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https://dx.doi.org/10.1016/j.matdes.2009.10.016

Contribution of nitrogen concentration to compressive elastic modulus of 18Cr–12Mn–*x*N austenitic stainless steels developed by powder metallurgy

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Abstract

It has been reported that nitrogen atoms affect the elastic constants of austenitic stainless steels differently. In this study, the effect of nitrogen content on the compressive Young's modulus of nanostructured 18Cr–12Mn austenitic stainless steels is evaluated. The alloys are processed by mechanical alloying under a nitrogen gas atmosphere and subsequent sintering. The results show that by increasing the nitrogen concentration from 0.99 to 2.31 wt.%, the modulus progressively decreases. This is attributed to an increase in the volume of the unit cells and the weakening of the metallic bonds.

Keywords: Nano materials (A); Powder metallurgy (C); Elastic behaviour (F)

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This is the accepted manuscript (postprint) of the following article:
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1. Introduction

It is well established that the nitrogen addition to stainless steels has advantageous effects on their mechanical properties [1–4] and corrosion resistance [5,6]. Since nitrogen is a strong austenite stabilizer element, in austenitic stainless steels this biocompatible element is capable of being a replacement for nickel that is expensive and toxic. Because of this, Cr–Mn–N austenitic stainless steels have recently attracted a lot of attention from scientific and technological points of view [7–10].

It is known that the elastic stiffness of materials depends on the nature of the interatomic bonding that may change during alloying. There are several reports in the literature on the effect of nitrogen on the elastic constants of austenitic stainless steels [11–18]. It has been realized that nitrogen atoms affect the elastic constants differently, where there is not a consensus on the behavior reported for various stainless steels tested at different temperatures.

This paper considers the influence of nitrogen content on the compressive Young's modulus of nanostructured 18Cr–12Mn–*x*N austenitic stainless steels prepared by mechanical alloying and sintering processes. The Young's modulus is determined according to the standard test described in ASTM E 111 [19] by compression tests. In spite of the fact that the compression test generally gives an underestimated value of Young's modulus; the comparison of the results is acceptable if accurate measurements are conducted.

2. Experimental procedure

Fe (>99.5%, $D_{av.}$ = 50 μm), Cr (>99.9%, $D_{av.}$ = 150 μm), and Mn (>99.9%, $D_{av.}$ = 50 μm) powders supplied by Merck with a composition of 70Fe–18Cr–12Mn (wt.%) were milled in a high-energy shaker mill. To introduce nitrogen in the alloys, milling was conducted under a continuous flow of pure nitrogen gas. Details of other milling variables can be found in Ref. [7]. Milling times of 48, 72, 96, and 120 h led to the development of alloy powders containing 0.992, 1.525, 1.917, and 2.312 wt.% nitrogen measured by a LECO gas analyzer (Corp., St. Joseph, MI). The characterization of the as-milled powders exhibited that amorphous/nanocrystalline powders have been synthesized. The same authors have recently studied the structure and some properties of Fe–Cr–Mn–N alloy powders synthesized by mechanical alloying in detail [7–10]. It would be worth mentioning that by increasing milling time and subsequently nitrogen concentration, the amorphous phase content increases [7].

The powders were uniaxially cold-pressed to cylinders with diameter and length of 5 mm at a compressive pressure of 1 GPa. To prevent oxidation during sintering and to preserve nitrogen in the structure, the compacts were encapsulated in quartz tubes under an evacuated condition (10^{-5} atm). Then, the densification was performed by sintering at 1200 ºC for 2 h and then water quenching to room temperature to obtain a fully austenitic structure. The density of the sintered samples was measured by Archimedes water immersion method. The theoretical density of the as-milled powder particles was measured as 7.705 g/cm^3 by a pycnometer using He gas. Additionally, the microstructures were investigated by X-ray diffraction (XRD) (Shimadzu Lab X-6000 with Cu Kα radiation) and transmission electron microscopy (TEM, JEOL-JEM 2010). The average crystallite size was estimated by Double-Voigt approach from the XRD results using TOPAS 3 from Bruker AXS. For the TEM observations, the selected sintered samples were first cut into discs of 3 mm diameter, manually ground to about 35 μm thickness, and then ion-milled at low temperatures. The sintering behavior of a mechanically alloyed Fe–Cr–Mn–N alloy powders with an amorphous/nanocrystalline structure has been investigated in detail by the same authors [10].

