [32], who obtained fully dense Al consolidates with high ductility. Erdeniz and Ando [17] were able to consolidate Al and Ni flakes into Al-Ni composites that had full potential for exothermic reactions between Al and Ni. Gheybi Hashemabad and Ando [70] recently reported their successful fabrication of bimetal-thermite by hybrid energetic composites with full potential for self-propagating exothermic reactions (SPER). Li [34], in his fundamental study of the densification during UPC of Al and Cu powders, noted that the metallurgical bonding of powder particles cannot occur until the powder particles deform to make the powder compact densified. Despite the striking results of these previous study, little is known as to why and how such rapid powder consolidation is possible in UPC.
2.3 Effects of High Strain-rate Plastic Deformation

In ultrasonic welding (joining), high-frequency ultrasonic vibration causes high strain-rate plastic deformation in materials. Vacancy concentrations in metals undergoing deformation have been estimated by different methods [25, 26, 71] to reach a level many orders of magnitude higher than equilibrium values. Awatani et al., who conducted ultrasonic fatigue tests with aluminum and observed jogs under TEM [71], believed that vacancies were generated by the non-conservative motion of jogs on screw dislocations. Excess vacancies may annihilate at grain boundaries or edge dislocations which results in climb, while other vacancies may condense to form dislocation loops and voids, as shown in Figure 2.1. Hull discussed the formation of strain-induced vacancies following application of a critical applied stress required for dislocation movement [72] and proposed that the glide of jogged screw dislocation produces trails of point defects (vacancies), schematically shown in Figure 2.2.

Figure 2.1: TEM micrographs showing (a) large dislocation loops and (b) voids [71].
Colanto [25] performed electrical resistivity measurements to assess the vacancy concentration in aluminum undergoing ultrasonic deformation, and investigate the ultrasonically deformed aluminum wires by TEM. Figure 2.3 presents a TEM micrograph of pure aluminum wire subjected to ultrasonic vibration (frequency: 20,000 Hz, amplitude: 9 μm, duration: 1s) for 1 second at a nominal temperature of 773 K (500 °C) [25]. Numerous vacancy clusters and Frank loops about 3 to 10 nm and 20 to 30 nm in diameter, respectively, are clearly found under TEM, suggesting a very high prior concentration of excess vacancies created by high strain rate deformation during ultrasonic vibration. Excess vacancies generated during ultrasonic vibration causes an increase of resistivity, from which vacancy concentration can be assessed [25]. In Colanto’s experiments, aluminum wires with different diameters were subjected to ultrasonic vibration, and a clear increase in electrical resistivity was determined from an increased voltage during the application of ultrasonic vibration, as shown in Figure 2.4. The measured increase of electrical resistivity of aluminum during ultrasonic vibration translates into a high value of excess $X_v$ of 0.06.
Figure 2.3: TEM image of Al wire subjected to ultrasonic deformation at 773 K (500 °C) [25].

Figure 2.4: Voltage vs. time plot from electrical resistance experiments [25].
Murty utilized a nuclear magnetic resonance (NMR) method to investigate the concentration of excess vacancies introduced by the deformation during tensile tests with ultrapure polycrystalline 25-mm-thick aluminum foil, at 2.7 % strain and 0.55s⁻¹ strain rate [26]. The NMR results are plotted in Figure 2.5, together with vacancy concentration curves calculated based on Estrin-Mecking’s mechanical jog model [73] for strain rates of 0.55s⁻¹ and 10⁻⁴s⁻¹. At the strain rate of 0.55s⁻¹, the NMR data match well with the prediction of the mechanical jog model. At low temperatures, the total vacancy concentration departs from the equilibrium values significantly, increases linearly with plastic strain and reaches a high value of 10⁻⁵ at around 310 K. At high temperatures above (550 K), the total vacancy concentration determined by NMR are close to the equilibrium values, indicating that excess vacancies do not exist in significant amounts, due to the annihilation of strain-induced vacancies via diffusion to sinks. Estrin-Mecking’s model [73] was further applied for the calculation of total vacancy concentrations at strain rates of 10⁵/s, 10⁴/s and 10³/s, as presented in Figure 2.6. [27]. The model predicts that at a strain rate of 10⁵/s, possible in ultrasonic welding, the total vacancy concentration would reach a plateau value of around 10⁻¹ at 660 K (387 °C).

![Figure 2.5: Arrhenius plot of total vacancy concentration: experimental results compared with predictions based on the mechanical jog (Estrin-Mecking) model [73] (solid line at 0.55s⁻¹ and dashed line at 10⁻⁴s⁻¹) [26].](image-url)
Figure 2.6: Total vacancy concentrations calculated based on Estrin-Mecking model [73] for various strain rates. The NMR data are represented by solid diamonds [27].

