

Thermal behavior of supersolidus bronze powder compacts during heating by hollow cathode discharge

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Abstract

Porous aluminum–bronze compacts formed from prealloyed metastable (supersolidus) powder were heated either by plasma or by a resistive furnace technique. The plasma heating was performed in two different setups: (i) Hollow Cathode Discharge (HCD) method and (ii) Shielded Cathode Discharge (SCD) method. All experiments were carried out for 12 min in hydrogen at temperatures ranging from 673 to 1323 K. In HCD, for temperatures above 773 K, a fully filled, non-porous region was obtained in the center of the compacts, exhibiting a quite different behavior than that obtained using either SCD or resistive techniques. In these cases, uniformly dispersed condensed micro-regions were detected in samples treated at temperatures higher than 1223 K. These observations are discussed in terms of the heating mechanism, mass transfer and behavior of supersolidus powder particles. A simple physical model for the creation of the central fully filled region obtained by HCD is introduced.

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1. Introduction

Sintering of new materials with novel structures and properties has been a focus of researchers around the world in the last few decades. Materials with controlled porosity (size, shape and distribution) such as cellular metals and metal foams have been developed [1]. New progressive techniques have been tested and recently the use of a plasma medium has been recognized to be advantageous in the preparation of hyperfine powder [2], synthesis of new ceramics [3,4] and in the heat treatment of compacted powders and sintered materials [5]. However, a material placed in plasma is exposed to a complex and hostile environment. This includes interaction with photons, bombardment by electrons, ions, atomic and molecular neutrals and radicals in ground and excitation states. In Ref. [6], many different possible interactions of plasma particles

with material surface and subsurface regions are described, including (i) surface diffusion, (ii) adsorption, reactions on the surface, desorption and reflection, (iii) nucleation and growth, (iv) sputtering, (v) implantation and collisional mixing, (vi) secondary electron emission, and (vii) surface and near-surface damage and others. In many cases, depending on the process parameters, a combination of these effects can take place during plasma treatment. A large portion of the energy introduced by particle bombardment is used to heat-up the material [7]. The nature of heating the samples is very different from that of conventional heating (e.g., resistive, flame and induction). Knowledge of the type of plasma, the particles involved, their fluxes and energy distributions is of primary interest. However, due to the complexity of the plasma processes and plasma–material interaction, not all these information are well known. That is why, for some of the observed phenomena in plasma–material processing, there is only a qualitative or semiquantitative understanding.

Thermal treatment by plasma of samples formed from traditional metal powder particles is discussed in various

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papers, e.g. [8,9]. However, none of these studies were of samples made from metastable metal powder particles created by a rapid cooling process.

In this paper, we present results obtained during hollow cathode plasma heating of porous aluminum–bronze compacts formed from rapidly cooled powder particles (supersolidus). Comparison of these results with simple resistive heating will also be shown. A simple physical model of the material behavior during the plasma process is discussed.

2. Experimental setup

The raw prealloyed aluminum–bronze powder produced by rapid solidification (supersolidus) containing Cu–9 wt.%Al–1 wt.%Fe was supplied by P/M Ind. & Com. Ltd. As can be seen in Fig. 1, the particle shapes are very irregular. The size of the powder particles varies between 38 and 150 μm (particle size distribution in Fig. 2) as obtained by the sieve method. The as-received material was pressed at 100 MPa in a single action die to produce cylinders of 10×6 mm (diameter \times height). The density of the samples was estimated to be 3.2 g cm^{-3} , corresponding to porosity of 50%. The porosity was measured by direct optical observations.

The experimental apparatus used for plasma heating is shown in Fig. 3. It consists of a vacuum chamber containing an anode and a hollow cathode, in which the sample is placed [10]. The distance between the cathode and the sample was 6.5 mm. Two setups, each one characterizing a different heating process, were used.

- 1) Hollow Cathode Discharge (HCD): the sample inside the crucible (23×15 mm; diameter \times height) is fully immersed in the plasma.
- 2) Shielded Cathode Discharge (SCD): the same crucible is used and covered by a metallic grid creating



Fig. 1. As-received bronze powder.

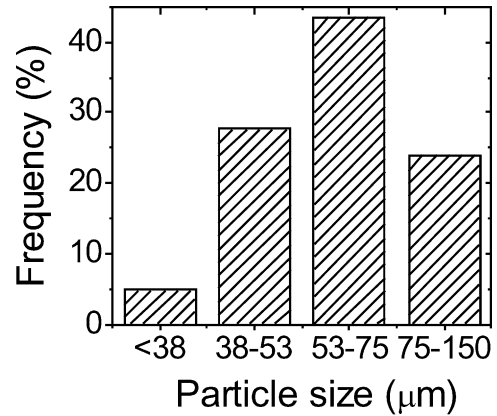


Fig. 2. Particle size distribution for the as-received bronze powder.

