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Development of non-eroding rocket nozzle throat for ultra-high temperature environment

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ABSTRACT

The powder processing methods including powder metallurgy (P/M) and powder injection molding (PIM) techniques for tungsten (W)–rhenium (Re) were employed to produce a W–Re rocket nozzle. The composition of W–Re was determined by 25 wt.% of Re to avoid the formatting brittle sigma (σ) phase. The samples for analysis of the densification behavior on sintering were prepared by die pressing and cold isostatic pressing (CIP). The feedstock for the PIM process was produced by mixing the W–25 wt.% Re powder and binder system based on a wax-polymer with an optimum solid loading through the twin-extruder mixer. The injection molded specimens were debound to extract and decompose the binders *via* the solvent and thermal debindings. The debound samples were sintered in a hydrogen atmosphere. After sintering, hot isostatic pressing (HIP) was carried out in an argon atmosphere to enhance the density.

The dilatometry experiments were performed to analyze and predict a densification behavior during sintering. The master sintering curve (MSC) model was used to characterize the densification behavior with a minimal set of preliminary experiments. The mechanical properties were evaluated through microstructure and chemical composition measured by EDX–SEM and X-ray diffraction (XRD).

Finally, the eroding test was conducted using the W–25 wt.% Re rocket nozzle produced by PIM under the high temperature. After carrying out erosion tests, the erosion rate, hardness and microstructure were evaluated.

1. Introduction

Rocket nozzles are widely used for a mechanical part such as a tactical missile and weather and surveillance satellite. Such a rocket nozzle works in the high temperature and pressure, because the enormous amounts of exhaust gas containing a high temperature produced by combustion pass through throat-area which is the smallest cross-section area. Therefore, the material for a rocket nozzle must have good mechanical properties such as a high melting point, a good thermal shock resistance, and a low coefficient of thermal expansion to retain propulsion performance. In general, graphite and carbon–carbon composites have been widely used as nozzle materials to reduce the erosion rate of throat-area. However, the erosion rate of those materials is not enough to maintain propulsion. In this regard, there have tried to employ different types of materials to reduce an increase of throat-area by erosion. A refractory metal is another representative material. Considering their thermal properties such as melting temperature, refractory metals are possible candidate materials for a noneroding rocket nozzle in the ultra-high temperature and pressure [1].

Refractory materials including niobium, tantalum, molybdenum and tungsten are the extraordinarily resistant materials against heat and wear. These materials have unique mechanical properties such as a high melting point, boiling point and density. Of all the refractory materials, rhenium has unique mechanical properties such that its melting temperature of 3180 °C exceeds all other metals except tungsten. Even though rhenium has a lower melting point than tungsten, rhenium has a better ductility at high temperature compared to other refractory materials [2]. In addition, rhenium has the highest tensile strength among the refractory materials under high temperatures.

Rhenium has a distinguishing mechanical property, the so-called rhenium effect. This mechanical property comes from its crystal structure *i.e.* rhenium has the closed-packed hexagonal structure, while other refractory metals have the body-centered cubic structure. Its hcp structure has a high solubility in transition metals having BCC and FCC structures [3]. This characteristic enables rhenium to form an alloy *e.g.* W–Re (tungsten–rhenium alloy) and Mo–Re (molybdenum–rhenium alloy). These alloys increase mechanical properties such as tensile strength and plasticity, and enhance weldability. In order to determine

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the optimum composition of Re-alloy, the phase change should be considered through the phase diagram. For instance, W–Re has the optimum solubility limitation of W with 26 wt.% Re to avoid the sigma (σ) phase which has a brittle mechanical property.

There have been several studies for the refractory materials, especially related to the production method for rhenium alloys [4–10]. As the most common method to form rhenium components, chemical vapor decomposition (CVD) and powder metallurgy (P/M) have been considered. Both methods are employed to fabricate the small or complex-shaped components. While CVD is considered as a clean method, it is not easy to produce the components in quantity. Although the P/M is suitable method for mass production, it is difficult to produce the required complex shape. In this regard, PIM is an attractive method from the manufacturing point of view including shape complex and mass production.

In manufacturing industries, the PIM process is a productive and cost-effective net-shaping process which combines advantages of both plastic injection molding and conventional powder metallurgy. This process has many advantages of shape complexity, tight tolerances, and material selection of metals and ceramics. Once desired materials, mold geometries, and process parameters are decided, PIM is an appropriate process for mass production. The PIM process consists of four steps; (i) mixing — producing the pelletized feedstock of the powder and organic binders, (ii) molding — injecting the feedstock melt into the mold cavity, similar with thermoplastics; (iii) debinding — extracting or removing the organic binders out of injection molded part *via* solvents or the thermal energy, (iv) sintering — densifying the debound part from the low initial density to the high final density, close to the full density [11–14].

