SINTERING IN GLOW DISCHARGE (PLASMA SINTERING)

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Abstract
Glow discharge as heat source for sintering has been recently investigated. Abnormal glow discharge, hollow cathode discharge and shielded cathode discharge have been applied for sintering iron, steel, non - ferrous alloys, and reinforced metal-matrix composites. The process can be carried out in a relatively simple apparatus - a vacuum chamber - and the process parameters, as e.g. the temperature and heating rate can be controlled by the voltage and pressure of the applied atmosphere a higher degree of surface densification and changes in the surface morphology were observed. These effects are ascribed to the enhanced condensation of atoms resulting from sputtering and the activated surface diffusion resulting from the ion bombardment of the sample surface. Lubricant and binder removal in glow discharge were also successfully tested.
Keywords: sintering in glow discharge, plasma sintering, hollow cathode discharge, abnormal glow discharge, shielded cathode discharge

INTRODUCTION

In the search for more efficient processes and more appropriate properties of sintered products, new sintering techniques have been developed. Activated sintering is one of the possibilities to alter favourably sintering parameters such as temperature and time or to achieve better final properties. The techniques of activated sintering range from additions of small quantities of chemical activators, radiation treatments to the application of plasma. These activation processes act either altering the kinetics or the driving force of sintering.

Recently sintering of metal powders has been investigated in glow discharge serving as an energetic source [1-3]. The name glow discharge comes from the fact that the plasma produced by applying a potential difference between two electrodes in a partially evacuated tube is luminous. The gas in the tube glows because the electrons originating at the cathode have enough energy to generate visible light by excitation collisions. A material placed in plasma is exposed to the interaction with plasma particles. A significant portion of the energy of these particles is transformed in heat which enables its application for sintering, among other processing possibilities.

In literature, the term plasma sintering is also often used for sintering in glow discharge. One other plasma sintering technique - *spark plasma sintering* - uses pulse electro-discharge, and therefore will not be treated here. Abnormal glow discharge (AGD), hollow cathode discharge (HCD) and shielded cathode discharge (SCD) have been applied for sintering iron, steel, non - ferrous alloys, hardmetal and reinforced metal-matrix composites, mostly by researchers in Brazil [1-10].

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HEATING IN GLOW DISCHARGE

While in the conventional sintering heat is transferred evenly to the sintered body by radiation and convection, in the glow discharge it is produced locally by the collision of plasma particles with its surface.

If the material to be processed is either the cathode or is in contact with it, the following effects will take place: (I) momentum transfer from the ion to the material, giving rise to surface defects; (II) local heat generation by the absorption of the ion's kinetic energy; (III) sputtering of surface atoms; (IV) physical adsorption of ions making possible surface reactions and (V) ion implantation in the processed material. The possible interactions with the material's surface and subsurface regions include also desorption reactions, surface diffusion, nucleation and growth, surface and near-surface damage [11].

The energy balance of Kersten et al. [12] of a body exposed to the action of plasma is expressed in the form of a surface integral:

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

where:

P_{in} - total power input
J_{rad} - heat radiation towards the surface
J_{ch} - power transferred by charged carriers
J_n - contribution of neutral species of the background gas
J_{ads} -energy released by adsorption and condensation
J_{react} - reaction energy of exothermic processes
J_{ext} - power input by additional external sources.

During sintering in glow discharge the powder compact positioned on the cathode is heated principally by bombardment of a flow of ions and fast neutrals (contributions J_{ch} and J_n). The total energy flux of ions (J_i) and fast neutrals ($J_{n\text{-}fast}$) can be expressed as the product of particle flux density (j_i for ions, $j_{n\text{-}fast}$ for fast neutrals) at the surface and the mean particle energy (E_i and $E_{n\text{-}fast}$, respectively) :

$$J_i = j_i E_i \quad (2)$$

$$J_{n\text{-}fast} = j_{n\text{-}fast} E_{n\text{-}fast} \quad (3)$$

The mean particle energy depends on the gas pressure in the tube, power and frequency. A relatively significant contribution is that of the heat radiation, which represents 5 to 10% of the total energy delivered to the material exposed to plasma in a low-pressure glow discharge [12].

The particles when colliding with the surface of the target material release a significant part of their energy, producing pressure and thermal spikes. These pressures and thermal spikes lead among other things to intense heating enabling the application of glow discharge for sintering. The following configurations of glow discharge have been applied successfully for sintering of metal powders:

1. Abnormal glow discharge. In a normal glow discharge the increasing current in a discharge tube leads to a very slow change in voltage. The current density to the cathode remains constant and the current increases by covering a greater cathode region. When the whole cathode is covered by the discharge the current can increase further only by applying more voltage. In the abnormal glow regime the voltage increases significantly with the increasing total current in order to force the cathode current density above its natural value and provide the desired current. A full covering of the cathode in abnormal glow discharge supplies the possibility of uniform heating. With the increasing current and voltage the cathode current density also increases,

heating the cathode and causing incandescence and thermionic emission. The thermionic emission practically transforms the glow discharge in an arc.

