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Highly porous Fe-2wt%P alloy produced by plasma assisted debinding and sintering of injection-molded parts

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ABSTRACT

Metal Injection Molding is a well-known powder metallurgy technology, which allows net-shaped parts to be produced with a high degree of automation and reduced costs in large-scale production. However, shape retention during sintering of porous parts remains a challenge. The present study demonstrates that plasma assisted debinding and sintering of injection-molded parts is a promising route for manufacturing highly porous Fe-P-based parts, improving porosity amount and dimensional accuracy, avoiding surface distortion of injection-molded parts while decreasing processing time. In this study, the effect of plasma sintering was analyzed regarding dimensional accuracy, porosity, phase composition and microstructure of highly porous Fe-2wt%P parts.

1. Introduction

Highly porous metals have attracted attention due to their low density, high porosity, good liquid and gas permeability, high surface area, and other unique properties. Among porous metals, porous Fe-P-based alloys have been highlighted because of their improved soft magnetic properties [1] and relative low price. They are suitable for many applications such as lightweight construction materials, biodegradable implants and scaffolds [2–4]. Cheng et al. [2] and Zhao et al. [3] produced scaffolds made of porous iron with the advantage of being biodegradable, non-toxic, and allowing drug delivery control by magnetic field [2,3]. Porous Fe-P-based alloys can also be applied in electrochemical devices such as current collector for proton exchange membrane fuel cell [5] or as electrodes in modern Ni-Fe batteries [6].

Metal injection molding (MIM) is a promising powder metallurgical technology for manufacturing porous parts, once it allows obtaining well-defined porosity by adjusting metal powder: binder system proportion or by the addition of space holder materials [7]. However, powder metallurgical manufacturing of porous materials has the challenge to retain the geometrical shape of highly porous components during sintering, which is more challenging in case of MIM because of the binder addition. Machado et al. have developed a reactor for plasma assisted debinding and sintering (PADS) of injection-molded parts, which has been successfully applied for manufacturing dense parts [8–10]. In recent studies [11,12], it was found that plasma treatment enhances dimensional accuracy and surface porosity of highly porous samples produced by MIM. Based on these results, PADS technique was for the first time applied aiming the production of highly porous parts. In this study, PADS of highly porous Fe-P-based parts was investigated regarding their porosity and microstructure.

2. Experimental procedure

MIM feedstocks with 50:50 and 53:47 metal powder: binder system ratios were produced. The metal powder was composed by Fe-2 wt% P alloy, produced by the mixture of Fe powder (Högänas D90 with particle size between 45 and 150 μm) and Fe_3P powder (Högänas, with 16 wt% P and particle size of 75 μm). The organic binder system consisted of 60 vol% paraffin, 35 vol% polyethylene (Hostalen GA 7260G) and 5 vol% stearic acid. Feedstocks were produced by mixing the powders and the binder system at 150 °C and then injected using MIM (Haacke MiniJet) into cylindrical parts of 30 mm diameter and 3 mm height. After

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injection molding, samples were immersed in *n*-hexane bath (50 °C, 24 h) to remove paraffin wax and stearic acid.

PADS was performed in a low-pressure system described in the literature [10]. First, samples were heated up to 500 °C at the rate of 1.6 °C to remove residual binder. Heating rate was chosen from our previous experiments to ensure a fast binder removal without leading to shape deformation of samples. Afterwards, samples were heated up to different sintering temperature (varying from 800 to 1100 °C) and held at sintering temperature for 2 h. Sintering cycle was performed under either argon or hydrogen atmosphere to investigate sintering behavior. Reference samples were conventionally thermal debinded and sintered in a resistive furnace under argon flow, for that samples were heated up to 500 °C at the rate of 1 °C/min and held at this temperature for 2 h to remove residual binder and then sintered at 1100 °C.

Sample's microstructure was characterized by light microscopy (B201, Olympus) and scanning electron microscopy (JSM 6360, Jeol). Analysis of open, closed and total porosity were determined by Archimedes method using a precision balance (EMB, Kern) equipped with a floating device, according to the work of Köhl

Table 1
Resulting porosity and shrinkage related to sintering parameters and feedstock composition.