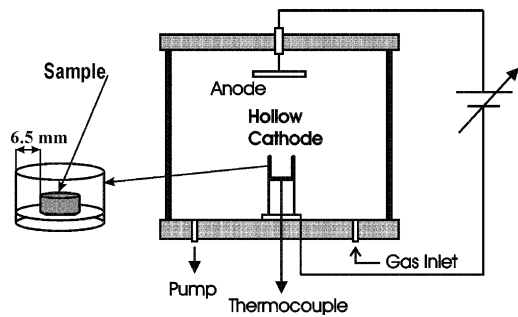


Fig. 3. Schematic illustration of the HCD system and the placement of sample inside the crucible.

a Faraday cup. This configuration does not allow the plasma to enter the crucible. However, the hot gas atmosphere enters and interacts with the sample.

For comparison, conventional sintering (CS) was performed in a common resistive furnace.

As shown in Table 1, all samples were treated for 12 min in flowing hydrogen. The flow of hydrogen was held

Table 1
Sintering conditions for all samples

Procedure	Pressure (Pa)	Atmosphere	Temperature (K)	Time (s)
HCD	700	H_2	1113	720
			1013	
			933	
			773	
			743	
			723	
			703	
			673	
SCD	700	H_2	1323	720
			1113	
			1013	
CS	1000	H_2	1323	720
			1223	
			1113	

constant at 15 sccm for all experiments. The temperature was measured by a chromel–alumel thermocouple inserted in the substrate holder, as indicated in Fig. 3. The temperature in the HCD and SCD procedures was controlled by varying continuously the voltage between the electrodes, e.g., the 673–1113 K temperature range corresponds to values of 400–700 V. To achieve maximum ionization, the pressure was adjusted to 700 Pa.

All samples were analyzed by a Olympus optical microscope, model BX60M and by a Phillips Scanning Electron Microscopy (SEM), model XL 30 ESEM equipped with an energy dispersive X-ray (EDX) analyzer for measuring elemental composition.

3. Why plasma medium?

As already indicated in Section 1, compacts placed into a plasma meet an environment completely different from that encountered in other classical forms of heating. In general, the total power input P_{in} at the compact surface is the surface integral over the sum of different contributions J_v (energy fluxes per time and area) [7]:

$$P_{\text{in}} = \int (J_{\text{rad}} + J_{\text{ch}} + J_{\text{n}} + J_{\text{ads}} + J_{\text{react}} + J_{\text{ext}}) dA, \quad (1)$$

where J_{rad} is the heat radiation towards the surface, J_{ch} the power transferred by charged carriers (electron and ions), J_{n} the contribution of neutral species of the background gas, J_{ads} the energy released by adsorption and condensation, J_{react} the reaction energy of exothermic processes (molecular surface recombination) and J_{ext} the power input by additional external sources (e.g., resistive heating).

Energy delivered by ion and fast neutral bombardment has been identified as the dominant contribution to the heating process in low-pressure glow discharge treatment (in our case, a process not present in SCD and CS) [11]. Between the glow and the substrate is a narrow region called the sheath or the cathode fall region (typically 0.01–1 cm, depending primarily upon pressure, power and frequency), in which the potential changes from the slightly positive plasma potential U_{pl} to the negative substrate surface U_{s} (or cathode) potential. Positive ions that diffuse to the sheath edge are accelerated towards the surface of the compact. Because of the existence of this voltage drop in the sheath region, the ions acquire energy

$$E_i = e|U_{\text{pl}} - U_{\text{s}}| \text{ (eV)}. \quad (2)$$

This energy is modified by the number of collisions (related to gas pressure) in which the ion loses its energy whilst traversing the sheath. These collisions are dominated by symmetrical charge transfer in which an energetic ion interacts with its neutral counterpart

producing a fast neutral and an identical ion with essentially zero energy, which is in turn accelerated by the electric field. Energies of arriving particles typically range between a few electron volts and several hundred electron volts. The total energy flux of ions and fast neutrals is then given by the product of particle flux density (j_i for ions, $j_{\text{n-fast}}$ for fast neutrals) at the surface and the mean particle energy:

$$J_i = j_i \bar{E}_i, \quad J_{\text{n-fast}} = j_{\text{n-fast}} \bar{E}_{\text{n-fast}}. \quad (3)$$

Electrons are repelled from the cathode and only those having sufficient energy (i.e., those in the high-energy tail of electron energy distribution) reach the surface, but with reduced energy and significantly lower flux density than that of the ions. Furthermore, the momentum associated with electrons is much less than that of positive ions and fast neutrals or metastable species. Heat radiation (whose photons are also of low momentum), however, is estimated to contribute as much as 5–10% to the total energy delivered to the material treated by low-pressure glow discharge [7].

