MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF NICKEL-FREE NANOCRYSTALLINE AUSTENITIC STEEL

Maciej Tulinski, Mieczysław Jurczyk

Summary

In this work, a nanocrystalline nickel-free stainless steels have been synthesized by the combination of mechanical alloying (MA), heat treatment and nitrogenation of elemental microcrystalline Fe, Cr, Mn and Mo powders. The process parameters, morphology and microhardness of obtained powders were determined. Phase transformation from the ferrite phase to austenite was confirmed by XRD analysis. Corrosion potentiodynamic tests were performed in H_2SO_4. The microhardness of the final bulk material was studied using Vickers method. According to existing conceptions, decreasing of material's crystallites size to nanometric scale allows to achieve much better mechanical properties (e.g. microhardness) compared to conventional materials. With regard to austenitic stainless steels it could help to obtain better products with better mechanical properties and corrosion resistance.

Keywords: Ni-free stainless steel, mechanical alloying, corrosion

Właściwości mechaniczne i odporność na korozję bezniklowej nanokrystalicznej stali austenitycznej

Streszczenie

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Introduction

Stainless steels are very important materials in regard of economical and technological point of view. To date, there are more than 200 different types of alloys that belong to stainless steel family. Stainless steels are used in a wide

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variety of services in which primary considerations are long service life, reliability, appearance and sanitary factors. Important interest is the use of these materials in the medical field. Presently, eg. most biomedical implants consist of a stainless steel framework. However, widely used 316L steel is not fully biocompatible, and has induced high occurrences of restenosis and thrombosis. Moreover, nickel ions produced due to corrosion are reported to cause allergies and even cancer. Nickel free austenitic stainless steels with nanostructure are one of the promising materials that fulfill these challenging criteria.

Nickel, which is austenite stabilizer, has to be replaced by another element with similar influence. One of the most promising austenitizing elements to replace nickel is nitrogen. Nitrogen increases austenite stability, corrosion resistance and prevents from formation of the sigma phase and martensite [1].

A new manufacturing process of nickel-free austenitic stainless steels with nitrogen absorption treatment has been developed [2]. In this method, small devices can be precisely machined in a ferritic phase and than during nitrogenization of their surfaces in nitrogen gas at temperature approx. 1200°C they become nickel-free austenitic stainles steels with better mechanical and corrosion resistance properties.

MA technique has been proven a novel and promising method for alloy formation [3]. Therefore all specimens were prepared using that technique in order to achieve nanocrystalline material.

Experimental

The Fe-Cr-Mn-Mo-N alloys were prepared by mechanical alloying of stoichiometric amounts of the constituent elements (99.9% or better purity). Mechanical alloying was carried out using a SPEX 8000 Mixer Mill fitted with a hardened steel vial and 10 mm diameter steel balls. The vial of the SPEX Mill was loaded with powder in a glove-box connected to a high purity argon supply to avoid oxidation of material. The elemental powders (Fe: 10 μm, Cr: 5 μm, Mn: 44 μm, Mo: 10 μm) were mixed and poured into the vial (Fig. 1a). The mill was run up to 48 h for every powder preparation (Fig. 1b). The as-milled powders were heat treated at 750°C for 0.5 h, under high purity argon, to form

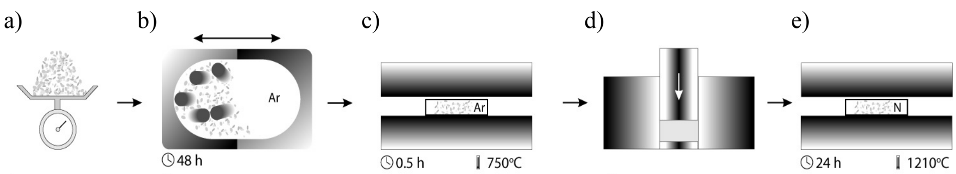

Fig. 1. Schematic representation of experimental process of manufacturing of nanocrystalline stainless steels: a) initial powders, b) mechanical alloying, c) heat treatment, d) cold pressing, e) nitrogen absorption

ordered phases (Fig. 1c). Cold pressing was carried on in hydraulic press. Samples obtained with pressure about 1 GPa were cylinder-shaped (8 mm in diameter and 2 to 4 mm height). Nitrogenation of cold pressed samples was carried out at temperature 1210^{o}C for 24 hours at 140 kPa nitrogen pressure (Fig. 1e).

The as prepared powders were characterized by means of X-ray diffraction (XRD). XRD was performed using an X-ray powder diffractometer with Co Kα radiation, at various stages during milling, prior to annealing and after annealing as well as after nitrogenation.

Microhardness measurements were carried out in Vickers method with the load of 200 g.

