Microstructure of Plasma-Sintered Aluminum Bronze Powder Compacts

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Abstract: Porous materials are successfully utilized for fabrication of many industrial components such as filters and selflubricating bearings. These products are made by powder metallurgy, where mixed or prealloyed powders can be used. The aluminum bronze is one of the most wanted due to its excellent properties in combination with low cost of the raw materials. In this work, single action compacted (100 MPa) prealloyed aluminum bronze (Cu-9wt%Al-1wt%Fe) cylinders were sintered using a hollow cathode discharge at temperatures between 400 and 750 °C with duration on the isotherm for 12 min. Microstructure changes, homogeneity, porosity and composition were analyzed after the treatment. Sintering below 550 °C led to uniform but porous structure. Above 550 °C it was observed a solidified central region and a porous structure that changes slightly throughout the cross-section. The diameter of the central region increased with treatment temperature. It is concluded that due to the intense plasma heating and subsequent surface melt formation a mass flow direction to the center of compacts occurred.

Introduction

Sintered aluminum bronze is a porous metal material, which due both the low cost of the raw materials and very interesting properties (such as higher mechanical strength, heat, corrosion and oxidation resistance in comparison to tin bronzes) is one of the most wanted systems for preparation of filters and autolubricating sleeves for sliding bearing [1]. Depending on the application, the porous structure with interlinked pores can be prepared either homogeneous or gradient [2]. Porous structure allows passing of fluids while not permitting fluid-inclusions down to certain diameter to pass to the other side. Such filters are used in food and beverage production, cryogenic, pharmaceutical, chemical processing industry and others [3]. The autolubricating sleeves for sliding bearing contain certain amount of absorbed lubricating oil. They are frequently employed for components with frequent rotational movement, such as motors, cars, trains, airplanes, ships, mining, agriculture and other industry machines, eletrodomestic systems and tools, etc. [3,4]. Outside of the porosity factor these porous metal materials possess excellent mechanical properties, good thermal conductivity, shock resistance and relatively low friction coefficient etc. [5]. Other porous metal materials of choice include: tin bronzes, stainless steel, nickel, aluminum and titanium and their alloys [4-5].

The use of aluminum bronze is relatively new in substituting higher-cost tin bronze material [6]. The use of prealloyed powders has been found advantageous because higher final density resulting in higher mechanical strength as compared to traditional powder metallurgy products can be reached [7]. Prealloyed powder is usually obtained by atomization (liquid alloy drop cools rapidly forming an alloy particle with core rich in copper and a shell rich in aluminum) and is frequently denominated as supersolidus [7]. A process which uses supersolidus sintering at temperatures between solidus and liquidus, is termed supersolidus liquid phase sintering (SLPS). It involves liquid formation inside the particles which spreads
to the particle contacts. Resulting capillary forces are responsible for the viscose liquid flow and high densification of sintered products during SLPS [7].

Outside of the isothermal sintering temperature, very important process factor is heating rate. Conventional heating processes can be substituted by plasma treatment, which offers higher heating rates [8]. Advanced surface modification processes that use thermal (such as arc) and non-thermal (such as glow discharge) plasmas have undergone substantial industrial development over the past several decades [9, 10]. A DC glow discharge is usually generated between two separated planar electrodes (a negatively charged cathode and an anode in most cases at the ground potential) placed in a chamber of low-pressure gas [9, 10]. Ions, electrons and active neutral species are formed after the breakdown of the gas. These active particles not only interact with each other within the plasma medium, but also with surfaces in contact with the plasma. In fact, the sample placed in the plasma is exposed to a complex and hostile environment. This includes interaction with photons and bombardment by electrons, ions, atomic and molecular neutrals and radicals in ground and excitation states. 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, 3000 °C spikes and pressures of $1.3 \times 10^{10}$ Pa ($1.2 \times 10^5$ atm) for $7 \times 10^{-11}$ s have been calculated for impinging particles with an energy of 100 eV [11]. 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 high heating rate, frequently observed surface densification, sputtering of the target material, formation of metastable materials on the surface, surface structure damage, etc.

In this work prealloyed aluminum bronze (Cu-9wt%Al-1wt%Fe) cylinders were sintered using a hollow cathode discharge. The effect of temperature on the microstructure changes, homogeneity, porosity and composition of sintered samples was studied.

**Hollow Cathode Discharge**

The hollow cathode discharge (HCD) used in the present experiments is based on the specially designed cylindrical structure of cathode (Fig. 1).

![HCD diagram](image)

Fig. 1 – Plasma sintering system. (a) The hollow cathode discharge. (b) Detail of compact placement inside the crucible.