The particle bombardment is a strongly nonequilibrium process. Upon contact with a surface, particles can release a significant part of their energy, producing pressure and thermal spikes. For example, 3283 K spikes and pressures of 1.3×10^{10} Pa (1.2×10^5 atm) for 7×10^{-11} s have been calculated for impinging particles with an energy of 100 eV [12]. Such pressures and spikes affect the results of the process taking place at the surface in contact with the plasma and are the reason for a frequently observed surface densification, sputtering of the target material, intense heating, formation of metastable materials on the surface, surface structure damage, etc. Batista et al. [5] heated compacts made of Fe powder at 1120 °C (1393 K) in a 80%Ar–20%H₂ gas mixture for 20 min. A high-density region near the surface was seen using SEM. In our case, however, pure H₂ was used as the plasma medium and no densification near the surface of any sample was observed. In fact, we detected higher porosity near the surface as will be shown later.

The hollow cathode effect is a special situation for the glow discharge between two closely separated cathode surfaces (in our case, this is the space between the inner wall of the crucible and the sample ~ 6.5 mm, which are both on the same negative potential). This effect occurs when the dimension of the cathode fall region becomes as large as the separation distance. The loss of electrons is low because they are repelled by negative walls of the cathode and in fact, they oscillate between the sample and the wall. The plasma density (i.e., the electron concentration) increases and reaches values of about 10^{12} cm^{-3} [13]. As a consequence, the production of ions rises too and the ion flux density at substrate surface increases. Depending on the separation distance, the gas pressure and the plasma density, the gas inside

the hole can be heated to extremely high temperatures affecting the surface temperature of treated sample.

4. Results and discussion

Observations by optical and electron microscopy revealed that the CS and SCD samples exhibit behavior quite distinct from the HCD sample when treated at the same elevated temperature. Fig. 4, obtained by optical microscopy, displays the structure of three samples (CS, SCD and HCD) heated to the same temperature of 1113 K. The CS and SCD samples exhibit a uniform porous structure, which is similar to that observed before heating. In contrast, the HCD sample shows a dense, non-porous region surrounded by voids and a shell whose porosity has increased over that of the untreated sample. This effect was observed at all temperatures above 773 K. As can be seen in Fig. 5, obtained by SEM, it is possible to further resolve the structure into: (1) an inner dense, non-porous region, (2) an intermediary one with a moderate porosity and (3) an external one with a high porosity. We did not detect any change in the weight of samples after treatment.

The formation of the central dense region with highly porous shell in samples treated by HCD is rather unexpected. It suggests the existence of mass transfer from the edge to the central region of the sample during plasma heating, since the weight of the samples, as indicated above, has not changed. This raises the question of the nature of this mass transfer. Diffusion as a dominant process is ruled out because of insufficient time. However, the formation of a liquid phase and its transfer by capillary force to the central part may be possible.

We now examine a possible physical model for the central region formation during HCD treatment. We will follow the idea that due to the intense plasma particle bombardment, the temperature of the surface region of the compact increases rapidly and (i) reaches a temperature sufficient for melt formation, and (ii) creates a temperature gradient in the treated compacts. Note that the sample temperature during HCD (and also during SCD) treatment was measured by a thermocouple inserted in the substrate holder in the vicinity of the compacts. Our very recent measurements with thermocouples inserted directly in the compacts show that, when the temperature 0.5 mm from the bottom of the sample was 728 K, the temperature 1 mm from the top was 325 K higher [14]. In case of SCD, only about 45 K thermal difference was obtained. This implies that the temperature at the substrate surface during HCD treatment will approach or even exceed the melting points of pure Al (~ 933 K) and Cu (~ 1357 K).

