The Effect of Porosity on Mechanical Properties of Porous FeCrN Stainless Steel

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Abstract. Porous FeCrN stainless steel has excellent corrosion resistance, biocompatibility and mechanical properties matching human bone because of non-nickel and manganese, which is a new direction of medical implants. In this paper, FeCrN stainless steel with porosity of 28.21\%-60.16\% was prepared by powder metallurgy method. The microstructure, pore morphology and mechanical properties of porous stainless steel were analyzed by means of XRD, SEM, EDS and compression test. The microstructure of porous stainless steel is mostly austenite + ferrite. With the increase of porosity, the compressive yield strength, compressive strength and elastic modulus of the material decrease.

1. Introduction

Medical stainless steel is widely applied for its mechanical properties, corrosion resistance, ease of manufacturing and cost effectiveness which has been a research hotpot in the field of medical implants. Stainless steel has been widely used clinically in orthopedics as artificial joints, bone repair materials and bone fixation. The mechanical compatibility of porous metal can be adjusted by introducing pores to reduce its elastic modulus. And physical properties of porous stainless steel such as large pore surface area and permeability can satisfy the functions of biological tissue growth, bonding and internal body fluid transportation. [1-3]

In terms of biocompatibility, high nitrogen nickel-free stainless steel has the potential to replace the medical grade 316L stainless steel as a new type of medical implant structure material because of the lower toxicity to human body. N and Mn are commonly used to replace precious metals and allergic Ni. Alvarez et al. [4] prepared lotus-type porous nitrogen-containing nickel-free stainless steel with a porosity of 0-50\% by vacuum melting zone melting method, but the structure and mechanical properties of lotus-type materials were anisotropic. Li et al. [5], Mondal et al. [6] and Hu et al. [7] used NH\textsubscript{4}HCO\textsubscript{3} as pore-forming agent and prepared porous titanium alloy and porous stainless steel by powder mixing and molding, respectively. The microstructure and properties of the samples showed isotropic characteristics. Porous materials with uniform structure and properties, controllable porosity and pore characteristics can be prepared by means of powder metallurgy that introducing pore-forming agent and removing pore-forming agent by preheating at low temperature.
The formation of sintering neck in powder metallurgy process depends on fresh metallic surface. The presence of oxide on the surface of powder particles not only hinders the diffusion of atoms, but also blocks the formation of sintering neck that inhibiting the sintering denseness of powder particles and reducing the performances. Therefore, it is necessary to remove the oxide on the powder surface through a reasonable process. Currently, the most common methods to used for reduced oxides include high vacuum reduction [8,9], hydrogen reduction [10,11], carbon reduction [12], etc.

In this paper, the porous stainless steel was prepared by ball milling Fe25Cr stainless steel powder through pore-forming agent removal, high vacuum reduction sintering and solid solution nitrification. The effect mechanism of porosity on mechanical properties of porous stainless steel were studied.

2. Materials used and experimental procedure

Fe25Cr powder prepared by ball milling was used in this paper. The particle size of Fe25Cr powder was 25-45μm. XRD pattern in Fig. 1(b) reveals that all ferrite of as-received powder. The as-received powder was mixed with 0.5wt.% polyvinyl alcohol (PVA) as binder, and then mixed with 30, 40, 50 and 60 vol.% ammonium bicarbonate (NH4HCO3) (< 300μm) as pore-forming agent, respectively. The powder was mixed at a V-type mixing machine for 24 h, and then cold pressed with 500 MPa. The samples are coded according to the porosity as G30, G40, G50 and G60, respectively. 3 steps process were used to prepare samples. The temperature was gradually heated from 25 to 675 °C with a heating rate of 10 °C/ min and hold for 25 min to degrease. The following parameters of the sintering process in high vacuum (3×10⁻³Pa) were used: 1250 °C(sintering temperature), 10 °C/ min, 120 min (holding time). Solution heat treatment were carried out at 1150 °C for 300 min in N₂, then quenched by water. A scanning electron microscope (SEM, NOVA NANOSEM430) was used to examine the morphology of the powder and sintered porous samples. Microstructural compositions of samples were analyzed with EDS (Oxford company, UK). Phase constituents were examined by X-ray diffractometer (XRD, Rigaku SmartLab SE, Japan) with scanning angle range of 30-100° and scanning rate of 0.04°/s. Cu Kα radiation was used. A universal testing machine (E45.105B, MTS) was used to run a compression test and the dimension of the samples were 2 mm (diameter) ×4 mm. Each sample was tested five times.
3. Results and discussion

![XRD patterns of porous FeCrN stainless steel](image)

