Phase Evolution in Cu-Zn Powder Mixtures Subjected to Ultrasonic Powder Consolidation and Ball Milling

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ABSTRACT

Ultrasonic powder consolidation (UPC) is a novel, low-temperature, rapid powder consolidation process, capable of producing full-density materials from powders in a few seconds.

The objective of this work was to investigate the phase evolution in a Cu-Zn powder mixture subjected to UPC in comparison with that in other high-strain rate materials processing methods such as ball milling. Systematic UPC experiments were performed with a Cu-48 wt% Zn powder mixture at nominal consolidation temperatures of 25 °C to 300 °C, using 20 kHz, 9 µm-amplitude ultrasonic vibration applied to the powder compact for a duration of 1 to 4 s. Optical microscopy and X-ray diffraction revealed the formation of γ-brass at the interface of Cu and Zn powder particles in the samples consolidated at or above 200 °C. The γ-brass formation increased with increasing consolidation temperature and vibration time and approached 70 vol% in a sample consolidated at 300 °C for 4 s. No new phase formed in a reference sample made at 300 °C but with no vibration, despite the close contact between Cu and Zn achieved in the reference sample.

The γ-brass formation in the UPC samples is contrasted by the direct formation of β-brass in ball-milled composite powders of the Cu-48 wt% Zn composition. The phase selection in UPC is governed by the local state at the Cu-Zn interface. The high excess vacancies generated at the Cu-Zn interface enhance the interdiffusion at the Cu-Zn interface by many orders of magnitude, allowing the interfacial Cu and Zn concentrations to exceed the normal solubility limits before a new phase can nucleate. This, in turn,
increases the driving force for the nucleation of γ-brass at the Cu-Zn interface. The driving for β-brass nucleation does not increase as much because of the large solubility of Zn in Cu.

Adding a pre-UPC step, such as a heat treatment or ball milling for a very short time (before any new phase formation is detectable), facilities β-brass nucleation which then grows in subsequent UPC. This shows the feasibility of β-brass production from elemental powders in a two-step UPC process.
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1. INTRODUCTION

Ultrasonic welding (USW) is a joining process that uses ultrasonic vibration to join different materials at low temperatures [1, 2]. USW is applicable to metals, polymers [3, 4] and ceramics [5] and is widely used in automotive, electronics and semiconductor industries [6, 7]. Ultrasonic powder consolidation (UPC) is a modified USW in which ultrasonic vibration and simultaneous uniaxial pressure is applied to consolidate metallic powders [8-11].

It is known that ultrasonic vibration results in local, high strain rate plastic deformation in metals [12-14]. Several studies have shown that the excess vacancy concentration in metals increases drastically above the thermal equilibrium values as a result of this high strain rate plastic deformation [15-18]. This high excess vacancy concentration may affect material behavior in three ways, through the effects on diffusion [8, 19-21], thermodynamic stability [8, 19] and mechanical flow stress [22].

Al-Zn and Al-Cu sheet joining with USW have verified the occurrence of excess vacancy enhanced diffusion [8, 19]. Gunduz et al. [23] also showed the possibility of melting point depression across the Al-Zn interface subjected to USW. Another important phenomenon reported in several studies is the dynamic softening in materials subjected to ultrasonic vibration [22, 24, 25].

Despite the above mentioned observations and hypotheses, there has been a lack of fundamental understanding of the mechanisms involved in USW and UPC. The motivation of this study was to provide a better understanding of thermodynamics and
kinetics of phase transformation in copper and zinc powder mixture subjected to ultrasonic vibration by comparing it with another well-understood high strain rate deformation such as ball milling.
2. BACKGROUND AND OBJECTIVES

2.1 Powder Consolidation

2.1.1. Conventional Powder Metallurgy Techniques

One of the metal forming processes which has been around for about a century is powder metallurgy (P/M) [26]. However, it has only been in the past 35 years that this process gained popularity in mass-producing high quality metal parts. As evidence of its widespread use, 80% of the total metal powder production in the US in 2005 was for P/M processes [27]. Major advantages of P/M process such as better control over the microstructure, facilitating ceramic and metal matrix composite manufacturing, producing near net shape parts at high material yield and its cost effectiveness have contributed to this popularity [26].

Any P/M process usually involves four steps: 1) powder manufacturing, 2) powder mixing, 3) compaction and 4) sintering. During compaction and consolidation, the particles initially go through a transitional restacking stage where they are rearranged due to the external forces. Above a certain threshold, the particles start to deform plastically and fill the voids which further increases the density. Finally, when the breaking stress of the particles is reached, fragmentation occurs which increases the density but only slightly. These compaction and consolidation stages are not always sequential and their significance depends on the ductility of the material [28]. Inherent in this process is the inevitable porosity in the final part which affects its mechanical,
thermal and electrical properties and limits its applications [29]. Obviously, full-density consolidation is desired in most applications and can be achieved through the following methods: 1) pressure-based consolidation 2) sintering-based consolidation 3) shockwave consolidation

**Pressure-based consolidation**

Pressure-based consolidation methods are characterized by the simultaneous application of high temperature and pressure. Several mechanisms are involved in the densification such as plastic flow by movement of dislocations and creep [30]. One of the popular pressure-based methods is hot isostatic pressing (HIP) in which the part is sealed in a flexible container inside a vessel and high pressure and temperature are applied via a gaseous medium [31].

As opposed to HIP which applies the pressure in all directions, methods like hot pressing and hot forging apply uniaxial pressure [32]. However, hot pressing and hot forging are different from each other in terms of initial powder density, strain rate and lateral constraint. Also due to the friction with the die walls, these methods usually result in non-uniform densification [33, 34].

Another method is hot extrusion which is suitable for manufacturing parts with fixed cross-sectional profile. The ease of extrusion is mostly controlled by the temperature which should not be too high to alter the microstructure [35].

Overall, all these methods are limited in application due to issues such as microstructural changes in high temperatures, non-uniform densification, regional anisotropy and surface contamination [36].
Sintering-based consolidation

In these methods, high density is obtained through improved green compaction followed by sintering. In order to improve the green compaction, methods such as axial cold pressing (ACP), cold isostatic pressing (CIP), roll compaction (RC), powder forging (PF) and cold powder extrusion (CPE) have been used [28, 37-40]. As improved green compaction is not enough for achieving a high-density final product, sintering plays an important role in removal of remaining pores [30, 41]. Removal of isolated pores during sintering is not always practical due to the dependence on slow diffusional mass transportation. Full densification can be achieved by liquid phase sintering (LPS) in the presence of persistent or transient liquid [42, 43]. The downfall to this process is that the presence of a liquid phase cause structural changes due to the rapid diffusion in the liquid [26, 32, 42].

Shock wave consolidation

Shock wave consolidation is achieved by a shock wave passing through the powder and causing the particles to weld rapidly. The shock wave can be generated either by an accelerated mass striking the powder at high speed (cold dynamic compaction) or by the detonation of an explosive charge around the powder (explosive compaction). The high strain rate accompanied by the momentary heating as a result of the shock wave, cause local melting of the particles leading to rapid, full-density consolidation [44]. The drawback of this method is its limited applicability to simple geometries and small volumes, high cost and low production rate [45].
2.1.2. Ultrasonic Powder Consolidation (UPC)

Ultrasonic powder consolidation (UPC) is an ultrasonic welding (USW) technique that is used for mainly metallic powder consolidation [8, 9, 25]. USW is a solid-state joining process applicable to joining sheets, foils and wires, producing metallurgically bonded joints. This method uses local high-frequency vibration and simultaneous normal pressure in parts. Parts are placed on a base (anvil) and an ultrasonic probe (sonotrode) compresses them under a desired normal force, while vibrating at a desired amplitude and frequency in a direction parallel to the joint plane [46].