Powder load (vol%)	Sintering		Porosity (%)			Shrinkage in (%)	
	Atmosphere	Temperature (°C)	Open	Closed	Total	Height	Diameter
50	Ar resistive	1100	9.7	6.8	16.5 ± 2.0	14.0 ± 3.5	16.7 ± 2.2
50	Ar plasma	900	47.1	11.5	58.6 ± 3.3	0.12 ± 0.5	0.25 ± 0.3
50	Ar plasma	1000	44.5	5.0	49.5 ± 2.4	0.0 ± 0.7	0.27 ± 0.2
50	Ar plasma	1100	38.4	6.4	44.8 ± 4.0	1.1 ± 0.5	0.54 ± 0.2
53	Ar plasma	1100	33.9	3.9	37.8 ± 1.5	1.1 ± 0.3	0.90 ± 0.3
50	H_2 plasma	1100	37.2	8.5	45.7 ± 0.6	2.2 ± 1.3	1.30 ± 0.3

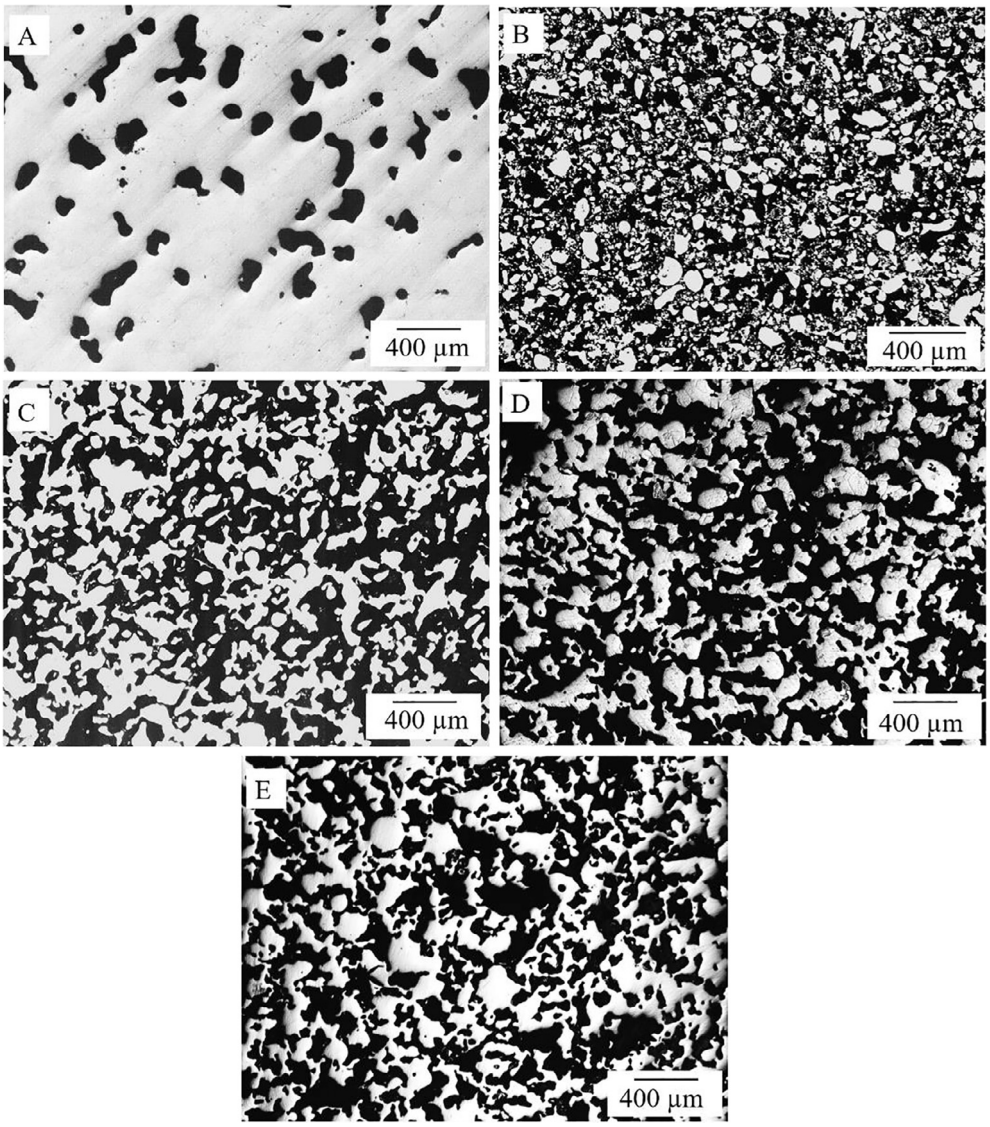

Fig. 1. Microstructure of injection-molded parts produced with 50 vol% of Fe-2%P and sintered in: (A) resistive furnace at 1100 °C, (B) Ar plasma at 900 °C, (C) Ar plasma at 1100 °C, (d) H_2 plasma at 1100 °C and (E) injection-molded part produced with 53 vol% of Fe-2%P and sintered in Ar plasma at 1100 °C.