2. Hollow cathode discharge. Hollow cathode discharge occurs when two cathode surfaces are separated with a distance equal to the cathode fall region. In this case the loss of electrons in the discharge is low because they are repelled by the negative walls of the cathode, and so oscillate between the two surfaces. This leads to an increase of plasma density and the ion flux density at the surface increases. Controlling the separation distance, gas pressure and plasma density, the gas inside the gap between the two surfaces can be heated to high a temperature which leads to an elevation of their temperature. A significant temperature gradient forms in the heated material due to the thermal spikes
3. Shielded cathode discharge. In shielded cathode discharge the hollow cathode is covered by a metallic grid creating a Faraday cup which impedes the plasma entering. Only radiation and neutral particles in basic and meta-stable states reach the surface. The hot gas, however, enters, and heats the treated material. As a result, no significant temperature gradient is produced.

In abnormal glow discharge the collisions between the ions and hydrogen molecules or argon atoms in the cathode sheath produce a flow of fast neutrals toward the cathode [13]. In the hollow cathode geometry the ionization rate is around ten times higher than in a linear abnormal glow discharge, making it possible to obtain an increased heating efficiency [14].

INTERACTION OF PLASMA WITH THE SURFACE OF A METAL POWDER COMPACT

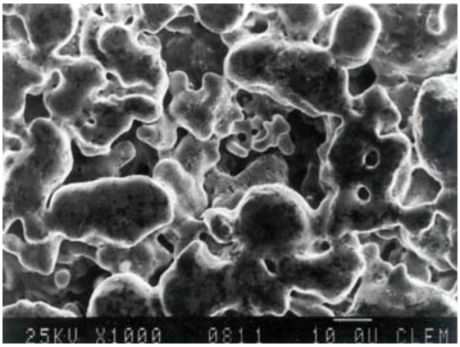
It is believed that the sputtered atoms impinging the surface of the compact activate the diffusion and condensation processes, resulting in a higher surface density. A cleaning effect taking place on the particle surfaces may also contribute to this activation. A higher degree of surface densification in plasma sintered iron compacts was related already in the early works about sintering in glow discharge [2].

A more detailed study in [15] revealed that when the green compact acted as the anode of the discharge, the surface porosity was equal or slightly lower than that measured on a sample sintered in a conventional process. When the sample acted as a cathode of the discharge, the surface porosity decreased significantly as compared with the case of anode configuration. The surface porosity decreased with the increase of the kinetic energy of ions bombarding the sample surface. This was ascribed to the enhanced condensation of atoms resulting from sputtering and the activated surface diffusion of iron atoms resulting from the ion bombardment of the sample surface.

The interaction of the plasma with the surface of the powder compact also results in different surface topography as described in [16,17]. Figure 1 a-b shows the differences in the surface topography of a sample sintered without the interaction with plasma, as well as interaction with it. The reason for these changes originates in the intense ion bombardment.

The exposition of the surface to the action of plasma resulted in the appearance of growth steps and fine open pores. The height of these growth steps was ~1 μm. Through measurements of the surface roughness a significant surface smoothening was found [17]. This implies that by sintering in glow discharge, different surface qualities can be produced exposing the surface to the action of the plasma, or shielding it.

In [4] using an annular hollow cathode geometry deposition of the elements Cr and Ni presence in the outer cathode into the sintered pure iron body was observed. By increasing time, the depth of this enriched layer increased, which makes it possible to intentionally modify the composition of the surface area of the sintered body. On the other hand, in this configuration a certain mass loss in the sintered body was also observed.



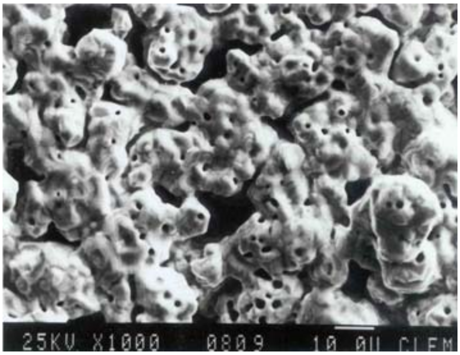


Fig.1. Surface topography of a metal powder compact sintered without the interaction with glow discharge (a) and with the interaction with glow discharge (b).

EQUIPMENT FOR SINTERING IN GLOW DISCHARGE

A relatively simple apparatus can be used for sintering in glow discharge. It consists of a vacuum chamber containing a cathode and anode. Different cathode/anode arrangements are possible depending on the regime employed for sintering. Figure 2 shows the equipment setup for sintering in hollow cathode discharge.

