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Original Research Paper

## Develop an effective oxygen removal method for copper powder

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## ABSTRACT

At present, one of crucial limitations for the hot isostatically pressed (HIPed) Cu-3Ag-0.5Zr alloy, which is used on the combustion chamber liner of aerospace engine, is the high oxygen content, which easily results in the intergranular fracture under high temperature, pressure, liquid hydrogen and oxygen environment during operation. In this study, a novel effective oxygen control method is developed, for which vacuum degassing process is integrated with a flowing hydrogen reduction reaction at an elevated temperature before HIP. For this technique, a container is designed with two gas pipes for hydrogen inflow and outflow, so the hydrogen circulation can be established. Allowing hydrogen to react effectively with oxygen, the oxygen content of HIPed alloy is found to drop significantly from 140 ppm (raw powder) to 28 ppm, which is equivalent to the oxygen-free copper and copper alloys. As a result of the reduction, no prior particle boundaries could be observed in the low oxygen content material. Although the tensile strength of the materials with and without employing this technique does not vary significantly, the ductility of low oxygen content material has improved by about 70% at 500 °C. This significant improvement of ductility is critical to ensure the safety critical PM components.

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## 1. Introduction

Compared to conventional thermal-mechanical manufacturing process for high performance, safety-critical materials e.g. the rocket engines, aero-turbine engines, the powder metallurgy (PM) method provides more uniform and finer grain distribution with minimum segregation, less internal defects, higher material performance, near-net-shape or net-shape final geometry and lower processing cost [1–5]. Nevertheless, the high oxygen content in the prealloyed powder in PM processing is of a great challenge as it can result in considerable reduction in the ductility of formed parts [6–9]. At present, to reduce the oxygen content of powder materials, there are two common methods adopted in the PM process. First, inert gases are used during the atomization of powder formation process to protect powder from reacting with oxygen [7,10–13]. Second, chemical reduction reactions [14–17] are used to extract oxygen from the powder and react with reduction agents such as hydrogen [16] or calcium [17].

Comparing these two methods, the second one has attracted more attention in the PM industry, because it can not only remove oxygen from the powder formation process but also be applied to

the powder storage and transportation processes. For example, Berglund, et al. [16] proposed a novel process for controlling oxygen content within stainless steel powder by using hydrogen, in that a canister with a getter layer and filled powder was evacuated. This canister was subjected to a hydrogen atmosphere at elevated temperatures. The hydrogen atoms diffused into the canister through the walls and formed H<sub>2</sub>O when reacted with the oxygen of the powder. The H<sub>2</sub>O was then reacted with the getter layer. Reacting with the getter materials, an oxide is formed to transfer the oxygen from the powder to the getter layer. Subsequently, the hydrogen atoms within the canister can be diffused out through the canister walls again. Less than 100 ppm oxygen content was reported. Oh, et al. [14] utilised a non-contact calcium pot to remove oxygen from the commercially pure Ti powder. The calcium pot was heated up closing to its melting temperature to react with the oxygen of the powder. The oxygen concentration was reduced to 814 ppm from the initial stage of 2200 ppm. Despite that, these relatively complicated methods, a simpler, more efficient and cost-effective oxygen reduction process is required for the PM industry.

One particular case in the aerospace industry is the combustion chamber (MCC) liner of NASA's space shuttle and rocket main engines [18,19], which are made of high strength and high thermal conductive Cu-3Ag-0.5Zr alloy, also known as NARloy-Z, by the

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PM and hot isostatic pressing (HIP) process. The high oxygen content within the PM/HIP formed MCC is a big structural integrity challenge. The oxidation process preferentially occurs around the grain boundaries with the formation of prioritized zirconium enriched precipitates (Zr as a getter for soluble oxygen in Cu-Ag-Zr alloy),  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  [18,20]. These grain boundaries react with hydrogen to form  $\text{H}_2\text{O}$  around grain boundaries within the propellants combustion (liquid hydrogen and oxygen) and liquid hydrogen cooling environment. This can result in less traceable, sudden brittle intergranular fracture of MCC parts, which is also commonly known as ‘hydrogen disease’, and may lead to a catastrophic disaster.

In this study, a novel and effective oxygen control approach for this Cu-3Ag-0.5Zr alloy is proposed and its feasibility and effectiveness is demonstrated. The variation of oxygen contents, mechanical performance, and microstructure have been obtained and compared.