The fact that USW is applicable for metals, polymers and ceramics joining and has the ability to weld dissimilar materials makes it widely practical in automotive and semiconductor industries [5, 47-50]. USW is also a low cost and high energy efficient method (85-90% of energy is delivered to the weld zone) and the welding time and temperature is very low in this process, preventing damage and deformation to the joint. More importantly, no atmosphere control is required as USW is not sensitive to surface oxides [51].

USW was developed in Germany in the 1940’s and it was then used industrially in the 1950’s. The first studies on this topic were done under a US Army contract during 1955-1956 where the design of the ultrasonic welder for the welding of aluminum alloys, copper and steel joints along with the metallurgical characteristics of the joints were discussed [46]. Later in 1960’s various studies focused on the fundamentals of bonding in USW. Frederick [52] concluded that bonding occurs in ultrasonic metal welding as a result of rapid plastic deformation which breaks up the oxide layer on the metals and
creates fresh metal surfaces, and then the fresh surfaces are pushed together to atomic distances leading to the creation of metallic bonding between two surfaces. Gencsoy et al. also stated that the in copper titanium ultrasonic welding oxide layers were disrupted and diffusion occurred across the fresh weld interface [53]. Hazlett et al. conducted series of ultrasonic welding experiments to investigate the bonding mechanism and suggested that metallurgical bonds could be a result of nascent metal contact across the interface, mechanical mixing as well as grain boundary diffusion [54]. Although these studies have discussed the bonding mechanisms in USW, the current understanding is only shallow and more research has to been done to fully address the bonding mechanisms.

Ultrasonic powder consolidation (UPC), developed at the Advanced Materials Processing Laboratory (AMPL) [9, 23, 25] is a new UWS technique in which ultrasonic vibration can produce bulk and metallurgically bonded metal powder consolidates at temperatures much below the metal’s melting point and in a few seconds, which is not possible by conventional powder metallurgy techniques [8, 25]. In UPC, simultaneous application of pressure and vibration at desired temperature promotes particle packing, deformation and bonding. Short processing time, low operation temperature, low energy consumption and adaptability to a continues process are some of the advantages of UPC [8, 9, 22, 55].
2.2 Kinetics of Ultrasonic Powder Consolidation

In USW and UPC, materials subjected to high-frequency ultrasonic vibration undergo high strain rate plastic deformation. In the high strain-rate deformation of metals, the concentration of vacancies stays high [16]. Vacancy mole fractions many orders of magnitude above the thermal equilibrium value have been estimated in metals subjected to high strain rate severe plastic deformation by electron microscopy [13, 16, 56, 57], calorimetry [14], electrical resistivity measurements [14, 25], X-ray diffraction (XRD) [14] and nuclear magnetic resonance (NMR) [18]. The deformation-induced excess vacancies are generated by the non-conservative motion of jogs on screw dislocations [15, 16, 56, 58] and/or possibly by other mechanisms [15, 56, 59, 60]. According to [61], a trail of vacancies follows the movement of a jogged screw dislocation as shown in Figure 2.1. This is due to the non-conservative motion of jogs on screw dislocations in low temperature deformation ($<$ 0.4 $T_m$) [62].

There are three conditions necessary to create a vacancy in this manner. First, the above mentioned critical stress must be applied within the material. Second, the energy of the formation of a vacancy must be less than the maximum energy that can be stored in a bent dislocation. The last condition requires that the created vacancies have enough time to diffuse away and in to the material to reduce the chance of void formation instead of individual vacancies [61, 63]. Aluminum has been shown to satisfy these conditions in a low temperature ultrasonic materials processing (UMP) [8, 64, 65].
The vacancy concentration may reach a high value even at lower strain rates as well, if temperature is sufficiently low. A NMR study by Murty, et al. [18] has shown that the mole fraction of vacancies ($X_V$) in pure aluminum deforming under tension at a strain rate of 0.55 s$^{-1}$ rises above the thermal equilibrium value below about 570 K and reaches a high plateau value of about 0.1 below about 310 K as shown in Figure 2.2.

Figure 2.1: Generation of vacancies by climb of jogs on screw dislocations [61].

Figure 2.2: Excess vacancy concentrations at various strain rates calculated with the model presented in [18]. The solid diamonds are NMR data.
The temperature at which $X_V$ hits the plateau value increases with increasing strain rate. At a strain rate of $10^5$ s$^{-1}$, typical of ultrasonic joining [66, 67], the model presented in [18] predicts $X_V = 0.1$ below about 660 K.

Furthermore, in a another study by Colanto [25], aluminum wires subjected to ultrasonic vibration, showed an increase in voltage which indicates an increase in electrical resistivity during the application of ultrasonic vibration, which translates into a high value of excess vacancies ($X_V = 0.06$), shown in Figure 2.3. TEM micrograph of the same aluminum sample (Figure 2.4) reveals numerous vacancy clusters and Frank loops which further verifies the presence of high excess vacancies in this sample.

![Figure 2.3: Voltage-time plot for Al wires subjected to ultrasonic vibration [25].](image)
Such a high value of vacancy concentration translates into diffusivity values that are several orders of magnitude over the normal values, giving rise to measurable diffusion distances in ultrasonically joined materials [8, 19, 22], even during such short times.

Since the diffusion coefficient is proportional to vacancy concentration, an increased diffusivity is expected [62]. This enhanced diffusion rate was demonstrated for a foreign element during continuous plastic flow by Seitz where vacancies were created by movement of dislocations [62]. In spite of the increased diffusivity, its magnitude has been a topic of disagreement in low temperature, high strain rate plastic deformation processes [20, 21, 68]. According to Ruoff and Ballufi, tracer diffusion studies provided no reliable correlation between enhanced diffusivity and the increased average vacancy
concentration. They also reported that enhanced apparent diffusivity is probably due to crack short circuiting and interface roughness effects, dismissing the claims role of enhanced lattice diffusion. Nevertheless, their theoretical calculations indicate a much larger than equilibrium vacancy concentration at $T = 0.5 T_m$ and sufficiently high strain rates ($>10^{-3} \text{ sec}^{-1}$) [68].

Despite the body of work strongly suggesting an excess vacancy concentration in metals undergoing high strain rate plastic deformation and its role in enhanced diffusivity, there existed little to no experimental data that clearly showed this. Specifically, high strain rate can cause an increase in temperature, and the effects of this rise on diffusivity needed to be separated from the effect of excess vacancies on diffusivity [20].

Hu et al. [19] experimentally determined the interface temperature during the ultrasonic joining of aluminum and copper, the data showed an increase in the interface temperature above nominal joining temperature, Figure 2.5
Figure 2.5: Interface temperature and increase in interface temperature above nominal joining temperature estimated for ultrasonic joining of Al and Cu [19].