In fact, this type of discharge appears also in holes drilled in the cathode or between any other closely separated cathode surfaces (typically several millimeters to about three centimeters in distance) at low gas pressures (typically 100 to 800 Pa) [12]. Due to such design of a cathode the loss of electrons (to the surfaces) is low because they are repelled by the negative potential of the cathode walls. In fact, the electrons oscillate in between the walls...
before they recombine with positive ions or escape out of the cavity. The plasma density (that is the electron concentration, ne) increases and reaches values of about $10^{13}$ cm$^{-3}$ (from typical $10^8$ to $10^{11}$ cm$^{-3}$ at such pressures) [12]. It means that degree of ionization ne/ng (electron concentration over concentration of neutral gas particles) rises and reaches values of about $10^{-3}$. As a consequence, the production of ions rises too and the ion flux density at the cathode surface increases. High luminosity of the glow can be seen inside the hollow cathode in comparisons to the rest of glow covering exposed cathode surfaces (Fig. 1a). Depending on the distance between cathode surfaces ($d_{cc}$), the gas pressure ($p$) and voltage applied ($U$), the gas inside the hollow cathode can be heated to high temperatures. For adjusted process parameters ($U$, $p$ etc.) the samples placed inside the hollow cathode will be treated at intensified conditions (higher gas ionization and current density approaching that of arc) in comparison to regions outside the cavity.

**Experimental setup**

The raw prealloyed aluminum bronze “supersolidus” powder produced by rapid solidification (atomization) containing 90wt%Cu, 9wt%Al and 1wt%Fe was supplied by Metalpó Indústria e Comércio Ltda. The powder presented irregular shapes. The particle size distribution was obtained using 325-mesh. Powder was pressed uniaxially using 100 MPa in a cylindrical matrix to obtain compacts 10 mm in diameter and 6 mm high. The green density of the samples was estimated to be 3.5 g/cm$^3$.

The system used for plasma sintering (Fig. 1) consists of a laboratory built high voltage DC source (maximum output 1500 V, 2 A), a vertically mounted cylindrical vacuum chamber (19 cm in diameter and 30 cm in height, made of borosilicate glass closed from both sides by stainless steel flanges), gas input and evacuation components, and process parameter sensors and controllers. Plasma was generated between a negatively polarized bottom electrode (cathode) isolated electrically from the rest of the system and an anode electrically connected with top flange, both held at ground potential. In the present experiments the top electrode’s actual size, geometry and its distance from cathode were insignificant. Fig. 1b shows how the sample (well centralized) was immersed in the plasma inside the hollow cathode crucible (23 x 12 mm - diameter x height, made from stainless steel). The distance $d_{cc}$ between the cathode walls and the sample was 6.5 mm in all experiments. Before each treatment, the system was pumped down by a two-stage mechanical pump until a residual pressure below 10 Pa was reached. Thereafter, dry hydrogen (99.99%) was introduced and its flow adjusted to $2.5\times10^7$ m$^3$s$^{-1}$ (15 sccm) using mass flow controller. Treatment pressure of 800 Pa, measured by a barocel capacitance manometer, was adjusted by manual valves. The specific treatment conditions (temperature, voltage, current and time) of all experiments are shown in Table 1.

**Table 1: Sintering conditions**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>Heating run-in time (min)</th>
<th>Time at isotherm (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>A2</td>
<td>400</td>
<td>590</td>
<td>0.19</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>A3</td>
<td>450</td>
<td>615</td>
<td>0.25</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>A4</td>
<td>500</td>
<td>570</td>
<td>0.28</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>A5</td>
<td>550</td>
<td>625</td>
<td>0.40</td>
<td>35</td>
<td>12</td>
</tr>
<tr>
<td>A6</td>
<td>600</td>
<td>640</td>
<td>0.49</td>
<td>35</td>
<td>12</td>
</tr>
<tr>
<td>A7</td>
<td>700</td>
<td>590</td>
<td>0.72</td>
<td>80</td>
<td>12</td>
</tr>
<tr>
<td>A8</td>
<td>750</td>
<td>600</td>
<td>0.80</td>
<td>75</td>
<td>12</td>
</tr>
</tbody>
</table>
The treatment temperature (measured by chromel-alumel thermocouple inserted in the cathode in the vicinity of the reaction zone where the compacts were treated) was adjusted by varying the DC voltage applied between the electrodes. Samples were plasma sintered at 400, 450, 500, 550, 600, 650, 700 and 750 °C for 12 minutes at the isotherm. Run-in time between 15 and 80 minutes was necessary to stabilize the treatment temperature. After the treatment the plasma was turned off and the sample was left inside the chamber to cool down for about 30 minutes (initial 15 minutes of cooling in flowing hydrogen, the rest time in vacuum). Then the chamber was opened and the compact was taken out for microstructural characterization.