## 2. Methodology

In this section, one of conventional and low-cost PM/HIP process (rather than the advanced atomizing integrated with HIP processing route with a full closed environment and no air contact) is briefly introduced and then the novel oxygen control process is described. The typical stages in this HIP process consist of powder preparation, classification and preservation, the design and fabrication of the stainless steel container, filling the prealloyed powder into a container, vacuum degassing and sealing of the container, HIP, and subsequent heat treatment [6,7]. It was noticed that three important factors that even with careful control, the powder is inevitably contacted with air and oxidized before container sealing in present PM/HIP case; second, once the powder is sealed within the vacuumed containers, the oxygen content will not change; third, after removing the containers, the free surface of HIPed parts is oxidized during the heat treatment, but can be easily removed. Thus, it was identified that the vacuum degassing before sealing powder into container stage is the key stage which determines the oxygen content of the final formed parts. Also, since the powder is contained within a closed environment, a reduction reaction before vacuum degassing can be effectively taken place. For Cu-3Ag-0.5Zr alloy, since its MCC liner is operated in high temperature and pressure hydrogen environment, high purity hydrogen (99.999%) is selected as the reducing agent without adding other impurities. The design of new containers and process are described as follows.

### 2.1. Container design

A novel stainless steel container for powder with two gas pipes was designed for the inflow and outflow of hydrogen and vacuum degassing, as shown in the schematic diagram in Fig. 1(a), for which the conventional container only has one pipe for vacuum degassing used in the PM industry. The stainless container with 60 mm internal diameter, 1 mm wall thickness and 150 mm length were designed in this study. Two circular holes with the diameter of 5 mm were located at the centre of the two ends as marked in Fig. 1(a). These two holes were further connected by two stainless steel pipes with 5 mm internal diameter and 1 mm thickness for gas flow. In order to avoid the powder loss during the powder filling, hydrogen reduction reaction and vacuum degassing, two layers of stainless filters with the mesh size of 25  $\mu\text{m}$  (less than powder size of 50–200  $\mu\text{m}$ , as detailed in the later section) were placed at the two ends of the container.

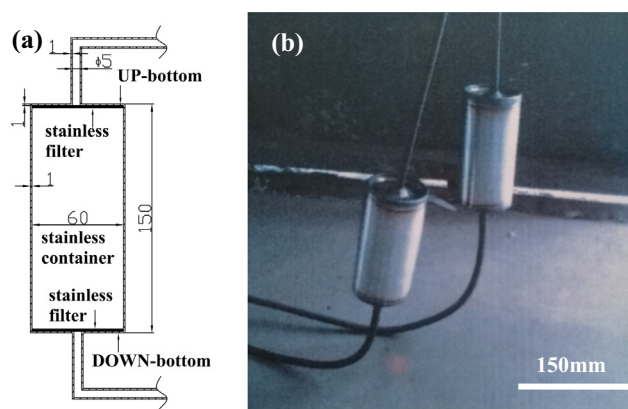


Fig. 1. (a) schematic diagram of newly designed stainless powder container with two pipes (unit of mm); (b) image of this novel stainless powder container.

### 2.2. Design of flowing hydrogen reduction and vacuum degassing

In this novel design, the hydrogen reduction reaction and vacuum degassing were combined into one process. This integrated process consists of four steps, namely, air tightness checking, hydrogen reduction, hydrogen cleaning and vacuum degassing. The schematic flow diagram is shown in Fig. 2.

In this design, the airtightness of the container and the up and down two gas channels is checked by a vacuum test. During this test, one end of the entire gas channel is sealed and another end is connected with a vacuum pump, as step 1 shown in Fig. 2(a).

In step 2, as seen in Fig. 2(b), the container is put into a furnace along the vertical direction. Hydrogen (density of 0.09  $\text{kg/m}^3$ ) flows into the container from the up gas channel to fully exhaust the air (density of 1.293  $\text{kg/m}^3$ ). During this process, the hydrogen reacts with oxygen on the powder surface and forms  $\text{H}_2\text{O}$  (density of 0.6  $\text{kg/m}^3$ ). The extra hydrogen flowed out from the down gas channel is ignited to avoid the hydrogen diffusing into the environment, which could lead to the potential explosion.

As hydrogen occupies the entire container and needs to be removed in order to avoid the potential risk of hydrogen-oxygen reaction at high temperature. In step 3, the container and gas channels are turned upside down and the gas inlet is connected to argon gas of higher density (1.784  $\text{kg/m}^3$ ) for extracting the remaining hydrogen in the container, as shown in Fig. 2(c).

After step 3, the inlet and outlet of gas channels are simultaneously connected to a vacuum pump for degassing, as step 4 shown in Fig. 2(d).

### 2.3. Experimental operation of flowing hydrogen reduction and vacuum degassing

The concept of the design is described in Section 2.2. The detailed description of practical operation is shown in this section. The prealloyed powder was filled into the designed stainless steel container, as shown in Fig. 1(b). Based on the proposed integrated design, the hydrogen reduction and vacuum degassing, the airtightness checking, hydrogen reduction, hydrogen cleaning and vacuum degassing were carried out in order as shown in Fig. 3(a)–(d).

For step 1, as shown in Fig. 3(a), hydrogen and argon cylinders were connected to a Y-type three-ways valve with two switches for control of the flow of hydrogen and argon respectively. The left outlet of this 3-ways valve was connected to the upside pipe of the container through a two-way valve (designated as 1# valve), which is used to ensure the container seal before step 4. The downside pipe of the container was connected to a vacuum pump also

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