The high diffusivity caused by excess vacancies play an important role in the metallurgical bond formation in kinetic joining processes. That can be summarized as below:

**Effects on diffusion and flow stress:** Formation of metallurgical bond requires that the mating metal surfaces be fresh with no oxides or contamination and in atomic-scale proximity and that the atoms at the mating surfaces have sufficient mobility to adjust their positions required for the crystal boundary being formed. The metallurgical bond formation in kinetic powder consolidation must occur in the sequence: (1) macroscopic shape change of powder particles for oxide film disruption and dense packing, (2) elimination of nano-scale surface asperities and steps at the interface for
atomic-scale mating surface conformity and (3) atom repositioning at the interface to configure a crystal boundary. The overall rate of metallurgical bond formation is limited by the slowest of the three steps, although these steps may overlap.

Steps 1 and 2 both require plastic deformation and hence would depend on the local flow stress of the material. A recent study on UPC of copper powder by Liu [55] has shown that both compact densification (i.e., deformation) and metallurgical bonding (of deformed particles) depended on consolidation temperature and time and hence are thermally activated processes. Moreover, UPC can produce full-density, metallurgically bonded consolidates within a few seconds at moderate temperatures [8, 22, 69]. All these findings suggest that the material subjected to ultrasonic deformation does not work harden as much as in conventional deformation processing and may even dynamically soften by some unknown mechanism. This phenomenon, referred to as ultrasonic softening, was originally proposed by Langencker [24] and has been observed in other studies [1, 16, 25, 64]. Langencker believed that ultrasound energy absorbed by dislocations will raise temperature at the dislocations, lowering the local flow stress, however, he never considered the effect of excess vacancies on the rate of dislocation climb. He suggested that dislocations may obtain thermal jogs but they may not move or intersect. This assumption however, contradicts his observation of increased dislocation density in his tensile test specimens [24]. Awatani et al. [16] on the other hand, did address possible excess vacancy generation in their study of ultrasonic fatigue tests on aluminum.

It is known that excess vacancies exert an osmotic climb force on the edge component of dislocations. This osmotic climb force acts as an effective pressure, which
exceeds 1100 MPa at excess vacancy concentrations around 100 times higher than the equilibrium concentration. This significantly increases the dislocation climb velocity. An analysis based on vacancy diffusion-controlled dislocation climb under no applied stress yields an equation for the climb velocity \( v_c \) in a crystal containing excess vacancies,

\[
v_c \approx D_V X_V / b,
\]

where \( b \) is the Burgers vector, \( D_V \) is the vacancy diffusivity, and \( X_V \) is the excess vacancy mole fraction [70]. It has been known that \( X_V \) in high strain-rate deformation may reach \( 10^{-4} \sim 10^{-1} \) [18, 25, 56], dislocations can climb at velocities significantly higher than normal climb velocity, encouraging rapid untangling and annihilation of dislocations [22].

**Effects on phase stability:** A high vacancy concentration may also affect the thermodynamic stability of the solid relative to that of the liquid, possibly causing melting below the equilibrium melting point. For aluminum, melting point may be depressed by as much as 400 K at a vacancy concentration of 0.1 [19], Figure 2.6. Such strain-induced melting point depression would play an important role in the bond formation in kinetic joining processes, particularly if the interface temperature exceeds the depressed melting temperature. Gunduz et al. [23] in an ultrasonic welding experiment of aluminum and zinc, observed featureless areas along the weld zone, indicating incidence of local melting, Figure 2.7. The joining temperature was 513 K and no temperature increase was monitored by the thermocouple during the experiment. This suggests the melting point depression as a result of high excess vacancies.
Figure 2.6: Normalized melting point of aluminum vs vacancy mole fraction calculated using a thermodynamic model [19].

Figure 2.7: SEM image of the featureless region along the Al-Zn weld interface [23].
2.3 Mechanical Alloying

Mechanical alloying (MA) is a solid-state powder processing technique that occurs by repeated fracturing and rewelding of the particles of a powder mixture in a ball mill [71]. This technique was originally developed in 1970’s for oxide-dispersion strengthened (ODS) super alloys production and since then has been widely used for synthesizing wide ranges of equilibrium and non-equilibrium alloy phases from elemental or pre-alloyed powders [72]. This process is carried out in different types of ball mills such as vibratory mills, attrition mills, planetary mills or conventional ball mills.

During ball milling the powder particles are constantly fractured, flattened, and cold welded. A mixture of powders and grinding media with variable ball to powder ratios is used. The impact force due to collision of two balls in the mill deforms the trapped powder particles, leading to work hardening and fracture. As a result of particle fracture, new surfaces are created, enabling the particles to weld together. In the early stages of ball milling, the powder particles are relatively soft, thus, the tendency to welding together and forming larger particles is high. The resulting composite particles at this stage have a characteristic layered structure of various concentrations of the starting compositions. As the process continues, the particles get work hardened and undergo fracture and fragmentation [71, 73, 74].

Currently, MA methods are proven to be successful for producing novel materials and structures, however, the limitations of this method are mainly the low efficiency and a lack of adequate models to predict the final outcome of this process [75-77].
The current models for MA by ball milling have not addressed all aspects of the process properties and structure relationships in MA; however, different models did their parts in addressing some of these aspects. The model presented in [78] only addresses the individual particle impacts as hertzian collision and evaluated the hardening and strains in particles as a function of their collision speed. It was assumed that some of the impact-welded particles were broken as a result of residual stresses while some remained welded. So to estimate the average particle size after ball milling, criteria for stress, fracture initiation and propagation were used. Aikin et al. expressed the reaction kinetics in terms of the probabilities of welding and fracture between particles [79, 80]. This model was then fitted to experimental results. The model in [81] used an energy criterion to further explain the phase transformations during ball milling. Also using the same model, Magini et al. [73] were able to predict the final phases after ball milling. Despite the above mentioned models, the fundamental principles and thermodynamics of microstructure evolution and phase transformation during ball milling are not yet fully understood.
2.4 Objectives

This study was aimed at understanding the phase evolution in Cu and Zn elemental powder mixture subjected to UPC in comparison with other high-strain rate materials processing methods such as ball milling. Systematic UPC and ball milling experiments were carried out with a Cu-48 wt% Zn powder mixture. Optical microscopy, image analysis and XRD were done on specimens to investigate the microstructure and phase evolution with particular interest in the unusual effects of excess vacancies on the thermodynamics and kinetics of phase transformation in UPC and ball milling.
3. EXPERIMENTAL PROCEDURE

3.1 Experimental Setup

3.1.1. Ultrasonic Powder Consolidation

The apparatus used in this study is a CONDOR ultrasonic welding unit shown in Figure 3.1 and Figure 3.2 manufactured by STAPLA Ultrasonic Corporation, Wilmington, MA. This welder operates at a maximum power of 3.5 kW and a fixed frequency of 20 kHz. The unit consists of a controller, a converter, an ultrasonic sonotrode and a booster. The high frequency signals are transmitted to the converter through the controller unit shown in Figure 3.3 and the booster unit amplifies and transmits the resulting vibrations to the ultrasonic sonotrode as shown in Figure 3.4. The amplitude of the vibration can be varied between 4-9 µm.

Figure 3.1: Schematic view of the ultrasonic powder consolidation setup.
Figure 3.2: STAPLA Condor ultrasonic welding unit.

Figure 3.3: ST30 Digital controller.
Figure 3.4: Amplitude enhancement of sonotrode.