Excess vacancies, introduced by high strain-rate deformation in ultrasonic vibration, may enhance diffusion [27,28], affect the thermodynamic stability of the solid that contains the excess vacancies resulting in melting point depression [28, 74] and also possibly cause dynamic softening [30].
2.3.1 Enhanced Diffusion

Enhanced diffusion has been observed in the ultrasonic welding of aluminum-zinc and aluminum-copper [27, 28]. In Gunduz et al.’s experiment [28], 50 µm thick 1100 H19 aluminum foil was ultrasonically welded to 250 µm thick 98.8 % pure zinc sheet at 517 K for 1 s. The EDS result obtained at the interfacial area of the weld showed significant inter-diffusion, as shown in Figure 2.7. The large amount of zinc diffusion into aluminum translates into a diffusivity of 1.9 µm²/s, a value five orders of magnitude higher than that of normal diffusivity at 513 K. Enhanced inter-diffusion was also noted in Hu et al.’s experiments [27] in which copper foil was ultrasonically welded to 1100 aluminum sheet for 1.25 s at nominal temperatures 298 K to 413 K (25 °C to 140 °C). Figure 2.8 shows the Cu concentration profiles in the aluminum side of the weld interface at different temperatures, which yield very high diffusivity values of $1.54 \times 10^{-13}$ to $2.22 \times 10^{-13}$ m²/s ($1.54 \times 10^{-1}$ to $2.22 \times 10^{-1}$ μm²/s). High values of excess vacancy concentration of 0.07~0.1 have been estimated in the aluminum/zinc and aluminum/copper ultrasonic welds.

Figure 2.7: EDS profile taken across the welding interface [28].
Figure 2.8: Cu concentration profile in the 1100 Al side of the diffusion couple of 1100 Al and Cu determined by EDS [27].
2.3.2 Melting Point Depression

Microscopic, electrical resistivity and NMR studies have shown that the vacancy concentration may reach high values during ultrasonic vibration [25, 26, 71]. Excess vacancies introduced by high strain-rate deformation affect the thermodynamic stability, potentially causing local melting well below the equilibrium melting temperatures. In Kreye’s TEM study [74], a continuous layer of fine grains (0.05 to 0.2 µm) along the weld interface were observed in 85 to 90% of the welds ultrasonically joined with 99.99% Cu, Cu₂Co and 99.95% Al at room temperature. Figure 2.9 presents a TEM micrograph showing the interface of an aluminum-copper ultrasonic weld, in which the arrows point to the extremely small grains along the interface. Kreye attributed formation of these fine grains to short-time melting and rapid cooling of thin surface layer. The melting observed in Kreye’s ultrasonic welding experiments was thought to have occurred at or above equilibrium melting temperatures, instead of a depressed melting temperature due to excess vacancies. However, no evidence supports that adiabatic heating actually caused the melting to occur above the equilibrium melting temperatures during ultrasonic welding.

Gunduz et al. [28] performed ultrasonic welding experiments of zinc and aluminum at 513 K, in which no increase in temperature was monitored by the thermocouples. SEM, carried out at the weld area of the ultrasonic aluminum-zinc weld, showed a featureless region along the weld interface, indicating occurrence of local melting, as presented in Figure 2.10. A thermodynamic model that accounts for the effect of ultrasonic of vacancies on free energy predicts local melting may occur, well below the equilibrium liquidus temperature, in the presence of excess vacancies at high concentration [27, 28, 75]. Figure 2.11 shows the normalized melting point of copper
calculated as a function of vacancy mole fraction [75]. Large melting point depression is predicted as vacancy mole fraction exceeds 0.01.

Figure 2.9: A TEM micrograph of interfacial region with arrows pointing to small new grains along the interface [74].

Figure 2.10: SEM micrograph showing the morphology of the weld after etching [28].
Figure 2.11: Melting point depression of copper due to strain-induced excess vacancies while exposed to ultrasonic vibration [75]
2.3.3 Dynamic Softening

High strain-rate plastic deformation caused by ultrasonic vibration may dynamically soften the materials being deformed. Langenecker presented experimental evidence demonstrating a softening effect in a material subjected to ultrasonic irradiation in 1966 [76]. Figure 2.12 shows stress-strain curves obtained from tensile tests performed with high-purity aluminum single crystals. The dashed curves indicate the plastic behavior of aluminum under continuous ultrasonic irradiation at different power levels. The left stress-strain plots show the apparent static shear stress necessary for plastic deformation of metals is significantly reduced during the application of intense ultrasonic stress waves; the amount of reduction is directly proportional to the acoustic energy input to the specimen. Langenecker proposed that at high power levels of ultrasonic irradiation, sufficient acoustic energy is absorbed at dislocations to free them from pinned positions, resulting in annihilation of dislocations and consequently causing dynamic softening.

![Stress vs. elongation for aluminum single crystals](image)

Figure 2.12: Stress vs. elongation for aluminum single crystals; dashed curve indicate straining during ultrasonic irradiation at 20 kc/s and solid curve indicate no irradiation [76].
Colanto, in his experiments of subjecting pure Al wires to ultrasonic vibration [25], observed unusual softening, instead of strain hardening expected for high strain-rate plastic deformation. TEM of the deformed aluminum reveal dislocation networks, indicating of recovery, and a high density of voids and dislocation loops that imply existence of large amount of vacancies during the ultrasonic deformation.

