

# Influence of Cryogenic Milling on the Mechanical / Corrosion Characteristic of ODS

## Hastelloy-N

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### 1. Introduction

Hastelloy-N (HN) is a Ni-based superalloy with good mechanical properties such as high strength, high-temperature mechanical stability, high erosion/corrosion resistance, and high creep resistance at elevated temperatures. Due to the excellent mechanical and corrosion properties, HN is a promising candidate material for future Generation IV advanced nuclear reactors. However, due to the high Nickel content HN will generate a significant amount of Helium due to (n,α) reactions when exposed to a neutron environment. One method of offering defect sinks, while concurrently improving the mechanical properties even further, involves the production of oxide dispersion strengthened (ODS) alloys. The oxide/metal interface provides a large amount of defect sinks for the Helium to accumulate.

In this study, we introduced the ODS HN made by cryogenic milling and spark plasma sintering (SPS) and performed tests to compare its mechanical properties to a commercial-grade alloy, highlighting the potential benefits of cryogenic milling for producing high-quality ODS alloys.

### 2. Methods and Results

#### 2.1 Material and alloying method

The commercial-grade Hastelloy-N (HN) (following ASTM B434 standard) was purchased from a commercial vendor to serve as a comparison with the ODS-fabricated alloys. The HN powder used to make the alloys for this study was also purchased from a commercial vendor (Powder Alloy Corporation, Inc., USA), and had particle sizes below 44 μm in diameter. Additionally, a sample of pure HN powder was pressed in a 0.5" (12.7 mm) diameter, 1" (25.4 mm) long die with an applied pressure of approximately 2.1 GPa (Fig. S1). Following pressing, the powder metallurgy HN was

sintered at 1125 °C for 2 hours in a vacuum furnace with a pressure of approximately 10<sup>-6</sup> mBar, with small amounts of tantalum included inside the die prior to pressing to act as an oxygen-getter during sintering. Table 1 displays the chemical composition of the samples in this study, which is provided from the supplier data sheet.

For the cryogenically-milled and room temperature-milled ODS HN samples, which have same chemical composition, 0.5 wt.% of Zr and 0.7 wt.% of Y<sub>2</sub>O<sub>3</sub> were added to the same HN powder. These powders were milled for 8 hours at 180 RPM using 3/16" (~5 mm) diameter 316 stainless steel milling media. The room temperature-milled ODS HN powder was milled at room temperature under an argon atmosphere, while the cryogenically-milled ODS HN alloy was milled under an argon atmosphere and a liquid N<sub>2</sub> cooling jacket for the attritor mill to maintain a temperature of approximately -196 °C. After preparing the ODS HN powders, a commercial vendor conducted spark plasma sintering (SPS) at 1150 °C for about 15 minutes with an applied pressure of approximately 2.1 GPa, which typically results in a density of 95% or greater with limited heat input in the material.

Table 1. Chemical composition of the alloys.

| Samples                        | Chemical composition (wt.%) |                               |      |     |      |        |        |          |          |           |           |           |          |          |
|--------------------------------|-----------------------------|-------------------------------|------|-----|------|--------|--------|----------|----------|-----------|-----------|-----------|----------|----------|
|                                | Zr                          | Y <sub>2</sub> O <sub>3</sub> | Ni   | Cr  | Mo   | Fe     | Si     | Mn       | V        | C         | Co        | Cu        | W        | Al + Ti  |
| Commercial-grade HN            | 0.0                         | 0.0                           | Bal. | 7   | 16   | 4 Max. | 1 Max. | 0.5 Max. | 0.5 Max. | 0.08 Max. | 0.02 Max. | 0.35 Max. | 0.5 Max. | 0.5 Max. |
| Powder metallurgy HN           |                             |                               |      |     |      |        |        |          |          |           |           |           |          |          |
| Room temperature-milled ODS HN | 0.5                         | 0.7                           | Bal. | 7.3 | 15.9 | 3.3    | < 1.0  | 0.1      | < 0.5    | 0.06      | 0.06      | 0.05      | 0.01     | < 0.5    |
| Cryogenically-milled ODS HN    |                             |                               |      |     |      |        |        |          |          |           |           |           |          |          |

#### 2.2 Mechanical tests

Microhardness measurements were conducted on polished the cryogenically-milled and the room

temperature-milled ODS HN samples using a Wilson/Tukon Microhardness Tester Model MO equipped with a Vickers indenter. Measurements were taken at two different load levels (0.2 kg and 1.5 kg) with an indenter dwell time of approximately 10-15 seconds. Tensile tests were carried out on the cryogenically-milled and the room temperature-milled ODS HN. Testing was performed using a Kammrath & Weiss Tensile/Compression Module (K&W) equipped with a 5 kN load cell, with strain rates of approximately  $2 \text{ Es}^{-1}$  (or a speed of  $1 \mu\text{m/s}$ ) at room temperature.