To determine the Young's modulus of the specimens (with a diameter of 5 mm and a height of 5 mm), uniaxial compression tests were carried out at room temperature with a crosshead speed of 2×10^{-5} m/s using a universal testing machine. To reduce the friction at the samples loading faces, the samples were lubricated with special grease. The compressive moduli of elasticity were determined by the slope of the stress-strain line in linear regions, according to ASTM E111 [19]. A calibrated strain gauge with an accuracy of 0.005 was employed for the strain measurements during testing. At least five replicates were carried out for each specimen and the average value is reported.

3. Results and discussion

Fig. 1 shows the XRD patterns of the specimens sintered at 1200 ºC for 2 h. It is noted that to obtain an austenitic structure, the samples were immediately water-quenched after sintering. The analysis of the XRD results suggests that fully austenitic (γ) structures have been obtained after the densification process. The crystallite size of the sintered samples is listed in Table 1, determined by the XRD analyses.

The TEM micrograph and the related selected area diffraction (SAD) pattern of the sintered sample containing 0.99 wt.% nitrogen is represented in Fig. 2, confirming the validity of the XRD results. That is, this confirms the validity of the crystallite size reported by the XRD analysis. Moreover, the SAD pattern suggests nanostructured austenite. This implies that even after sintering, the nanometric structure of the material has been retained. The retarded grain growth during sintering is attributed to the segregation of nitrogen atoms to grain boundaries and the retarded crystallization of the amorphous phase existing in the as-milled powders. Since the solubility of nitrogen is limited in the crystalline structures, nitrogen atoms tend to segregate toward grain boundaries to decrease strain energy. The accumulation of considerable nitrogen contents at grain boundaries retards grain growth by decreasing grain boundary mobility. It is noted that LECO analyses after sintering on the samples revealed that the nitrogen loss during sintering is negligible (less than 0.03 wt.%), attributed to the small internal volume of the sealed quartz capsules. On the other hand, preserved nitrogen increases the stability of the amorphous phase, retarding its crystallization and affecting the resultant grain size.

Table 1 also tabulates the relative density of the sintered specimens, indicating relative densities almost ranging form 95.5 to 97 %. The compressive Young's modulus of the sintered specimens as a function of the nitrogen concentration is given in Fig. 3. It is emphasized that in addition to the nature of the interatomic bonding (matrix), porosity has a considerable contribution to the Young's modulus. One of the valid equations expressing the correlation between Young's modulus and porosity is the following relationship [20]:

$$E = E_0\,(1 - f_1 p + f_2 p^2) \tag{1}$$

where E is the Young's modulus of the porous sample, E_0 is the Young's modulus of the matrix, p is the porosity fraction, and the constant f_1 and f_2 are equal to 1.9 and 0.9, respectively. The Young's modulus of the matrix calculated by Eq. 1 is also demonstrated in Fig. 3. It should be considered that the initial length/diameter ratio of the samples affects the measured values. Note that in this work, the initial length/diameter ratio was 1. The relatively low Young's modulus of the alloys compared to other stainless steels can also be owing to the significant concentration of manganese. Because it has been found that manganese lowers the elastic constants of austenitic stainless steels [21,22]. Since the crystallite sizes of all the specimens are in a very narrow range, the Young's modulus variation merely is as a result of the nitrogen content contribution, *i.e.* the Young's modulus decreases by increasing the nitrogen content.

The results of the present research are compatible with those reported in Refs. [11–15]. It has been found that by increasing carbon and nitrogen content, the Young's moduli of AISI 304 (Fe–18Cr–10Ni–1Mn) [11] and Fe–18Cr–19Mn [12] stainless steels decrease. Furthermore, it has been realized that nitrogen in solid solution decreases all the elastic stiffnesses of 316LN stainless steels; on the contrary, the precipitation of Cr_2N contributes to an increase in all the elastic constants [13]. Theoretical models [14,15] predict a decrease in the elastic stiffnesses with the interstitial addition. In these studies, the decrease in the Young's modulus has been attributed to the unit cell expansion due to the nitrogen addition. On the other hand, our findings contradict those of a number of studies [16–18]. It has been revealed that at room temperature, nitrogen rises the Young's modulus of both cast and powder metallurgy austenitic stainless steels when the nitrogen concentration exceeds 1.5 at.% [16]. In addition, carbon and nitrogen increase all the elastic constants of AISI 304 stainless steels at liquid helium temperature [17]. It has been also concluded that nitrogen increases the elastic modulus of Fe–21Cr–20Ni alloys in the case of both solid solution and precipitation [18].