A hypothesis [30] suggests that in the presence of high concentration of excess vacancies [25, 26, 71], dislocations may climb at velocities many orders of magnitude higher than the normal climb velocity, promoting rapid untangling and annihilation of dislocations, hence rapid recovery.
3 EXPERIMENTAL

Systematic UPC experiments were well performed with a copper powder to investigate the process of densification and metallurgical bonding of powder compact in UPC.

3.1 Material

The material used in the experiments was a water-atomized copper powder consisting of spherical particles, shown in Figure 3.1 The powder was provided by Fukuda Metal Foil and Powder Co. Ltd., Kyoto, Japan. The size of the powder particles ranged approximately from 1.7 µm to 9 µm, with a mean of about 5 µm. The oxygen content was 0.1-0.3 %.

Figure 3.1: SEM image of the spherical copper particles.
3.2 Ultrasonic Powder Consolidation

3.2.1 Ultrasonic Powder Consolidation Apparatus

A STAPLA condor ultrasonic welder was used to perform the ultrasonic consolidation experiments with copper powder. The whole apparatus for the ultrasonic powder consolidation experiments is presented schematically in Figure 3.2. The converter produced ultrasonic vibration, which is boosted in amplitude and transferred to the sonotrode by the oscillation system shown in Figure 3.3. The amplitude is open to be adjusted from 0 µm to 10 µm, and it was set 9 µm for all the experiments performed in the present work. The controller, connected with the converter, allows to vary the duration of vibration (consolidation time), while fixing the frequency at 20 kHz. A positioning system enables the heating plate to move in the x and y directions. By rotating the knob, the sonotrode can be moved downward to apply a clamping force to the powder via the punch. In the present work, the normal pressure was kept constant at 100 MPa for all the experiments.

![Figure 3.2: Schematic of ultrasonic powder consolidation system.](image)
Figure 3.3: Amplitude enhancement of sonotrode due to booster configuration.

The heater plate shown in Figure 3.4, with two cartridge heaters and a K-type thermocouple, is used to heat the powder and monitor the temperature. The heater plate is machined from AISI 304 stainless steel into a cuboid of dimensions 5.1 cm x 5.1 cm x 1 cm, as shown in Figure 3.3. Three holes are drilled to carry two identical cartridge heaters purchased from TUCTO and a K-type thermocouple purchased from Omega. The length and diameter of the heaters are 51 mm and 6.3 mm, respectively. The heaters are rated 500 W and are capable of heating to temperatures up to 1147 K (874 ºC). The schematic, on the right in Figure 3.4, illustrates a 3D view of the heating plate. As shown in Figure 3.5, signals from the thermocouple are transferred through a National Instruments PCI-6035E DAQ board to a computer with LabView installed. The numerical data of temperature and a profile of temperature versus time are both displayed on the LabView interface. The controller box allows to heat the powder compact under the command from LabView. Figure 3.6 shows the wiring diagram of the heaters and the control box.
Figure 3.4: Mechanical drawing of the heater plate (left) and schematic of the heating plate configured with a K-type thermocouple and two cartridge heaters (right).

Figure 3.5: Heating and temperature monitoring system.
Figure 3.6: Wiring diagram of the heater and control box [25].

Figure 3.7 shows a drawing of the punch and the die used in the UPC experiments. The punch, 4 mm in diameter and 6 mm in height, was machined from a metric alloy steel dowel pin of 4 mm in diameter and hardened to a minimum Rockwell hardness of C52. The die was made by drilling a 4.1 mm through hole in a 5 mm thick piece of cold rolled steel. The die hole was made slightly larger than the diameter of the punch to allow for the vibration to take place without interference, while minimizing powder loss through the gap between the punch and the die during ultrasonic powder consolidation.

Figure 3.8 illustrates the powder loading procedure. A piece of steel foil is first placed in the recess on the heating plate, in order to avoid contaminating the powder from the direct contact with the plate. After the die is mounted into the recess, copper powder is placed in the die hole. The punch is then inserted without hard pressing on the powder. The sonotrode is moved just above the punch by the positioning system. A plexiglass box, with tubing to connect to an argon gas cylinder, is used to keep the die/punch and powder in a flowing argon bath. Then the heating plate is turned on. Once the desired temperature is reached, the sonotrode is lowered to apply a normal pressure to powder via the punch. Ultrasonic vibration is then applied to the powder through the punch under the desired uniaxial pressure.
Figure 3.7: Drawing of the punch and the die.

Figure 3.8: Schematic of the placement of all parts during powder loading.
3.2.2 Investigated UPC Conditions

The ultrasonic powder consolidation experiments were performed under a constant pressure of 100 MPa at nominal consolidation temperatures of 300-600 °C for durations of 2-6 s. Table 3.1 summarizes the UPC processing conditions investigated.