The sonotrode is made of high speed tool steel and has a 3680 µm x 3680 µm square tip with a 14 x 14 grid of square knurls spaced 100 µm apart. Each knurl is a 150 µm x 150 µm square as shown in Figure 3.5.

Figure 3.5: Schematic diagrams showing the sonotrode tip [25].
A heater plate was designed to allow experiments at elevated temperature. Two high temperature cartridge heaters from McMaster (6.28 mm in diameter, 51 mm in length and 250 W in power) are inserted in a stainless steel plate along with a K-type thermocouple probe from OMEGA as shown in Figure 3.6. The cartridge heaters have a stainless steel armored lead covering and a maximum operating temperature of 760 °C (1033 K).

Figure 3.6: Schematic view of the heater plate.
This setup is connected to a computer through a control box shown in Figure 3.7 and a National Instruments PCI-6035e DAQ board. A computer program, coded in LabView 8.6, acquires the temperature data from the thermocouple and controls the temperature of the cartridge heaters to ensure that the set temperature is reached. This program records the temperature data at a rate of 1000 data points per second. Additionally, an external K-type thermocouple is used to further monitor the specimen temperature during each experiment. Figure 3.8 shows the detailed wiring diagram of the heater and control box.

Figure 3.7: The heater plate control box.
In order to consolidate the specimen, UPC experiments employ a die-punch setup made of A2 tool steel hardened to minimize high temperature deformation. The die and punch are 2 mm and 3.5 mm thick, respectively, and have a matching diameter of 4.1 mm.

Figure 3.8: Wiring diagram of the heater and control box [25].

Figure 3.9: Drawing of the die and the punch.
3.1.2. Ball mill

The ball mill used in this study is a PQ-N04 planetary ball mill from Across International with a maximum speed of 600 rpm. This ball mill has four grinding stations placed on a Sun Wheel as shown in Figure 3.10.

![Figure 3.10: PQ-N04 planetary ball mill.](image)

In this study a 100 ml stainless steel vacuum grinding jar was used as shown in Figure 3.11. The pre-mixed powders and stainless steel grinding balls with 10 mm diameter purchased from McMaster were placed inside the grinding jar and the jar was then evacuated and backfilled with argon gas to ensure an inert atmosphere. A ball to powder mass ratio of 10 to 1 was selected for the ball milling experiments.
Figure 3.11: Stainless steel vacuum grinding jar.
3.2 Materials

The materials used in this study were copper and zinc powders with 5 µm and 75 µm mean diameter, respectively. The copper powder was obtained from Fukuda Metal Foil and Powder Co. LTD. and the zinc powder was purchased from Alfa Aesar. SEM micrographs of the as-received powders are shown in Figure 3.12.

![Figure 3.12: SEM pictures of as-received (a) Cu powder (b) Zn powder.](image-url)
3.3 Experimental Procedure

A mixture of Cu-48 wt% Zn was prepared and dry mixed in a rotary plastic container for 3 hours to ensure a homogenous distribution. Systematic UPC experiments with powder mixture of Cu-48 wt% Zn composition were conducted to investigate the effects of ultrasonic vibration on the microstructural evolution of specimens.

As seen in the Cu-Zn phase diagram is in Figure 3.13, the Cu-48 wt% Zn powder mixture composition was chosen such that the consolidated material lies in the β-brass region.

Figure 3.13: Cu-Zn phase diagram [82].
In order to consolidate a sample, the die was first placed on the heater plate. Then, approximately 0.1 g of powder mixture was placed in the die and finally the punch was positioned on top of the die. The whole setup was then placed under an acrylic (Plexiglas) box with tubing connected to an argon gas cylinder to avoid oxidation during the experiment by providing a flowing argon bath as shown in Figure 3.14.

![Figure 3.14: The acrylic box connected to an argon gas cylinder.](image)

The powder mixture was then heated to the consolidation temperature. Once the system was reached the desired temperature the die-punch setup was subjected to normal pressure applied through the sonotrode to the punch. Then the whole setup was kept at the consolidation temperature for a few minutes under the applied pressure, to make sure the temperature distribution was uniform in the die-punch setup. Soon after the holding time was over, in-plane ultrasonic vibration was applied through the sonotrode and punch
for a few seconds (1-4 s). Once the process was over and the consolidated sample was cooled down enough, the sample was removed from the die. Figure 3.15 shows the heating-cooling profile as well as the pressure profile for each sample, during the UPC process.

![Figure 3.15: Temperature and pressure profile during the UPC process.](image)

The pre-mixed powder mixture was subjected to ultrasonic vibration in the argon atmosphere for 1, 2, 3 and 4 s at the nominal consolidation temperature ranging from room temperature to 300 °C (573 K) and under 100 MPa uniaxial pressure. For all the experiments, the amplitude of ultrasonic vibration was kept at 9 µm. A reference sample was also made at 300 °C (573 K) under identical pressure and temperature conditions but without ultrasonic vibration to compare and investigate the effect of ultrasonic vibration on phase transformation.
The processing conditions used for sample consolidation are summarized in Table 3-1.

**Table 3-1: Processing conditions for consolidated Cu-48wt% Zn samples.**

<table>
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<th>Temperature (°C)</th>
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3.4 Metallographic Characterization and Microscopy

The consolidated specimen was mounted in an acrylic resin and cured for 1 hour at room temperature. Metallographic specimen preparation was performed on the samples to allow sample observation under an optical microscope. For this process a Buehler ECOMET 5 two speed grinding/polishing table was used. First, the sample was ground in several steps on SiC abrasive papers with continuously reducing abrasiveness. The grit sizes used were 240, 400, 600, 1000, 1500 and 2000. This process is continued until all previously visible scratches were removed and the finest possible surface condition was achieved. Between the grinding steps, the specimen was rinsed with tap water to reduce the risk of contamination. After grinding, the specimen was polished on a rotating wheel using a final polish-blue color-medium nap cloth purchased from Mark V laboratory. A solution consisting of 1.0 µm alumina (aluminum oxide) powder suspended in distilled water was used as an abrasive material which aids the scratch removal from the surface of the sample. To obtain the best surface quality, the sample was then successively polished with 0.3 µm and 0.05 µm alumina suspensions. Finally the prepared sample was metallurgically characterized under an Olympus VANOX-T optical microscope with the highest magnification of 1000x.
3.5 Image Analysis

Image analysis was performed on the resulting micrographs to determine the areal fractions of phases formed during the UPC process.

First, using the Photoshop software, the image was transformed to a binary image such that it contained only two colors. The new phase formed in the UPC process was kept in its original light blue color while copper and zinc particles are transformed to a darker color. This image was then converted to a black and white image using the ImageJ software. The area fraction of the new phase can be easily calculated as the number of white pixels divided by the total pixel count in the image as shown in Figure 3.16.

Figure 3.16: The sequence of creating a black and white image.
3.6 X-Ray Diffraction

X-ray diffraction (XRD) was carried out to investigate the phase changes in ball-milled and UPC-consolidated Cu-Zn samples. XRD patterns were obtained for various ball-milled and UPC samples using a PANalytical X'Pert PRO diffractometer with Cu kα (λ=0.15418 nm) incident radiation at a scanning rate of 5°/min located at the Center for Materials Science and Engineering (CMSE) at the Massachusetts Institute of Technology (MIT), shown in Figure 3.17.

