Densification behavior of high Co–Ni steel prepared by spark plasma sintering

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Abstract—High Co–Ni steel with excellent mechanical properties has been extensively used in aerospace and military industries. In this study, spark plasma sintering (SPS) method was used to sinter high Co–Ni steel powders. The powder compacts were heated at 100 °C/min to the desired sintering temperature under 40MPa with 10 min holding. Microstructure of the samples sintered at different temperatures were observed and their mechanical properties were tested. The results show that the as-sintered sample obtained at 1050 °C is nearly full density. The sintered high Co–Ni steel mainly composed of lath martensite shows a high level of ultimate tensile strength and yield strength.

1. INTRODUCTION
Due to excellent comprehensive performance, high Co–Ni steel has gained considerable attention during the past several decades [1, 2]. In the 1960s, the United States successfully developed HY180 steel with precipitation strengthening as the main strengthening method. With the development of the aerospace industry, a new generation of high Co–Ni secondary hardening steel AF1410 was developed. However, AF1410 steel still had some limitations in engineering applications. In 1991, the United States successfully developed Aermet100 steel based on AF1410 steel. And the fracture toughness of Aermet100 steel was significantly improved. In 2011, QuesTek New Technology developed a high-purity M54 steel using dual vacuum smelting technology [3-6].

M54 steel has an optimum combination of high strength and toughness, which frequently serves as load-bearing structural components in aerospace and military industries. The excellent properties of M54 steel depend on the lath martensite matrix with high dislocation density and the secondary hardening produced by precipitated carbides [7-9]. Compared with Aermet100 steel, the chemical composition of M54 steel reduces cobalt element, resulting in cost reduction. But M54 steel still shows the same mechanical properties as AerMet100 steel [10].

Spark plasma sintering (SPS) is a new type of powder metallurgy technology with the advantages of fast heating rate, uniform heating and short sintering time [11, 12]. Compared with samples prepared by traditional powder metallurgy, the samples prepared by SPS are characterized by high density, uniform structure and fine grains [13, 14]. Currently, SPS technology has been applied in the preparation of a variety of metal materials. Wang et al. [15] fabricated a CoCrNi medium-entropy alloy by gas atomization and spark plasma sintering. The magnetization loop indicated that this CoCrNi MEA showed good soft magnetic properties. Deirmina et al. [16] investigated strengthening mechanisms in
hot work tool steel produced by high energy mechanical milling and spark plasma sintering. The results explained that dislocation strengthening and Hall-Petch strengthening were the major contributing mechanisms in strengthening the as-sintered steel.

Although SPS has been successfully used to prepare some metal materials such as magnetic alloy and hot work tool steel, there are only a few reports on the application of this method to manufacture high Co–Ni steel. This paper attempts to obtain a new sintered high Co–Ni steel prepared by SPS technology. The densification behavior, microstructure evolution and mechanical properties of the sintered high Co–Ni steel were studied.

2. EXPERIMENTAL

The high Co–Ni steel powders with particle sizes ranging from 25 to 50μm were produced by the high-pressure nitrogen gas atomization method. The chemical composition of the powders is similar to that of M54 steel. The nominal composition of the as-supplied powders is given in Table 1.

| TABLE 1. CHEMICAL COMPOSITION OF THE HIGH CO–NI STEEL POWDERS IN WEIGHT PERCENTAGE |
|-----------------|---|---|---|---|---|---|---|
| C               | Co | Ni | Cr | Mo | W  | V  | Fe |
| 0.3             | 7  | 10 | 1  | 2  | 1.3| 0.1| Bal. |

40 g prepared powders were loaded in a graphite die with an inner diameter of 30 mm and then placed in the SPS equipment for sintering. All the sintering experiments were performed on DR. SINTER type SPS-3.20-MV equipment. The powders were subsequently consolidated at different temperatures (750°C, 900°C, 950°C, 1000°C, 1050°C) with 40MPa uniaxial pressure and 10min holding time in vacuum atmosphere. The samples were heated with a heating rate of 100°C/min up to the final temperature and the temperature was monitored with an infrared thermometer. Finally, cylindrical samples with a diameter of 30mm and different heights were obtained.

The value of theoretical density of this steel is 8.05 g/cm³. Archimedes method was carried out to measure the density of the as-sintered samples. The relative density was calculated using the ratio between the real and theoretical density values. The morphology and microstructure of etched samples were examined using optical microscope and scanning electron microscope. Hardness value was measured on Rockwell hardness tester, taking the average of five points each time. Tensile testing was conducted at room temperature via a material testing machine with an engineering strain rate of 1×10⁻³ s⁻¹. To ensure repeatability, each value was calculated from the average of three tests.