Table 3.1: Ultrasonic Powder Consolidation Conditions

<table>
<thead>
<tr>
<th>T in °C (K)</th>
<th>Consolidation Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>300 (573)</td>
<td></td>
</tr>
<tr>
<td>350 (623)</td>
<td></td>
</tr>
<tr>
<td>400 (673)</td>
<td></td>
</tr>
<tr>
<td>450 (723)</td>
<td></td>
</tr>
<tr>
<td>500 (773)</td>
<td></td>
</tr>
<tr>
<td>550 (823)</td>
<td></td>
</tr>
<tr>
<td>600 (873)</td>
<td></td>
</tr>
</tbody>
</table>

*Punch Diameter: 4 mm, Die Diameter: 4.1 mm, Atmosphere: High-purity Argon, Pressure: 100MPa

3.3 Characterization

3.3.1 Microscopy and Energy-dispersive X-ray Fluorescence Spectroscopy (EDS)

Consolidated specimens were mounted in epoxy, and cross sections were ground and polished by standard metallographic procedure. An Olympus VANOX-T optical microscope was used for optical microscopy. The lowest and highest magnifications of the objective lens on the microscope are 5 X and 150 X. The magnification of the eyepiece is fixed at 5 X. Thus, observation was performed under magnifications ranging from 50 X to 1500 X. Micrographs were taken with an Olympus DP-12 digital camera attached to the microscope.
A JEOL-6360 scanning electron microscope was used for low-magnification SEM; while the high-magnification SEM images were taken under a Hitachi S-4800 SEM equipped with an energy-dispersive X-ray spectrometer (EDS).

3.3.2 Etching

The as-consolidated specimens were etched to reveal metallurgical features. The etchant used for optical microscopy and low-magnification SEM was a solution of 1g FeCl₃, 30 ml HCl and 100 ml ethanol. For high-magnification SEM, a solution of 1.5 g FeCl₃ in 20 ml ethanol was used to preserve the fine feature of the microstructure. The contents of the etchants are summarized in Table 3.2. The time of etching was adjusted from 5 seconds to 1 minute for the best result. The as-etched surfaces were flushed with ethanol and then dried in airflow.

<table>
<thead>
<tr>
<th>Etchants</th>
<th>Compositions</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 g FeCl₃, 30 ml HCl, 100 ml ethanol</td>
<td>Optical Microscopy and Low-magnification SEM</td>
</tr>
<tr>
<td></td>
<td>1.5 g FeCl₃, 20 ml ethanol</td>
<td>High-magnification SEM</td>
</tr>
</tbody>
</table>
3.3.3 **Hardness Test**

A SHIMADZU HMV-2T hardness tester was employed to measure the hardness of the consolidated specimens. The hardness tester permits hardness testing at nine levels of loading, 19.61 mN being the maximum. The magnifications of the eyepiece and the objective lens are, respectively, 10X and 40X. The specific setting used in the present work is given in Table 3.5. The same setting was applied to all the specimens.

<table>
<thead>
<tr>
<th>Indenter</th>
<th>Load</th>
<th>Cursor</th>
<th>Loading Time</th>
<th>Lens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vickers</td>
<td>245.2 mN</td>
<td>HV0.025</td>
<td>5 s</td>
<td>40X</td>
</tr>
</tbody>
</table>
3.3.4 Washing Test

After taking optical and SEM micrographs, the specimens were subjected to an ultrasonic washing test to investigate the bonding among the particles in the specimens. As shown in Figure 3.9, a specimen submerged in water, was subjected to ultrasonic vibration transferred via water from the transducer located at the bottom of the cleaner. Particles not bonded well were washed off from the specimen, leaving surface pores. For each specimen, the ultrasonic washing was operated in five sessions of 2 min, 3 min, 5 min, 5 min and 5 min, with a total of 20 min. The specimen was then examined under the microscope and several micrographs were taken. The micrographs were image-analyzed with ImageJ to determine % porosity after washing for 2, 5, 10, 15 and 20 min. % Porosity is defined as the areal percentage of surface pores. Likewise, % density (% surface density), calculated by 100% - % porosity, is the percentage of the surface area filled with material.

Figure 3.9: Schematic of ultrasonic washing.
4 RESULTS

4.1 Assessment of Compact Densification

The as-consolidated specimens were well-shaped discs 4 mm in diameter and around 2 mm in thickness, with a small material extruded into the gap between the die and the punch which was easy to remove. Figure 4.1 shows such a specimen consolidated at 500 °C for 4 s. Figure 4.2 shows a cross section of another specimen consolidated under the same condition where good uniform consolidation is apparent.

Figure 4.1: A specimen as-consolidated with copper at 500 °C for 4 s.

Figure 4.2: A montaged cross section image of the specimen consolidated at 500 °C for 4 s.
Figure 4.3 presents optical micrographs of the specimens consolidated at 300-500 °C for 4 s. All the specimens exhibit a high degree of densification except for the ones consolidated at 300 °C and 350 °C, in which several pores are seen. Virtually, no porosity is noted in specimens consolidated at/above 400 °C. Thus, full densification was achieved at 400 °C in 4 s.