Figure 3.17: PANalytical X’Pert PRO XRD instrument at MIT.
4. RESULTS AND DISCUSSION

4.1 Ball Milling of Copper and Zinc Powders

Systematic ball milling experiments were performed on Cu-48 wt% Zn pre-mixed powder mixture with ball milling durations of 1, 5 and 10 hours. Figure 4.1 shows optical micrographs of the cross sections of composite powder particles from the three batches. The three samples all show an outer region in yellowish color and a core regions consisting of thin reddish and light blue alternating layers and some dark holes between the layers. The thickness of the yellowish outer region is seen to increase with increasing ball-milling time. A close look at the core regions of the samples reveals that some parts of the core region has also turned yellow, which is most clearly seen in the sample ball milled for 10 h.

Figure 4.2 shows the XRD pattern of the sample ball milled for 10 h. Three phases are identified; the fcc Cu-rich solid solution (α-brass), the hcp Zn-rich solid solution and bcc β-brass. From the colors of the phases seen in Figure 4.1, it is deduced that the yellowish phase that formed in the outer region of the samples, and also in the core region as evident in the sample ball milled for 10 h, is bcc β-brass, and the reddish and light blue layers in the core region of the samples are, respectively, the fcc α-brass phase and the hcp Zn-rich solid solution. This suggests that during the ball milling of Cu and Zn powder mixture, thin alternate layers of Cu and Zn were first produced by repeated deformation and welding, which then promoted interdiffusion and hence formation of the intermediate phase β-brass between the welded Cu and Zn layers. As
seen in Figure 4.1, this process is complete in the outer regions of the samples whereas in the core regions where much of the elements still remained unreacted as α-brass and the Zn-rich solid solution. It is also seen that the outer β-brass layer thickened with increasing ball-milling time, while the amount of β-brass increased in the core region as well. The fact that the outer layers of the samples are all yellow in one color suggests that the outer layer must consist of a single phase that has the Cu-48 wt% Zn composition, which cross-verifies that the yellow phase is β-brass.

Figure 4.1: Ball-milled copper and zinc powder mixture at room temperature and argon atmosphere for (a) 1 hour, (b) 5 hours, (c) 10 hours.
Figure 4.2: X-ray diffraction pattern for mechanically alloyed Cu-48 wt% Zn powder mixture, ball-milled for 10 hours.
4.2 Ultrasonic Powder Consolidation of Copper and Zinc Powders

Systematic UPC experiments were conducted under the conditions shown in Table 3-1 to investigate the phase evolution in a Cu-48 wt% Zn powder mixture during UPC.

4.2.1. Metallographic Characterization

In addition to the UPC specimens prepared under the conditions in Table 3-1, a reference sample was first made at 300 ºC and under 100 MPa uniaxial pressure but with no ultrasonic vibration. Figure 4.3 shows a micrograph of the reference sample where reddish Cu particles are seen to form a network and Zn fills the cells in the network. The individual particles of Cu in the Cu network are discernible and largely in their original spheroidal shape, indicating a low degree of compact densification in the Cu network. We note also some holes in the Cu network. They were created during sample preparation which indicates a lack of bonding among the Cu particles. Thus, the conditions applied, i.e., 300 ºC, 100 MPa and no ultrasonic vibration, did not produce good metallurgical consolidation of the Cu particles in the Cu network. The densification of the Zn particles in the cells, however, is more complete. Individual Zn particles are hardly discernible, and no voids or gaps are visible in the Zn-filled cells, up to the interface with the Cu network.
Despite the intimate contact between Cu and Zn at their interface, no new phase formed in the reference specimen which was produced at 300 °C, but without ultrasonic vibration. Thus there was not enough interdiffusion to allow for diffusional transformations in the reference sample under the condition applied.

Figure 4.3: Reference sample made at 300 °C and under 100 MPa uniaxial pressure.

Figure 4.4 - Figure 4.7 show micrographs of samples consolidated at nominal temperatures of 25, 100, 150, 200, 250 and 300 °C with 1, 2, 3 and 4 s of ultrasonic vibration. Overall, the samples all exhibit a network of Cu regions and Zn-filled cells as in the reference sample, but with increasing degrees of particle densification at higher consolidation temperature and time. Moreover, a new phase formed between Cu and Zn which became evident above about 150 °C regardless of ultrasonic vibration time.
In the samples consolidated at room temperature, micrographs (a) of Figure 4.4 - Figure 4.7, individual Cu particles are discernible, many of which were lost from the polished surface of the samples during sample preparation. Thus, little densification or bonding of Cu particles was achieved at room temperature, regardless of the ultrasonic vibration time applied. A higher degree of densification, and most probably bonding, of Zn particles is achieved even at room temperature. However, there is no indication of phase transformation in the samples consolidated at room temperature.

The samples consolidated at 100 °C, micrographs (b) of Figure 4.4 - Figure 4.7, exhibit higher degrees of densification in the Cu region, as well as full densification in the Zn region. The individual Cu particles in these samples are still largely discernible and some Cu particles have even come off the polished surface during sample preparation. The Cu region became more intact as the ultrasonic vibration time was increased, with virtually full densification achieved at 4 s. This suggests that densification depended on both the vibration time temperature. No evidence of phase transformation is noted in these specimens consolidated at 100 °C.

Even higher degrees of consolidation are observed in the Cu regions of the samples consolidated at 150 °C, micrographs (c) of Figure 4.4 - Figure 4.7, where good metallurgical consolidation of Cu and Zn particles also seems to be achieved at 2 s and longer times. At 1 s, however, some Cu particles are still discernible. While the achievement of full densification does not necessarily guarantee good metallurgical bonding in the consolidated sample, the absence of particle detachment during sample preparation implies good bonding in the Cu regions of the samples consolidated for 2 s
and longer. Thus, both the densification and bonding in the Cu region (network) are time-dependent processes. Still no new phase is found in these samples consolidated at 150 °C.

The samples consolidated at 200 °C, micrographs (d) of Figure 4.4 - Figure 4.7, exhibit well-consolidated Cu and Zn regions, except at the shortest consolidation time of 1 s applied, at which the Cu particles are still somewhat discernible. Thus, the thermal activation at 200 °C was sufficient for rapid metallurgical consolidation of Cu particles to complete within 1+ s. Furthermore, a new phase has just appeared at the interface between the Cu and Zn regions. The new phase, appearing in gray in the micrographs, just formed in the sample consolidated for 1 s, Figure 4.4(d), and increased significantly with increasing ultrasonic vibration time, Figure 4.5(d), Figure 4.6(d) and Figure 4.7(d).

More extensive formation of the new phase occurred in the samples consolidated at 250 °C, micrographs (e) of Figure 4.4 - Figure 4.7. The gray new phase has just covered most of the Cu-Zn interface as early as 1 s. At 2 s, the new phase has formed a well-developed continuous layer between the Cu and Zn regions, which further thickened into the Cu and Zn regions over the next 2 s. At 4 s, the new phase has grown to consume most of the Zn and much of the Cu. A close look at the gray new phase regions in these samples reveals dark features that appear to coincide with the prior inter-particle boundaries in the Cu regions.