3. RESULTS AND DISCUSSION

3.1. Microstructure evolution

According to the powder sintering theory, the densification process of the samples can be divided into three stages. Figure 1(a) and (b) show the OM micrographs of the sample heated to 750°C, which reveal the evolution of the powder in the initial stage of sintering. Before densification, high density current acts on the alloy powders to produce instantaneous high temperature, which promotes the escape of gas, the volatilization of water and the rearrangement of particles. The shape of the alloy powders remain spherical, indicating no significant change.
Figure 1. Optical micrographs of the as-sintered samples heated to different temperatures: (a)-(b) 750℃, (c)900℃, (d)950℃, (e)1000℃, (f)1050℃.
In the middle stage of sintering, elevating the temperature makes the atoms quickly migrate to the bonding surface between the particles to form sintering necks. From figure 1(c) and (d), the sintering necks of the as-sintered samples are manifested clearly. A large number of sintering necks between the powders are formed at 900°C (seen in figure 1(c)). As the temperature increases, the sintering necks continue to grow and the grain boundaries diffuse into nearby grains. At 950°C, some distorted grains recover and recrystallize (seen in figure 1(d)). At this stage, the samples shrink rapidly and the density increases significantly.

When sintering enters the final stage, the samples are already highly densified and the change of shrinkage is little. It can be seen from figure 1(e) that the continuous pores in the sintered sample disappear at 1000°C. Figure 1(f) shows that grains grow slightly and many carbides appear in the steel matrix at 1050°C. SE images of the sample heated to 1050°C are shown in figure 2. It can be found that the matrix phase of the as-sintered sample is lath martensite. In addition, some small spherical pores still exist on the lath martensite matrix.

3.2. Densification and hardness

Figure 3 illustrates that relative density and hardness as a function of sintering temperature for the as-sintered samples. As the sintering temperature increases, the relative density of high Co–Ni steel is increasing. The relative density increases rapidly when the sintering temperature is below 1000°C, but it changes little when the sintering temperature is above 1000°C. The relative density of the sample sintered at 1050°C is slightly lower than that of the sample sintered at 1000°C, which may be due to the test error.
The change trend of hardness values is similar to that of the relative density. Increasing the relative density of sintered alloys and reducing the number of defects make the unit area able to withstand larger load, which results in increased hardness. For the as-sintered sample, nearly full density of 8.02 g/cm³ (the relative density is 99.6%) and hardness of 56.5HRC are approached at 1050°C.

![Graph showing relative density and hardness of samples sintered at various temperatures.](image1)

Figure 3. Relative density and hardness of the samples sintered at various temperatures.

![Graph showing tensile properties of samples sintered at various temperatures.](image2)

Figure 4. The tensile properties of the samples sintered at various temperatures.

3.3. Tensile properties
The average tensile properties of high Co–Ni steel sintered at different temperatures are presented in figure 4. It is obvious that the ultimate tensile strength, yield strength and elongation to failure all increase with increasing sintering temperature. This steel exhibits a high strength level when it reaches almost full density. The highest ultimate tensile strength and yield strength can even reach 1934MPa and 1134MPa at 1050°C, respectively. It is known that the lath martensite with high density of tangled dislocations inside it can provide high strength. Moreover, the precipitated carbides distributed on the matrix can also strengthen the as-sintered sample [17, 18]. Based on the above discussion, the high density dislocations and precipitated carbides in lath martensite matrix result in high strength of this steel. In addition, the plasticity of the high Co–Ni steel produced by SPS is acceptable. The elongation to failure of the sample heated to 1050°C can reach 3.7%.
4. CONCLUSION
The current study investigates densification behavior of high Co–Ni steel fabricated by spark plasma sintering in terms of microstructure evolution and mechanical properties. The main conclusions of this study can be summarized as follows.

- The densification process of high Co–Ni steel can be divided into three stages: the initial stage of sintering (<900°C), the middle stage of sintering (900°C-1000°C) and the final stage of sintering (1000°C-1050°C). The microstructure and properties change greatly during the middle stage of sintering, which is the main densification stage.
- The high Co–Ni steel with the relative density of 99.6% was prepared by SPS at 1050°C for 10 min with a heating rate of 100°C/min and a uniaxial pressure of 40MPa.
- At sintering temperature of 1050°C, high Co–Ni steel exhibits ultimate tensile strength of 1934MPa, yield strength of 1134MPa, elongation to failure of 3.7% and hardness of 56.5HRC. The high strength level of this steel can be attributed to the joint strengthening of lath martensite and carbides.

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