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Development of niobium powder injection molding. Part II: Debinding and sintering

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Abstract

This article is a continuation of feedstock preparation and powder injection molding (PIM) of pure niobium. Part II discusses debinding and sintering of injection molded niobium. PIM of pure niobium powder was analyzed for efficiency of the process. After solvent and thermal debinding, sintering of injection molded material was conducted up to 2000 °C in vacuum as well as inert-gas low-oxygen partial pressure atmosphere. This paper investigates the effect of sintering time, temperature and atmosphere on the processing of pure niobium. Under all sintering conditions the oxygen content is reduced from ∼19,000 in the as-received powder to as low as 300 ppm, at e.g. 2000 °C for 2 h in a low-vacuum atmosphere. The carbon content increased from the as-received 70 to 200–300 ppm, depending on the sintering conditions. However, this amount of carbon is not considered detrimental for structural application. Master decomposition and sintering curves are introduced for pure niobium to study the optimum debinding and sintering conditions. Further, sintering parameters (atmosphere, peak temperature and hold time) are optimized for achieving maximum densities with minimal impurities.

Keywords: Nb; Niobium; Powder injection molding; Solvent debinding; Thermal debinding; Sintering of Nb; Master decomposition curve; Master sintering curve

1. Introduction

Niobium is the lightest refractory metal (density = 8.57 g/cc). Approximately 75% of all niobium metal is used as an addition to low-alloyed steels. Another 20–25% is used as an additive in nickel base superalloys and heat-resisting steels. Only 1–2% is used in the form of pure niobium and niobium-base high temperature alloys [1,2]. Due to its limited application and reactive nature during processing, little work has been done in processing of pure niobium. In 1944, for the first time pure niobium powder was pressed into bars and sintered in vacuum by resistance heating [3]. But there were no details on the processing parameters. Since then, reports on the powder metallurgy processing of pure niobium have been erratic. Klopp et al. [4] observed 91% density after sintering niobium bars at 2150 °C for 4 h. The initial powder size was 3.2 μm and final oxygen and carbon contents were 0.079 and 0.03 wt%, respectively. In investigating porous niobium, sintering in the range of 1000–1600 °C under ultra-high vacuum and low-oxygen partial pressure has been done of fairly large powder size (32–63 μm) [5]. In a similar study, fine niobium powder (1.3 μm) was sintered in the range of 1200–1800 °C under vacuum [6]. Both studies provided minimal details with regard to final density and impurity content. Cold isostatically pressed niobium ($D_{50} = 6.7$ μm, $O = 0.62$ wt%) was sintered up to 2000 °C under vacuum [7]. Abnormal grain growth above 1800 °C was observed and the final oxygen content was 0.05 wt%. All of the above work consisted of simple pressing of niobium powder into bars, and little to no work has been done in processing of pure

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niobium via powder injection molding. Only recently niobium has been introduced as mint metal—via ingot melting and cold deformation [8].

Powder injection molding (PIM) is a relatively new manufacturing process, modified from the plastic injection molding process where a significant volume fraction of the plastic is replaced by small metal particles [1,9]. It is a net-shape process targeted at intricate shapes produced at a high production rate. For refractory metals, PIM as shaping process has a relative cost advantage since it uses the same powders at the same price as used in alternative processes [10]. So, for big lot sizes PIM has a clear economic advantage in producing complex shapes. Dropmann et al. [11], in 1992 applied powder injection molding to Nb-base superalloys. They achieved 94% density after sintering up to 2350 °C.

This article is the second in the series of development of niobium powder injection molding. In Part I [1], the potential of PIM for pure niobium and a systematic approach based on rheological properties were discussed in detail. The primary purpose of Part II is to report the debinding and sintering of injection molded niobium. The discussion covers factors which affect the optimum debinding and sintering conditions. Results are provided for sintered densities, impurity contents (carbon and oxygen), and microhardness. Each of the properties is analyzed against sintering temperature, time, and atmosphere. Finally, an optimum sintering window is provided for niobium based on the master sintering curve (MSC).

2. Experimental procedures

Details on the powder and binder characteristics, feedstock development and injection molding have been detailed in Part I [1], see Table 1. Debinding and sintering of injection molded niobium is described in Part II.

2.1. Solvent and thermal debinding

A two-step debinding process was selected. First, solvent immersion debinding was carried out by immersing the parts in heptane (debinding tank model: 1235; supplier: Sheldon Manufacturing Inc., Cornelius, OR) at 60 ± 1 °C. Parts with a thickness of 3.17 mm were placed on perforated steel trays and dipped into heptane once the temperature reached 60 °C. A debinding time of 2 h was used, which was optimized experimentally using thermo-gravimetric analysis (TGA). Solvent debinding removed most of the wax in the binder, leaving backbone polymers for component handling strength. The next step was to remove the binder by heat. The parts were placed on an alumina setter and debound in a high purity argon atmosphere. After thermal debinding, pre-sintering was done in the same retort to provide handling strength.

2.2. Sintering

Sintering was performed in three different atmospheres at various times and temperatures. The goal was to determine the effect of atmosphere, temperature, and time on the sintered density, impurity content, and mechanical properties. Table 2 shows the set of sintering experiments undertaken. The first three experiments were performed at 1600 °C for three different hold times in atmosphere hV (high vacuum of 1.3×10^{-4} Pa). The next four experiments were performed in higher pressure vacuum (ℓV—low vacuum of 0.13 Pa) at various times and temperatures. The last three runs were performed in a high-purity inert atmosphere (iG—inert-gas low-oxygen partial pressure/argon).

2.3. Property measurement of sintered parts

After sintering, tensile bars were sectioned into two pieces with a diamond cut-off saw and further sectioned on an abrasive cut-off saw. The chips were analyzed for carbon in a combustion carbon/sulfur analyzer (model: EMIA-8200; supplier: JY Horiba, Edison, NJ). A sample weight of 0.5 g was used and three measurements for each sample were performed. Further, the samples were cut to

Table 2
Sintering experiments at various processing parameters

Temperature/time	Atmosphere		
1600 °C/1.0 h	hV	ℓV	–
1600 °C/1.5 h	hV	–	iG
1600 °C/2.0 h	hV	–	–
1800 °C/1.5 h	–	ℓV	–
1800 °C/2.0 h	–	–	iG
2000 °C/0.5 h	–	ℓV	–
2000 °C/1.0 h	–	ℓV	–
2000 °C/1.5 h	–	–	iG

hV—high vacuum.
ℓV—low vacuum.
iG—inert-gas low-oxygen partial pressure.

Table 1
Characteristics of binder components used in binder system [1]

Binder	Paraffin wax	Polypropylene	Polyethylene	Stearic acid
Vendor	Dussek Campbell	PolyVISIONS	DuPont	FisherScientific
Density (g/cm^3)	0.90	0.90	0.92	0.94
Melting range (°C)	42–62	110–150	60–130	74–83
Melting peak (°C)	58	144	122	79
Decomposition range (°C)	180–320	350–470	420–480	263–306