The samples consolidated at 300 °C, micrographs (f) of Figure 4.4 - Figure 4.7, exhibit a well-developed layer of the gray phase even at the shortest consolidation time of 1 s. At 4 s, the gray new phase has consumed almost all of the remaining Zn. The dark features noted in the samples consolidated at 250 °C are more clearly seen in the samples consolidated for 1 - 3 s. The matching between the dark features and the prior boundaries
of Cu particles is very evident in the samples consolidated for 2 s and 3 s, Figure 4.5(f) and Figure 4.6(f). Careful observation of the gray new phase regions reveals that most of these dark features are terminated at a certain distance from the interface with the remaining Cu. This implies that the gray new phase regions that contain the dark features were created by the diffusion of Zn into the Cu and that the gray regions that extend beyond the position at which the dark features are terminated were created by the diffusion of Cu into the Zn. The dark features in the gray new phase regions are largely erased in the sample consolidated at 300 °C for 4 s, Figure 4.7(f).
Figure 4.4: Optical micrographs of Cu-48 wt% Zn powder mixture consolidated under 100 MPa for 1 s at (a) room temperature (b) 100 °C (c) 150 °C (d) 200 °C (e) 250 °C (f) 300 °C.
Figure 4.5: Optical micrographs of Cu-48 wt% Zn powder mixture consolidated under 100 MPa for 2 s at (a) room temperature (b) 100 ºC (c) 150 ºC (d) 200 ºC (e) 250 ºC (f) 300 ºC.
Figure 4.6: Optical micrographs of Cu-48 wt% Zn powder mixture consolidated under 100 MPa for 3 s at (a) room temperature (b) 100 °C (c) 150 °C (d) 200 °C (e) 250 °C (f) 300 °C.
Figure 4.7: Optical micrographs of Cu-48 wt% Zn powder mixture consolidated under 100 MPa for 4 s at (a) room temperature (b) 100 °C (c) 150 °C (d) 200 °C (e) 250 °C (f) 300 °C.
4.2.2. Phase Identification

The new phase that formed above 150 °C was identified by XRD as γ-brass, an equilibrium phase of the Cu-Zn phase system that has the nominal composition of Cu₅Zn₈, Figure 3.13. Figure 4.8 and Figure 4.9 show the XRD patterns of the sample consolidated at 100 °C for 2 s and the sample consolidated at 300 °C for 2 s, respectively. The XRD pattern of the sample consolidated at 100 °C, Figure 4.8, shows only the fcc Cu (α-brass) and hcp Zn reflections. Thus, no new phase formed in this sample consolidated at 100 °C, as expected from the micrograph in Figure 4.5(b). The XRD pattern of the sample consolidated at 300 °C, Figure 4.9, however, shows additional peaks that are indexed as γ reflections. Thus, the new phase in Figure 4.5(f) must be γ-brass. Since the new phase that formed in all other UPC samples consolidated at/above 200 °C also was in the same gray color, it is deduced that γ-brass was the only new phase that formed in all of the UPC samples consolidated at/above 200 °C, despite the Cu-48wt%Zn composition of the powder mixture at which β-brass is the phase expected in the eventual equilibrium state.
Figure 4.8: X-ray diffraction pattern for the specimen consolidated at 100 °C with 2 s vibration and under 100 MPa uniaxial pressure.

Figure 4.9: X-ray diffraction pattern for the specimen consolidated at 300 °C with 2 s vibration and under 100 MPa uniaxial pressure.
4.2.3. Gamma-brass Growth Kinetics in UPC

As seen from the micrographs in Figure 4.4 - Figure 4.7, the $\gamma$-brass formation was observed only in the samples consolidated at 200 °C and above. The volume fraction of the $\gamma$-brass in the UPC samples was determined by the image analysis described in Section 3.4. Figure 4.10 shows the volume fraction of $\gamma$-brass against the nominal consolidation temperature for the vibration times of 1 - 4 s. Figure 4.11 re-plots Figure 4.10 to show the increase in $\gamma$-brass volume fraction with time at 200, 250 and 300 °C. Clearly, the volume fraction of $\gamma$-brass increased with increasing temperature and time.

To investigate the rate-limiting step of the $\gamma$-brass growth, the cube root of the $\gamma$ volume fraction was plotted against the vibration time. The resultant growth curves shown in Figure 4.12 imply a parabolic growth, which is indicative of diffusion-controlled growth. In fact, when the cube root of the $\gamma$ volume fraction is re-plotted against the square root of vibration time, the resultant plots are nearly linear, Figure 4.13. Thus, the growth of $\gamma$-brass in the UPC samples seems to be diffusion-controlled.
Figure 4.10: Volume fraction of Gamma-brass as a function of nominal temperature for samples made under 100 MPa pressure and 1, 2, 3 and 4 s ultrasonic vibration.

Figure 4.11: Volume fraction of Gamma-brass as a function of vibration time for samples made under 100 MPa pressure and at 200 °C, 250 °C and 300 °C.
Figure 4.12: Cube root of Gamma-brass volume fraction as a function of vibration time for samples made under 100 MPa pressure and at 200 °C, 250 °C and 300 °C.

Figure 4.13: Cube root of Gamma-brass volume fraction as a function of square root of vibration time for samples made under 100 MPa pressure and at 200 °C, 250 °C and 300 °C.
The kinetic equation for the diffusion-controlled growth of a phase in a material has the general form:

\[ x = \alpha \sqrt{Dt} \]  

(1)

Where \( x \) is the growth distance, \( D \) is the diffusivity of the element whose diffusion is limiting the growth kinetics, \( t \) is the growth time and \( \alpha \) is a factor that depends on the far-field and interfacial concentrations of the element in concern.

Since the \( \gamma \)-brass region in the Cu-Zn phase diagram is narrow and nearly vertical, Figure 3.13, the value of \( \alpha \) for the growth of \( \gamma \)-brass is not strongly dependent on temperature. We may assume that the cube root of the \( \gamma \) volume fraction crudely represents the growth distance \( x \) in our case. We may also assume that the vibration time is the growth time. Then, the slope of the cube root of the \( \gamma \) volume fraction plot vs. \( t^{1/2} \) in Figure 4.13 may be regarded as \( \alpha \sqrt{D} \), the rate constant in Eq. (1). Therefore, plotting the logarithm of the slope against the inverse of the temperature in Kevin may yield a straight line. In the absence of knowledge of the exact temperature in the material being consolidated, we use the nominal consolidation temperature as the actual temperature in the material during UPC, although this is not strictly correct [19].

Figure 4.14 shows the Arrhenius plot obtained in the manner described above which gives an activation energy of 18,660 J/Mol. This value of activation energy is in a range comparable to the activation energy of Zn in a dilute Cu-Zn solution which is reported to be 191 kJ/Mol [83] and that of the diffusion in Cu in a dilute Zn-Cu solution which is about 125 kJ/Mol [83].
The above analysis based on Eq. (1) requires a constant interfacial concentration. This, however, is not guaranteed in UPC where the interfacial concentrations may not be limited at the equilibrium solubilities. Moreover, the excess vacancies are not thermally generated, and as such the activation energy of substitutional diffusion is not necessarily the same as the sum of the activation energies of vacancy jump and formation. Further work is needed to more correctly address the kinetics of γ-brass growth in the UPC of Cu-Zn powder mixture.

