Ultrasonic Materials Processing – with Applications to Powder Consolidation of Cu-Cr Composites and Surface Hardening of Aluminum

A Thesis Presented

By

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ABSTRACT

Ultrasonic materials process (UMP) has been found to produce unusual effects on the thermodynamic state and kinetics of structural changes in metals and alloys. This research was conducted with the objective of applying UMP to the consolidation of Cu and Cr powder mixtures into Cu-Cr composites suitable for electric contact and welding electrode applications, and also to the surface hardening of aluminum by rapid diffusion of Cu into Al and in-situ age hardening in the diffusion zone.

The process variables involved in the ultrasonic powder consolidation (UPC) study were the temperature and time of consolidation, clamping pressure, punch-die geometry and the atmosphere of consolidation. Both air and argon gas atmospheres were used. The aluminum surface hardening study involved the same variables except only air atmosphere was used.

Simultaneous consolidation of Cu-10~30wt% Cr composites on a Cu substrate with near theoretical density was achieved without using a lubricant at clamping pressures as low as 17.5 MPa and moderate temperatures ≤ 500 °C (773 K) within a very short consolidation time of a few seconds or less. Metallographic observation by optical microscopy and scanning electron microscopy (SEM) indicated near full-densification and metallurgical bonding of the Cu powder particles into a Cu matrix in which nearly undeformed particles of Cr were distributed uniformly. In the composites consolidated under optimal conditions, only a small amount (<~1%) of isolated porosity was detected at some of the Cu matrix-Cr particles interface. Full metallurgical bonding was achieved also at the interface between the composite and the Cu substrate. Energy-dispersive X-ray fluorescence spectroscopy (EDS) revealed no trace of oxygen in the Cu-Cr composites.
produced under optimal conditions, suggesting that oxygen gas was effectively purged out during UPC without leaving significant amount of oxide in the consolidates. Compacts made without ultrasonic vibration but under otherwise identical conditions had significantly lower fractional density than those processed with ultrasonic vibration. In addition, no metallurgical bonding occurred at the compact-substrate interface in the absence of ultrasonic vibration.

Rapid diffusion of Cu into Al took place when the surface of Al sheet covered with Cu foil was subjected to ultrasonic vibration parallel to the surface at temperatures as low as 160 °C (433 K). The interdiffusivity determined form EDS profiles was as high as 0.14 µm²/s at 250 °C (523 K), a value four orders of magnitude higher than the normal value of diffusivity of Cu in Al. The microhardness of the diffusion zone of the specimens measured significantly higher than that of the interior of the Al sheet where no Cu reached. The hardening peaked at a processing temperature of 160 °C (433 K), suggesting that the rapid diffusion of Cu promoted in-situ precipitation hardening. Much less hardening, due primarily to strain hardening and dynamic recovery, was noted with Al sheet processed without Cu foil.

The above results of both the Cu-Cr composite consolidation and Al surface hardening studies reflect the high concentration of lattice defects, particularly vacancies, introduced in the material by the high strain-rate deformation caused by UMP which is estimated to be of the order of 10³ s⁻¹.
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# TABLE OF CONTENTS

ABSTRACT.................................................................................................................1

ACKNOWLEDGEMENTS...............................................................................................3

TABLE OF CONTENTS..................................................................................................4

LIST OF FIGURES.........................................................................................................6

LIST OF TABLES............................................................................................................8

LIST OF EQUATIONS.....................................................................................................9

1. Introduction..................................................................................................................11

2. Literature Review.......................................................................................................12

   2.1 High Strain Rate Processing of Materials and Its Subsequent Effects..............12

   2.2 Surface Hardening of Materials.........................................................................20

   2.3 Powder Metallurgy (P/M)..................................................................................26

       2.3.1 Pressure-based Consolidation.................................................................28

       2.3.2 Sintering-based Consolidation.................................................................32

       2.3.3 Shock Wave Consolidation.......................................................................33

   2.4 Cu-Cr Composites...............................................................................................37

3. General Hardware Setup...........................................................................................40

4. Enhanced Cu Diffusion in Al and In-Situ Age Hardening during Ultrasonic
   Deformation.............................................................................................................42

   4.1 Research Objectives...........................................................................................42

   4.2 Experimental Setup and Procedure...................................................................42

   4.3 Results and Discussions....................................................................................46

5. Powder Consolidation of Cu-Cr Composites............................................................52

   5.1 Research Objectives...........................................................................................52

   5.2 Experimental Procedure.....................................................................................52
5.3 Results and Discussions..................................................................................................................58
  5.3.1 Metallurgical Results..................................................................................................................59
    5.3.1.1 Composites produced using the Small Punch.................................................................59
    5.3.1.2 Composites produced using the Big Punch........................................................................67
  5.3.2 Hardness Results.........................................................................................................................76
6. Conclusions........................................................................................................................................78
Appendix................................................................................................................................................81
7. References...........................................................................................................................................82
LIST OF FIGURES

Figure 1: Glide of a jogged screw dislocation producing trails of point defects [3] ........ 12

Figure 2: The influence of 20 kHz acoustic energy on the age hardening kinetics of a Cu-
Be alloy annealed at 573 K. Maximum acoustic stress $\sim 3.5 \times 10^8$ dyn cm$^2$
[16] ..................................................................................................... 18

Figure 3: Precipitation start times in austenitic Nb microalloyed steels at two distinct
strain rates [18]. ....................................................................................... 19

Figure 4: Al-Cu phase diagram showing the metastable GP zone, $\Theta'$ and $\Theta$ solvuses
[20]. ........................................................................................................ 21

Figure 5: Schematics of mechanisms which contribute to densification and pore
elimination [35] ..................................................................................... 29

Figure 6: A schematic of the classic hot isostatic pressing process [35] .................... 30

Figure 7: Hot powder extrusion is accomplished using canned powder and a penetrator
ram that forces the powder to densify as it is flowing through the constricting
die........................................................................................................... 31

Figure 8: Copper-chromium phase diagram [58] ..................................................... 39

Figure 9: Amplitude enhancement of sonotrode due to booster configuration ........ 41

Figure 10: Ultrasonic controller unit ..................................................................... 41

Figure 11: USW equipment laboratory setup. ......................................................... 43

Figure 12: SEM micrograph of as-received 99.8% Al sheet cross section. .............. 44

Figure 13: Schematic of the UPC experiments for rapid aluminum surface hardening. .. 45

Figure 14: Aluminum hardness at 3 µm from the surface versus temperature with 120
MPa pressure of sonotrode in 1 second of ultrasonic vibration. ........................ 50

Figure 15: Hardness vs. vibration time for aluminum specimens processed at 433 K with
and without copper foil. ........................................................................... 50

Figure 16: Hardness at 3 µm from the surface vs. pressure applied by sonotrode at 433 K
for 1 s...................................................................................................... 51

Figure 17: EDS profile of copper diffusion in aluminum at 523 K in 2 s. The arrow shows
a line along which analysis was taken....................................................... 51

Figure 18: SEM micrograph displaying precipitates at grain boundaries at 523 K....... 51
Figure 19: UPC equipment laboratory setup. ................................................................. 53
Figure 20: As-received copper powders................................................................. 56
Figure 21: As-received chromium powders......................................................... 56
Figure 22: Cumulative particle size distribution of Cr powders......................... 57
Figure 23: Schematics of die-punch geometry. ....................................................... 57
Figure 24: Side and top view of heater plate. ......................................................... 57
Figure 25: As-consolidated Cu-10 wt%Cr composites with 120 MPa pressure of sonotrode at (a) 773 K for 5 s (b) 673 K for 8 s (c) 573 K for 8 s. ............... 61
Figure 26: Effects of post UPC heat treatment (Cu-10Cr) (a) as consolidated at 573 K for 8 s, (b) heat treated at 800 K for 1 h, (c) heat treated at 800 K for 2 h, (d) heat treated at 1000 K for 1 h................................................................. 62
Figure 27: SEM micrographs of Cu-10 wt%Cr composite consolidated on substrate at 773 K for 5 s of ultrasonic vibration with 120 MPa pressure. Porosity of the composite measured to be less than 1%. a) 270 x, b) 1.08 kx, c) 3.35 kx. ..... 62
Figure 28: Cross section of Cu-10wt%Cr composite on copper substrate at 773 K with 120 MPa pressure of sonotrode with duration of 5 s at the edges. Porosity of the edges of composite measured to be 23.6%......................................................... 63
Figure 29: EDS analyses of the Cu-10 wt%Cr sample consolidated under 120 MPa pressure at 773 K for duration of 5 s of ultrasonic vibration............... 65
Figure 30: EDS analyses of the Cu-10 wt%Cr sample heat treated at 800 K for 1h, previously consolidated under 120 MPa pressure at 773 K for duration of 5 s of ultrasonic vibration. ................................................................. 65
Figure 31: EDS analyses of the Cu-10 wt%Cr sample consolidated under 120 MPa pressure at 573 K for duration of 8 s of ultrasonic vibration..................... 66
Figure 32: EDS analyses of the Cu-10 wt%Cr sample heat treated at 800K for 1h, previously consolidated under 120 MPa pressure at 573 K for duration of 8 s of ultrasonic vibration. ................................................................. 66
Figure 33: 1.1 mm Cu-10wt%Cr composite consolidated on 0.67mm copper substrate using 4 s of ultrasonic vibration and 35 MPa pressure of sonotrode at 773 K. ........................................................................................................... 68
Figure 34: 1.1 mm Cu-10wt%Cr composite consolidated on 0.67mm copper substrate using 4 s of ultrasonic vibration and 35 MPa pressure of sonotrode at 573 K. ......................................................................................................................................................................................................................68

Figure 36: Composite consolidated at 773 K by a) pure pressure without ultrasonic vibration, b) ultrasonic vibration under a 35 MPa clamping pressure for 1 s using a 6.3 mm die diameter.........................................................................................................................................................................................................................69

Figure 35: SEM micrographs of a) Cu-30wt%Cr, b) Cu-20wt%Cr, c) Cu-10wt%Cr composite consolidated on substrate at 773 K for 4 s of ultrasonic vibration with 35 MPa pressure using a Big Punch................................................................................................................................................................................69

Figure 37: Comparision of fractional density versus time between samples consolidated with or without vibration using a Big Punch......................................................................................................................................................................................................71

Figure 38: Cu-10wt%Cr composite consolidated on substrate in Ar at a) 573 K, b) 673 K, c) 773 K for 4 s under 35 MPa clamping pressure. ........................................................................................................................................................................................................73

Figure 39: Micrographs of etched Cu-10wt%Cr composites at a) ×5, b) ×10, c-d) ×100 magnifications made at 773 K using 35 MPa clamping pressure in 4 seconds in Ar atmosphere by the Big Punch..................................................................................................................................................................................................74

Figure 40: Micrograph of Cu-10wt%Cr composites made at 773 K using 17.5 MPa clamping pressure in 4 seconds in air by the Big Punch..................................................................................................................................................................................................74

Figure 41: Detached surface of Cu-10wt%Cr composite consolidated on Cu substrate at 773 K for 4 s with 35 MPa clamping pressure. ........................................................................................................................................................................................................75

Figure 42: Substrate-side fracture surface of Cu-10wt%Cr composite consolidated on Cu substrate at 773 K for 4 s with 35 MPa clamping pressure. ..................................................................................................................................................................................................75

LIST OF TABLES

Table 1: Full density variables used for copper and other alloys........................................35
Table 2: Ultrasonic materials processing parameters used for in-situ hardening project..46
Table 3: Cu-10wt%Cr composites using a punch 3.4 mm in diameter and 0.63 mm in thickness (Small Punch). .................................................................................................................................58
Table 4: Cu-10wt%Cr composites using a punch 6.3 mm in diameter and 5.04 mm in thickness (Big Punch). .................................................................................................................................................58
Table 5: EDS results of Cu-Cr samples consolidated in air and Ar using a Big punch. 73
Table 6: Hardness Cu-10wt%Cr composite consolidated at 573 K for 8 s and as-received powders. ................................................................. 77
Table 7: Hardness Cu-10wt%Cr composite consolidated at 673 K for 8 s with 120 MPa pressure using the Small Punch. .......................................................... 77
Table 8: Hardness Cu-10wt%Cr composite consolidated at 773 K for 5 s with 120 MPa pressure using the Small Punch. .......................................................... 77
Table 9: Hardness Cu-10wt%Cr composite consolidated at 773 K for 4 s with 35 MPa pressure using the Big Punch. .......................................................... 77
1. Introduction

Ultrasonic materials processing (UMP) may produce unusual microstructural changes in materials. However, no fundamental understanding of the metallurgical processes in UMP is firmly established due primarily to the complex nature of the interaction between the ultrasonic energy and the structural changes in the material being subjected to UMP. Unlike other deformation processes, UMP can induce high strain-rate deformation in a material in a few seconds without altering the macroscopic geometry of the material. High concentrations of crystalline defects, particularly of vacancies, caused by UMP may produce unusual effects on the diffusion and thermodynamic phase stability. This property makes UMP a unique means to alter material structure without applying high temperature, large macroscopic deformation or long time.