Figure 4.4 presents high-magnification micrographs from the same specimens which were consolidated for 4 s at 300-500 °C. Dark appearing regions located at prior particle boundaries are noted in the specimens consolidated at 300 °C, 350 °C and 400 °C, however there is no such regions in the specimens consolidated at 450 °C and 500 °C. The dark inter-particle regions decreased with increasing temperature, as shown in histogram in Figure 4.5. The values of % dark region were determined from high-magnification optical micrographs of as-polished surfaces of the specimens. It is clear that % dark region sharply decreased to virtually 0 % at/above 450 °C.
Figure 4.3: Optical micrographs of as-polished specimens consolidated for 4 s at 300, 350, 400, 450 and 500 °C. Small amounts of pores are noted in the specimens consolidated at 300 and 350 °C.
Figure 4.4: High-magnification optical micrographs of as-polished specimens consolidated for 4 s at 300, 350, 400, 450 and 500 °C. Regions between prior particles appear dark in specimens consolidated at 300 - 400 °C. There is no noticeable dark inter-particle region in the specimens consolidated at 450 and 500 °C.
Figure 4.5: Change in % dark inter-particle regions with consolidation temperature for specimens consolidated for 4 s. The area of the regions decreases with the increase of temperature.
The amount of dark inter-particle regions depended on the consolidation time as well. This is seen in Figures 4.6 and 4.7 which show optical micrographs of as-polished specimens consolidated at 450 °C for 2, 3 and 4 s at low and high magnifications. Dark inter-particle regions are clearly seen in the specimens consolidated for 2 s and 3 s, but not in the specimen consolidated for 4 s. This is true for the specimens consolidated at 500 °C (presented in Figure 4.8 and 4.9) in which a small amount of dark inter-particle regions remained at 2 s of consolidation time but no dark regions were found at longer times. The inter-particle regions in the specimens consolidated for 2, 3 and 4 s were neither voids nor holes, and were actually filled as seen in Figure 4.10.

The histogram in figure 4.11 summarizes the areal percentage of the dark inter-particle regions determined with ImageJ for the specimens consolidated at 400, 450 and 500 °C for 2, 3 and 4 s. A set of high magnification optical micrographs taken on the specimens consolidated at 400-500 °C for 2-4 s are organized into the 3 × 3 matrix shown in Figure 4.12 to summarize the variation of dark regions with increasing consolidation temperature and time. From the above observations and data, we confirm:

• Dark inter-particle regions are not pores; they are part of the consolidated material.

• Dark inter-particle regions decrease with increasing consolidation temperature and time.
Figure 4.6: Optical Micrographs of as-polished specimens consolidated at 450 °C for 2 s, 3 s and 4 s.
Figure 4.7: High-magnification optical micrographs of as-polished specimens consolidated at 450 °C for 2 s, 3 s and 4 s. Dark regions appear only in the consolidations for 2 s and 3 s.
Figure 4.8: Low magnification optical micrographs of the specimens consolidated at 500 °C for 2 s, 3 s, 4 s and 6 s.
Figure 4.9: High magnification optical micrographs showing, at 500 °C, dark inter-particle regions appeared at consolidation time of 2 s. No dark regions are noted at 3 – 6 s.
Figure 4.10: Optical (left) and SEM (right) micrographs of the specimens consolidated 450 °C for 2 s, at 400 °C for 3 s and at 350 °C for 4 s. The SEM micrographs prove the dark inter-particle regions are actually filled.
Figure 4.11: Change in % dark inter-particle regions with consolidation temperature and time.
Figure 4.12: Matrix of micrographs of consolidated specimens summarizing the change of dark inter-particle regions with consolidation temperature and time.
Carefully differentiating the pores and the dark inter-particle regions, we were able to determine the % porosity on polished specimen surfaces with ImageJ. The degree of compact densification (% density) was then calculated as $100\% - \%\text{ porosity}$. Figure 4.13 shows the % density against the nominal consolidation temperature for specimens consolidated for 2, 3, 4 and 6 s together with their % dark region from Figure 4.11. We see that compact densification of the specimens consolidated for 3 s and longer times depended almost singly on temperature, whereas that of specimens consolidated for 2 s lagged behind. This is more clearly seen in Figure 4.14 where the % density is plotted against the consolidation time for specimens consolidated at 400, 450 and 500 °C. Obviously, most of the compact densification occurred within the first 3 s regardless of the consolidation temperature. We also note that densification occurred in specimens that exhibited a high value of % dark region.
Figure 4.13: Compact densification vs. consolidation temperature for specimens consolidated for 2, 3, 4 and 6 s. Also shown are the percentages of dark inter-particle regions.