Figure 4.14: Arrhenius plot for Gamma-brass growth.
4.2.4. Phase Evolution

The formation of γ-brass from Cu and Zn powders in the UPC samples is contrasted by the direct formation of β-brass from Cu and Zn in the ball milled composite powders shown in Figure 4.1. Since the Cu$_5$Zn$_8$ composition of γ-brass differs from the Cu-48wt%Zn composition of the powder mixture, the UPC samples have not reached the final equilibrium state expected at the Cu-48wt%Zn composition.

In order to investigate the effect of powder mixture composition on the phase formation in the UPC of Cu-Zn powder mixture, additional UPC experiments were carried out with powder mixtures of 10 wt% Zn, 20 wt% Zn, 30 wt% Zn and 40 wt% Zn compositions. The samples in these experiments were all consolidated at 300 °C for 2 s of ultrasonic vibration under 100 MPa uniaxial pressure. Figure 4.15 shows optical micrographs of these samples in which formation of gray colored γ-brass between the Cu and Zn regions is evident, even in the sample with only 10 wt% Zn. Increasing the zinc concentration only produced higher volume fractions of γ-brass. Thus γ-brass was the phase that nucleated and grew in the UPC of Cu-Zn powder mixture, regardless of the Zn content in the powder mixture. No β-brass formation is noted in these specimens.
Figure 4.15: Optical micrographs of consolidated specimens at 300 °C with 2 s of ultrasonic vibration, under 100 MPa uniaxial pressure and powder mixture of (a) Cu-10 wt% Zn, (b) Cu-20 wt% Zn, (c) Cu-30 wt% Zn, (d) Cu-40 wt% Zn.

The above results suggest that the phase selection in UPC Cu-Zn is not affected by the global chemical state of the material. Rather, it is an event governed by the local state at the Cu-Zn interface in the powder mixture. γ-brass, however, is not a stable phase in samples with overall chemical compositions less than about 50 wt% Zn, Figure 3.13. The stable phases should be α-brass in the samples with 10, 20 and 30 wt%Zn, α-brass and β-brass in the samples with 40 wt%Zn, and β-brass in the samples with 48 wt%Zn. This was confirmed by heat treatment experiments of samples with 48 wt%Zn consolidated at
300 °C for 2 s under 100 MPa pressure. Figure 4.16 shows micrographs of the samples after heat treatment at 100 °C for 15, 30, 60 and 300 minutes where β-brass formed between the remaining Cu and the γ-brass and increased with increasing heat treating time. At 300 minutes, the β-brass has grown to occupy the entire volume of the sample, which in turn verified the overall Cu-48 wt%Zn composition of the sample. XRD also confirmed the complete transformation to β brass in this sample, Figure 4.17.

Figure 4.16: Optical micrographs of consolidated specimens at 300 °C with 2 s of ultrasonic vibration, under 100 MPa uniaxial pressure after heat treatment process at 100 °C for (a) 15 min, (b) 30 min, (c) 60 min, (d) 300 min.
As shown in Figure 4.16, after heat treating the sample at 100 °C for 15 min, the β-brass starts to grow at the interface of copper rich phase and γ-brass. As the heat treatment time increases, the amount of β-brass becomes more significant and finally after 300 min of heat treatment the whole sample transforms to β-brass. The XRD result shown in Figure 4.17 confirms this observation.

![X-ray diffraction pattern](image)

**Figure 4.17:** X-ray diffraction pattern for the specimen consolidated at 300 °C with 2 s vibration and under 100 MPa uniaxial pressure and heat treated at 100 °C for 300 min.
The selection of \(\gamma\)-brass, instead of \(\beta\)-brass, as the phase to nucleate at the Cu-Zn interface seems unique to the UPC process as it was the \(\beta\)-brass that formed in ball milled Cu-Zn powder mixtures, Figure 4.1. Since there was no \(\beta\)-brass in the UPC-consolidated Cu-Zn samples, \(\gamma\)-brass nucleation must have been exclusively more active than \(\beta\)-brass nucleation.

This may be explained with the Gibbs free energy curves, or G curves, in Figure 4.18 schematically drawn for the temperature of the sample during UPC. Although the equilibrium Cu-Zn phase diagram, Figure 3.13, has another intermediate phase, \(\varepsilon\), that is stable below 598 °C, G curves are shown only for \(\alpha\)-brass, \(\beta\)-brass, \(\gamma\)-brass phases and the hcp Zn-rich solution since no \(\varepsilon\) phase was observed in the samples. The G curve of \(\alpha\)-brass, \(G_\alpha\), is wide reflecting the large solubility of Zn in \(\alpha\)-brass, whereas the G curves for \(\beta\)-brass and \(\gamma\)-brass, \(G_\beta\) and \(G_\gamma\), are narrow to match with their narrow composition ranges. The G curve of the hcp Zn-rich solution, \(G_{(Zn)}\) must also be narrow as expected from the limited equilibrium solubility of Cu in Zn.

When a Cu-Zn powder mixture is subjected to UPC, interdiffusion causes a rapid increase of the concentration of Cu in the Zn and the Zn concentration in the Cu at the Cu-Zn interface. Since the substitutional diffusivity is proportional to vacancy concentration, the diffusivity is increased over the normal value by a factor of \(X_{V}^{ex}/X_{V}^{eq}\) where \(X_{V}^{ex}\) is the excess vacancy concentration and \(X_{V}^{eq}\) is the equilibrium (thermal) vacancy concentration [19, 23]. Recent NMR studies has shown that \(X_{V}^{ex}\) can be as high as 0.1 in pure aluminum being subjected to tensile testing [18]. Such a high \(X_{V}^{ex}\) value translates into a diffusivity several orders of magnitude above the normal value [19].
Under such conditions, significant interdiffusion may occur at the interface before any intermediate phase can nucleate. This would allow the interfacial Cu concentration in the Zn to exceed the usual equilibrium solubility before the ε phase can nucleate. The arrow on the $G_{(Zn)}$ curve indicates the increase in Cu concentration at the interface. The interfacial Cu concentration may even exceed the metastable solubility limit defined by the common tangent on the $G_{(Zn)}$ and $G_{\gamma}$ curves, (Point P on the $G_{(Zn)}$ curve), so that γ-brass gains a large driving force for its nucleation in the Zn at the interface.

The Zn concentration in the Cu at the interface may also increase as indicated by the arrow on the $G_{\alpha}$ curve in Figure 4.18. This, however, would not increase the driving force for the nucleation of β-brass or γ-brass on the Cu at the interface as much because of the wide $G_{\alpha}$ curve which mandates its tangent lines to go below the $G_{\beta}$ or $G_{\gamma}$ curve, Figure 4.18.

![Gibbs free energy curves for different Zn concentrations in Cu-Zn UPC samples.](image-url)
The excess vacancies in the hcp Zn-Cu solution impose another important effect on the phase evolution as they would also increase the Gibbs free energy of the phase in which they are created. For a crystal consisting of \(n_0\) atoms, the free energy is increased by an amount given by:

\[
\Delta G = n_v G_v - T \Delta S_v
\]  

(2)

Where \(n_v\) is the number of thermal and excess vacancies, \(G_v\) is the free energy of a vacancy and \(\Delta S_v\) is the configurational entropy change for the inclusion of vacancies. For random mixing of vacancies in the crystal, \(\Delta S_v\) is given by:

\[
\Delta S_v = k \left[ (n_0 + n_v) \ln(n_0 + n_v) - \ln n_v - n_0 \ln n_0 \right]
\]  

(3)

For one mole of such ‘atom – vacancy solutions’ i.e., \(n_0 + n_v = N_a\),

\[
\Delta G_{(Zn)}(X_v) \equiv \frac{RT}{1 - X_v} \left[ (1 - X_v) \ln(1 - X_v) + X_v \ln X_v \right] + \frac{X_v}{1 - X_v} G_v
\]  

(4)

Where \(G_v\) is the free energy for the formation of one mole of vacancies.