One of the industrial processes where UMP may have impact is powder metallurgy where UMP-enhanced diffusion may produce drastic effects on the process parameters. This research was motivated by the opportunity to fabricate full-density Cu-Cr composites on a Cu substrate suitable for high current-density electric contact and welding electrode applications by the simultaneous rapid powder consolidation and joining by UMP at low temperatures and pressures. In addition to the composite consolidation study, this research was motivated also by the opportunity to exploit the enhanced diffusion caused by UMP in the surface treatment of metals. Specifically, UMP was applied to aluminum sheet covered with Cu foil to study the diffusion of Cu into Al and possible in-situ precipitation hardening with the objective of exploring innovative ultrasonic surface hardening methods for aluminum.
2. Literature Review

2.1 High Strain Rate Processing of Materials and Its Subsequent Effects on Structural Changes

In theory, in the diffusion by the vacancy mechanism, the diffusion coefficient $D$ is proportional to the concentration of vacancies ($c$). If then $c$ is increased above its equilibrium value, for example if excess vacancies are created by dislocation movements during plastic deformation [1], then $D$ should be increased. The excess vacancies during low temperature deformation ($>0.4 \ T_m$) are generated by the nonconservative motion of jogs on screw dislocations [2]. Figure 1 shows the glide of a jogged screw dislocation producing trails of point defects. Seitz [1] was one of the first to illustrate that movement of dislocations generally would lead to production of vacancies, and in proposing experiments to test his theory. He suggested that the rate of diffusion of a foreign element or a radioactive tracer can be increased by continuous plastic flow.

![Slide 1](image.png)

Figure 1: Glide of a jogged screw dislocation producing trails of point defects [3].
The screw dislocation pinned by sessile jogs bends under stress until a critical stress is reached, after which the jog travels one atomic distance leaving a vacancy behind it. Therefore, the first necessary condition to produce vacancies is that the maximum energy that can be stored within a bent dislocation be larger than the vacancy formation energy. The second necessary condition requires that this critical shear stress to produce a vacancy actually be induced within a material. The third and last conditions necessary to reach these high vacancy concentrations require that there is enough time for the vacancies to move away from the jogs and diffuse into the material, otherwise large voids rather than individual vacancies would form in the wake of the moving jogs. For all three conditions above, Gunduz [3] has shown that these conditions are met for aluminum in ultrasonic materials process (UMP) at low enough temperatures.

There has been a disagreement over the past years concerning the magnitude of diffusion during low-temperature, high strain rate plastic deformation processes. Ruoff and Balluffi [4-6] reviewed the status of the whole debate in these articles. It was deduced by them that at that time there was no reliable evidence in all the enhanced diffusion results obtained by tracer-diffusion studies for any increase in the average vacancy concentration. They also criticized prior claims of observing enhanced lattice diffusion under the low strain rate conditions investigated, pointing crack short-circuiting and interface roughness effects as possible reasons for the apparent diffusivity enhancement. However, theoretical calculations by Ruoff and Balluffi indicate that in the lower portion of the high temperature region, at $T=0.5T_m$, and at sufficiently high strain-rate magnitudes ($>10^{-3} \text{ sec}^{-1}$), the average vacancy concentration within the specimen will be much larger than the equilibrium concentration.
Brown [7] proposed a simple model for the enhanced diffusion due to excess vacancies. The model concentrates on vacancy effects whether in undirectional [4] or in vibrational deformation [7]. He came up with the equation for the diffusion distance $X$:

$$X = \sqrt{D_s t} = \sqrt{\left( \alpha a^2 n_0 P \varepsilon \right)}$$  \hspace{1cm} (2.1)

where $D_s$ is diffusivity under strain, $a$ is the lattice spacing, $\alpha$ is a geometrical factor, where $\varepsilon$ is the strain, $P$ the atomic fraction of vacancies produced by unit strain, $n_0$ is the mean number of jumps a vacancy makes before being captured by defects (vacancy annihilation). Equation (2.1) is apparently independent of temperature as well as of strain rate and depends only on total strain. The huge amounts of enhanced diffusion were all refuted, supposedly, by Brown [7] in 1971 by putting numerical values in Equation (2.1).

The numerical values put by Brown are as follows:

For f.c.c. metals, if $a$ is taken as the unit cell edge, then $a^2 \sim 10^{-19}$ m$^2$ and $\alpha=1/12$. As most experiments carried out back then reached the total strain of about unity, $\varepsilon$ is replaced by value of one; Thus $P$ and $n_0$ are the only adjustable factors. Now the maximum credible value of $P$, about $10^{-3}$, was obtained from Brown’s experiments on the diffusion under stress by assuming that all the mechanical work used to deform the specimen went to form vacancies. As for $n_0$, Brown assumed the main traps of vacancies are dislocations, then $n_0=10^9$ corresponds to a dislocation density $f$ of about $10^2$ m$^{-2}$ and to a vacancy lifetime of about $10^{-1}$ s at $T=2/3T_m$ (622 K for aluminum). On the basis of quenching experiments, this is, if anything, a rather high value for $\tau$ (and consequently for $n_0$) in a well annealed metal. Thus $n_0=10^9$ but no higher, can be accepted as relevant to those experiments where the stress diffusion runs were carried out at diffusion temperatures. Higher values of dislocation density and correspondingly lower values of
$n_0$ are relevant to those experiments where the deformation took place at temperatures lower than those of normal diffusion (for instance insonation experiments) and the diffusion was observed by the growth of precipitates or by annealing. This means that at relatively low strain rates and high temperatures, high vacancy diffusivity leads to their annihilation [8].

Thus, after calculating using Equation (2.1), for well annealed metals at temperatures of normal diffusion, the maximum diffusion distance proposed by Brown is

$$\sqrt{D_a t} \sim 100 \text{ nm},$$

The maximum possible enhanced diffusion calculated by Brown seemed correct back then as the usual strain rate of the deformation processes was around one per second and the atomic fraction of vacancies calculated by electrical resistivity was around $10^{-3}$; however today ultrasonic and explosive deformation can reach up to a $10^3 \text{ s}^{-1}$ strain rate [9]. Also, NMR techniques used by Murty et al. [10] measured that the maximum vacancy concentration in Al can reach $10^{-1}$. Even if the mean number of jumps a vacancy makes before being captured by a trap decreases to $10^5$, still the maximum diffusion distance will be

$$\sqrt{D_a t} \sim 316 \text{ nm}.$$

Buffington and Cohen [11] deformed α-iron in compression during diffusion annealing and compared the self-diffusion coefficient under strain, $D_s$, with the self diffusion coefficient in unstrained α-iron, $D_u$. The authors proposed a linear relation

$$D_s/D_u - 1 = 180000 \dot{\varepsilon}$$

(2.2)

where $\dot{\varepsilon}$ is the strain rate in s$^{-1}$ and 180000 is a constant relevant to a anneal temperature of 1163 K. At their highest strain rate ($\dot{\varepsilon} = 7.5 \times 10^5 \text{ s}^{-1}$) the enhancement ($D_s/D_u$) was
about 16. These results were replaced by another set [12] not essentially different but giving enhancement of about 24 times at 1023 K.

Militzer [8] et al. modeled the effects of deformation induced vacancies on enhanced self-diffusion, non-equilibrium segregation and precipitation and compared their predictions with previous experiments performed on steels, confirming the fact that vacancy concentration increases rapidly with increasing strain rate and that significant enhancement of self diffusivity is a result of materials being deformed at high strain rates. They asserted that after deformation, the lifetime of free vacancies may extend to several hundred seconds, especially if industrial finish rolling temperatures and strain rates are employed.

Early research efforts, specifically on the effects of ultrasound in metals, were conducted by Langenecker [13]. He did several experiments in which metal specimens such as aluminum and zinc were attached directly to ultrasonic sonotrode that is allowed to vibrate at various levels of intensity. They observed “acoustic softening” for aluminum when using intensities of up to 50 Watt/Cm² at 291 K and attributed the observation to acoustically excited areas of dislocation which act as “spotsinches” in the metal.

Li et al. [14] ultrasonically bonded aluminum pad-in-chip with gold wire. In very short times, on the order of milliseconds, atoms of Au/Al bonding materials can be made to diffuse across the bond interface under the combined influence of ultrasonic and thermal energy. The thickness of the atomic inter-diffusion layer was measured as about 500 nm for an Au/Al bond. The mechanical effect mobilizes dislocations in the metal crystalline lattice and enhances atomic diffusion across the bonding interface. Their TEM images taken before and after the ultrasonic treatment showed a significant increase in
dislocation density in annealed aluminum. They also merely did the same procedure with Al/Ni to evaluate the effects of power, time, and load on the feature of bond interface and interface thickness. The Al/Ni interface reached 3 µm at 200 °C under the load of 0.76 N [15].

Recently, Gunduz et al. [9] studied the phase stability and diffusion mechanism during the ultrasonic welding of aluminum and zinc pairs at elevated temperatures. New phase diagrams of Al-Zn for different vacancy concentrations with a modified sub-regular solution model in which free energy curve of Al-Zn solutions under normal conditions were calculated with Thermo-Calc. The experiments showed evidence of melting point depression as well as enhanced diffusion which occurred due to strain induced excess vacancy formation during the ultrasonic welding of Al/Zn pairs. Since the thermocouple measurements did not exceed the eutectic temperature for the Al-Zn binary system, this phenomenon was explained by possible melting point depression caused by deformation-induced excess vacancies. The enhanced diffusion was verified by calculations made in correlation with the EDS data obtained which yielded a diffusivity five orders of magnitude higher than that of normal diffusivity at 513 K. During the high strain-rate (10^3 s^-1) deformation in ultrasonic welding, effective vacancy concentrations up to 7×10^-2 were reached. The latter value is only slightly less than the reported physically possible maximum vacancy concentration of ~ 10^-1 measured directly by NMR techniques [10]. The microstructure of the welds revealed formation of a featureless region, which penetrated the grain boundaries in the aluminum side, whereas the interface with the zinc side was flat. The results suggest that the ratio of the deformation-enhanced diffusivity to the normal diffusivity is equal to the ratio of the strain-induced vacancy concentration to
the equilibrium vacancy concentration and that the vacancy mechanism applies to the enhanced diffusion in ultrasonically deformed aluminum.