Figure 4.14: Compact densification vs. consolidation time for specimens consolidated at 400, 450 and 500 °C. Also shown are the percentages of dark inter-particle regions. Densification occurred rapidly within 3 s.
4.2 Assessment of Metallurgical Bonding

The nearly full densification of the consolidated specimens attests to the achievement of particle shape change within about 3 s, but this does not necessarily mean that the particles were all bonded metallurgically. The degree to which metallurgical bonding was achieved was examined by subjecting the consolidated specimens to ultrasonic washing in water as shown in Figure 3.9, with the idea that any material that was not bonded well would come off as the specimen surface was subjected to ultrasonic washing. Figure 4.15 shows optical micrographs of specimens consolidated for 4 s at 300 °C after 2, 5, 10, 15, and 20 minutes of ultrasonic washing. Clearly, the surface porosity increased with increasing washing time, indicating insufficient bonding in the specimens.

Figure 4.16 plots the “surface density” calculated as 100% - % surface porosity for specimens consolidated at 300, 350, 400, 450 and 500 °C as a function of ultrasonic washing time, where the % surface porosity was measured on the washed specimen surface. The values at time zero are the densities of the as-consolidated specimens, whereas those at 5-20 min. are values of “surface density”. We see that the “surface density” decreased with increasing washing time for specimens consolidated at or below 400 °C, but virtually no reductions in “surface density” are noted for the specimens consolidated at 450 and 500 °C. This indicates attainment of good bonding in the latter specimens. The reductions in “surface density” leveled off after about 15 minutes, indicating that the material that remained in the specimen surface was sufficiently bonded. Thus, we may regard the “surface density” after 20 minutes as a measure of bonding.
Figure 4.15: Micrographs of the specimen consolidated at 300 °C for 4 s, before and after ultrasonic washing for 2 min, 5 min, 10 min, 15 min and 20 min.
Figure 4.16: “Surface” density vs. washing time of specimens consolidated under 100 MPa, for 4 s at 300-500 °C.

Figure 4.17 presents a set of optical micrographs from the specimens consolidated for 4 s, at 300-500 °C. Clearly, the metallurgical bonding in the consolidated specimens increased with increasing consolidation temperature, and virtually no surface porosity developed in the specimens consolidated for 4 s at 450 °C and 500 °C after 20 min of ultrasonic washing.
Figure 4.17: Micrographs of specimens consolidated for 4 s under 100 MPa at 300 - 500 °C after ultrasonic washing for 20 min.
The as-consolidated density (densification) and after-washing density (bonding) curves of specimens consolidated for 4 s are presented in Figure 4.18. The two curves show both compact densification and metallurgical bonding increased with increasing consolidation temperature. The densification curve is above the bonding curve. Thus, metallurgical bonding lagged behind compact densification, and extra time was necessarily required for bonding to catch up with compact densification. The hardness data plotted in Figure 4.19, re-confirms metallurgical bonding increased with increasing temperature, resulting in the development in hardness.
Figure 4.18: As-consolidated (in blue) and after-washing density (in red) curves of the specimens consolidated under 100 MPa, at 300-500 °C for 4 s.

Figure 4.19: Hardness of the specimens consolidation for 4 s vs. consolidation temperature.
Figure 4.20 plots the “surface density” after 20 minutes of washing against the consolidation temperature for the specimens consolidated for 2, 3, 4 and 6 s. The same data are re-plotted in Figure 4.21 to show how the “surface density” increased with increasing consolidation time for specimens consolidated at 400, 450 and 500 °C. Good bonding is seen to be achieved at/above 450 °C and when consolidation time was 4 s or longer. At 400 °C, consolidation times up to 6 s were not enough to produce good bonding. Specimens consolidated for 3 s had good bonding only when consolidated at 500 °C. By referring to the values of % dark region from Figures 4.5 and 4.11 (also shown in Figure 4.20 and Figure 4.21), it is seen that the temperature and time at which good bonding was obtained coincide with those at which % dark region reduced to virtually zero. This is verified by the micrographs in Figure 4.22, where specimens consolidated at 500 °C for 3 s, at 450 °C for 4 s and at 500 °C for 4 s, which are free of dark regions, remained intact during the 20 minutes of washing, whereas significant surface porosity developed in the specimens consolidated at lower temperatures or for shorter time, that had some dark regions. Thus, good bonding was obtained in specimens, in which dark inter-particle regions were eliminated.
Figure 4.20: Surface density against temperature for the specimens consolidated for 2 s, 3 s, 4 s and 6 s, after washing for 20 min.

Figure 4.21: Surface density against consolidation time for specimens consolidated at 400 °C, 450 °C and 500 °C, after washing for 20 min.
Figure 4.22: Matrix of optical micrographs summarizing the change in bonding as measured by ultrasonic washing tests with consolidation temperature and time. Bonding increased with decreasing % dark region.
4.3 Mechanisms of Densification and Metallurgical Bonding

The above results reveal that densification proceeded quickly in specimens that exhibited a high value of % dark region, whereas good bonding was attained only in specimens in which dark regions were eliminated. As the elimination of dark regions takes time, bonding necessarily lags behind densification.