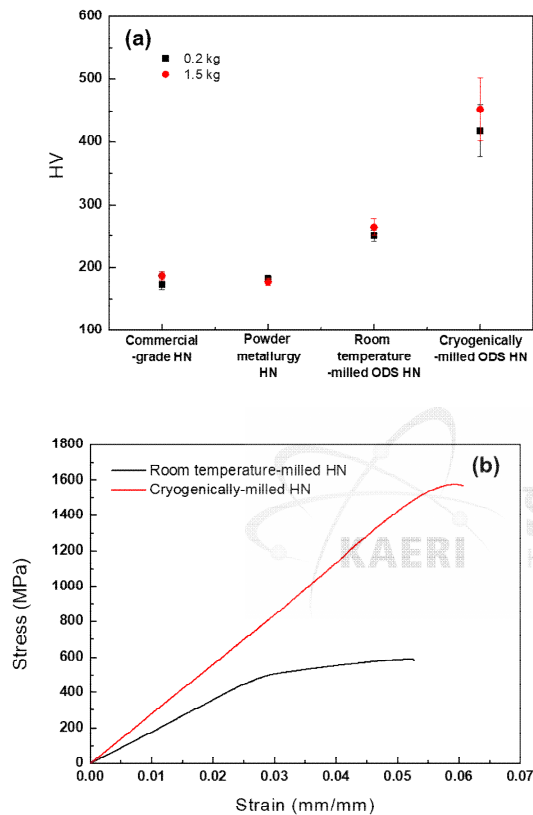


Fig. 1. (a) Vickers hardness and (b) tensile tests results of the HN samples (error bar: standard deviation)

The Vickers hardness and tensile test results are shown in Fig. 1. In the case of the hardness measurement, commercial-grade HN and powder metallurgy HN had similar values ( $172.69$  ( $0.2 \text{ kg}$ ) /  $187.50$  ( $1.5 \text{ kg}$ )  $\text{kgf/mm}^2$  and  $182.13$  /  $177.31$   $\text{kgf/mm}^2$ , respectively.) The alloys containing additional alloying elements showed higher hardness than the pure HN samples. The hardness of the room temperature-milled ODS HN was measured as 1.3 times higher, and the cryogenically-milled ODS HN was recorded as 2.6 times higher than the hardness value of the commercial-grade HN.

Due to the size limitation in the powder metallurgy HN samples, the tensile tests were only performed on the room temperature-milled ODS HN and the cryogenically-milled ODS HN. The yield strength of the room temperature-milled ODS HN was

measured as 1.57 times larger than the commercial-grade HN, while UTS (Ultimate Tensile Strength) was 0.69 times lower. In the case of the cryogenically-milled ODS HN, there was no elastic deformation as shown in the tensile test curve; however, the yield strength of the cryogenically-milled ODS HN was 5.5 times larger than commercial-grade HN, and UTS was almost double the value listed in literature. Although cryogenically-milled ODS HN has higher strength than that of the room temperature-milled ODS HN, higher Young's modulus was recorded at the cryogenically-milled ODS HN. However, both ODS alloys showed quite a low Young's modulus relative to the commercial-grade HN.

