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Microstructure and mechanical properties of a new group of nanocrystalline medical-grade stainless steels prepared by powder metallurgy

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Abstract

This paper focuses on the structure and mechanical properties of powder metallurgy stainless steels (Fe–Cr–Mn–Mo–Si–N–C) developed for biomedical applications. The samples were prepared by mechanical alloying and subsequent liquid-phase sintering with a eutectic Mn-Si alloy additive. By changing the sintering aid content, the pore configuration, compressive strengths, and impact properties of the samples were assessed. The Rietveld X-ray diffraction analysis showed after sintering at 1050 °C for 60 min followed by water-quenching, a nanocrystalline austenitic structure was formed in the material. According to the mechanical experiments, by increasing the additive content from 0 wt% to 6 wt%, sintering densification, yield stress, compression strength, and absorbed impact energy were improved, where spoiling occurred when adding 8 wt% additive. Also, as realized from the impact fracture surface features, despite the presence of some unmelted additive particles, the role of the pore elimination in toughness prevailed over that of these particles.

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Keywords: Nanostructured materials; Powder metallurgy; Microstructure; Mechanical properties

1. Introduction

Metals and alloys are the oldest materials used in surgical purposes to make devices for fracture fixation, joint replacement, external splints, braces, and traction apparatus, as well as dental amalgams [1]. Nowadays, the widely used metallic biomaterials include stainless steels, titanium and its alloys, cobalt-chromium-based alloys, as well as tantalum, niobium, and gold. Stainless steels, typically AISI 316L, are conventionally used in orthopedics, with the main advantages of low cost, good mechanical properties, sufficient corrosion resistance, and easy processing. However, problems have been found with this type of medical-grade stainless steels. The most important problem is the negative effect of metal ions or fretting debris released from the implant due to corrosion and wear. Nickel and chromium are known as potentially harmful elements in the medical stainless steels. Nickel ions act as allergens in the human body, which may cause inflammations like swelling, reddening, eczema, and itching on skins [2,3].

Due to the harmful effect of nickel ions on the human body, nickel-free austenitic stainless steels, generally Fe–Cr–Mn–Mo–N system, are being considered as a potential replacement for conventional nickel-containing alloys. Because of this, with the development of new surgical stainless steels and the modification of ASTM medical standards, the nickel content is decreasing and the nitrogen content is increasing. Currently, in ASTM standards, two nickel-free medical-grade stainless steels are imported: ASTM: F2229 and ASTM: F2581.

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To produce nitrogen-containing nickel-free austenitic stainless steels, there are several methods, such as melting processes, solid nitrogen absorption treatment, and powder metallurgy. Powder metallurgy is a continually and rapidly growing technology which includes most metallic and alloy materials in a wide variety of shapes and applications. The high precision forming capability of powder metallurgy generates pieces with a near net shape and complex features, without the need of subsequent machining. In addition, the powder metallurgy process has a high degree of flexibility, allowing the tailoring of the physical characteristics of a product to suit specific properties and performance requirements. In this regard, mechanical alloying is a capable process to synthesize a wide variety of equilibrium and non-equilibrium structures, including supersaturated, metastable crystalline, quasicrystalline, intermetallic, nanostructured, and amorphous powders [4].

It is known that to meet the best mechanical and corrosion behaviors of powder metallurgy parts, high densities are imperative. To do so, a number of approaches like warm compaction, increasing sintering temperature and time, and using proper additives to activate liquid-phase sintering are under consideration. In the liquid-phase sintering process, the formation of a liquid phase promotes densification via providing a particle rearrangement, faster diffusion rate, and pore elimination [5]. Recently, mechanically-alloyed stainless steel powders with the nominal composition of ASTM: F2581 were liquid-phase sintered with a Mn–11.5 wt% Si additive [5-7]. Also, the suitable corrosion resistance and biocompatibility of this novel material were verified [8]. In this work, the effect of the additive amount on their mechanical properties is investigated by uniaxial compression and impact experiments.

2. Materials and methods

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Mechanical alloying was used to synthesize stainless steel (with the composition of ASTM: F2581: Fe-17Cr-10Mn-3Mo-0.4Si-0.5N-0.2C in wt%) and sintering aid (Mn-11.5 wt% Si) powders. The samples with 0, 2, 4, and 6 wt% additive were sintered at 1050 °C for 60 min and were then quenched in water to obtain a single-phase austenitic structure. More details on the mechanical alloying and sintering parameters are available in Refs. [5-8].