Thus, the excess vacancies would lift the \(G_{(Zn)}\) curve by \(\Delta G_{(Zn)}(X_v)\), as shown with the broken curve in Figure 4.18. This would have an effect of increasing the driving force for \(\gamma\) nucleation by \(\Delta G_{(Zn)}(X_v)\).

The excess vacancies may potentially have yet another effect. Figure 4.19 shows \(G_{\alpha}, G_{(Zn)},\) and \(G_L\), the G curve of the liquid Cu-Zn phase. As the \(G_{(Zn)}\) curve is lifted by \(\Delta G_{(Zn)}(X_v)\), the mid part of \(G_L\) may get under the common tangent between the \(G_{\alpha}\) and \(G_{(Zn)}\) curves. This constitutes a thermodynamic condition for ‘eutectic melting’ between the \(\alpha\)-brass and the (Zn) solution. However, whether such thermodynamic conditions for
strain-induced melting can actually occur in the Cu-Zn system in the presence of excess vacancies is not known at present.

![Gibbs free energy curves](image)

**Figure 4.19:** Gibbs free energy curves for different Zn concentrations and corrected Gibbs free energy curves for compounds with high excess vacancy concentration.

The direct formation of β-brass from Cu and Zn during ball-milling, Figure 4.1, implies that the interdiffusion in the ball-milled Cu-Zn powder mixture was not as much enhanced as in UPC. Although the instantaneous strain rate in ball-milling may be high, the deformation is intermittent, i.e., it happens in a composite powder particle only when the particle is impacted by the balls, and excess vacancies may be lost to sinks, i.e., dislocations, during the intervals between impacts. The lower process temperature (which is nominally room temperature for ball-milling) may also keep the diffusion more limited
than in UPC. With limited diffusion, the Cu concentration in the Zn at the Cu-Zn interface would not be increased as much as in UPC, and the driving force for $\gamma$-brass nucleation hence stays low. Under such conditions, the $\beta$-brass phase, which has a large overall driving force for formation at the Cu-48wt%Zn composition, is the phase that forms. $\gamma$-brass may also form in intermediate stages where high Zn regions remains, although ultimately the $\gamma$-brass must all transform to $\beta$-brass.

To further investigate the reason behind the selection of the phase to form in Cn-Zn powder mixture, two new experiments were performed. In the first experiment, a Cu-48 wt% Zn powder mixture, encapsulated in a pre-evacuated and Ar gas-backfilled quartz tube, was placed in a furnace at 100 °C for 5 minutes. Once the powder was cooled to room temperature, it was taken out of the quartz tube and consolidated by UPC at 300 °C for 2 s of ultrasonic vibration under 100 MPa uniaxial pressure. In the second experiment, a Cu-48 wt% Zn powder mixture was first ball-milled in Ar atmosphere for 5 minutes and consolidated by UPC under the same conditions as those of the first experiment. In either experiment, the Cu concentration in the Zn at the interface is not expected to increase to the extent that $\gamma$-brass nucleation is favored.

Figure 4.20(a) and Figure 4.20(b) shows the cross sections of the consolidated samples from the first and second experiments, respectively. Both samples exhibit significant amount of $\beta$-brass formation despite the very short duration of the pre-heat treatment or ball milling. Although no $\beta$-brass formation was detected using XRD in the heat treated or ball-milled powder mixture, Figure 4.21 and Figure 4.22, $\beta$-brass must have nucleated during the short pre-heat treatment and ball milling and subsequently
grew further during UPC, while $\gamma$-brass also formed as a result of the enhance diffusion in UPC. These new experiments demonstrate the feasibility of producing $\beta$-brass by UPC in a two-step procedure with a pre heat treatment or ball milling.

![Figure 4.20](image)

**Figure 4.20:** Cu-48 wt% Zn powder (a) Heat treated at 100 °C for 5 minutes (b) Ball-milled for 5 minutes, then consolidated at 300 °C with 2 s of ultrasonic vibration, under 100 MPa uniaxial pressure.

![Figure 4.21](image)

**Figure 4.21:** X-ray diffraction pattern for Cu-48 wt% Zn powder heat treated at 100 °C for 5 minutes.
Figure 4.22: X-ray diffraction pattern for Cu-48 wt% Zn powder ball-milled for 5 minutes.
5. CONCLUSION

The objective of this work was to study the phase evolution in Cu and Zn powder mixtures subjected to UPC in comparison with that in Cu and Zn powder mixtures subjected to ball milling. The following results have been obtained during this study:

1. Systematic UPC experiments with a Cu-48wt% Zn powder mixture at different nominal processing temperatures have shown that the densification and bonding between powder particles increase with increasing temperature and vibration time.

2. Consolidated samples made at and above 200 °C exhibited a reaction zone, composed of an intermediate phase identified as γ-brass (Cu₅Zn₈). The growth of the γ-brass increased with increasing temperature and vibration time.

3. The γ-brass region exhibited dark linear features that coincide with the prior particle boundaries of the Cu powder particles and are terminated at some distance from the interface with the remaining Cu in the sample. This implies that the regions of the γ-brass that contained the dark features were created by the diffusion of Zn into the Cu and that the gray regions that extend beyond the dark features were created by the diffusion of Cu into the Zn.

4. The dark features in the intermediate phase regions were largely eliminated in the sample consolidated at 300 °C and with 4 s of vibration.

5. UPC of Cu-Zn powder mixtures with Zn contents from 10 to 40 wt% all produced γ-brass, suggesting that the phase selection in UPC Cu-Zn is not affected by the
global chemical state of the material. Rather, it is an event governed by the local state at the Cu-Zn interface in the powder mixture.

6. When a Cu-Zn powder mixture is subjected to UPC, interdiffusion, enhanced by the high excess vacancy concentration, causes a rapid increase in the Cu concentration in the Zn and the Zn concentration in the Cu at the Cu-Zn interface. Since the substitutional diffusivity is proportional to the vacancy concentration, the diffusivity is increased over the normal value by as much as several orders of magnitude. This permits the interfacial Cu concentration in the Zn to exceed the usual equilibrium solubility of Zn in the hcp Zn-Cu solid solution above which the ε phase can form, or even the metastable solubility above which the γ-brass phase can form, yielding a large driving force for the nucleation of γ-brass in the Zn at the interface.

7. Zn diffusion into the Cu would also be significant, but was not sufficient to cause fcc β-brass (CuZn) to nucleate because of the much larger solubility of Zn in Cu.

8. Ball milling of Cu-48wt% Zn powder mixture for 10 h caused β-brass, the equilibrium phase at the composition, to nucleate directly between Cu and Zn, but with much slower growth than the γ-brass growth in UPC.

9. Ball milling or heat treatment may be used as a pre-treatment to cause β-brass to nucleate in the Cu and Zn powder mixture, so that the β-brass can grow in the pre-treated powder mixture when subjected to UPC.
REFERENCES


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