Numerous experiments have also been performed to investigate whether strain-induced precipitation takes place more rapidly than precipitation in the absence of deformation. Some of the papers are mentioned below:

Hynes and Shyne [16] presented that the precipitation hardening of beryllium-copper alloy has not changed in early minutes of insonation at 573 K. The hardness versus time for samples with and without ultrasound is shown in Figure 2.

![Figure 2](image.png)

Figure 2: The influence of 20 kHz acoustic energy on the age hardening kinetics of a Cu-Be alloy annealed at 573 K. Maximum acoustic stress ~3.5×10^8 dyn cm^-2 [16].

They suggested that the large increases in hardening claimed by earlier workers could be attributed to failure to take account of sonic heating. The small increase in hardness which they did find was entirely caused by acoustic enhancement of grain boundary precipitation. They proposed that energy in the kHz frequency range (which was
universally used in all previous experiments) cannot be absorbed by, or produce to-and-fro motion of, dislocations. It can, however, be absorbed at grain boundaries.

Sun et al. [17] showed that both dislocations and grain-boundaries act as nucleation sites for strain-induced MnS precipitates in electrical steels. The experimental data were analyzed using classical nucleation theory. As the temperature is decreased, however, nucleation on dislocations becomes more important. Such a transition is usually attributed to a corresponding increase in dislocation density, which then provides more nucleation sites in the grain interiors. In addition, the higher nucleation and growth rates of intermetallics lead in turn to a decrease in the precipitation start time [17]. The effect is also supported by start time measurements of niobium borocarbonitride precipitation in microalloyed steels [18]. Figure 3 shows precipitation start time versus temperature in austenitic Nb microalloyed steels at different strain rates.

![Figure 3: Precipitation start times in austenitic Nb microalloyed steels at two distinct strain rates [18].](image)
2.2 Surface Hardening of Materials

Aluminum and its alloys are attractive for many applications in industry because of low density, high electrical and thermal conductivities and good formability. However, their hardness, wear resistance and other mechanical properties are poor in comparison to those of steels. Continuous research is made into new possibilities for making use of the advantages of the aluminum in applications that were reserved up to now for harder and more wear-resistant materials.

It is generally known that many properties of materials such as aluminum and steel depend on their surface characteristics. This applies not merely to physical properties but also and particularly to technological characteristics such as friction, abrasion, or wear properties, which often decide the reliability and service life of components and tools. Nearly all industrial applications today demand for optimum bulk mechanical and physical properties of materials. The requirements on the surface therefore often differ from those of the interior of a material. The treatments that are conventionally used to enhance surface properties are classified as diffusional, thermal, and coating or plating. Examples of diffusional treatments include carburizing, nitriding, and carbonotriding (case hardening methods). Example of thermal and applied energy treatments include flame hardening, laser hardening, shot peening and induction hardening. Coating or plating processes include hard chromium plating and electroless nickel plating, as well as various other hardfacing methods [19].

The traditional method to hardene Al and some of its alloys is solution heat treating the alloy followed by quenching to room temperature. After quenching of the alloy, aging at specific temperatures will result in the formation of precipitates. In alloys based on the Al-Cu system, the hardening observed at room temperature is attributed to localized
concentration of copper atoms forming clusters and Guinier-Preston zones designated GP zones. As aging temperature increases, clusters of GP zones are replaced by $\Theta''$, $\Theta'$ and $\Theta$ (Figure 4).

![Figure 4: Al-Cu phase diagram showing the metastable GP zone, $\Theta''$ and $\Theta'$ solvuses](image)

Maximum strength and hardness occur when the amount of $\Theta''$ is essentially at a maximum. However, this conventional water-quenching followed by secondary machining and straightening of the part in the precipitation-hardened condition, causes large residual stresses and reduced fatigue life, not to mention the huge amount of time needed to complete the aging process [21].

Case hardening or surface hardening is the process of hardening the surface of a metal, often a low carbon steel, by infusing elements into the material's surface, forming
a layer of a harder alloy. The most traditional and obsolete method to execute carburizing involves packing the low-carbon iron within a substance high in carbon, then heating this pack to encourage carbon migration into the surface of the iron. This forms a thin surface layer of higher carbon steel, with the carbon content gradually decreasing deeper from the surface. The resulting product combines much of the toughness of a low-carbon steel core, with the hardness and wear resistance of the outer high-carbon steel. Nowadays, more advanced methods such as gas, and plasama carburizing have replaced the “packing” method; as they are more adaptable to mass production and environmentally more friendly and flexible in terms of component treatment.

Nitriding shares a similar procedure with carburizing, except with nitriding process, the atmosphere at the surface is enriched with atomic nitrogen and this atomic nitrogen will combine with surface iron to form Fe₃N and/or Fe₄N which are very hard intermetallics, and once formed, require no further heat treating to achieve a higher degree of hardness. The advantages of nitriding over other forms of conventional surface hardening are that the hard surface is produced with no subsequent heat treatment operations; however distortion is present in the metal. This is the principal reason why the process is still used at present [22].

Boronizing provides high surface hardness for steel (3800 kg/mm²), however distortion and micro cracks caused from high processing temperatures is a major problem for boronized steel surfaces which consequently limit its use mostly to tool steels [22]. Also, the techniques for boronizing are inflexible and rather labor intensive making the process less cost effective than other diffusional processes [19].
Induction heating is a non-contact heating process which utilizes the principle of electromagnetic induction to produce heat inside the surface layer of a work-piece. By placing a conductive material into a strong alternating magnetic field, electrical eddy currents can be induced in the steel thereby creating heat due to the $I^2R$ losses in the material. By quenching this heated layer in water, oil or a polymer-based quench medium, the surface layer is altered to form a martensitic structure which is harder than the base metal [19].

Shot peening is a cold working process used to produce a compressive residual stress layer and modify mechanical properties of surfaces. It entails impacting a surface with shots (round metallic, glass or ceramic). The cold work produced during shot peening is not directly controlled, but is a consequence of the extensive coverage, shot size, and peening parameters. The high cold work is often a drawback because the dislocation density produced in the deformed layers accelerates thermal relaxation and develops yield strength gradients, making the surface subject to both thermal and mechanical imperfections [23].

Nearly all of the above mentioned processes to have surface-hardened materials intrinsically have drawbacks. Heating followed by quenching a lengthy process and excessive heating will coarsen the microstructure which will degrade mechanical properties. Also, quenching itself induces unwanted residual stress to the surface of metal because of thermal gradients which ultimately will provide a source for crack initiation and propagation. The relation between the thermal stress $\sigma_{th}$ during cooling and the corresponding temperature gradient in the component is given by [24]:

$$\sigma_{th} = E. \Delta T. \alpha$$  \hspace{1cm} (2.3)
where $E$ is the modulus of elasticity and $\alpha$ is the linear thermal coefficient of thermal expansion of the material. It is quite unlikely that high temperature gradients develop in good thermal conductors (e.g., Cu and Al), but is much more likely in steel and titanium.

Plating and coating treatments deposit hard surface layers of completely different chemistry, structure, and properties on steel and aluminum substrates and are applied by different technological processes. Hard chromium plating is produced by electrodeposition from a solution containing chromic acid and a catalytic anion in proper proportion. In electroless nickel coating, the coating is deposited by an autocatalytic chemical reduction of nickel ions by borohydrate compounds. Both electroless nickel coating and chromium plating are extensively used for hardening steel structure, however electrolytic nickel coating has recently been proposed for the surface hardening of aluminum alloys [25]. Surface hardening by coating or surface modification especially by electroless nickel coating and chromium plating usually lacks sufficient quality, adhesion and uniformity of layers. Environmental problems are also associated with most plating processes especially chromium plating. High pressures used in laser processing causes surface cracking, cavities, blisters, and condensation of evaporated portions of the metal in the form of droplets has been observed [23]. Other disadvantages of laser surface hardening are high equipment cost, safety issues against radiation and preparation of surface with absorbents because of poor light-laser absorption [26]. The absorptivity of the laser light ranges from 2 to 5 % whereas the remainder of the energy is reflected and represents the energy loss.

Therefore, novel processes have been developed to eliminate the drawbacks of traditional hardening routines. The new solutions for surface hardening of aluminum are
listed as: laser surface alloying and laser surface hardening by induced shock waves [27], plasma vapor depositing (PVD) [28], chemical vapor depositing (CDV) [29], diamond-like hydrocarbons coatings [30], high current Fe-ion implantation [31] and plasma focus assisted carburizing [32].

The plasma vapor deposited TiN on aluminum has been investigated by Lugscheider et al. [28]. Several problems such as immediate formation of oxide top layer and long processing times are mentionable. The oxide layer showed adverse effects on the bond strength of TiN to aluminum since they form a dense, inert surface boundary which prevents diffusion processes or other interactions between coating and substrate material.

Gao et al. [31] modified aluminum surface by high current Fe-ion implantation using a metal vapor vacuum arc ion source. The major hardening phase formed by high current Fe-ion implantation into Al was of Al\textsubscript{13}Fe\textsubscript{4} intermetallic compound which increased the hardness of Al films.

Laser surface processing (melting, alloying, and deforming) has been used extensively in recent years to obtain hardened material surface, especially aluminum. In laser surface hardening, the intense laser beam strikes the metal surface which will instantly vaporize the surface layer. The rapidly expanding high temperature vapor exerts a pressure on the target surface which then propagates into the specimen as a stress wave. A laser induced stress wave produces the highest inelastic stress (in order of GPa) in the near surface region of metals especially aluminum alloys [33], similar in effect to shot peening. Shock conditions developed by high intensity laser irradiations were sufficient to produce significant strengthening and hardening. Fairand et al. [34] showed by
transmission electron microscopy that the cause of these property changes was a significant increase in dislocation density produced by the passage of the shock wave.

The laser radiation also used to induce power density up to $10^{16}$ Wm$^{-2}$ and to supply high rate heating followed by cooling. In some cases, the temperature gradient per unit time is as high as $10^6$ K.s$^{-1}$. In laser processing of steels, the high heating rates result in a shift of transformation temperatures to higher values as well as to a change of the austenitisation mechanism. In laser hardening the martensitic transformation is achieved by self-cooling, which means that after the laser light interaction the heat has to be very quickly conducted into the workpiece interior. The rates of cooling by heat conduction into the surrounding material are lower by about one order of magnitude than heating rates; so that finely grained martensite will form [23].

A new method for the hardening of aluminum surface is introduced. In the present study, using ultrasonic deformation, combination of strain hardening and solid solution strengthening will result in hardened aluminum surface.

### 2.3 Powder Metallurgy (P/M)

Powder Metallurgy (P/M) is a process of forming metal parts by heating compacted metal powders to below their melting points. Although the process has existed for more than 100 years, over the past quarter century, it has become widely recognized as a superior way of producing high-quality parts for a variety of important applications. P/M constitutes an important path 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 rechargeable batteries, bio-implanting materials, tungsten
filaments for light bulbs and various automotive parts such as transmission gear and clutch [35]. The various applications of P/M are substantiated by the large metal powder shipments in United States, which exceeded 500,000 metric tons in 2005, of which about 400,000 metric tons were specifically used for P/M use. For instance, iron powder shipments in North America have been doubled from 1980 to 2000 [35]. One of the significant advantages of P/M is its ability to control the microstructure of materials such as tool steels and super alloys, which otherwise are difficult to process and fabricate. Also, P/M is capable of developing advanced materials such as metal matrix composites (MMC) and ceramic matrix composites (CMC).