The supersolidus aluminum–bronze powder from which the samples are compacted possesses a very

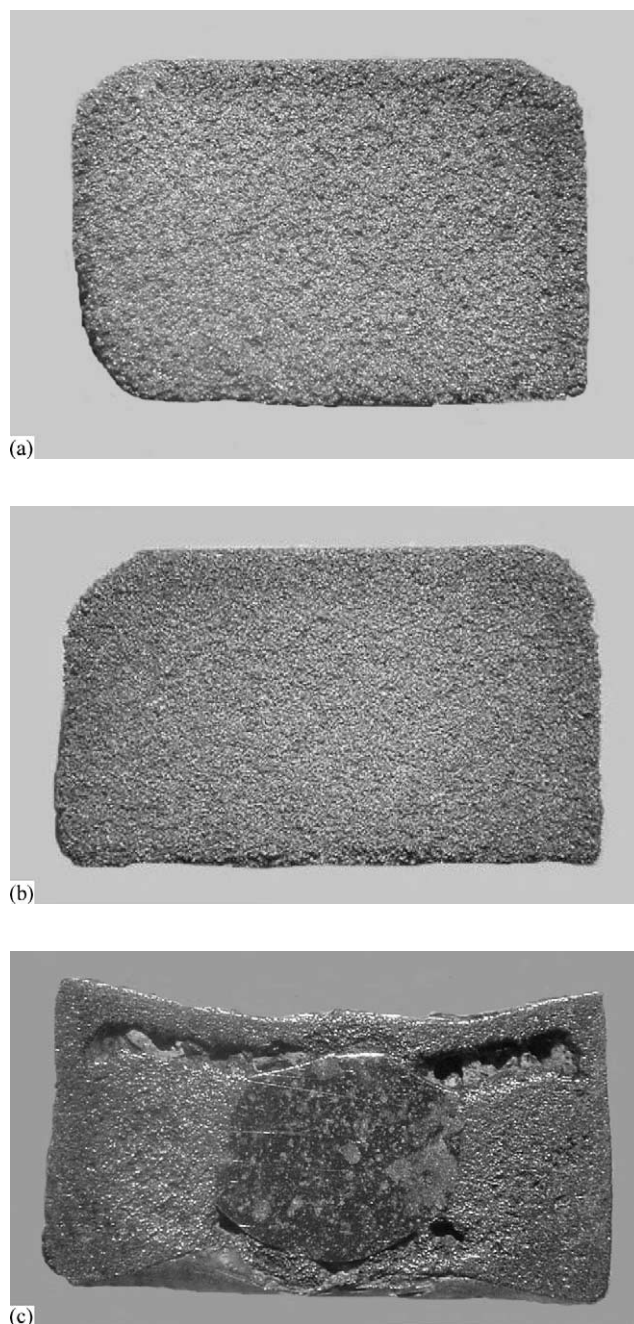


Fig. 4. Optical micrographs of samples heated to 1113 K by (a) CS, (b) SCD and (c) HCD. Scale: the height of the sample (6 mm) does not change during the cutting of the sample.

interesting property. Because it is produced by a rapid cooling process, it contains an Al-rich central region [15,16]. This structure is metastable. When such a powder is heated, the particles break, due to a difference in volume expansion, and the Al-rich central region melts at a temperature below 1323 K (the upper limit given by the Cu–Al phase diagram for Cu–10 wt.%Al). This decomposition is very fast for supersolidus materials and is, in fact, the inverse process of its rapid creation (solidification), with a velocity reaching a value

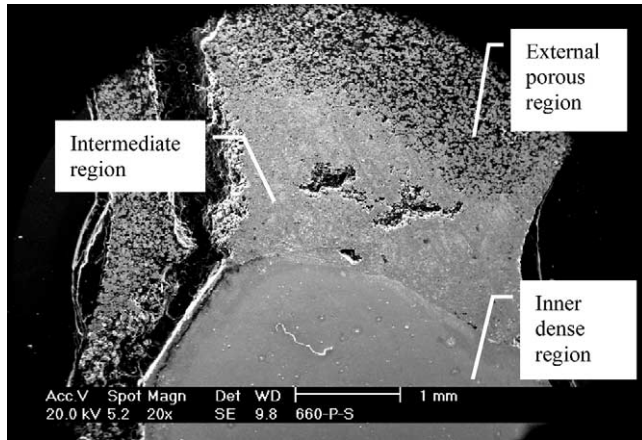


Fig. 5. Detailed SEM image of HCD sample heated to 1113 K.

between 10 and 100 ms⁻¹ [17]. In our case, direct SEM observations of different parts of the surface and near-surface region show many broken particles such as in Fig. 6.