To analyze the size and shape of pores in the sintered samples, optical microscopy was used. In order to determine the final microstructure, including the formed phases and crystallite sizes after sintering, X-ray diffraction (XRD, Shimadzu Lab X-6000, Cu Kα) analysis was used, where the results were interpreted by the Rietveld method using the Double-Voigt approach.

To study the uniaxial compressive behavior of the samples, according to ASTM: E9, cylindrical samples with the aspect ratio of 1.5 were used. The compression tests was done at a constant crosshead speed of 0.1 mm/s, with at least three replicates. Additionally, in order to compare the absorbed impact energy of the samples, Charpy impact tests on the stainless steel samples of 5 × 5 × 75 mm in size (ASTM: E23), were conducted. To do so, a sample containing 3 wt.% additive was also prepared and the tests were done on the specimens containing 0, 3, and 6 wt.% additive. Finally, fractured surfaces after the impact tests were studied by a scanning electron microscope, SEM.

3. Results and discussion

According to the Mn-Si phase diagram [9], the used sintering aid was a eutectic alloy with a melting point of 1040 °C. Obviously, at sintering temperatures below 1040 °C, no additive liquation occurs and solid-state sintering merely governs [5-7]. On the other hand,

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very high temperatures accelerate the undesirable phenomenon of fast grain growth and are not cost-effective. Therefore, in this work, only the sintering temperature of 1050 °C is focused on, albeit with different additive amounts. Fig. 1 presents the effect of the additive content, from 0 to 6 wt%, on the porosity features, suggesting the evolution of densification with increasing the additive content. Sintered densities measured by the water Archimedes method have been reported in Ref. [6]. Note that, as indicated in Fig. 2, the addition of 8 wt% sintering aid leads to the detrimental phenomenon of spoiling due to the high level of liquid formed during sintering; thus, the higher contents were not tested.

Fig. 3 shows the XRD pattern of the sintered sample containing 6 % additive. The Rietveld analysis of the XRD data depicted the formation of a single-phase austenitic structure after sintering, as confirmed with ferritoscopic measurements. Note that to have an austenitic structure, after sintering at 1050 °C, the samples were water-quenched. In addition, the mean crystallite size was measured to be less than 50 nm, where mechanical alloying had been previously created the nanostructured powders [10-15]. This nanoscale structure, even after the sintering process, have been also verified by microscopic studies [6,7], reflecting a significant resistance to grain growth. The solute drag effect combined with the contribution of carbon and nitrogen are expected to be responsible for the retarded grain growth in this material. The solubility of nitrogen and carbon atoms in crystals is limited; therefore, they segregate at grain boundaries [16-18] and retard grain boundary mobility at high temperatures [18-21].

Fig. 4 represents the true compressive stress-strain curve of the sintered samples. The yield and compression strengths extracted from the curves are also summarized in Fig. 5. As can be seen, both increases by increasing the sintering aid content, due to the progress in

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densification and the decrease of retained porosity. Moreover, an increase in elastic modulus by decreasing the pore level is observable in the curve, which is in agreement with previously-reported models [22]. It is also noticeable that, despite the presence of some porosity in the samples, considerable compressive strengths were found. This is due to the strengthening contribution of the interstitially dissolved atoms of carbon and nitrogen, on the one hand, and the obtained nanometric structures, on the other hand. Note that the presence of retained porosity in implants can be advantageous for medical applications. Porosity decreases the elastic modulus mismatch of the bone and implant, and subsequently decreases the probability of loosening [23]. Also, surface porosity can help the mechanical fixation of implants [24]. As well as the better strength of these materials, their higher biocompatibility of these nickel-free stainless steels is another benefit, as compared to conventional stainless steels like AISI 316L [8].

The absorbed energy of the samples during the Charpy impact tests is indicated in Fig. 6, showing an increase in the energy by increasing the amount of the additive and thereby reducing the porosity content. Indeed, porosity acts as stress concentration sites and has a negative effect on the absorbed energy for fracture, via encouraging crack initiation and propagation.