So what really was the matter that filled the inter-particle regions and how did the bonding develop in the powder compact? To elucidate what actually happened, we first examine the SEM micrographs of as-polished specimens consolidated under four different conditions: 350 °C x 4 s, 400 °C x 3 s, 450 °C x 2 s and 500 °C x 2 s (see Figure 4.23). The specimens consolidated at 350 °C for 4 s and 400 °C for 3 s have similar values of % dark region (~13%) and hence their after-wash surface density values (degrees of bonding) are also similar (93.5 and 93.6%). The specimens consolidated at 450 °C for 2 s has a lower % dark region of 12% and consequently a higher after-wash density of 96%, and the specimen consolidated at 500 °C for 2 s has an even lower % dark region of 6% and a higher after-wash density of 98.5%. The dark regions in the specimens consolidated at 350 and 400 °C are seen to penetrate between the powder particles, keeping them unconnected with each other. However, in the specimens consolidated at 450 and 500 °C, the powder particles became progressively contiguous with each other as the % dark inter-particle regions decreased. It is this increase in contiguity that brought about the increased bonding observed in Figure 4.20 and 4.21. The observed structural change strikingly resembles that in transient liquid phase sintering, as schematically shown in Figure 4.24, but was it really a liquid phase that filled the inter-particle regions?
Figure 4.23: Bonding develops as particle contiguity increases.

Figure 4.24: Schematic of liquid phase sintering.
Energy-dispersive X-ray fluorescence (EDS) analysis was run to identify the material that filled the inter-particle regions. Figure 4.25 shows the results obtained at inter-particle and prior particle regions in a specimen consolidated at 350 °C for 4 s. Both EDS spectra show identical copper peaks although a small oxygen peak is noticed in the spectrum of the inter-particle region. Therefore, the dark inter-particle regions are filled essentially with copper. A small amount of oxygen might be trapped, probably in oxide form.

Figure 4.25: EDS analysis of the specimen consolidated at 350 °C for 4 s.
The progressive microstructural changes in the specimens are seen in Figure 4.26 that shows SEM micrographs of specimens consolidated at 400 °C for 3 s, 450 °C for 4 s, 500 °C for 3 s and 500 °C for 4 s after etching with a solution of 1.5 g FeCl\textsubscript{3} in 20 ml of ethanol. The specimen consolidated at 400 °C for 3 s exhibits a microstructure in which prior particles are well separated by the inter-particle regions. The inter-particles regions, which must be copper according to the EDS results, appear to have a very fine microstructure that is not resolved in the low-magnification SEM micrograph. High-resolution SEM for a specimen consolidated at 350 °C (Figure 4.27) revealed that the material that filled the space between particles has a ragged interface with the particles and as such might not be well bonded with the particles. Moreover, in the SEM micrograph in Figure 4.28, the inter-particle regions are seen to have a high density of nano-sized voids. This may explain why good bonding was not attained in specimens that exhibited dark inter-particle regions. The ragged interface also implies that the space between particles was not filled with stable liquid since, if it was stable liquid, it would have wetted the particle surface, forming a smoother interface with the particles.

So what was there to fill the inter-particle regions? One thing we already know is that this material should be copper that came from the parent particles during UPC. It is of interest to note that the particles in the specimens consolidated at 400 °C for 3 s (Figure 4.26) resemble pebbles on riverbeds in that both have a rounded shape. A recent mathematical model [77] predicts that rocks in rivers erode quickly by abrasion that occurs mainly at their protruding regions, losing a large amount of mass (debris) that is carried away by the water while they settle as pebbles on the riverbed. It is conceivable that the powder particles in the compact, when subjected to ultrasonic vibration, experience similar effects, i.e., the rubbing action among the particles causes debris to form and fill the interstices of the powder particles, thereby increasing compact
densification. The process of debris production in UPC, however, may differ from that of pebble formation in rivers since, in the latter, abrasion (brittle material failure) creates the debris whereas ductile failure and/or even melting may be involved in the former.

The debris-filled inter-particle regions, however, were not well bonded and appeared dark under the microscope. At higher consolidation temperatures and longer consolidation times, the dark inter-particle regions were replaced with well-defined grains as seen in Figure 4.26. These new grains are about 2-4 \( \mu \text{m} \) in the specimens consolidated at 450 °C for 4 s and 500 °C for 3 s and somewhat larger in the specimen consolidated at 500 °C for 4 s. The new grains were created by grain growth and recrystallization, which took place as the inter-particle regions were ‘consolidated’ into integral (bonded) parts of the material. At 500 °C, the ‘consolidation’ of inter-particle region into well-defined grains was completed in 4 s, as seen in Figure 4.29. Both grain coarsening and recrystallization being a thermally activated process, the progress of bonding depended on temperature and time as seen in Figures 4.20 and 4.21.