After the sintering compacts were cut (along their vertical axes) and the exposed surfaces treated by a chemical reagent made of 5 g FeCl₂, 2 ml HCl and 95 ml ethanol for microstructural analyses, which was carried out using Olympus BX60M optical microscope and a Philips XL 30 Scanning electron microscope (SEM). Some of the photos were obtained also using Sony digital camera (Mavica 90) coupled with a magnifying glass. Porosity was calculated using simple program analysing image obtained by optical microscope.

**Results and Discussion**

The Fig. 2 shows structures of samples A2, A5 and A6 sintered at temperatures of 400, 550 and 600 °C, respectively in comparison with only-compacted, not plasma-treated sample A1.

![Fig. 2 – Structure evolution of plasma-sintered compacts. Samples are cut in the middle along their vertical axes. Rectangular area 10x6 mm (diameter x height of the compact) of the internal structure is revealed. (a) Not-sintered sample; Samples sintered at temperatures of (b) 400 °C, (c) 550 °C and (d) 600 °C.](image)

All samples were cut in the middle along their vertical axes. Rectangular area 10 x 6 mm (diameter x height of the compact) of the internal structure was revealed. Compact A2 treated at 400 °C exhibits uniform porous structure which is similar to that observed of not plasma-treated sample A1. The same structure characteristics were also observed for samples A3 and A4 treated at 450 and 500 °C, respectively. During the cutting of the sample A1, frequent particle detachment occurred; on the other hand, during the cutting of plasma treated compacts A2, A3 and A4, the particles clearly held together indicating for consolidation of the particles.
Samples A5, A6, A7 and A8 plasma-treated at temperatures of 550 °C (Fig. 2c), 600 °C (Fig. 2d), 700 and 750 °C, respectively show a dense, non-porous central region, which size increases with treatment temperature. Detailed SEM observation of the structure of samples A2 (Fig. 3a) and A6 (Fig. 3b) show that the porosity of the structure of sample A2 (and also A3 and A4) changes slightly through out the cross-section, while porosity gradient such as in Fig. 3b is clearly visible for sample A6 (and also for A5, A7 and A8).

![Fig.3 – SEM images showing details of the structure of sample treated at (a) 400 °C and (b) 600 °C.](image)

Several specific regions can be identified: (1) a dense, non-porous central region (the one already identified using optical microscope), (2) near-central region, (3) intermediate region with a moderate porosity and (4) an external shell-like region whose porosity has increased over that of the untreated sample. Samples treated at highest temperatures of 700 and 750 °C are more deformed and they exhibit some extensive internal empty spaces. A simple physical model explaining the formation of the dense and non-porous central region obtained specifically using hollow cathode discharge treatment was introduced by C. Alves Jr. et al. [13]. The mechanism consists of these steps: i) The ion bombardment triggers thermal spikes in the supersolidus particle at substrate surface. This leads to particle fragmentation and melt formation. (ii) The liquid travels by capillary forces to the central region. (iii) Liquid fills the pores and solidifies. The model requires that (1) the temperature at the substrate surface during HCD treatment will approach or even exceed the melting point of supersolidus is 1323K and (2) temperature gradient in the treated compacts exists. Note that the sample temperature during HCD 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 450 °C, the temperature 1 mm from the top was 320 °C higher [14]. Plasma treatment is strongly nonequilibrium process allowing reaching rapidly high temperatures at substrate surface, melting it and provoking the above-mentioned process while the central region is still at lower temperature.

In Fig. 4 details of the regions indicated in Fig.3b of the sample A6 are shown. Fig. 4a shows that the central dense region exhibits lamellar structure formed by rapid cooling process from liquid phase. It indicates that the central region was filled by molten material before it solidified. Fig. 4b shows the near-central region with clear evidence that the process of densification would continue and the central region would grow if there would be enough time at the treatment temperature. Fig. 4c is specifically interesting image because it shows something which seems to be a solidified liquid in between the not molten or only partially molten original particles. A surface region is shown in Fig. 4d. An increase of the size of voids with round shape is evident. It indicates that many particles were molten and that the material was lost by liquid flow through the pores presumably to the center.
Fig. 4 – Details of the regions indicated in Fig. 3b of sample treated at 600 °C. (a) Image from optical microscope showing dendritic structure of the central region. SEM images of the (b) near-central region, (c) solidified liquid flowing in between not molten or only partially molten original particles in intermediate region and (d) large round shape voids in the external surface regions.

Conclusions

In this work we show that samples treated at temperature of 500 °C and below (measured by thermocouple inserted in sample holder) have uniform, but porous sintered structure with no indication of liquid phase formation while compacts sintered at temperature of 550 °C and higher presented central dense region formed by liquid transfer by capillary forces from melted surface region. The porosity gradient increased with treatment temperature.

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References