One of the key steps for the PIM process is sintering which is a thermally activated diffusion process. Sintering is a complex process involving the evolution of the microstructure as well as simultaneous actions related to several transport mechanisms. The processing conditions for sintering can affect the mechanical properties such as the microstructure and density. The density especially plays a vital role to evaluate the merchantability of sintered parts. The density of sintered parts is strongly correlated with final dimension as well as strength of a part, since the occupied pores in the parts are eliminated by bonding together into a coherent, solid mass during sintering. Therefore, not only does it demand intense effort to understand the sintering behavior but also to determine the proper processing conditions. Understanding the densification behavior during sintering is especially difficult, because the sintering mechanism is associated with many factors such as particle size, morphology and processing conditions. The densification behavior for sintering can be analyzed using a master sintering curve (MSC) model and linearized form of MSC. Many researchers have analyzed and predicted a densification behavior through the MSC [15–24]. The MSC suggested by Su and Johnson [15] can characterize the densification behavior regardless of different heating rates. The linearized form of MSC was proposed by Blaine et al. [21] by a simpler means of determining the model parameters, n and $\ln \Theta_{ref}$. Those parameters, n and $\ln \Theta_{ref}$, have the physical meanings that n for a power law exponent is how fast densification occurs, and Θ_{ref} for the half-way point between initial density and final density during the sintering is how much densification occurs. Those parameters can be obtained from experimental data.

This study investigates the powder processing for W–25 wt.% Re. In Section 2, the experimental procedures including characteristics of W–25 wt.% Re powders, binder system, experimental conditions and setups are briefly mentioned to produce the specimens. Section 3 presents the results of experiments and analysis of MSC and then the results are verified and discussed using the analysis of several respects including densification behavior, microstructure and mechanical properties. After evaluating the characteristics of samples, the rocket nozzles were produced and then the mechanical properties were evaluated through an eroding test that was performed. Finally, conclusions and contributions of this study are presented in Section 4.

2. Experimental procedures

2.1. Powder characterization

The W–Re powder (produced by CetaTech, Inc.) was prepared by a reduction process. The optimum composition of W–Re is highly related to the solubility limit as shown in Fig. 1 [25]. In this study, in order to avoid the formation of the hard and brittle σ-phase, W–25 wt.% Re powder was fabricated and used for the P/M process.

The particle size of this powder was measured by particle size analyzer (Particle Size Analyzer, CILAS 1064), as illustrated in Fig. 2. The particle sizes of D_{10}, D_{50}, and D_{90} are 3.22, 9.74, and 18.35 μm, respectively. The powder has a slightly bi-modal distribution. The distribution slope parameter (S_w) calculated by Eq. (1) is 3.387. This parameter is a just value to represent how broadly particle is distributed. Considering that the easiest powders to mold exhibit S_w of less than 4, the obtained value of 3.387 is within a reasonable range.

$$S_W = \frac{2.56}{\log_{10}\left(\frac{D_{90}}{D_{10}}\right)} \tag{1}$$

Fig. 3 shows the morphology of powders observed using a scanning electron microscopy (FE-SEM, Philips XL30S FEG). Some particle surfaces were covered with wavy rods with submicron size, but the variation in chemical composition with particle morphologies was not distinctive. The carbon content in the W–25 wt.% Re powder, measured by inductively coupled plasma (ICP, ICP-OES), was 0.024 wt.%.

2.2. Sample preparation

The samples were prepared by P/M and PIM methods. In order to evaluate the mechanical properties as well as densification behavior, the sample was produced by P/M method. The P/M process consists of the following steps; (i) die pressing (DP) was used as the method of compaction. Cylindrical compacts, 10 mm in diameter, were made at a compaction pressure of 50 MPa, (ii) cold isostatic pressing (CIP) — compacted samples were uniformly pressed at pressure of 180 MPa from multiple directions for achieving uniformity of compaction compared to the uniaxial pressing, (iii) pressureless sintering — CIPed samples were heated in a H_2 atmosphere using the following thermal cycle: ramp up to 1550 °C, hold for 10 h, ramp to 2350 °C and hold for 4 h, (iv) hot isostatic pressing (HIP) — sintered samples were compacted with a temperature of 1900 °C and pressure of 100 MPa for 2 h in an Ar atmosphere to obtain full density.

In order to evaluate the eroding rate, the samples were fabricated by the PIM method. PIM was carried out as the following; (i) mixing — the powder and binder system were mixed at 50 vol.% solid loading of W–25 wt.% Re powder by twin-extruder mixer (CetaTech Inc.) to produce the pelletized feedstock. The binder system composed of wax, polypropylene (PP), polyethylene (PE) and stearic acid (SA). The material properties for each component of the binder system are summarized in Table 1, (ii) injection molding — the feedstock was shaped by injection molding into the mold cavity to fabricate the desired shape, (iii) solvent debinding — the binder in the injection molded part was dissolved at 50 °C for 20 h in an n-hexane solution. (iv) thermal debinding was carried out at 900 °C for 1 h in a H_2 atmosphere, (iv) pressureless sintering — debound samples were heated under the same conditions of P/M process, (v) hot isostatic pressing (HIP) — sintered samples were heated and compacted under the same conditions as the P/M process.

The samples were produced by two methods. The manufacturing procedures according to production method are summarized in Table 2.