### 2.3 Immersion tests and surface analysis

The corrosion media used for the immersion tests was a eutectic FLiNaK salt (46.5 mol% LiF-11.5 mol% NaF-42 mol% KF). The FLiNaK was prepared by mixing LiF (99.9% purity, Alfa Aesar, USA), NaF (99.9% purity, Alfa Aesar, USA), and KF (99.8% purity, Alfa Aesar, USA) powders in the correct ratio. The mixed salt powder (85 g in total) was placed in a Ni crucible (inner diameter: 50 mm; height: 55 mm). The crucible was then loaded into a 304 stainless steel chamber and dried at  $300 \text{ }^\circ\text{C}$  for 5 hours by flowing high purity Ar ( $> 99.998\%$ ) over the salt. Finally, the chamber was heated to  $600 \text{ }^\circ\text{C}$  for another 3 hours to melt the mixed salt. The immersion tests were performed by placing the commercial-grade HN, the powder metallurgy HN, the room temperature-milled ODS HN, and the cryogenically-milled ODS HN samples in the molten FLiNaK at  $700 \text{ }^\circ\text{C}$  for 48 hours.

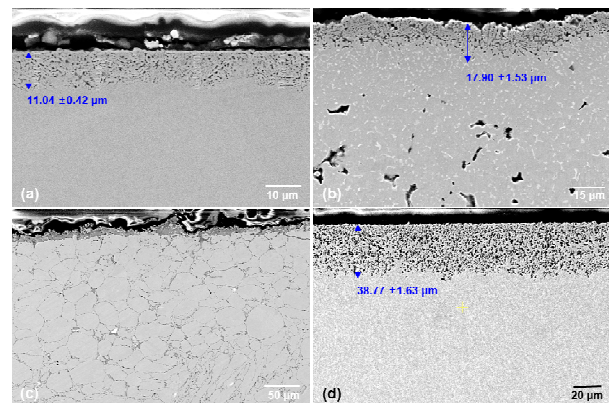


Fig. 2. Cross-sectional SEM images and corrosion depth of the samples after the immersion tests in the molten FLiNaK salt for 48 h at  $700 \text{ }^\circ\text{C}$ ; (a) Commercial-grade HN, (b) Powder metallurgy HN, (c) Room temperature-milled HN, (d) Cryogenically-milled HN (the corrosion depth was measured at least 10 times in different sites.)

In Fig. 2, cross-sectional SEM images of the samples after immersion tests in the molten FLiNaK salt for 48 hours at  $700 \text{ }^\circ\text{C}$  are shown. In the case of the commercial-grade HN, the corrosion-affected layer consists of small voids, which are formed by alloying

element dissolution, particularly Cr. The corrosion depth of the commercial-grade HN was  $11.04 \pm 0.42 \mu\text{m}$ . Upon comparison with the commercial-grade HN, the powder metallurgy HN exhibited a comparatively deeper corrosion penetration depth of  $17.90 \pm 1.53 \mu\text{m}$ . It is presumed that the molten salt infiltrated the manufacturing defects during the immersion test, where these defects contribute to an increased corrosion-exposed surface area and penetration depth. The room temperature-milled ODS HN exhibited inferior corrosion resistance compared to the previous alloys. Corrosion spread through the entire thickness of the sample, primarily along the grain boundaries and pores, resulting in an estimated corrosion penetration depth of over  $500 \mu\text{m}$ . The cryogenically-milled ODS HN exhibited better corrosion propagation depth than the room temperature-milled ODS HN, but it showed approximately 3.5 times deeper corrosion propagation depth than the commercial-grade HN. Overall, it can be concluded that the corrosion resistance of specimens manufactured via powder metallurgy is lower than that of the commercial-grade HN. The reason for the difference in corrosion resistance is further discussed in the following section.

### 3. Conclusions

In the present research, we assessed the mechanical and corrosion characteristics of ODS HN fabricated through cryogenic milling and spark plasma sintering (SPS). The ODS specimens demonstrated superior Vickers hardness relative to both the commercial-grade HN and the metallurgic HN variant. Among these, the cryogenically-milled ODS HN manifested outstanding strength, whereas the room temperature-milled ODS HN exhibited diminished UTS. From a corrosion standpoint, both ODS samples trailed the commercial-grade HN in resistance capabilities. The room temperature-milled ODS HN was characterized by Zr at grain boundaries. Owing to its elevated Gibbs free energy relative to Cr, Zr was predisposed to dissolve into the salt at the outset. Conversely, while the cryogenically-milled ODS HN integrated Zr, it eluded grain boundary segregation. The presence of finely dispersed Mo-based oxide bolstered mechanical prowess but inadvertently hastened corrosion progression, outpacing the commercial-grade HN, primarily due to Mo's higher Gibbs free energy when contrasted with Ni/Fe.

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