There usually exist four basic steps for any P/M process: 1- powder manufacture, 2- blending or mixing, 3- compaction, 4- sintering. The mechanism of compaction of powders followed by consolidation can be divided into three stages: transitional restacking, plastic deformation with or without fragmentation or attrition [36]. The transitional-restacking stage refers to the flow of particles past each other, rearranging themselves as determined by the forces exerted on them. This stage involves the greatest movement and, therefore, the largest increase in density. In the second stage, further densification occurs as the limiting interparticle friction forces of stage one are exceeded and the particles deform plastically to fill the voids in the powder. The final stage of compaction is attributed to plastic deformation and flow-induced work hardening. When the compaction forces exceed the breaking stress within the powder body, fragmentation and fracture of the particles occur, leading to comminution. In this stage, density increases only slightly. It must be recognized that these stages are not necessarily sequential, and, in some powders, namely ceramics and brittle metals like chromium, the
second stage is absent. In extremely soft metals, like lead, stages one and three are of little significance. [36].

A drawback in P/M is the porosities originating from the particle interstices in the powder compact. Although a high sintered density is desired in many applications, sintering to full density demands a large shrinkage, often resulting in difficulties with dimensional control. In practice, all net shape P/M parts used in mass-producing have some porosity, which limits their mechanical, electrical and thermal properties. Therefore, an important technical requirement in P/M is full-density consolidation of powders. In general, three fundamental approaches to full-density consolidation are identified: (1) pressure-based consolidation, (2) sintering-based consolidation and (3) shock wave consolidation.

### 2.3.1 Pressure-based Consolidation

In pressure-based consolidation both excess temperature and pressure are used simultaneously. This kind of consolidation takes various forms such as hot isostatic pressing (HIP), forging, extrusion, equal channel angular pressing (ECAP) and uniaxial hot pressing [35, 37]. During deformation the particle contacts have a high local stress that induces densification by plastic flow via dislocation motion, creep via dislocation climb, diffusion, and diffusional creep via lattice or grain boundary diffusion. When pressure and/or stress are applied to powders, several mechanisms contribute to densification and pore elimination, as illustrated in Figure 5.
A popular means to consolidate powders to full density is hot isostatic pressing (HIP). Unlike hot pressing and spark sintering, which apply pressure along one axis, hot isostatic pressing applies pressure from all directions simultaneously. Here the powder is sealed in a flexible, air tight, evacuated container and then subjected to a high-temperature, high pressing environment. Since the powder is totally isolated and compaction and sintering are executed simultaneously, the process is attractive for reactive and brittle materials. Powder consolidation takes place in a heated pressure vessel. High-pressure gas, such as argon or nitrogen, is mostly used to transfer heat and pressure to the consolidate [35]. The pressure and temperature variations versus time in HIP are shown schematically in Figure 6.

A fairly new HIP-like process has been patented by the name of Ceracon, CERAmic CONsolidation, in the mid 1970's to consolidate powder metals [38]. This process is a
quasi-isostatic, hot consolidation technique which utilizes a ceramic/carbonaceous particulate material as a pressure transmitting medium instead of a gas media as used in HIPing. Relatively, the Ceracon process can apply significantly higher pressures than HIPing or hot pressing. The pressure values available are less than in the explosive compaction process, but the process possesses none of the inherent constraints on size and shapes associated with explosive compaction. The amount of time any sample is subjected to consolidation is significantly shorter (1-2 minutes) compared to 1-8 hours needed for HIPing processes. The Ceracon process results in benefits equal to or better than isostatic processing while minimizing interfacial reaction and grain growth at orders of magnitude because of the reduced consolidation time.

Figure 6: A schematic of the classic hot isostatic pressing process [35].

Hot pressing and powder forging are both uniaxial hot compaction techniques but they differ in two major aspects. Hot pressing usually starts with loose powder and slow strain rates for densification. Hot forging usually starts with a sintered preform that undergoes lateral flow as it is subjected to plastic flow in a high strain rate stroke. Furthermore, hot pressing has full lateral constraint while powder forging starts without lateral constraint, causing the preform to bulge. Pressure is applied along a single axis by a ram in
unidirectional direction. Since friction exists between the object and die walls, this contributes to a variation in pressure with positions in the composite and, hence, to nonuniform densification.

Hot extrusion of a powder is another way to achieve full density composites. However, the reduction ratio (the cross sectional area of the billet divided by the cross-sectional area of product) in hot powder extrusion must sometimes exceed 10 for adequate densification. Long shapes with a constant cross-section are the main products. Both densification and shaping are achieved in one operation. A schematic drawing of hot powder extrusion is given in Figure 7. Although the intrinsic materials properties have an effect on the ease of extrusion, temperature is the main process control variable. Too high a temperature damages the microstructure and shortens the life of the extrusion tooling. Alternatively, too low a temperature makes the extrusion difficult because the powder is resistant to deformation [35].

![Diagram of hot powder extrusion](image)

Figure 7: Hot powder extrusion is accomplished using canned powder and a penetrator ram that forces the powder to densify as it is flowing through the constricting die.

Many limitations exist with conventional pressure-based consolidation methods mentioned above. Conventional extrusion requires high pressures and often imposes nonuniform deformation on the workpiece, machinery and tooling. Many of the
limitations involved with area reduction extrusion stem from the need for substantial extrusion ratios to achieve good interparticle bonding. Also, non-uniform deformation may cause inhomogenous flow and regional anisotropy in consolidated sample [39]. Several aspects of HIP process make it expensive and unattractive for high volume production. The first is the high cost of “canning”, placing the powder in a flexible isolating medium that can resist the subsequent exposure of temperature and pressure, and then later removing the product or the decanning. Still after decanning, the surface is contaminated by the container and needs to be removed after HIP by chemical dissolution, machining, or abrasion. Secondly, HIPing requires high temperatures for long times that may alter microstructural properties and outweigh the benefits of the materials produced. Long process duration also coarsen the grains of metals which is not favorable in respect to mechanical properties. These add up to the cost and makes HIP less of a net-shape industrial and practical technology. In addition, hot extrusion and HIP do not impart significant material shear strain helpful for breaking up surface oxides and contamination required for the bonding of certain powders, even when full density is achieved. HIP is also limited in its ability to achieve adequate particle-to-particle bonding, remove all void space and even accomplish full density for specific materials [39]. In the case of ECAP, inferior ductility compared to extrudants has been reported [40] for the consolidation of ultra-fine aluminum particles due to their disadvantageous microstructure texture reflecting deformation along ECAP shearing plane.

2.3.2 Sintering-based Consolidation

In sintering-based consolidation, higher density is obtained through a series of compaction followed by solid sintering or liquid phase sintering (LPS). Evidently, LPS
involves sintering under conditions where solid grains coexist with a wetting liquid. The methods used for sintering-based consolidation include roll compaction, cold isostatic pressing (CIP), cold powder extrusion, axial cold pressing, and powder forging. Also, near-full-density can be achieved by metal injection molding or liquid phase sintering; although these methods can produce up to 98% dense composites [41]. Obtaining full-density composites during subsequent sintering must depend on slow diffusional transport, which is hardly practical. In case of powder injection molding, dimensional control can be challenging as during injection, shrinkage will occur. There exist some design restrictions such as features size (must be larger than 0.1 mm) and shape of corners (must have round corners). Also, full binder removal is inevitable which in some cases can decrease mechanical properties. In case of LPS, liquid infiltration of a porous P/M composite also produces a near-full-density material. However, the presence of a liquid phase causes grain coarsening in the sintered material [35].

2.3.3 Shock Wave Consolidation

In shock wave consolidation, densification and bonding of the particles is facilitated by the passage of a strong shock wave through the powders [42]. The shock wave may be generated by detonating a shaped explosive charge placed around the powder (explosive compaction) or by the impact of a projectile, or hydrostatic shock [43]. The explosive compaction has the advantage of lower capital investment, the feasibility of producing large composites, and the possibility of designing configurations which impart little net momentum to the sample.
The resulting heating from shock waves produce partial melting as observed in metals, followed by a rapid solidification via heat conduction into the particles which may cause rapid full-density consolidation. This aspect of shock wave consolidation is of particular importance in the consolidation of rapidly solidified alloy powders since rapid cooling of interparticle melt may be sufficient to retain the unique properties of these alloys. Since no powder preheating is required in this process, the consolidated sample suffers minimal structure changes if parameters are adjusted properly. 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 and simple geometries. In addition, the impactors used in shock wave consolidation have a very short life because they operate under very high stresses [44]. The rapid release of high compressive stress generates a tensile rarefaction wave which often produces severe radial cracking in the compacted sample [45].

It should be pointed out that hydrostatic shock techniques are different from conventional isostatic pressures, plus they are cheaper and simpler to construct. However, a wide range of parameters, such as explosive charge and volumes of the chamber, working liquid/medium and powder affect the outcome of the compaction using these techniques. This restricts their usefulness as an empirical tool for investigating a range of variables, such as composite materials and shock pressures and thus makes the process undesirable to study the physics of consolidation. Consequently, hydrostatic shock techniques are commercially unattractive and find little practical and industrial application [45].

In any consolidation and joining processes, joining necessarily requires diffusional mass transport and strong interparticle bonding. This normally accompanies use of high
process temperature and pressure, which sometimes adversely affects the microstructure of consolidated material. An ideal full-density consolidation process is defined as one in which both full densification and metallurgical particle joining are achieved rapidly, simultaneously, economically and without affecting the microstructure of the as-received powders. Some of near full-density processes and the parameters used for some alloys are displayed in Table 1 to corroborate the fact that none of current full-density consolidation processes satisfies all of these needs mentioned above.

Table 1: Full density variables used for copper and other alloys.

<table>
<thead>
<tr>
<th>Material</th>
<th>Process</th>
<th>Fractional Density</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-20wt%Nb[35]</td>
<td>HIP</td>
<td>0.99</td>
<td>1073</td>
<td>310</td>
<td>1</td>
</tr>
<tr>
<td>Cu [37]</td>
<td>HIP</td>
<td>0.99</td>
<td>1223</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>Cu-20wt%W[46]</td>
<td>CIP</td>
<td>0.75</td>
<td>298</td>
<td>400</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu[47]</td>
<td>HIP</td>
<td>0.98</td>
<td>698</td>
<td>76</td>
<td>1</td>
</tr>
<tr>
<td>Cu-50wt%Cr[48]</td>
<td>LPS,CIP, annealing</td>
<td>0.95</td>
<td>873</td>
<td>600</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The extraordinary features of ultrasonic welding (USW) such as excess vacancy concentration, melting point depression and enhanced diffusion [9] can be utilized in many other processing routes especially for powder consolidation. In addition, none of the current rapid manufacturing and prototyping methods possess the favorable characteristics of ultrasonic rapid manufacturing, which include the following: low heat generation, no radiation, no electromagnetic fields, no toxic fumes, no additional
chemicals, low power consumption, composite equipment, quick, quiet, inexpensive and consistent process when adjusted to optimal settings [49]. Some of the previous studies in this field will be presented below.