The SEM micrograph of the impact fracture surfaces is also presented in Fig. 7. Non-spherical, irregular, and stretched pores are observed in the fracture surface of the additive-free sample (Fig. 7a), similar to those observed in the optical images. No evidence of the formation of dimples is also observed in the micrograph. All justify the low absorbed energy of this sample during the impact fracture test. However, the decrease of the level of pores is recognizable by increasing the additive content in Fig. 7, since they have been filled with the

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additive melt. As Figs. 7b and 7c suggest, the diameter and depth of dimples for the sample containing 6 % additive is higher than those for the sample containing 3 % additive, which is another evidence for the improvement of impact toughness with adding the sintering aid. Nonetheless, some discrete particles are still observed in the facture surface of the additive-containing samples. The energy-dispersive X-ray spectrum of one of these particles for the sample containing 6 % additive, as shown by an arrow in Fig. 7c, is presented in Fig. 7d. The analysis of this spectrum suggests that they are unmelted additive particles which are common in liquid-phase sintered parts, as also reported in Refs. [25,26], and can affect the impact properties via stress concentration. However, the observed improvement of toughness with increasing the additive content infers that the contribution of the pore elimination prevails over that of the presence of these unmelted particles to the impact fracture behavior.

4. Conclusions

The structure and mechanical properties of powder metallurgy Ni-free stainless steels were investigated. The outcome of this work can be summarized as follows:

1. After 60 min of sintering at 1050 °C, a fully austenitic structure with a mean crystallite size of about 50 nm was achieved.

2. A decrease in the pore level was realized by increasing the sintering aid, via optical microscopy, where by adding 8 wt% sintering aid, spoiling was observed.

3. By increasing the additive amount from 0 wt% to 6 wt%, the compressive yield strength and compression strength were increased from about 475 MPa to 700 MPa and 550 MPa to 1050 MPa, respectively. Also, an increase in the impact resistance was found by

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increasing the additive content, from the Charpy impact tests and fractographic microscopic observations.

4. Some unmelted additive particles were observed in the impact fracture surfaces of the additive-containing samples, despite the improved toughness.

