Effect of sintering temperature and solution treatment on microstructure and mechanical properties of high-N Ni-free austenitic stainless steel prepared by metal injection molding

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Abstract: High-N austenitic stainless steel was prepared by injection molding and sintering under nitrogen atmosphere by using gas atomized Cr-Mn-Mo-N duplex stainless steel powders. The powders and binder were mixed, injected, debinded and sintered. Effect of sintering temperature and solution treatment on microstructure and mechanical properties were studied. It shows that sintering temperature has significant effect on N content and density. With the increase of sintering temperature, the sample density was increased, but the N content was decreased. Samples sintered at 1200 °C was composed of austenite and Cr₂N, while only austenite can be detected by XRD for samples sintered at 1250 and 1300 °C. The fracture mode of the samples sintered at 1200 and 1250 °C is brittle fracture, along the 45° direction and stress axis, but samples sintered at 1300 °C did not fractured at the maximum load (21 kN) and showed ductility during compression. After solution treatment, the Cr₂N was disappeared and samples sintered at 1250 °C did not fractured during compression.

1. Introduction

Austenitic stainless steel with high N are widely used in many industries such as cryogenic, medical, as well as high temperature applications, due to their good combination of mechanical properties, corrosion resistance and biocompatibility [1, 2]. N can not only improve the strength of the stainless steel, but also improve the corrosion resistance, especially the pitting resistance [3]. On the other hand, N is a strong austenite stabilizer, it's capacity is about 20-30 times higher than that of Ni. Use N instead of Ni to stabilize austenite in stainless steel not only improves the strength of steel, but also avoids the risk of Ni allergy [4]. High-N austenitic stainless steel (HNASS) is usually produced by high pressure melting and powder metallurgy. The former face many problems such as expensive casting equipment, uneven distribution of N and dangerous high gas pressure [1, 4]. HNASS produced by powder metallurgy (PM) is favorable for obtaining fine grain, supersaturated N content etc. [5]. Effects of powder metallurgy process route and N content on the properties of high-N Ni-free austenitic stainless steel were studied by Lefor [6]. They find that gas-solid reaction in the sintering process can conveniently adjust the N content in high-manganese austenitic steel and higher N content can be achieved compared to casting. The advantages of fabricating HNASS by PM were obvious, but
Gas-solid nitriding is a complex and slow process. Unless a special PM process is developed, gas-solid nitriding is only suitable for porous parts or thin-wall parts with small cross section [7].

Metal injection molding (MIM) is an emerging technology suitable for large-scale production of high precision small-sized parts with complex shape. The large number of pores that formed after debinding can facilitate the nitridation process during sintering [8, 9]. Moreover, the large specific surface area of the fine powder that used in MIM can provide easy access of N and shorten the diffusion distance, so that higher N content and more uniform N distribution can be obtained. Uggowitzer [10] prepared P.A.N.A.C.E.A nickel-free austenitic stainless steel by MIM and its N content reached up to 0.8 -1.0 wt. %. HNASS prepared by injection molding and sintering under nitrogen combined with solid solution treatment can obtain complete or nearly complete austenitic microstructure [11]. Solid solution treatment can homogenize the N content, dissolving the nitrides, intermetallic compounds precipitated in the cooling process and inhibiting the diffusion of N in the subsequent quenching, so as to improve the properties of the HNASS.

Effects of sintering temperature and solution treatment on the microstructure and mechanical properties of HNASS prepared by injection molding and sintering under nitrogen were studied. The relationship between N content and mechanical properties of the samples is discussed.

2. Experiment

Spherical N₂ gas atomized duplex stainless steel powder with an average particle size of 14.3 μm provide by Sandvik Osprey was used. Chemical composition of the powder is 16-18%Cr, 11-12%Mn, 3-4%Mo, 0.8%Si, 0.3%N, 0.03%C (wt.%), and balanced with Fe. The binder consist of 65 Vol.% microcrystalline wax (MW), 25 Vol.% high-density polyethylene (HDPE), 5 Vol.% ethylene-vinyl acetate copolymer (EVA) and 5 Vol.% stearic acid (SA). The powder loading is 68 vol.% in the feed.

The fabrication process consists of mixing, injection, debinding and sintering. Mixing was performed by using a rolling mixer with rotating speed of 30 r/min, mixing temperature of 140 °C, and mixing time of 90 min. Injection molding was performed by using an injection machine (Foshan Lijuan LQ-98A, China) with injection temperature of 160 °C, injection pressure of 100 bar, injection speed of 30 cm³/s, holding pressure of 80 bar, injection time of 3s, and mold temperature of 45 °C. Solvent (n-heptane) debinding was carried out in an oil bath at a temperature of 58 °C and a holding time of 8 hours. Thermal debinding was carried out under the protection of cracked ammonia. The solvent debinded samples were placed in an alumina crucible filled with alumina ceramic beads of 2 mm diameter (pre-fired at 800 °C). The thermal debinding schedule is shown in Fig. 1. Sintering and solution treatment was carried out in a tube furnace under flowing high-purity N₂. Typical sintering schedule is shown in Fig. 1. Solution treatment was performed at 1150 °C for 1.5 h. Samples sintered at 1200 °C for 2 h are named N1200, while N1250 and N1300 represent samples sintered at 1250 and 1300 °C for 2 h. After solution treatment, they were named GN1200, GN1250 and GN1300.