Gunduz [3] proposed the ultrasonic consolidation of aluminum powders by using a simple punch and die arrangement that can consolidate powders to full density in extremely low processing parameters like time and temperature. The microstructure clearly indicated that ultrasonic vibrations were extremely effective in particle rearrangement and gas removal. The reasonable ductility of the consolidates, tested by manual bend, indicated that surface oxides were effectively removed allowing for fresh metallic contact during ultrasonic consolidation.

Also, Gulsoy [50] investigated the effect of ultrasonic powder consolidation technique on consolidation of ignitable nickel and aluminum powders and nanoflakes. Systematic experiments were performed to optimize processing parameters to produce fully dense aluminum and nickel powder and nanoflakes consolidates. Ultrasonic vibrations successfully broke up the surface oxide films of aluminum particles, thus enhancing metallic contact and forming metallurgical bonding between the aluminum particles. The fracture micrographs demonstrated that no metallurgical bonding was established between aluminum and nickel powders. However, good contact between aluminum and nickel particles was revealed in the microstructures of as-consolidated samples. Consequently, fully dense powder composites and nanoflakes consolidates were fabricated using the ultrasonic technique.
2.4 Cu-Cr Composites

High electrical-conductive and strength materials are expected to be applied to the strong field magnets, lead-frame, trolley wire, electric contact, welding electrodes, furnace parts, cylinder heads and electrical switchgear [9, 51]. Copper is used in these applications for its high electrical conductivity as it has the highest electrical conductivity of any base metal, being exceeded in this respect only by silver. Also, copper is being utilized on account of its high thermal conductivity, good corrosion resistance and mechanical workability. Occasionally, when slightly greater conductivity or ductility is required, oxygen-free high-conductivity copper may be used. The special grades of copper such as phosphorus dioxidized copper or arsenical coppers are not commonly used for conductors, since they have inferior conductivity [52].

As monolithic Cu does not fulfill mechanical requirements needed in most applications, many types of new Cu alloys were developed to satisfy these needs. Improvement in the strength of Cu can be achieved by forming either a solid solution or a fine dispersion of a second phase in the matrix or by fiber reinforcement. Among the several Cu-X composites that have been studied [53-54], Cu-Cr composites have a desirable combination of attributes, in that they offer low cost (the cost of Cr is roughly one-tenth of Nb) and the low solubility of Cr in Cu matrix, and exhibit a high elastic modulus. Cu-Cr composites provide a solution to mechanical properties concerns by the introduction of a stiffer reinforcement phase which bears a significant proportion of the applied stress. One of the advantages of using Cu-Cr composites is that the second phase can contribute to the conductivity, unlike traditional ceramic reinforcements. In order to maximize electrical conductivity in a copper-X (in this case chromium) composite
material, a microstructure with continuous three-dimensional copper matrix and homogenous fine dispersed reinforcement particles must be formed during processing [55]. It has been established that bcc metals are particularly suited for reinforcing an fcc metal matrix, because when subjected to high degrees of deformation, they elongate preferentially, resulting in a fine ribbon-like morphology [56].

According to the phase diagram of Cr and Cu (Figure 8), the two elements cannot react with each other to form compounds. They also have little mutual solubility. The miscibility gap in the liquid state of this alloy was confirmed using thermal and metallographic work [57]. The immiscible nature of the two elements makes the liquid of this binary system unstable below the liquidus temperature. Thus, Cu-Cr alloys are not well suited for conventional solidification processing where liquid tends to phase-separate during solidification, causing undesirable chemical segregation. The Cu-Cr phase diagram is a simple eutectic system with minimal change in solid solubility of chromium in copper as the temperature decreases. The solid solubility of Cr in Cu is well established now as 0.7 wt% at the eutectic temperature. Alloys containing 0.2 to 0.6 wt% Cr show age hardening upon quenching from 1323 K and reheating in the range of 673 to 873 K. Commercially important alloys contain about 1% Cr. Solidification starts with the formation of α and the composition of the liquid moves down the liquidus line to the eutectic. At 1343 K the eutectic mixture of α and Cr is formed and this is seen in the microstructure as a typical lamellar structure. Slow cooling from this temperature will allow precipitation of chromium in the solid solution, but this is not done in practice because much superior mechanical properties can be obtained by quenching to retain the chromium in the supersaturated solid solution and then ageing to allow a very fine
dispersion of chromium particles to form throughout the matrix. The great advantages of this alloy in the fully heat-treated condition are high conductivity and retention of good mechanical strength continuously at temperatures up to approximately 673 K and, for short times, much higher strength will be sustained.

![Copper-chromium phase diagram](image)

Figure 8: Copper-chromium phase diagram [58].

Lots of properties and characteristics such as interface and ageing characteristics, thermo-mechanical and corrosion behaviors and resistivity of Cu-Cr composites have been examined in literature [48, 59-62]. However, composite fabrication methods used were conventional powder metallurgy techniques which have several flaws that prevent their expansion to manufacturing products. In addition, nowadays both the mostly used manufacturing techniques, namely traditional powder metallurgy and metal infiltration are unsuccessful in obtaining the requested microstructure suited in conduction
applications [63]. Even high quality casting of Cu-Cr alloys is inefficient as Cr tends to segregate under gravity, leading to large anisotropic precipitates with thin copper layers and to substantial decrease in conductivity [48]. Therefore, novel industrialized fabrication method for Cu-Cr composite should be introduced.

3. General Hardware Setup:

The CONDOR ultrasonic welding unit manufactured by STAPLA® Ultrasonics Corp. has a maximum power of 3.5 kW, operating at a frequency of 20 kHz. The peak-to-peak vibration amplitude can be adjusted between 7.5 to 18 µm giving a total displacement of 15 to 36 µm. The controller unit supplies high frequency signals that are fed into the converter unit consisting of a stack of piezoelectric crystals. The resulting vibrations are transmitted to the ultrasonic sonotrode, also known as the horn, through the booster unit and their amplitude can be amplified at a 2:1 ratio during the transmission (Figure 9). Using feedback, the controller unit adjusts the output power to produce steady amplitude. The clamping load was measured using a load cell stage which was mounted on the anvil at four mounting points at the center of the anvil. The load reading was calibrated using known dead weights. The clamping load is manually adjusted using a linear Z-axis vertical stage. The welding parameters are adjusted using the appropriate buttons and knobs on the controller unit shown in Figure 10. The parameters that can be altered using a controller unit are load, time and amplitude.
Figure 9: Amplitude enhancement of sonotrode due to booster configuration

Figure 10: Ultrasonic controller unit.
4. Enhanced Copper Diffusion in Aluminum and In-situ Age Hardening during Ultrasonic Deformation

4.1 Research Objectives

This research was conducted to investigate the enhanced diffusion in aluminum being subjected to ultrasonic deformation. Of particular interest was to examine the possibility for surface hardening of aluminum surface by the diffusion of copper from externally placed copper foil into the aluminum surface and possible in-situ age hardening in the diffusion zone. The above was thought to be possible as ultrasonic deformation would produce a high concentration of excess vacancies in the aluminum, thereby increasing the diffusivity by many orders of magnitude [9]. To envision a low-cost continuous commercial production, copper foil was chosen as the external reservoir of copper which would be rubbed against the surface of aluminum sheet by UMP to facilitate metal to metal contact and rapid copper diffusion into the aluminum surface. After Ump, copper foil would come off the aluminum surface allowing for reuse in the continuous UMP.

4.2 Experimental Setup and Procedure

The Ultrasonic Welding unit setup used in this part of study is shown in Figure 11 showing the components and the positioning system.
The materials used were 1 mm thick 99.8% aluminum sheet and 10 µm thick 99.8% pure copper foil obtained from Alfa Aesar\textsuperscript{®} and Fukuda Metal Foil and Powder Co. LTD., respectively. The foil surface condition is a critical factor in this process as thick adherent surface oxides scales, large-scale surface roughness [63] and moisture [64] are undesirable and eventually will alter the outcome of the process. Therefore, the surface contaminants and roughness on the aluminum sheets were removed by polishing, started with coarse coated abrasive discs and graduated to fine ones, followed by ultrasonic cleaning in an acetone bath. An SEM micrograph of the as-received Al sheet is shown in Figure 12.
The aluminum sheet and the copper foil were ultrasonically processed with the copper foil on top of the aluminum sheet (Figure 13) with the STAPLA Condor® [65] device at a frequency of 20 kHz and an amplitude of 9 µm for different welding durations using a high speed steel sonotrode which has two tip surfaces with dimensions 320×380 µm and 3800×3800 µm located on each side which could be utilized by rotating the sonotrode in its case. In these experiments only the tip that had the dimensions of 3800×3800 µm and a surface with a 14 by 14 matrix of knurls to provide high friction between the tip and the work pieces was used. The temperature of the samples during the ultrasonic processing was controlled using a flat plate heater that was connected to a Variac type power supply. The heater unit was placed on top of the scale to set temperature and measure clamping load simultaneously. The input power was adjusted such that the measured temperature reached the target value. A point load cell was employed beneath the sample to measure the clamping load on the specimen at the initial point of contact.

Figure 12: SEM micrograph of as-received 99.8% Al sheet cross section.
Figure 13: Schematic of the UPC experiments for rapid aluminum surface hardening.

The grinding marks on the top and bottom of aluminum sheet were parallel to each other and perpendicular to the horizontal vibration direction. UMP was carried out in air at a temperature monitored by a 100 µm wire K-type thermocouple press-fitted at the interface between copper foil and aluminum sheet. Aluminum samples were heated to different temperatures and then copper foil was put on the aluminum sample before the ultrasonic deformation. Upon contact of the sonotrode tip, the interface temperature dropped by 2 to 7 K. However, the desired temperature was restored in 2 to 5 seconds, depending on the set temperature, and remained constant during deformation according to the thermocouple reads. Ultimately, after the deformation, the sample was instantly, within 2 seconds, removed from the stage and cooled in air.

Cross sections of the processed Al sheets after removing the Cu foil, were etched with Keller reagent (1 mL HF, 1.5 mL HCl, 2.5 mL HNO₃, 95 mL H₂O) for a period of one minute and examined by optical microscopy and scanning electron microscopy (SEM) with accelerating voltage of 20 kV. Vickers microhardness measurements were performed using a Shimadzu® HMV unit. The selected loads were 0.25, 0.49, and 0.98
N, corresponding to Vickers microhardness designations of HV0.025, HV0.05 and HV0.1. A dwell time (i.e., the peak load holding) of 20 seconds was applied to all samples during microhardness tests. The spacing of adjacent indentations was set at 30 or 40 µm to avoid interference between the work-hardened regions of indentation. Also, hardness measurements were performed 3 µm from the surface of aluminum with a Knoop indentor by the force of 490.3 mN. Energy dispersive X-ray spectroscopy (EDS) was performed normal to the surface to determine the concentration profile, which was utilized to analytically determine the average diffusivity of copper in aluminum during the ultrasonic deformation.

4.3 Results and Discussion

The process parameters employed for the experimental UMP conditions were the temperature and time of ultrasonic vibration and the normal pressure under which the specimen was subjected to the ultrasonic vibration. Table 2 shows the range of the parameters that were applied to the present study.