In the present work, the decrease in the Young's modulus by increasing the nitrogen concentration is explained as follows. Since nitrogen atoms occupy octahedral interstitial sites in austenite, the unit cells expand by adding nitrogen. This is because of the smaller volume of the interstitial sites of the lattice compared with the size of interstitial nitrogen atoms. This fact is completely in contrast to the effect of substitutional atoms with radii less than the radius of the parent atoms on the variation of the unit cell volume. The volume expansion decreases the Young's modulus, according to theoretical predictions based on lattice dynamics and elastic continuum models (Eshelby's model) [11,23]. Moreover, the decrease in the Young's modulus can be a consequence of the weakening of the intercluster couplings. Due to strong interatomic interactions between the Fe–N, Cr–N, and Mn–N pairs [7,9], some electrons in the metallic bonds are transferred to the metal-nitrogen bonding regions. As a result of the fact that N atoms have a higher electronegativity than Fe, Cr, and Mn atoms, a strong accumulation of electrons forms towards N atoms, giving rise to an electrons depletion near Fe, Cr, and Mn atoms. This results in the weakening of the metallic bonds that connect atomic clusters in the crystalline network [9]. Accordingly, the Young's modulus of the materials decreases by increasing the nitrogen content. That is, in this range of nitrogen concentration, the weakening effect of the metallic bonds dominates the effect of the formation of some stiff metal-nitrogen bonds on the Young's modulus.

Meanwhile, since the solubility of nitrogen in crystalline phases, especially austenite is limited and since the alloys contain considerable amounts of nitrogen, nitride compounds may exist locally in the structure, inducing localized electrons. This is in accordance with studies suggesting a decrease in the concentration of conduction electrons at nitrogen contents higher than 0.4 wt.%. In other words, in these cases nitrogen increases the covalent contribution of the interatomic bonds, inducing clustering [24]. This localized-electron bonding can increase the Young's moduli, which is in agreement with the work reported by Shankar et al. [13]. Nevertheless, as the amount of these probable precipitations is very low, they were not detected by characterization methods. The results of the present research, in which the Young's modulus decreases by increasing the nitrogen content, reflect that the contribution of probable nitrides (if they exist) does not prevail over that of the volume expansion and the weakening of the intercluster couplings. Albeit, in high-manganese stainless steels where the probability of presence of the local compounds is lower, it is believed that M–X electrons behave more itinerantly than locally (where M is a Fe, Cr, or Mn substitutional atom and X represents an N interstitial atom) [12]. Hence, this justifies the minor role of probable nitride compounds in the observed Young's modulus behavior in the high-manganese stainless steels studied here.

4. Conclusions

Nanostructured high-nitrogen 18Cr–12Mn austenitic stainless steels were developed by mechanical alloying and subsequent sintering. The results of compression tests demonstrated that by increasing the nitrogen concentration, the Young's modulus decreases. This behaviour was considered from the viewpoints of the variation in the volume of the unit cells and the weakening of the metallic bonds with increasing the nitrogen concentration. Interstitial nitrogen atoms in austenite expand the unit cell, thereby decreasing the modulus according to the Eshelby's model. Moreover, nitrogen gives rise to the electron depletion near the metallic bonds, weakening the metallic bonds and decreasing the modulus.

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Figures:

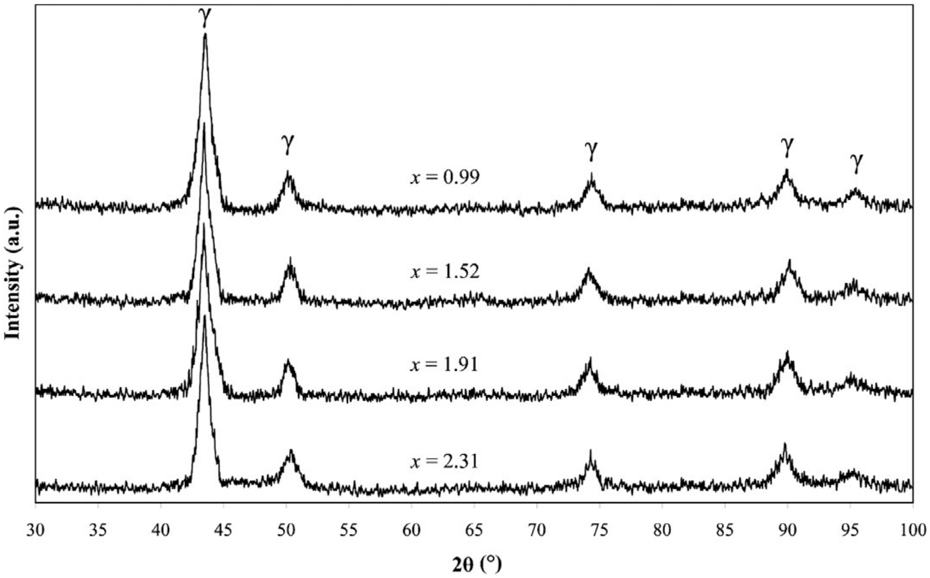

Fig. 1. The XRD traces of the Fe–18Cr–12Mn–*x*N samples sintered at 1200 ºC for 2 h (*x* is the nitrogen concentration in wt.%).

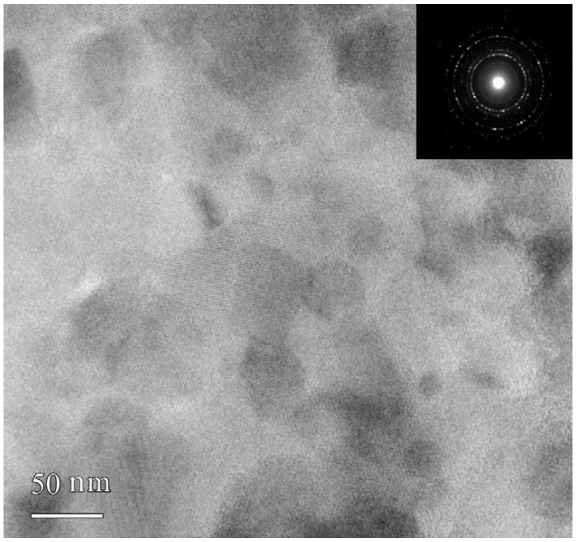

Fig. 2. The TEM micrograph and the corresponding SAD pattern of the Fe–18Cr–12Mn–0.99N specimen sintered at 1200 ºC for 2 h.

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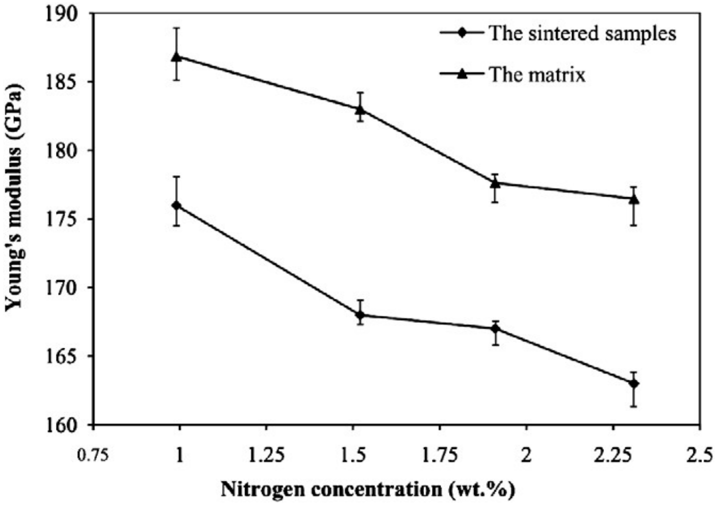

Fig. 3. The compressive Young’s modulus of the porous sintered specimens and that of the matrix vs. the nitrogen concentration.

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Table 1. The austenite crystallites size and the relative density of the sintered specimens

Nitrogen concentration (wt.%)	Crystallite size (nm)	Relative density (%)
0.99	53	96.9 <0.6>
1.52	51	95.6 <0.3>
1.91	48	96.8 <0.4>
2.31	49	95.9 <0.5>

Error value: <X> = ±X