The analyses of the corrosion were conducted on a Solartron 1285 potentiostat in Princeton Applied Research corrosion cell system. This system was connected to a personal computer. The experiments were controlled and the data were analyzed using a CorrWare analysis software. Counter electrodes are graphite and the reference electrode is SCE (Hg/Hg_2Cl_2 – Sat. KCl). The method of polarization resistance was employed to investigate the change in corrosion. The etching solution was 0.1 M H_2SO_4. Scanning range and speed were from –1 to 2.5 V and 0.5 mV/s, respectively. Experiments were carried out at 25^{o}C. From the analyses, the corrosion current, I_{corr}, were recorded. The corrosion rate (mmPY) can be then calculated, using CorrWare software, by as follows:

$$\text{Corrosion rate} = 0.00408\ I_{corr}\ A/\ n\ D,$$

where I_{corr} is the corrosion current (A/cm^2), D is the density and A/n is the effective weight, 0.00408 is Corrosion Rate Constant.

The value D for stainless steel was 7.8 g/cm^3. The value of the effective weight, A/n, was 25.29 g.

The steel specimens were in the form of rods. The specimens were prepared and mounted according to the following steps. The stainless steel rods were formed in the dimensions of 8 mm diameter and 3 mm long. A stainless steel rod 200 mm long and 3.5 mm diameter was used for establishing the electrical contact. The whole assembly was inserted in a glass tube. Silicon resin was used to ensure the exposure of a determined apparent surface area of 0.5 cm^2.

Results and discussion

After 48 h of MA the alloy had decomposed into an amorphous phase and nanocrystalline α-Fe. Heat treatment performed after MA process results in crystallization into ferritic phase. Then, compacted material was nitrided at 1210^{o}C which resulted in phase transformation from ferrite to fully austenie

(Fig. 2). Average crystallite size of so produced material increased from 16 to 27 nm during processing and was estimated by Scherrer's method.

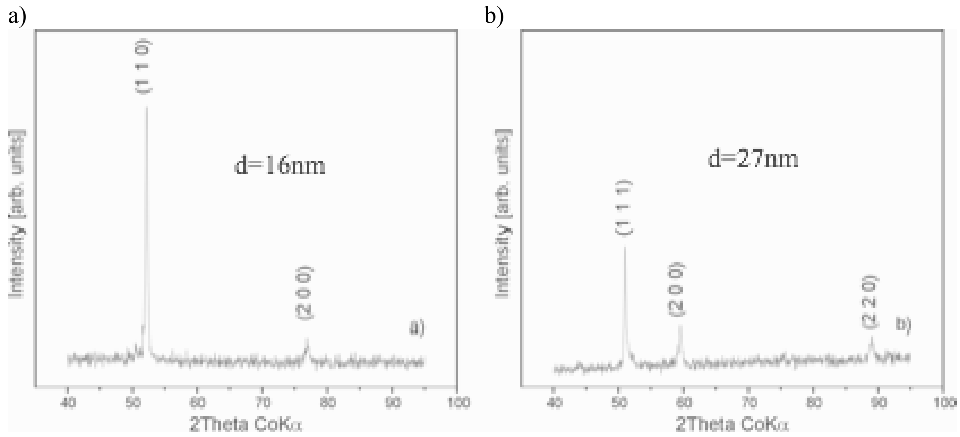

Fig. 2. Phase transformation from ferritic (a) to austenitic (b) in $Fe_{74}Cr_{24}Mo_2N$ stainless steel

Using confocal laser scanning microscope Olympus LEXT, it was possible to reveal the surface of nanocrystalline nickel free austenitic stainless steels. The surface of $Fe_{54}Cr_{24}Mn_{21}Mo_1N$ sample shown in Fig. 3 reveals pores. These pores have irregular shapes and dimensions.

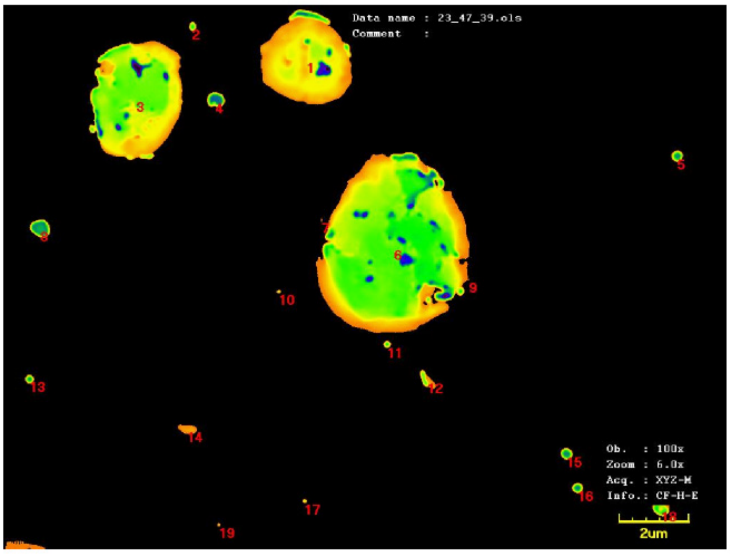

Fig. 3. Surface of $Fe_{54}Cr_{24}Mn_{21}Mo_1N$ sample under confocal laser scaning microscope

From an analysis of the surface profile it can be derived that pores penetrate to a depth of 152 to 460 nm. On the other hand, their percentage of the entire surface of the material is 9.5% and the largest pore diameter up to 4 μm.