Table 2: Ultrasonic materials processing parameters used for in-situ hardening project.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Pressure (lbf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Cu &amp; Al sheet</td>
<td>140-150-160-180-200-240</td>
<td>1</td>
<td>250</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>160</td>
<td>1-2-4-8</td>
<td>250</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>160</td>
<td>1</td>
<td>50-100-150-175-200-225-250</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>200-250</td>
<td>2</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 14 shows the micro-knoop hardness measured on the cross section 3 µm from the surface of Al sheet subjected to UMP at 140 °C – 240 °C for 1 s with and without Cu foil on top of them. For the specimens processed with Cu foil, the hardness measurements
were done after removing the Cu foil. The Cu foil was not metallurgically bonded to the Al surface and could be manually peeled off from the Al sheet. Every data point was obtained as the average of at least 5 hardness measurements. The hardness of aluminum sheet processed with copper foil maximized at 433 K to 268 HK, whereas that of the aluminum sheet without copper foil decreased monotonically with increasing temperature while staying lower than the hardness of Al sheet processed with copper foil at all temperatures treated.

Figure 15 shows the Knoop hardness of the Al sheet processed with and without Cu foil determined 3 \( \mu \)m from the contact surface as a function of vibration time. One of the specimens was processed with Cu foil only for the first 1 s, after which the Cu foil was removed and the specimen was subjected to further processing without Cu foil. It is clearly seen that the hardness of the specimen processed with Cu foil kept increasing within the range of processing time of 8 s investigated, whereas the hardness of the specimen processed with Cu foil only for the initial second followed the same pass for the first 2 s but leveled off beyond 4 s. The hardness of the specimen processed entirely without Cu foil is much lower than that of the specimens processed with Cu foil and showed only a moderate initial increase beyond 1 s and leveled off after 4 s.

Two important observations are made: the higher hardness of Al sheet with copper foil evidences diffusion of copper into the aluminum surface and the hardening (characterized by the peak at 433 K) is likely caused primarily by in-situ precipitation hardening. The monotonic decrease in hardness of the aluminum sheet processed without Cu foil is considered to occur due primarily to dynamic recovery that increased with increasing temperature.
Figure 16 shows that the hardening in the surface region increases sharply at a pressure of about 80 MPa, suggesting that good metallic contact between Al and Cu required for the transfer of Cu in the Al sheet is achieved above 80 MPa.

To further confirm such observations, EDS was performed to determine the copper concentration in the surface region of the specimen processed with Cu foil. Figure 17 shows an EDS profile of Cu concentration of an Al specimen proceed with Cu foil at 433 K for 2 s.

Using the data obtained from the data points, the effective diffusion depth, $x$, of Cu can be determined as the distance of which the copper concentration is half the surface value. Taking the surface value to be 15.3 wt% Cu, $x$ is estimated on the trendline to be 0.73 µm. The enhanced diffusivity $D$ then is given by

$$D = \frac{x^2}{t}$$

which at $t=2$ s gives a diffusivity of 0.26 µm$^2$/s, a value 4 orders of magnitude higher than the normal diffusivity of copper in aluminum at 523 K.

By assuming that the enhanced diffusion is solely due to the formation of excess vacancies, an estimate of the excess vacancy concentration in aluminum in this experiment can be obtained from [9]:

$$\frac{X^\text{excess}_V}{X^\text{equil}_V} = \frac{D_{\text{enhanced}}}{D_{\text{normal}}}$$

where $X^\text{excess}_V$ and $X^\text{equil}_V$ are the excess and equilibrium vacancy concentrations, respectively, and $D_{\text{normal}}$ is the normal lattice diffusivity. Lattice diffusion is dependent on $T$ via

$$D = D_o \exp\left(\frac{-q}{kT}\right)$$
where $Q$ is an activation enthalpy, $T$ is temperature and $R$ is gas constant. The terms that are virtually independent of temperature have been grouped into a single material constant $D_0$.

For the lattice diffusion of copper in aluminum, $D_0$ and $Q$ are $0.647 \text{ cm}^2/\text{sec}$ and $32,270 \text{ cal/mol}$, respectively [66], which yield to $3.5 \times 10^{-6} \text{ } \mu\text{m}^2/\text{sec}$ at $523 \text{ K}$. The equilibrium vacancy concentration of aluminum at $523 \text{ K}$ is estimated to be $5 \times 10^{-7}$ using Reversible Work (RW) results [67]. Also, for the aluminum case in the present study, the $X_{v}^{equi}$ value of aluminum may be given by $2.226 \exp \left(- \frac{59.82 KJ}{R.T} \right)$ which yield to $2.3 \times 10^{-6}$ [9]. Therefore the excess vacancy concentrations of aluminum, respectively, were estimated to be $0.037$ and $0.17$ according to the former and latter references, a value slightly less and higher than the reported physically possible maximum vacancy concentration of $\sim 10^{-1}$ measured directly by NMR techniques [10].

It has been reported that nucleation of precipitates often occurs at lattice defects, such as grain boundaries and dislocations [2, 68]. Thus, the generation of excess vacancies induced by high strain-rate ultrasonic deformation would enhance the diffusion of copper in aluminum, making both nucleation and growth very fast. The excess vacancies may also decrease the driving force needed for the nucleation of precipitates. The nucleation sites of precipitates were also investigated by means of SEM in the present work. As seen in Figure 18, precipitates are formed on grain boundaries at $523 \text{ K}$. Precipitates in the interior of the grains were not discernible by SEM, however fine scale strengthening precipitates (e.g., GP zones and $\Theta''$) must have formed. As age hardening, observed in this present study, would not occur without such intragranular precipitation.
Figure 14: Aluminum hardness at 3 µm from the surface versus temperature with 120 MPa pressure of sonotrode in 1 second of ultrasonic vibration.

Figure 15: Hardness vs. vibration time for aluminum specimens processed at 433 K with and without copper foil.
Figure 16: Hardness at 3 µm from the surface vs. pressure applied by sonotrode at 433 K for 1 s.

![Graph showing the relationship between Knoop Hardness (HK) and Pressure (MPa).]

\[ y = 15.323e^{-0.962x} \]

Figure 17: EDS profile of copper diffusion in aluminum at 523 K in 2 s. The arrow shows a line along which analysis was taken.

![EDS profile image showing copper concentration over distance.]

Figure 18: SEM micrograph displaying precipitates at grain boundaries at 523 K.

![SEM micrograph image with 2 µm scale.]

51
5. Powder Consolidation of Cu-Cr Composites

5.1 Research Objectives:
This research is conducted to examine the feasibility of simultaneous ultrasonic consolidation and joining of Cu-Cr composites on a copper substrate suitable for the applications to high current-density electric switches and electrodes.

For this purpose, the following objectives were defined:

- To achieve full-density consolidation of Cu-Cr composite on a Cu substrate by a ultrasonic powder consolidation (UPC) technique.
- To optimize UPC parameters for full-density consolidation and simultaneous joining of Cu-Cr composite-Cu substrate duplex materials.
- To characterize UPC consolidated Cu-Cr composite/substrate specimens and determine the process-structure relationship involved.

5.2 Experimental Setup and Procedure:
Figure 19 shows the ultrasonic welder used for the UPC experiments together with its components.
Figures 20 and 21 show SEM micrographs of the as-received copper and chromium powders provided by Fukuda Metal Foil and Powder Co., LTD. As seen in Figure 20, the Cu powder particles exhibit dendritic morphologies as they were produced by electrolytic deposition. The Cr particles shown in Figure 21 were produced by comminution and therefore have irregular morphologies. Cumulative particle size distribution of the Cr powder is shown in Figure 22.

Copper (>99%) and chromium (>99%) powders were mixed with ethanol for 30 minutes in a cylindrical container with 3.55 cm in diameter at an average rotational speed of 600 rpm. Powders were blended to the nominal compositions of Cu–10wt%Cr, Cu–20wt%Cr and Cu–30wt%Cr. The powder mixtures were then subjected to ultrasonic consolidation in air and argon atmospheres with a punch and die arrangement shown schematically in Figure 23.
The dies, which were made of a 0.8 mm thick nickel plate with a 3.8 mm die hole (Small Die) or a 2.5 mm thick nickel plate with a 6.6 mm die hole (Big Die), were tightly fitted into the die fixture (Figure 24). Punches with dimensions of 3.4 mm in diameter and 0.63 mm in thickness (Small Punch) or 6.3 mm in diameter and 5.08 mm in thickness (Big Punch) were used to consolidate powders on the die. The die was fitted to the top of the heater plate which is bolted to a weight scale to measure the normal loading. Two high-temperature 200 W cartridge heaters 5.08 cm in length and 0.63 cm in diameter obtained from McMaster-Carr® were inserted into the side of the heater plate (Figure 24) alongside a thermocouple. High-temperature ceramic insulation was provided in a box (0.2×0.2×0.06 m) and placed beneath the heater (Figure 19) to confine heat. The copper substrate situated under the die was 70 µm in thickness for the Small Punch and 675 µm for the Big Punch.

The welding tip was lowered to apply a specified normal load during heating. In order to prevent the sticking of the powders to the sonotrode, 0.025 mm thick nickel foil was placed between the punch and the powders. The powder mixture was placed in the die after the specified temperature of the heater was reached and maintained constant. Another thermocouple was used between the copper substrate and die to measure the temperature at the moment of contact. After 1-2 seconds, depending on the temperature, the temperature came back to the set value.

Cu-Cr mixtures placed in the die hole were processed ultrasonically at 573, 673 and 773 K to study the effects of temperature on resultant composite and the joining microstructure between the composite and the substrate. Ultrasonic vibration was applied parallel to the die surface at a frequency of 20 KHz with a vibration amplitude of 9 µm.
Composites were made under 1,112 N force (250 lbf) which translates to a pressure of 120 MPa using the Big Punch and 35 MPa using the Small Punch at different duration of ultrasonic vibration ranging from 0.5 to 8 s. After consolidation, the die was ejected from the stage, cooled to room temperature in air and the composite (either joined or not joined to the copper substrate) was removed from the die. As a result, composites ranging from 3.4 to 6.3 mm in diameter were produced. The samples were heat treated in air at different temperatures between 600 K and 1000 K in a LINDBERG/BLUE furnace. The samples were prepared by standard metallographic procedure and etched with a solution constituting of 1 part HNO₃ and 4 part H₂O for 30 s.

Vickers microhardness measurements were performed using a Shimadzu® HMV unit at loads of 0.25 N, 0.49 N, and 0.98 N, which corresponded to the Vickers microhardness designations of HV0.025, HV0.05 and HV0.1. A dwell time (i.e., the peak load holding) of 20 s was applied to all samples. The spacing of adjacent indentations was set at 30 µm or 40 µm to avoid interference between the work-hardened regions of adjacent indentations. The porosity of the samples was measured using the ImageJ image analysis software. The microstructural characterization of both as-consolidated and heat treated samples was done using an Olympus VANOX-T optical microscope and a Zeiss Surpa 25 SEM with accelerating voltage of 20 kV. EDS was performed to determine the chemical composition of the as-consolidated and heat treated samples.
Figure 20: As-received copper powders.

Figure 21: As-received chromium powders.
Figure 22: Cumulative particle size distribution of Cr powders.

Figure 23: Schematics of die-punch geometry.

Figure 24: Side and top view of heater plate.
5.3 Results and Discussions:

The UPC experiments were performed under the conditions shown in Tables 3 and 4. The UPC experiments performed with the Small Punch are shown in Table 3, and more with the Big Punch are shown in Table 4.

Table 3: Cu-10wt%Cr composites using a punch 3.4 mm in diameter and 0.63 mm in thickness (Small Punch).