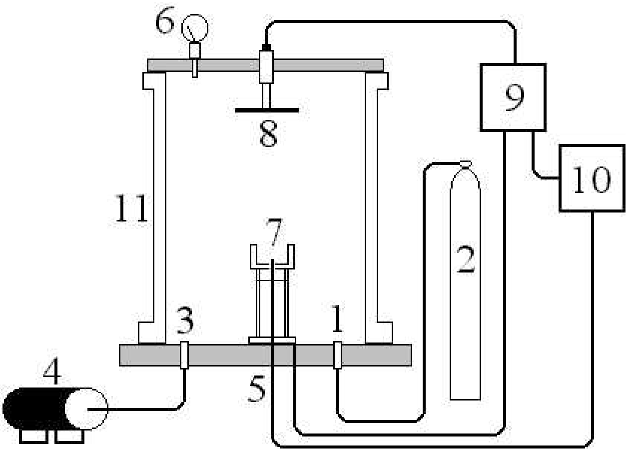


Fig.2. Apparatus for sintering in hollow cathode glow discharge. 1 gas inlet, 2 gas container, 3 vacuum inlet, 4 vacuum pump, 5 thermocouple, 6 pressure measurement, 7 hollow cathode (holder), 8 anode, 9, 10 power source and control units, 11 vacuum - tight tube.

The process parameters as e.g. the temperature and heating rate can be controlled by the voltage and pressure of the applied atmosphere. The sintering is usually carried out in a flow of hydrogen, argon and their mixtures. The advantage of the presence of hydrogen in the mixture enables the reduction of the oxides present in the green compacts for most metals. The related pressure ranges are between 133 Pa and 2660 Pa.

MATERIALS SINTERED IN GLOW DISCHARGE

Iron based systems .Most of the work on sintering in glow discharge was done with iron and steel powder compacts. One of the first works [3] on sintering in linear abnormal glow discharge already related that, due to the activation of the mass transport, a higher surface densification occurs. It was attributed to the back-scattering of atoms sputtered from the surface of the sintered body. In [4] the time dependence of neck growth between the powder particles was accompanied for time periods from 30 to 240 min, and it was found that simultaneously with the neck growth the small pores tended to disappear resulting in an increase of pore size.

Systems by the presence of liquid phase. There are only a few works on sintering with the presence of liquid phase in glow discharge. Copper based alloys such as 90Cu10Sn and aluminium bronze were used for plasma sintering with the presence of the liquid phase [5,6,10]. Density gradients were observed after sintering with the presence of liquid phase, suggesting the possibility of a production of functionally gradient materials from metal powder compacts by this treatment. In [5] was related that a compositionally homogeneous α bronze microstructure was obtained by sintering industrially pressed compacts of self-lubricating bearings in glow discharge at lower nominal sintering temperatures than in the conventional process. A surface layer of higher density was observed in the sintered bearings. In [10] during sintering in hollow cathode discharge a Cu9Al1Fe bronze, a fully filled non-porous region was formed in the central area of the sintered body. The formation of this region was ascribed to the melting of the surface area due to a pronounced temperature gradient in the hollow cathode discharge. This melted volume, due to the capillary forces, penetrated into the central areas with lower temperatures where it rapidly resolidified.

Metal matrix composites. Sintering Fe-NbC composites in glow discharge resulted in a more effective densification (95 % of the theoretical density at 750°C) than in a conventional resistive furnace, where significant densification occurred only above 1240°C [18]. Enhanced densification was observed also in the W-Cu system at 700°C although it was accompanied by copper loss due evaporation and sputtering [19].

LUBRIFICANT REMOVAL AND DEBINDING IN GLOW DISCHARGE

Lubricant removal from green iron compacts by heating them in glow discharge was related by Santos et. al. [20], both in hydrogen and argon atmospheres. They found that the efficiency of the removal increases with an increasing temperature up 350°C, the hydrogen atmosphere being more efficient. Temperatures above 350°C resulted in carbon deposition on the surface of the compacts.

The removal of a polypropylene binder from injected metal parts by glow discharge is related in [21]. The extraction of the binder occurs due to the action of the high kinetic energy of the electrons that dissociate the hydrocarbon molecules. The injected parts are exposed to a gas flow and the light radicals or molecules produced by the dissociation of the binder are pumped out of the furnace. A total removal of polypropylene from the injected body positioned on the anode of a confined anode-cathode hydrogen glow discharge, maintaining the temperature at 400°C, was obtained with a treatment of 10 min. Debinding and sintering can be performed in a unique thermal cycle, using the same equipment. This activated debinding cycle enables one to significantly reduce the processing time in comparison to the conventional vacuum process.

Binder removal using abnormal glow discharge in cemented carbides was related by Escobar et al. [22].

CONCLUDING REMARKS

Sintering in glow discharge can be classified as a process of activated sintering. This activation comes from the fact that the sputtered atoms impinging the surface of the compact activate the diffusion and condensation processes. Higher surface densification and surface morphology changes are the result of this interaction. The localised action of the plasma on the surface region therefore enables one to produce intentionally different properties in the cross section - materials with functional gradients.

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