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Figures

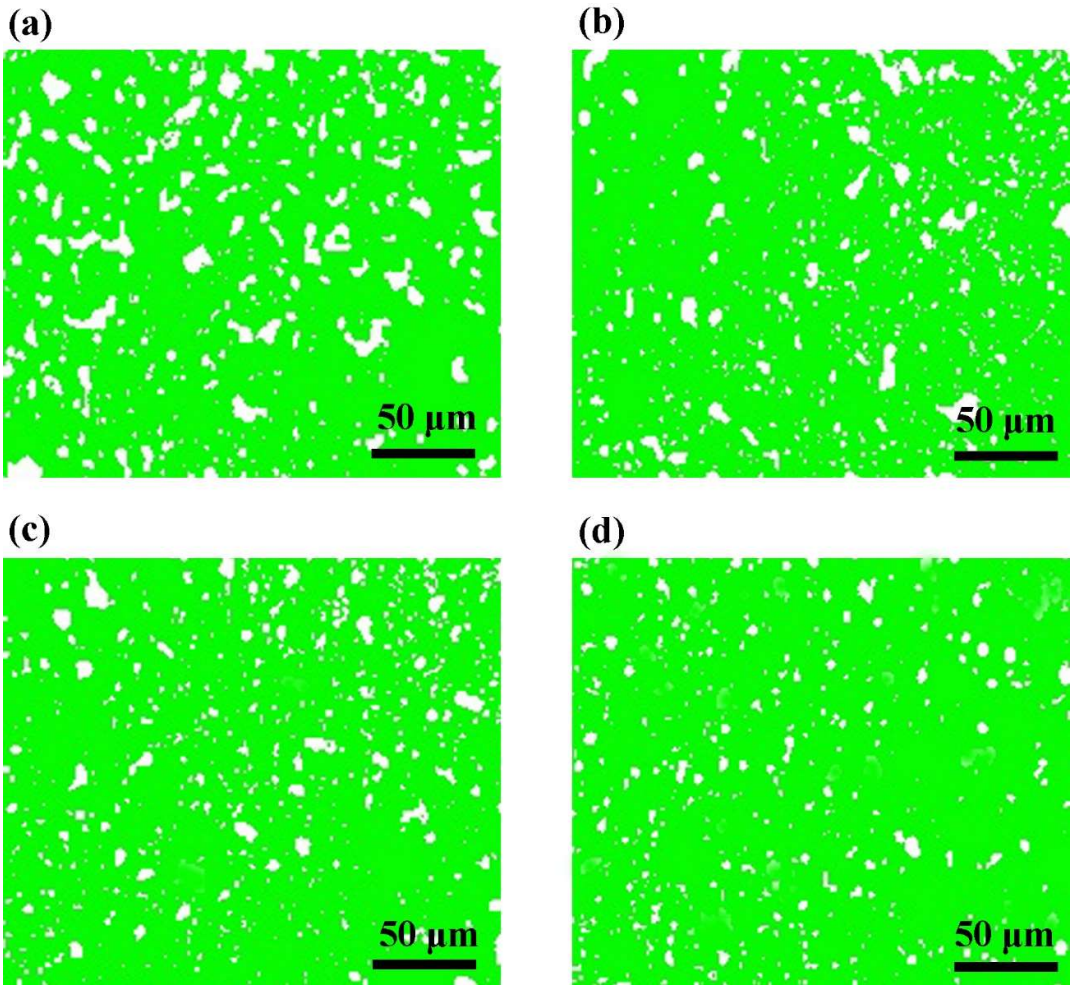

Fig. 1. Optical image analyzed photos of the sintered samples with (a) 0, (b) 2, (c) 4, and (d) 6 % additive.

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Fig. 2. Macroscopic photo of the samples after sintering.

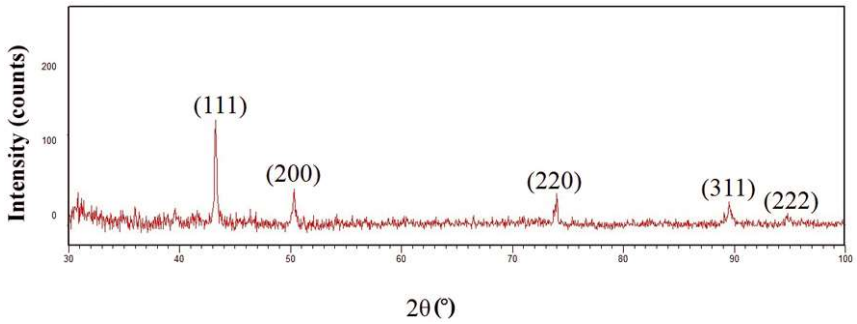

Fig. 3. XRD pattern of the sintered sample containing 6 % additive.

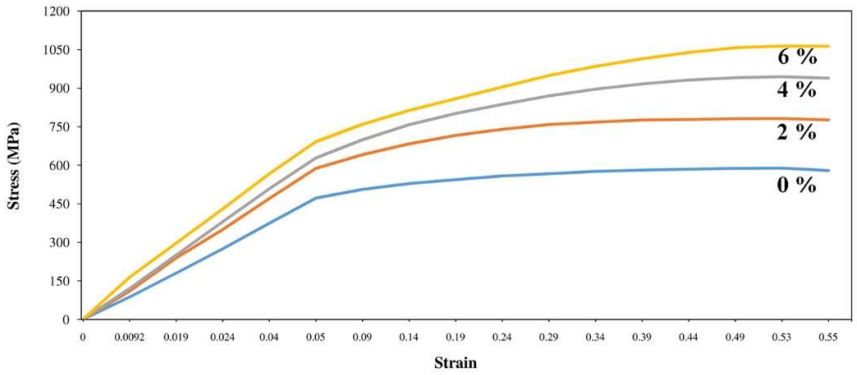

Fig. 4. Compressive true stress-strain curves of the sintered samples.

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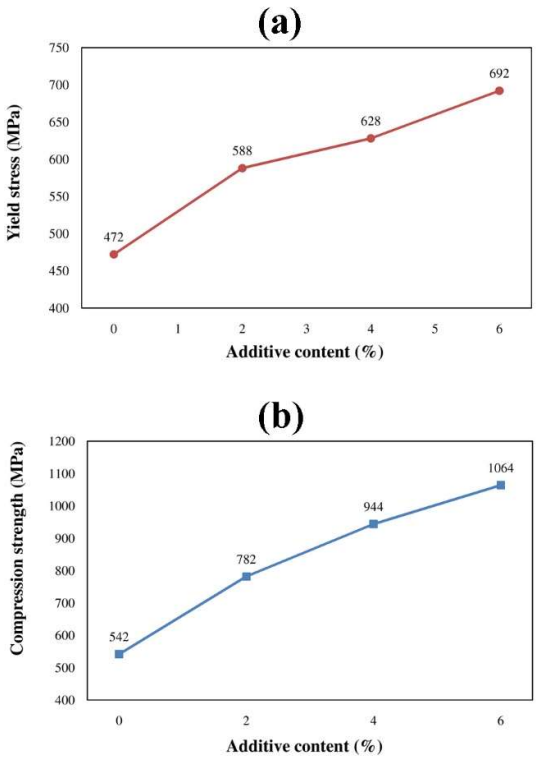

Fig. 5. (a) Yield strength and (b) compression strength of the samples, extracted from Fig. 6.