We believe that the central dense region is formed by the flow of either melted Al or Al–Cu melt from the hot surface region to the center. EDX analysis of the near-surface region reveals that the concentration of Al drops down to ~2 wt.% providing clear evidence of the mass disappearance. However, the transfer of a small amount of Al from the near-surface region may not be sufficient

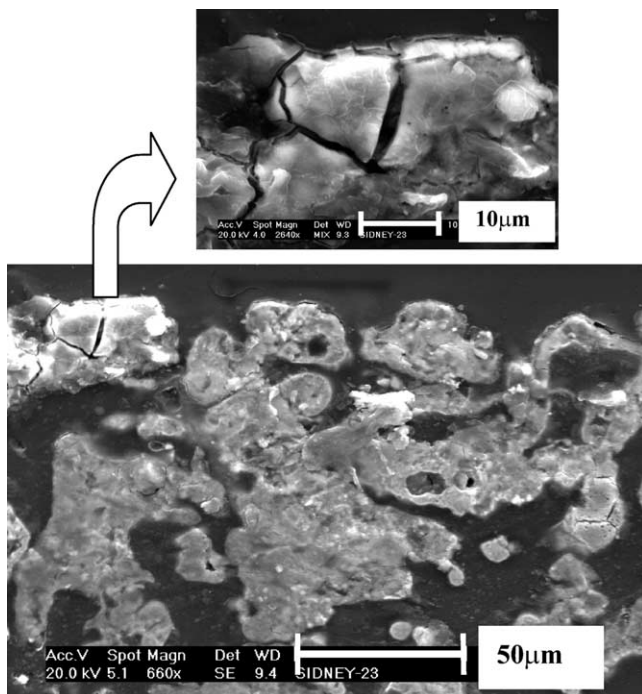


Fig. 6. SEM image of compact surface region showing particle breakdown.

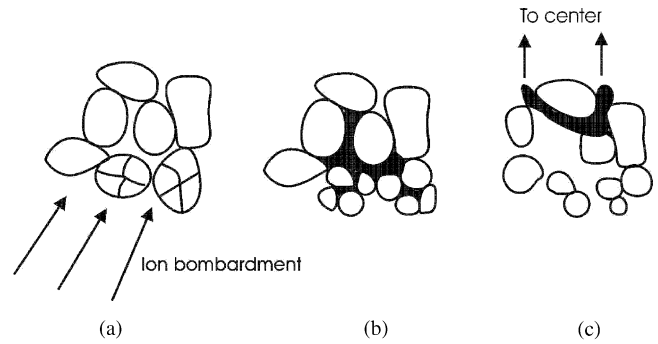


Fig. 7. Illustrative physical model of the process showing (a) plasma particles bombardment at compact surface, (b) supersolidus powder particle fragmentation and melt formation, and (c) liquid transfer.

to explain the central region formation and we suggest that Cu also contributes to the mass flow.

Melting at the substrate surface and the existence of the temperature gradient creates a pressure gradient, the driving force for the capillarity. Melted material travels by capillarity towards the central region. The liquid fills the pores in the central region without the surrounding particles being melted (because the temperature there is low).

The above-discussed mechanism is illustrated in Fig. 7 with these steps: (i) The ion bombardment (Fig. 7a) triggers thermal spikes in the supersolidus particle. This leads to particle fragmentation and melt formation (Fig. 7b). (ii) The liquid travels by capillary forces to the central region (Fig. 7c). (iii) Liquid fills the pores and solidifies.

In comparison with HCD, SCD and resistive heating do not involve ion and fast neutral particles bombardment at the compact surface. In SCD, the plasma is separated from the compacts by a mesh, allowing only radiation and neutral particles in basic and metastable states to reach the surface. With no additional acceleration, this particle bombardment does not create thermal spikes and there is no significant temperature gradient formation. With a relatively uniform temperature throughout the samples, the porous aluminum–bronze compacts start to melt homogeneously at equilibrium sample temperature higher than 1223 K and only uniformly dispersed condensed micro-regions formations are detected.

5. Conclusion

The present experiments show the difference between thermal treatment by conventional and plasma procedures for supersolidus powder. While the porous aluminum–bronze compacts are homogeneously melted by resistive heating and SCD at a uniform sample

temperature higher than 1223 K, in plasma (HCD) a fully filled region is observed at temperatures above 773 K (measured in the substrate holder). Strong energetic plasma particle bombardment is believed to melt the surface region and to create a thermal gradient. A simple physical model for the formation of the melted region in HCD is proposed with these main steps: (i) melt formation at compact surface, (ii) material transfer, and (iii) resolidification.

The observed phenomena are believed to be due to the nature of plasma heating, which involves mass transfer by capillary forces and the metastability of powder produced by rapid solidification.

We suggest that this kind of phenomenon (appropriately controlled) can be used in material processing where functional gradient is important, such as, for example, in the production of graded cellular metals and metal foams.

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