et al. [13]. The obtained results were double-checked by numerical analysis of light microscopy images. Surface average roughness (*Ra*) was measured through a roughness tester (SJ-410, Mitutoyo) according to ISO 4287 [14]. Phase composition was analysed by X-Ray diffraction using Cu K_α radiation in a Bruker AXS, D8 Advance diffractometer.

3. Results and discussion

Injection-molded samples sintered in plasma had a significant lower shrinkage than samples sintered in resistive furnace (Table 1). As consequence of lower shrinkage, porosity was higher in the plasma-sintered samples. Sintering of metallic materials in plasma seems to start from the surface in direction to bulk due to collision between plasma specimens and sample surface, which leads to thermal spikes at the surface as reported in the literature [12]. Once the samples are sintered at the surface, shrinkage is reduced.

Fe-2wt%P parts with porosity as high as 58.6 vol% could be achieved. Porosity was obviously higher in samples sintered at lower temperatures (Table 1). Samples sintered at 800 °C had very poor mechanical properties and even collapsed. So that, sintering temperatures between 900 and 1100 °C were the most suitable for producing highly porous Fe-2wt%P parts. By comparing, samples produced with 50 and 53 vol% powder load, it was observed that, as expected, higher powder load resulted in lower porosity (Table 1). So that, porosity amount could be adjusted by the sintering temperature and the powder load. Porosity distribution was homogeneous and mostly interconnected in the plasma-sintered samples (Fig. 1).

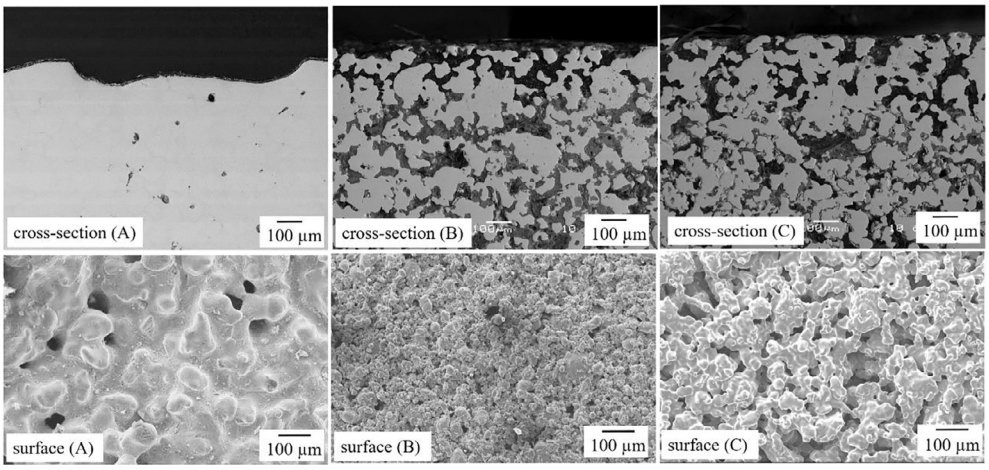

Fig. 2. SEM of the cross-section and top surface of Fe-2wt%P parts sintered at 1100 °C: (A) in resistive furnace, (B) in Ar plasma and (C) in H_2 plasma.