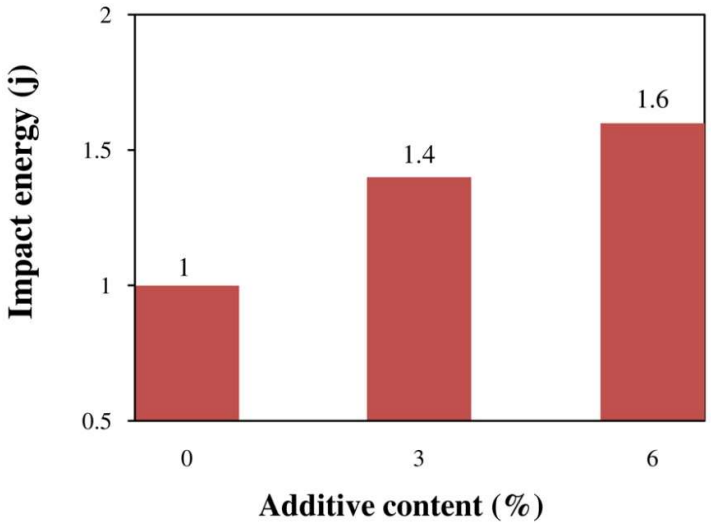

Fig. 6. Charpy impact energy of the samples at room temperature.

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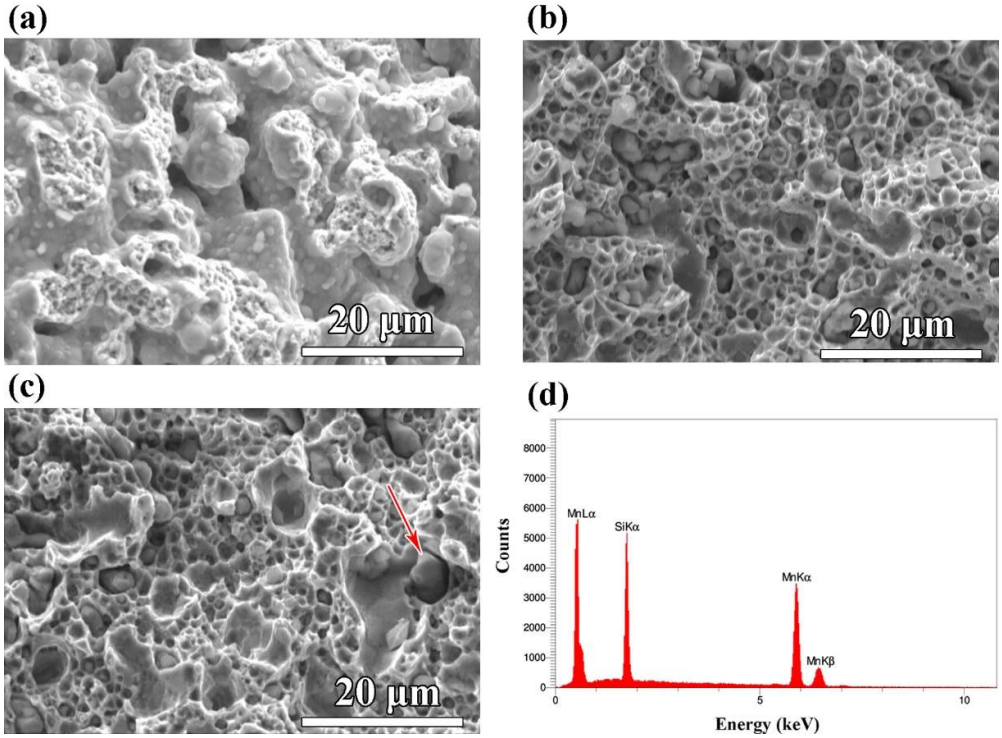

Fig. 7. SEM micrographs of the impact fracture surfaces for the samples containing (a) 0, (b) 3, and (c) 6 % additive. (d) Energy-dispersive X-ray spectrum of the particle shown with the arrow in part "c".