Microstructure of the samples was examined by scanning electron microscopy (SEM, FEI, Nova Nano 430). The N content was analyzed by EDS and the values were averaged from 10 data measurements. Phase constituents were examined by X-ray diffraction (XRD, Panalytical X’pert) using Cu Kα radiation with a scanning speed of 1°/min. Sintered density was measured by Archimedes method. Compressive tests were performed using a universal testing machine (MTS E45.105B) with a constant strain rate of 1 × 10⁻³ s⁻¹. Vickers hardness was examined using a load of 9.8 N (HV1) with a dwell time of 15 s, and the hardness values were calculated by averaging 10 measurements.
3. Result and discussion

A. XRD phase analysis. XRD patterns of original powder, N1200, N1250 and N1300 sample are shown in Fig. 2. The XRD patterns of the powder show that it is composed of ferrite and austenite. However, the ferrite completely disappeared after sintering. When sintered at 1200 °C, the sample is composed of austenite and Cr₂N. Yet, only austenite can be detected in the XRD patterns for samples sintered at 1250 and 1300 °C. Although peaks of Cr₂N have not been observed in the XRD patterns for N1250 and N1300 sample, Cr₂N can be seen in the microstructure, as shown in Fig. 3. After solution treatment, Cr₂N was disappeared which can be proved by XRD (Not given here). The N content of the samples sintered at different temperature is given in Table 1. With the increase of sintering temperature, the N content was decreased gradually, and so the Cr₂N in samples was decreased which can improve both the plasticity and corrosion resistance of the HNASS.

B. Microstructure analysis. Fig. 3 presents SEM backscattering images of N1200, N1250 and N1300. The porosity in sample N1200 is the highest and most of them are inter-connected pores. The
pores in N1250 are almost completely closed and large pores were basically disappeared. Meanwhile, the pores in N1300 were spheroidized and the number is reduced. It is shown that densification between 1200 and 1250 °C are obvious, while between 1250 °C and 1300 °C is not as significant, and the density data listed in Table 1 also support this argument. Fig. 4 presents SEM backscattering images of GN1200, GN1250 and GN1300. There are no nitrides can be seen at these images after solution treatment.

Fig. 3 SEM backscattering images of samples (a) N1200, (b) N1250, and (c) N1300.

Fig. 4 SEM backscattering images of samples (a) GN1200, (b) GN1250, and (c) GN1300.

C. Mechanical properties. Fig. 5 is the compressive stress-strain curve of N1200, N1250 and N1300 sample at room temperature. Table 1 shows the N content, Vickers hardness, relative density and compressive properties of the HNASS. Table 2 shows the Vickers hardness and compressive properties of the HNASS after solution treatment. As reported earlier, the nitrides that formed in the sintered samples decreased and the relative density increased gradually as the sintering temperature increased from 1200 to 1300°C, the fracture mode of N1200 and N1250 is brittle fracture, along the 45° direction and stress axis, but the N1300 have enough ductility so that it did not ruptured although the compressive force reach at 21 kN. When the sintering temperature was 1250 °C, the compressive strength (σbc) was 2156 MPa and the fracture strain was 46%. As the sintering temperature was 1200 °C, since the existence of the nitrides, the hardness reaches the maximum (among the three reported) value of 321 HV. After solution treatment, the compressive strength of N1200 slightly reduced and the fracture mode was still brittle fracture, but the fracture strain increased by about 10%. However, For GN1250, it did not fracture during compressive test and showed ductility. The hardness was slightly increased with the increase of sintering temperature after solution treatment, as a result of the increase of their density.
Fig. 5 Engineering compressive stress-strain curves.

Table 2 Vickers hardness, compressive properties of the HNASS after solution treatment.

| Sample code | Hardness | $\sigma_{bc}$ (MPa) | Fracture strain (%) |
|-------------|----------|---------------------|---------------------|
| GN1200      | 237      | 1775                | 47                  |
| GN1250      | 243      | No fracture         | No fracture         |
| GN1300      | 252      | No fracture         | No fracture         |

4. Conclusion

High-N Ni-free austenitic stainless steel was prepared by injection molding and sintering under nitrogen atmosphere. Effect of sintering temperature and solution treatment on the microstructure and properties were studied. Results are summarized as follows:

1. With the increase of sintering temperature, the N content decreased but density increased and the pores are gradually closed and spheroidized.
2. Samples sintered at 1200, 1250 and 1300 °C consist of austenite and small amount of Cr$_2$N.
3. Samples sintered at 1200 and 1250 °C were brittle fracture along the 45° direction and stress axis, but samples sintered at 1300 did not fractured and showed ductility during compression.
4. The Cr$_2$N was disappeared and samples sintered at 1250 °C did not fractured during compression after solution treatment.

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