<table>
<thead>
<tr>
<th>UPC Temperature (°C)</th>
<th>Time (s)</th>
<th>Pressure of sonotrode (MPa)</th>
<th>Heat treatment</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60-100-120</td>
<td>600 K x 1 h, 700 K x 1 h, 800 K x 1 h, 2 h</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td>300</td>
<td>1, 2, 4, 6, 8</td>
<td></td>
<td>NA</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td>400</td>
<td>1, 2, 4, 6, 8</td>
<td>60-100-120</td>
<td>N/A</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td>500</td>
<td>1, 2, 5, 8</td>
<td>60-100-120</td>
<td>800 K x 1 h</td>
<td>Cu-10wt%Cr</td>
</tr>
</tbody>
</table>

Table 4: Cu-10wt%Cr composites using a punch 6.3 mm in diameter and 5.04 mm in thickness (Big Punch).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Pressure of sonotrode (MPa)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1-2-4</td>
<td>35</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td>400</td>
<td>1-2-4</td>
<td>35</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td>500</td>
<td>0.5-1-2-4-6</td>
<td>With vibration</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Without vibration</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>4</td>
<td>35</td>
<td>Cu-20wt%Cr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu-30wt%Cr</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>4</td>
<td>17.5</td>
<td>Cu-10wt%Cr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>
5.3.1 Metallurgical Results:

5.3.1.1 Composites Produced Using a Small Punch

Figure 25 a-c shows cross sections of composites ultrasonically processed under uniaxial pressure of 120 MPa at temperatures 573, 673 and 773 K. The porosity decreases with increasing temperature of consolidation and reaches 0.99 at 773 K. The porosity in the specimen consolidated at 773 K is observed mostly at the interface of Cu/Cr; however in the specimen consolidated at lower temperatures, porosities are distributed throughout the cross section of the composites. It should also be pointed out that some of the pores can be attributed to pull-outs of chromium particles during the metallographic preparation such as grinding and polishing.

The consolidated composites were then subjected to a heat treatment in an attempt to further ‘sinter’ the composites and eliminate the porosity. Figure 26 shows Cu-10wt%Cr composites consolidated at 573 K for 8 s (a) in the as-consolidated state and (b) - (d) after a heat treatment at (800 K) for 1 and 2 h or at 1000 K for 1 h. The porosity appears to have somewhat decreased with increasing time at 800 K, but largely remained in the material. The pores in a specimen heat treated at 1000 K were even somewhat larger. This implies that the heat treatment left air-filled isolated pores. Such pores may bulge at high temperatures and could not be eliminated unless the gas is removed from the material by diffusion, which takes time.

Simultaneous ultrasonic consolidation and joining of Cu-10wt%Cr composite on copper substrate at 773 K was successful with 120 MPa pressure of sonotrode with duration of 5 s (Figure 27). The composite is densified to a fractional density of 0.99 and a composite microstructure where chromium particles are uniformly dispersed in a well
compacted copper matrix. Despite the high degree of densification seen in the composites produced at 773 K, these composites showed little ductility when subjected to manual bending with pliers. However, the interface between the copper substrate and the Cu-Cr composite is barely recognizable at higher magnifications, which means that the copper substrate and the copper matrix of the composite are fully bonded metallurgically. The original copper powder particles deformed extensively during UPC to produce the consolidated Cu matrix while the chromium powders virtually remained undeformed.

Figure 28 shows a cross section of a Cu-10wt%Cr composite produced on the copper substrate at 773 K with 120 MPa pressure of sonotrode and with a duration of 5s on edge of the sample where the sonotrode tip was not present to exert pressure. The porosity in the edge region of the composite was measured to be about 24%. In the central region of the same specimen (Figure 27), particle boundaries are absent, whereas in the edge region, most of the boundaries are still discernible. This indicates that the shear stress induced by the ultrasonic vibration was more significant at the central region and that there exists density gradients along the sonotrode width.
Figure 25: As-consolidated Cu-10 wt%Cr composites with 120 MPa pressure of sonotrode at (a) 773 K for 5 s (b) 673 K for 8 s (c) 573 K for 8 s.
Figure 26: Effects of post UPC heat treatment (Cu-10Cr) (a) as consolidated at 573 K for 8 s, (b) heat treated at 800 K for 1 h, (c) heat treated at 800 K for 2 h, (d) heat treated at 1000 K for 1 h.

Figure 27: SEM micrographs of Cu-10 wt%Cr composite consolidated on substrate at 773 K for 5 s of ultrasonic vibration with 120 MPa pressure. Porosity of the composite measured to be less than 1%. a) 270 x, b) 1.08 kx, c) 3.35 kx.
Figure 28: Cross section of Cu-10wt%Cr composite on copper substrate at 773 K with 120 MPa pressure of sonotrode with duration of 5 s at the edges. Porosity of the edges of composite measured to be 23.6%.

Figure 29 shows the EDS results of a Cu-10wt%Cr composite consolidated on a Cu substrate at 773 K for 5 s of ultrasonic vibration under a 120 MPa pressure. No presence of oxygen in the matrix is noted. This suggests that at 773 K the Cu-Cr powder particles were very quickly consolidated into a dense composite before significant oxidation could take place. However, after the sample was heat treated at 800 K for 1 h, oxygen was detected in the matrix (Figure 30), as the heat treatment was not performed in an atmosphere-controlled environment. The high shear stress exerted on the copper particles by the ultrasonic vibration is considered to break down the surface oxide and removes the broken oxide scales from the bonding region.

The EDS results of a Cu-10wt%Cr composite consolidated at 573 K for 8 s of ultrasonic vibration under 120 MPa pressure is shown in Figure 31. The presence of oxygen confirms that oxidation occurred in this composite during the consolidation. In addition, when this sample was subjected to a heat treatment in air at 800 K for one hour,
the oxygen content increased to 10.95 wt% (Figure 32) while the porosity approximately remained unchanged, indicating the presence of surface-connected pores in the composite, at least initially. Significant oxidation took place during the 8 s of ultrasonic consolidation despite the relatively low temperature of 573 K. This may be attributed to the high vacancy concentration expected during UPC which may promote mass diffusional transport of oxygen into the Cu. Such internal oxidation may be enhanced in the presence of excess vacancies and dislocations. Crude calculations, assuming the formation of CuO, suggest that up to 14.5wt% oxygen is possible if the entire volume of Cu in the composite is oxidized (refer to Appendix). Thus, the high values of oxygen content in Figures 31 and 32 are not unrealistic. Porosity remained unchanged during the heat treatment as the oxide present in the as-consolidated sample would hinder the densification. The effect of oxidation on the densification has been addressed in the literature, especially for low melting metals such as aluminum and tin at temperatures below three-quarters of their absolute melting point [69-70].
Figure 29: EDS analyses of the Cu-10 wt%Cr sample consolidated under 120 MPa pressure at 773 K for duration of 5 s of ultrasonic vibration.

Figure 30: EDS analyses of the Cu-10 wt%Cr sample heat treated at 800 K for 1h, previously consolidated under 120 MPa pressure at 773 K for duration of 5 s of ultrasonic vibration.
Figure 31: EDS analyses of the Cu-10 wt%Cr sample consolidated under 120 MPa pressure at 573 K for duration of 8 s of ultrasonic vibration.

Figure 32: EDS analyses of the Cu-10 wt%Cr sample heat treated at 800K for 1h, previously consolidated under 120 MPa pressure at 573 K for duration of 8 s of ultrasonic vibration.
5.3.1.2 Composites Produced Using a Big Punch

Figure 33 and 34 show digital pictures of 1.1 mm thick Cu-10wt%Cr composite consolidated on 0.67 mm copper substrate using 4 s of ultrasonic vibration and 35 MPa pressure of sonotrode at 573 and 773 K, respectively. Full consolidation of the Cu-Cr composite on the copper substrate identifies this technique as a net shape manufacturing process. It is also contemplated that this technique would apply to fabricate a Cu-Cr composite layer on Cu electrodes for improved erosion resistance.

Figure 35 shows cross sections of composites with different Cr content up to 30 wt%Cr consolidated on a Cu substrate at 773 K with 35 MPa normal pressures and a duration of 4 s of ultrasonic vibration. The Cr content does not seem to adversely affect the joining of copper substrate with the copper matrix of the composite nor the consolidation of the composites. All of these samples analyzed by ImageJ software showed less than three percent porosity.

To evaluate the effect of ultrasonic vibration on the consolidation and joining processes, Cu-10wt%Cr powder compacts were subjected to 35 MPa clamping pressure at 773 K for 1 s with and without vibration. Micrographs of both samples are shown in Figure 36. Both yielded a composite; however, the composite consolidated without ultrasonic vibration did not join to the copper substrate and showed a much lower fractional density (0.79) than the composite consolidated with ultrasonic vibration (0.96). In addition, the sample processed ultrasonically exhibits much smaller voids which are distributed more homogenously in the sample. It should also be mentioned that composites could not be made when powders were not subjected to vibration at 573 and 673 K while using 6.3 mm die diameter.
Figure 33: 1.1 mm Cu-10wt%Cr composite consolidated on 0.67mm copper substrate using 4 s of ultrasonic vibration and 35 MPa pressure of sonotrode at 773 K.

Figure 34: 1.1 mm Cu-10wt%Cr composite consolidated on 0.67mm copper substrate using 4 s of ultrasonic vibration and 35 MPa pressure of sonotrode at 573 K.
Figure 36: Composite consolidated at 773 K by a) pure pressure without ultrasonic vibration, b) ultrasonic vibration under a 35 MPa clamping pressure for 1 s using a 6.3 mm die diameter.

Figure 35: SEM micrographs of a) Cu-30wt%Cr, b) Cu-20wt%Cr, c) Cu-10wt%Cr composite consolidated on substrate at 773 K for 4 s of ultrasonic vibration with 35 MPa pressure using a Big Punch.
Increasing the time of vibration produced denser Cu-10wt%Cr composites at consolidation temperature of 773 K under a 35 MPa clamping pressure. All the Cu-10wt%Cr composites were metallurgically consolidated and joined to the copper substrate except for the composite consolidated in 0.5 s. Figure 37 compares the changes in fractional density with time between samples consolidated with and without vibration using the Big Punch. The fractional density of the samples consolidated with vibration reached a plateau at 4 s of vibration. No porosity gradients or localized consolidation were seen in the samples with fractional densities higher than 0.98. Also, another set of samples were simply put under pure pressure for specified amounts of time (1, 2, 4 and 6 s). The red data points show the fractional density of those samples processed without vibration. These fractional densities are significantly lower, by almost 20%, than those of the specimens consolidated with vibration and show only slight increases with increasing time, while also showing a large scatter. None of the composites that were processed just by pure pressure were joined to the copper substrate. Thus, the application of apparently ultrasonic vibration is essential for the joining between the copper substrate to the copper matrix of the composite.
Figure 37: Comparision of fractional density versus time between samples consolidated with or without vibration using a Big Punch.

To investigate the effects of atmosphere on ultrasonic composite consolidation, Cu-10wt%Cr composites were made in Ar gas at 573, 673 and 773 K under a 35 MPa clamping pressure with a vibration duration of 4 s (Figure 38). EDS results showed that samples consolidated at 573 K in Ar gas contains less oxygen than samples consolidated in air (Table 5). Neither of the Cu-10wt%Cr composites fabricated at 773 K in air and Ar atmospheres showed presence of oxygen. Figure 39 shows micrographs of polished and etched Cu-10wt%Cr composites made 773 K with the Big Punch at under a 35 MPa clamping pressure and a duration of 4 s. The high magnification micrographs in Figure 41 (c) and (d) show that joining of the copper substrate and the composite is achieved.