The results of 30-60% XRD patterns show all the soluted samples consist of austenite and little ferrite. The ferrite in as-received powder transformed to some austenite in as-fabricated samples after nitriding solid solution. It is necessary to increase the nitriding time and obtain higher nitrogen content to get more austenite.
Fig. 3 SEM morphology of porous FeCrN stainless steel with porosity of: (a),(b)30%; (c),(d)40%; (e),(f)50%; (g)(h)60%

The pores are composed of three kinds of pores. One is the pore derived from oxide reduction, which presents a round hole in the powder particle with a size of less than 1μm. Another pore left between powder particles after sintering, with irregular shape and a size of less than 10μm. The large pores were formed after the pore-forming agent was removed. The pores were evenly distributed in the sample with the shape of the pore-forming agent and the size was less than 300μm.

EDS results show that there is a small amount of chromium nitride inside the particles and chromium oxide at the junction of the particles. Sintering was hindered by the oxide and thus decrease the strength. EDS-mapping results showed that the overall nitrogen content of G30-G60 samples was 0.62-0.77 wt.% after 3-hours nitriding. Porous 25Cr stainless steel is more conducive to nitriding compared with plate nitriding [13].

Table 1 EDS mapping results of porous FeCrN stainless steel

|       | N   | O   | Cr  | Fe  |
|-------|-----|-----|-----|-----|
| G30 Mapping | 0.77 | 0.45 | 19.92 | Bal. |
| G40 Mapping | 0.71 | 0.43 | 20.21 | Bal. |
| G50 Mapping | 0.62 | 0.30 | 18.61 | Bal. |
| G60 Mapping | 0.75 | 0.43 | 18.64 | Bal. |

Fig. 4 Compressive stress-strain curve of porous FeCrN stainless steel

The compressive stress-strain curves (Fig.4) of 30%-60% porous stainless steel fabricated by powder metallurgy show similar three-stage stress-strain behavior:

In stageⅠof the stress-strain curve, the deformation of porous stainless steel with different porosity shows linear elastic behavior, and the elastic modulus and yield strength decrease with the increase of porosity. In stageⅡof the stress-strain curve, the porous stainless steel with different porosity
deformation shows an obvious stress platform with unsteady flat stresses. In stage III of the stress-strain curve, the low porosity porous stainless steel fracture after the compressive stress peak, the high porosity porous stainless steel platform stage in the later stress slightly decreased, followed by denseness stage.

As can be seen from the Fig.4, the slope of the curve in the second stage is related to the porosity. As the porosity increases, the slope of the curve in stage II decreases gradually, which is determined by the porosity of the porous stainless steel: the smaller the porosity, the less space pores of the porous stainless steel, and the pores are compacted faster during the compression process.

Table 2 shows the elastic modulus and compressive strength of porous stainless steel prepared by powder metallurgy with pore-forming agent content of 30-60 vol.% are roughly in the range of 14.69-43.46 GPa and 344.46-1107.85 MPa. The elastic modulus and compressive strength of porous FeCrN stainless steel decrease with the increase of porosity.

Table 2 Compressive yield strength, compressive strength and elastic modulus of porous FeCrN stainless steel

| Sample codes | Porosity (%) | Yield strength (MPa) | Compressive strength (MPa) | Compressive strain (%) | Elastic modulus (GPa) |
|--------------|--------------|----------------------|---------------------------|------------------------|-----------------------|
| G30          | 28.21        | 86.91±2.01           | 1107.85±12.47             | 48.32±3.31             | 43.46±1.01            |
| G40          | 39.22        | 54.96±1.96           | 457.06±9.23               | 41.28±1.21             | 23.31±0.85            |
| G50          | 53.90        | 37.64±1.55           | 425.01±18.53              | 42.89±2.10             | 17.10±0.67            |
| G60          | 60.16        | 31.49±1.40           | 344.46±14.43              | 40.26±1.38             | 14.69±0.61            |

4. Conclusion

The microstructure of porous nitrogen-containing Fe25CrN stainless steel prepared by powder metallurgy method is transformed from pure ferrite to austenite after 3 steps of degreasing, high vacuum reduction and nitriding solid solution. The nitrogen content was also increased to the range of 0.62-0.77 wt. %.

The compressive stress-strain curves of 30%-60% porous stainless steel prepared by powder metallurgy show similar three-stage stress-strain behavior: elastic linear stage, plastic compact stage and fracture stage.

With the increase of porosity, the compressive strength of porous stainless steel decreases from 1107.85 MPa to 344.46 MPa, the elastic modulus decreases from 43.46 GPa to 14.69 GPa, and the compressive strain decreases slightly from 48.32% to 40.26%.

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