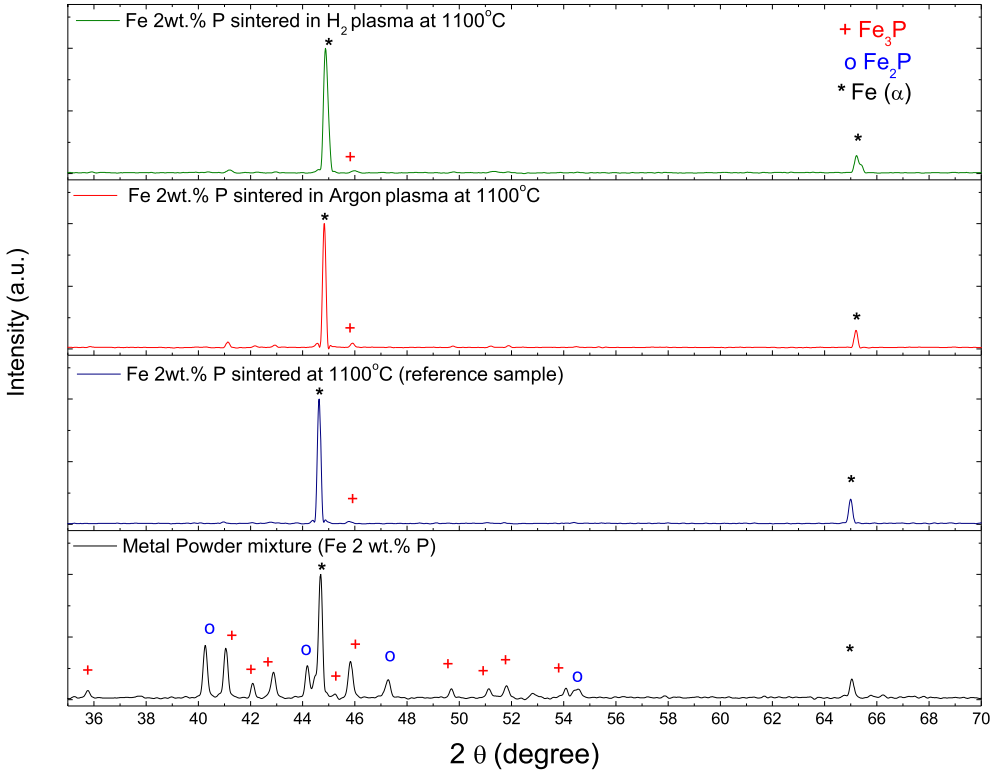

Fig. 3. X-ray pattern of injection-molded parts regarding sintering parameters.

During plasma assisted thermal debinding a higher heating rate (1.6 °C/min) and a shorter dwell time (1 min) could be applied without any shape loss of samples compared to conventional thermal debinding in a resistive furnace (1 °C/min and 120 min dwelling time). Plasma specimens interacted with binder components promoting a breakdown of polymeric chains leading to a faster binder evaporation, whereas binder could be easily removed from injection-molded samples as discussed in the literature [10,12]. In case of thermal debinding in a resistive furnace, a higher heating rate results in a severe loss of sample shape. Therefore, PADS allows a shorter processing time.

Injection-molded parts sintered in plasma had a smaller grain growth, which is related to lower density compared to samples sintered in a resistive furnace (Fig. 2-bottom). Sintering in H_2 plasma resulted in an increased grain growth at the surface compared to sintering in Ar plasma. As proposed by Pavanati et al. [9], the presence of H atoms may contribute to eliminate impurities from grain boundaries. A grain boundary with lower level of impurities has higher mobility, therefore leading to a higher grain growth. Smaller particles are preferred for many applications since grain growth may lead to severe loss of mechanical and electrochemical properties. Furthermore, the presence of hydrogen atoms can weaken mechanical properties. Therefore, the mechanical properties will be investigated in our ongoing studies to be published in the future. Plasma sintering also contributed to a decrease in the bending of the sample surface (Fig. 2 top) and in the surface average roughness (Ra). Ra decreased from 10.9 ± 1.3 μm in samples sintered in a resistive furnace to 6.5 ± 0.9 μm and 9.2 ± 0.9 μm in samples sintered in Ar and H_2 plasma, respectively.

All sintered samples showed the same phase composition. Fe-α (ferrite) was mainly the only observed phase, Fe_2P and Fe_3P decreased considerably. P atoms from Fe_2P and Fe_3P diffused to Fe-α matrix forming a solid solution. Furthermore, X-ray diffraction results indicated that injection-molded parts did not form oxide, nitride or carbide compounds during PADS (Fig. 3).

4. Conclusions

This study demonstrated that plasma assisted debinding and sintering (PADS) of injection-molded parts is a suitable technique for production of highly porous metals. PADS decreases shape loss during sintering and increases porosity, allowing the production of highly porous Fe-P-based parts with higher dimensional accuracy and an interconnected porosity. The amount of porosity can be controlled by adjusting the sintering temperature and the feedstock composition. PADS of injection-molded parts has potential for manufacturing metallic scaffolds for controlled drug delivery, where a high dimensional, an open and interconnected porosity are required. Furthermore, PADS can reduce manufacturing time.

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