Cu-10wt%Cr mixtures were also subjected to 17.5 MPa and 9 MPa clamping pressures for 4 s at 773 K using the Big Punch. A composite with fractional density of 0.98 was joined to the copper substrate under a 17.5 MPa clamping pressure (Figure 40). However, 9 MPa clamping pressure was not sufficient to fabricate Cu-10wt%Cr
composites. The comparison between the fabrication parameters of UPC and Table 1 shows that UPC requires far less pressures and time than current full-density methods.

The composite-substrate specimens were fixed to a bench clamp and the substrate was bent with pliers to open a crack along the composite-substrate interface. The composites were then forced to be gripped off the substrate. The fractured surfaces were then subjected to dry air blast to remove, if present, any loosely adhering particles, debris and contaminants. Figure 41 shows the detached surface of the composite/substrate specimen consolidated at 773 K under 35 MPa pressure of sonotrode. The ductile fracture surface in the copper suggests that full metallurgical bonding of Cu powders has occurred. Figure 42 shows the substrate-side of the detached surface. The fracture micrograph of the substrate is indicative of full metallurgical joining at the interface of the composite and the substrate.
Table 5: EDS results of Cu-Cr samples consolidated in air and Ar using a Big punch.

<table>
<thead>
<tr>
<th>UPC</th>
<th>wt% Cu (at.%)</th>
<th>wt% Cr (at.%)</th>
<th>wt% O (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573 K x 4 s (Ar)</td>
<td>90.9 (86.4)</td>
<td>8.0 (9.4)</td>
<td>1.1 (4.2)</td>
</tr>
<tr>
<td>573 K x 4 s (air)</td>
<td>78.1 (69.2)</td>
<td>18.7 (20.3)</td>
<td>3.2 (11.5)</td>
</tr>
<tr>
<td>773 K x 4 s (air)</td>
<td>92.3(87.2)</td>
<td>7.7(9.0)</td>
<td>0</td>
</tr>
<tr>
<td>773 K x 4 s (Ar)</td>
<td>79.0(74.7)</td>
<td>21.0(24.6)</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 38: Cu-10wt%Cr composite consolidated on substrate in Ar at a) 573 K, b) 673 K, c) 773 K for 4 s under 35 MPa clamping pressure.
Figure 39: Micrographs of etched Cu-10wt%Cr composites at a) $\times 5$, b) $\times 10$, c-d) $\times 100$ magnifications made at 773 K using 35 MPa clamping pressure in 4 seconds in Ar atmosphere by the Big Punch.

Figure 40: Micrograph of Cu-10wt%Cr composites made at 773 K using 17.5 MPa clamping pressure in 4 seconds in air by the Big Punch.
Figure 41: Detached surface of Cu-10wt%Cr composite consolidated on Cu substrate at 773 K for 4 s with 35 MPa clamping pressure.

Figure 42: Substrate-side fracture surface of Cu-10wt%Cr composite consolidated on Cu substrate at 773 K for 4 s with 35 MPa clamping pressure.
5.3.2 Hardness Results:

Tables 6, 7 and 8 show the micro-Vickers hardness of the as-received powders and the Cu-Cr composites consolidated at 573, 673 and 773 K under the consolidation conditions shown in Table 3. The hardness values of the Cr particles range closely around 530 - 590, regardless of the process conditions. The hardness values of Cu, in the absence of oxidation, also range narrowly around 80 - 133. Somewhat increased hardness values of 115 - 161 are noted for the oxidized regions of the Cu matrix. The decrease in hardness of the Cu matrix depends on the heat treatment temperature, and is significant at 800 K and 1000 K, but is limited at 600 K (Table 7).

The hardness measurements of the Cu-10wt%Cr composites consolidated at 773 K for 4 s with 35 MPa pressure using the Big Punch are shown in Table 9. The hardness of the copper matrix remained nearly constant indicating that chromium content has no effect on the mechanical flow of the copper matrix. This is expected from the nearly zero solubility of Cr in Cu. The hardness of chromium particles could not be measured in the Cu-30wt%Cr composite, as the indentor, under the 490 mN force, moved the chromium particles in the copper matrix. This indicates that chromium particles are not firmly situated in the copper matrix in the as-consolidate state, and as such the interfacial bond strength between copper and chromium in the Cu-30wt%Cr is not as strong as in Cu-10wt%Cr and Cu-20wt%Cr composites.
Table 6: Hardness Cu-10wt%Cr composite consolidated at 573 K for 8 s and as-received powders.

<table>
<thead>
<tr>
<th>Vickers Hardness (HV 0.05) (490 mN)</th>
<th>Chromium</th>
<th>Copper</th>
<th>Gray regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powders</td>
<td>541</td>
<td>96</td>
<td>N/A</td>
</tr>
<tr>
<td>As-consolidated</td>
<td>591</td>
<td>110</td>
<td>126.5</td>
</tr>
<tr>
<td>Heat treated at 600 K for 1h</td>
<td>540</td>
<td>94</td>
<td>121</td>
</tr>
<tr>
<td>Heat treated at 800K for 1h</td>
<td>533</td>
<td>90</td>
<td>115</td>
</tr>
</tbody>
</table>

Table 7: Hardness Cu-10wt%Cr composite consolidated at 673 K for 8 s with 120 MPa pressure using the Small Punch.

<table>
<thead>
<tr>
<th>Vickers Hardness (HV 0.05) (490 mN)</th>
<th>Chromium</th>
<th>Copper</th>
<th>Gray regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-consolidated</td>
<td>573</td>
<td>119</td>
<td>125</td>
</tr>
<tr>
<td>Heat treated at 600K for 1h</td>
<td>491</td>
<td>133</td>
<td>147</td>
</tr>
<tr>
<td>Heat treated at 800K for 1h</td>
<td>533</td>
<td>95</td>
<td>132</td>
</tr>
<tr>
<td>Heat treated at 1000K for 1h</td>
<td>477</td>
<td>105</td>
<td>161</td>
</tr>
</tbody>
</table>

Table 8: Hardness Cu-10wt%Cr composite consolidated at 773 K for 5 s with 120 MPa pressure using the Small Punch.

<table>
<thead>
<tr>
<th>Vickers Hardness (HV 0.05) (490 mN)</th>
<th>Chromium</th>
<th>Copper</th>
<th>Gray regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-consolidated</td>
<td>589</td>
<td>122</td>
<td>N/A</td>
</tr>
<tr>
<td>Heat treated at 800K for 1h</td>
<td>540</td>
<td>81.5</td>
<td>111</td>
</tr>
</tbody>
</table>

Table 9: Hardness Cu-10wt%Cr composite consolidated at 773 K for 4 s with 35 MPa pressure using the Big Punch.

<table>
<thead>
<tr>
<th>Vickers Hardness (HV 0.05)</th>
<th>Chromium</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-10wt%Cr</td>
<td>512</td>
<td>106</td>
</tr>
<tr>
<td>Cu-20wt%Cr</td>
<td>497</td>
<td>107</td>
</tr>
<tr>
<td>Cu-30wt%Cr</td>
<td>N/A</td>
<td>95</td>
</tr>
</tbody>
</table>
6. Conclusions

The intrinsic effects of high strain-rate plastic deformation by ultrasonic materials processing (UMP) on diffusion were applied to the simultaneous consolidation and joining of Cu-Cr composites on a Cu substrate and surface hardening of Al sheet. The following are the major results obtained.

• Application of ultrasonic vibration to Cu-Cr powder mixture, placed in a die placed on a Cu substrate and subjected to moderate normal pressure as low as 17.5 MPa at warm temperature up to 773 K, was shown to produce a fully dense Cu-Cr composite consolidated on the Cu substrate within a few seconds or less.

• Cu-10wt.%Cr, Cu-20wt.%Cr, Cu-30wt.%Cr composites were fabricated on a Cu substrate. Such materials are potentially suitable for high-current density electrical contact and electrode applications where both high conductivity and erosion resistance are required.

• Optimal process conditions produce full metallurgical joining of the Cu-Cr composite to the Cu substrate as well as between the Cu powder particles in the Cu-Cr composite.

• Virtually no oxygen was detected in Cu-Cr composites consolidated in air at a sufficiently high temperature (773 K) where the oxygen in the powder compact was purged out during rapid densification before it oxidized the powder. Composites consolidated in air at 573 and 673 K had isolated pores with significant amounts of
oxygen, reflecting their insufficient ultrasonic densification. Use of Ar atmosphere eliminated oxidation.

- Compacts processed with no ultrasonic vibration, but under otherwise identical process conditions, never reached full density or exhibited interparticle or composite-substrate bonding.

- The ultrasonic powder consolidation (UPC) technique investigated for the consolidation of Cu-Cr composites provides an innovative route for the full-density, rapid consolidation of composites from powders.

- Subjecting the surface of Al sheet covered with Cu foil to UMP at warm temperatures up to 523 K for just a few seconds causes rapid diffusion of Cu into Al without joining the Cu foil onto the Al sheet. EDS revealed significant depths of Cu diffusion that translated into diffusivities many orders of magnitude higher than normal values. Based on the vacancy mechanism for substitutional diffusion, vacancy concentrations up to about 0.05 in mole fraction were calculated for the Al under UMP. This result is consistent with previous work on ultrasonically produced Al-Zn weldments.

- The diffusion zone of the Al sheet specimens subjected to UMP with a Cu foil overlay had significantly higher hardness than Al sheet specimens subjected to the same UMP but without Cu foil. The hardness of the diffusion zone, measured at a depth of 3 μm from the Al surface, peaked at a UMP temperature of 473 K, suggesting that the hardening is
due to in-situ precipitation of strengthening phases, which also was enhanced by the high diffusivity.

• The rapid diffusion of Cu in Al and in-situ age hardening in the diffusion zone discovered in the present research suggests that similar effects may result with other combinations of elements. This may lead to the development of innovative rapid hardening technologies of metallic surfaces.
Appendix

The high values of oxygen content in the Cu-Cr composites produced by UPC (shown in Figures 31 and 32) may need to be examined for verification. For this purpose, consider the Cu-10wt.%Cr specimen processed in air at 573 K using the Small Punch for which EDS indicated an oxygen content of 10.95%. As can be seen in Figure 26(c), the Cu matrix of this specimen appears to be severely oxidized. The oxidized part is distinguishable from the rest of the matrix because of the discoloration of this area. Image analysis showed that 81% of the matrix was oxidized. Such a high degree of oxidation occurring in such a short period of time is considered to reflect a high concentration of vacancies and dislocations induced by the UMP.

The greenish discoloration implies that the oxidized region may consist not only of oxides but also other compounds that might have formed during the wet grinding and polishing of the specimen. However, for simplicity, assume that the oxidized region is monolithic, consisting of either of cupric oxide (CuO) or cuprous oxide (Cu$_2$O). Also assume that the oxidation of Cu into cupric or cuprous oxide does not change the specific volume of the matrix. Then, the overall oxygen content, wt.%$O$, of the Cu-10wt.%Cr composite due to the formation of Cu$_x$O is calculated by:

$$\text{wt.}\%O = \frac{M_O}{M_O + xM_{Cu}} \cdot 90 \times 0.81$$

where $M_O$ and $M_{Cu}$ are the atomic mass of oxygen and copper, respectively. Thus, for $x=1$ (i.e., for CuO), %$O = 14.5$ wt.% and for $x=2$ (i.e., for Cu$_2$O), %$O = 8.1$ wt.%

Thus, the calculated values of wt.%$O$ are in reasonable agreement with the value obtained by EDS, although the EDS value may not be exact.
7- References


65. [www.staplaultrasonics.com](http://www.staplaultrasonics.com).