The microhardness of the final bulk material was studied using Vickers method and the results are presented in Table 1. Compared with widely used 316L stainless steel (245 HV0.2), microhardness of sintered nanocrystalline austenitic nickel-free nitrogen containing stainless steels obtained by mechanical alloying is significantly higher (397 to 520 HV0.2). The result is two times greater than in austenitic steel obtained by conventional methods. This effect is directly connected with structure refinement and obtaining of nanostructure as well as introduction of nitrogen. Nitrogen dissolved in austenitic stainless steel increases its strength which is caused by large amount of solution hardening. The grain size hardening in N-alloyed austenitic stainless steels is based on the grain size dependance of the yield strength described by the Hall-Petch equation. The effect of N content on grain boundary hardening increases proportionally as the N content of the steel increases. Grain boundary hardening increases therefore with increasing N content of the steel and is related to the strong affininty between Cr, Mo and N atoms.

Table 1. Microhardness of synthesized nanocrystalline materials in comparision to microcrystalline OOH17N14M2 stainless steel

Sample	**Microhardness HV0.2**
OOH17N14M2	245
$Fe_{76}Cr_{24}N$	486
$Fe_{74}Cr_{24}Mo_2N$	397
$Fe_{54}Cr_{24}Mn_{21}Mo_1N$	520
$Fe_{59}Cr_{23}Mn_{12}Mo_6N$	487
$Fe_{62}Cr_{18}Mn_{18}Mo_2N$	417
$Fe_{64}Cr_{24}Mn_{10}Mo_2N$	470

Table 2 summarizes results of corrosion tests in H_2SO_4. The corrosion current, I_{corr}, is highest in the case of $Fe_{59}Cr_{23}Mn_{12}Mo_6N$ is 1.3×10^{-5} A/cm^2 . That is two orders of magnitude lower result comparing to classic OOH17N14M2 austenitic steel. The corresponding values of $Fe_{54}Cr_{24}Mn_{21}Mo_1N$ and $Fe_{64}Cr_{24}Mn_{10}Mo_2N$ are 1.6×10^{-4} and 5.1×10^{-4} A/cm^2, respectively. I_{corr} values indicate that addition of Mo and reduction of Mn resulted in appreciable decrease in the corrosion current and corrosion rate. Measured values, in most cases, are considerably improved compared to widely used OOH17N14M2 stainless steel. As presented elsewhere [4-6] these materials also posses capability of implementation in the field of medicine due to very good corrosion resistance in physiological solutions.

Table 2. Results of corrosion tests in H_2SO_4

Sample	Icorr A/cm^2	Corrosion rate mm/year
316L	3.6×10^{-3}	1.0
$Fe_{76}Cr_{24}N$	1.7×10^{-3}	3.82
$Fe_{74}Cr_{24}Mo_2N$	6.1×10^{-3}	1.2
$Fe_{54}Cr_{24}Mn_{21}Mo_1N$	1.6×10^{-4}	1.2
$Fe_{59}Cr_{23}Mn_{12}Mo_6N$	1.3×10^{-5}	0.18
$Fe_{62}Cr_{18}Mn_{18}Mo_2N$	3.5×10^{-4}	6.2
$Fe_{64}Cr_{24}Mn_{10}Mo_2N$	5.1×10^{-4}	2.1

Conclusions

High solubility of N in the solid phase of austenite combined with low pressure and short diffusion distance make solid-state nitriding of austenitic stainless steel an effective method for introducing high N contents and connected with it enhancement of mechanical properties and corrosion resistance.

Nitrogen alloying, especially of Mo-alloyed austenitic stainless steels, improves the resistance to corrosion. The beneficial effect of Cr, Mo and N can be utilized even in conventionally manufactured bulk materials obtained by cold pressing.

On the basis of the results of this study, nickel free austenitic stainless steel with a significantly improved performance can be pointed. This steel has a chemical composition: $Fe_{59}Cr_{23}Mn_{12}Mo_6N$ and its parameters are considerably better than parameters of OOH17N14M2 steel, which is the reference point. Microhardness is almost two times higher and despite 9% porosity, obtained material has better corrosion resistance (two orders of magnitude lower corrosion current). All these effects are directly connected with structure refinement and obtaining of nanostructure as well as introduction of nitrogen. The results demonstrate the great potential of this material and the possibility of its use in the wide range of fields where corrosion resistance is most important.

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