The above process is further verified in the optical micrographs in Figures 4.30 and 4.31 that show the progressive metallographic changes with consolidation temperature and time. In the specimens consolidated for 4 s at 350 °C (Figure 4.30), the dark regions are seen to fully penetrate between particles, whereas those in the specimen consolidated for 2 s at 500 °C (Figure 4.31) are isolated. With increasing temperature or time, bridges formed and grew between the particles, increasing the contiguity among particles, while the ultrasonic vibration continued to deform the material (see the specimen consolidated for 4 s at 400 °C in Figure 4.30 and the one consolidated for 3 s at 500 °C in Figure 4.31). Concurrent recrystallization and deformation are evident in the specimens consolidated for 4 s and 6 s at 500 °C.
Figure 4.26: Progressive microstructural changes in specimens consolidated at 400–500 °C, etched with a solution of 1.5 g of FeCl₃ in 20 ml of ethanol.
Figure 4.27: High-resolution SEM micrograph of the specimen consolidated at 350 °C for 4 s, after etching with a solution of 1.5g FeCl₃ and 20 ml ethanol. Inter-particle regions have ragged interface.
Figure 4.28: High-resolution SEM micrographs of the specimen consolidated at 350 °C for 4 s, etched with a solution of 1.5g FeCl₃ and 20 ml ethanol, and sputter-coated 0.3 nm thick with platinum.
Figure 4.29: High-resolution SEM micrograph of the specimen consolidated at 500 °C for 4 s, after etching with a solution of 1.5g FeCl₃ and 20 ml ethanol. Well-defined grains are seen.
Figure 4.30: Optical micrographs of the specimens consolidated at 350-500 °C for 4 s, etched with a solution 1 g FeCl₃, 30 ml HCl and 100 ml ethanol.
Figure 4.31: Optical micrographs of the specimens consolidated at 500 °C for 2-6 s, etched with a solution of 1g FeCl₃, 30 ml HCl and ethanol 100 solution.
4.4 Discussion: Nature of the debris

The debris that filled the inter-particle regions might have been molten when they were produced from the parent particles. This is implied by the thin films at PPBs in Figure 4.32 which shows high-resolution SEM micrographs of another specimen consolidated at 350 °C for 4 s. The thin films likely formed as molten films and solidified very quickly, while the imposed ultrasonic vibration caused the solidified material (debris) to accumulate in the inter-particle regions. The ragged appearance of the inter-particle material, in Figure 4.27, also attests that the particle interstices were not occupied by liquid at once. Rather, the liquid, forming in small amounts, solidified immediately as it formed, adding to the inter-particle debris, as shown in Figure 4.33.

Such a liquid might not have been a stable liquid, i.e., it might have formed as a result of strain-induced melting point depression as illustrated in Chapter 2 [28]. In another possible scenario, stable liquid could form as the friction and high strain-rate deformation at the peripheries of the powder particles heat up the material to the equilibrium melting temperature (1084 °C). However, the apparent transient behavior of the liquid cannot be explained well in the latter scenario. Further work is required to determine the nature of the melting phenomenon.
Figure 4.32: High-resolution SEM micrographs of specimens consolidated at 350 °C for 4 s, etched with a solution of 1.5 g FeCl₃ and 20 ml ethanol. The thin film formed at PPBs implies liquid formation.

Figure 4.33: High-resolution SEM micrograph of the specimen consolidated at 350 °C for 4 s, etched with a solution of 1.5 g FeCl₃ and 20 ml ethanol.
5 CONCLUSIONS

Ultrasonic powder consolidation (UPC) has been proven capable of rapidly consolidating copper powder into full-density, metallurgically bonded bulk materials at moderately elevated temperatures. The following knowledge has been gained that may help determine the mechanisms involved in ultrasonic powder consolidation.

1. Comprehensive UPC experiments with a water-atomized spherical Cu powder at 300 °C to 600 °C have shown that both compact densification and particle bonding increase with increasing consolidation temperature and time.

2. With 9 μm-amplitude, 20 kHz-ultrasonic vibration, the minimum nominal consolidation temperature required for full densification in 3 s is 400 °C and that in 2 s is 500 °C. The minimum consolidation temperature required for good metallurgical bonding (determined by ultrasonic washing tests) is 500 °C for a consolidation time of 3 s and 450 °C for a consolidation time of 4 s.

3. Compact densification occurred as the inter-particle regions are filled with ‘debris’ from the parent particles that rub against each other when subjected to the ultrasonic vibration. The inter-particle regions have been identified as copper by EDS.

4. Despite the complete filling of the inter-particle space by the debris, the inter-particle regions appear darker than the remaining parent powder particles under the optical microscope because the debris regions are not well bonded metallurgically. This has been confirmed by ultrasonic washing tests.

5. The debris-filled regions have a ragged interface with the remaining parent particles and contain nano-sized voids. The debris likely form due to melting at the rubbing particles
surface, possibly by strain-induced melting point depression, although further work is required to determine the exact nature of the debris.

6. The dark inter-particle regions decreased with increasing consolidation temperature and time as they became integral parts of the consolidated material. Metallurgical bonding is attained when the debris-filled inter-particle regions are completely transformed to well-defined grains by grain coarsening and recrystallization under imposed ultrasonic vibration. This happened at 500 °C for consolidation time of 3 s and at 450 °C for 4 s, the critical conditions for metallurgical bonding addressed in Conclusion 2 above.

7. Since the transformation of the debris-filled regions required extra time and temperature, metallurgical bonding necessarily lags behind compact densification.
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