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Evolution of structure in austenitic steel powders during ball milling and subsequent sintering

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Abstract

The aim of this work was to obtain bulk nanocrystalline austenitic steel by ball milling of steel powders and their compaction. For powder compaction pulse plasma sintering method was used. Ball milling of 316L austenitic steel powders in a planetary Fritsch P5 mill resulted in the two-phase structure consisting of austenite and martensite. Both phases exhibited crystallite size in the range 10–20 nm. The maximum content of martensite reached 66% and was observed after short processing time. The decrease of its contribution was observed after prolonged milling and was explained by stabilization of nanocrystalline austenite and residual stresses. Pulse current sintering technique allowed obtaining fully dense samples exhibiting austenitic structure characterized by grain size in the range 150–300 nm and microhardness 400 $HV_{0.3}$.

Keywords: Nanostructures; High-energy ball milling; X-ray diffraction; Magnetic measurements

1. Introduction

Steels, as the most widely applied materials, have been a subject of studies for many years. Many processing methods have been applied to improve their structure and properties. It is expected that further improvement of steels can be achieved by refinement of their structure, down to a nanocrystalline range. In recent years a number of methods for refining the structure of metals and alloys by severe plastic deformation have been developed, like equal channel angular pressing, hydrostatic extrusion and high pressure torsion [1]. Ball milling is also regarded as an effective method for obtaining nanocrystalline alloys, if followed by successful powder compaction allowing for preservation of nanocrystalline structure. In this work an attempt was made to obtain austenitic steel in the nanocrystalline state by ball milling of powders followed by their compaction.

2. Experimental details

Commercial (Höganas) atomized powders of 316L austenitic steel (17% Cr, 13% Ni, 2.2% Mo, 0.2% Mn, 0.8% Si, 0.02% C, balance Fe) were subjected to ball milling. Fritsch P5 planetary ball mill equipped with hardened steel vials and balls was used for milling experiments. The mill operated at 250 rpm. The mass of powder was 10 g and ball-to-powder weight ratio was 10:1. All powder handling was performed in a glove bag under an argon atmosphere. X-ray diffraction (XRD, Philips PW 1830, Cu Kα radiation) was applied for phase analysis and determination of crystallite size using Hall–Williamson method [2], as well as for estimation of the fraction of austenite and martensite in the structure of steel from the area of diffraction peaks corresponding to both phases. Differential scanning calorimetry (Perkin-Elmer DSC 7) allowed thermal effects registration during heating the powders. The samples were continuously heated within the temperature range from 50 to 720 °C applying the heating rate of 20 $^\circ C\,min^{-1}$. Transmission Mössbauer spectra were measured at room temperature using a 25 mCi ^{57}Co-in-Rh source. The relative contents of the phases present in the samples were calculated as a ratio of the area of the relevant subspectrum to the total spectral area, assuming similar Debye–Waller factors for each phase. Magnetization measurements were performed in a broad temperature interval with the Faraday balance in magnetic field up to 1.5 T. The contribution of martensite in the structure of steel was calculated assuming the mass magnetization of martensite to be equal to 146 $A\,m^2/kg$ [3]. The ball milled powders were compacted by pulse current sintering technique [4], applying the optimised parameters: discharge voltage 8 kV, pulse current 70 kA, impulse duration 500 μs, temperature 1050 °C, time 5 min and pressure 40 MPa. Transmission electron microscopy (TEM) observations were carried out for compacted samples using Philips EM 300 unit. Density was measured using a Gibertini E154

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balance equipped with a device for measuring the density of solids (Archimedes method).

3. Results

Fig. 1 shows a sequence of XRD patterns recorded for the samples subjected to milling for increasing time. The starting powders reveal fully austenitic structure. Ball milling of powders results in very fast partial transformation of austenite into martensite, observed already after 1 h of processing. Further milling changes the proportions between both phases only. The significant broadening of the diffraction lines belonging to both phases testifies their nanocrystalline nature. The changes of crystallite size of both phases with milling time are shown in Fig. 2. A typical behaviour for metallic powders is observed, i.e. a significant decreasing of crystallite size down to 10–20 nm. Simultaneously, an increase of lattice strain up to 1% was observed.

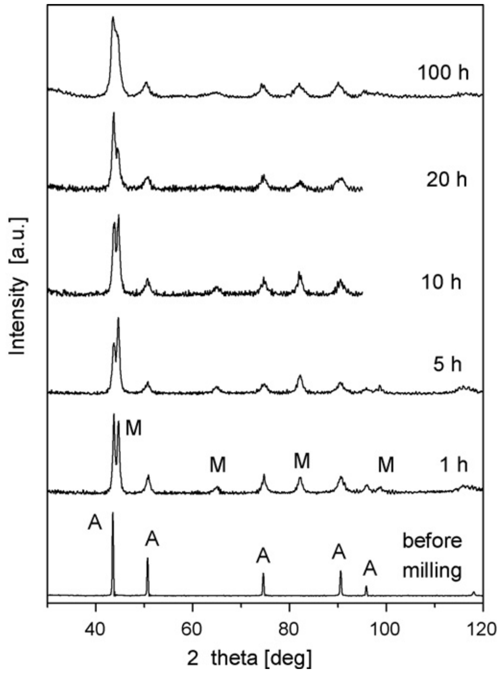

Fig. 1. XRD patterns of powders milled with increasing time. A, austenite; M, martensite.

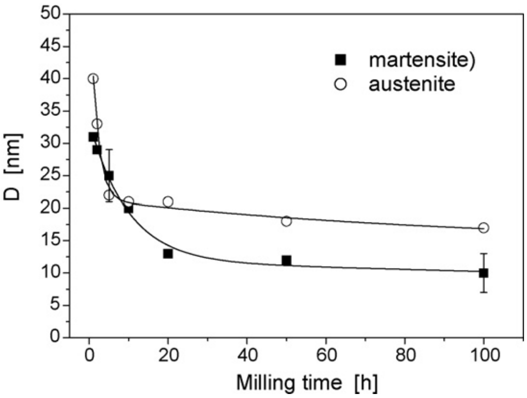

Fig. 2. Dependence of crystallite size of martensite and austenite on milling time.

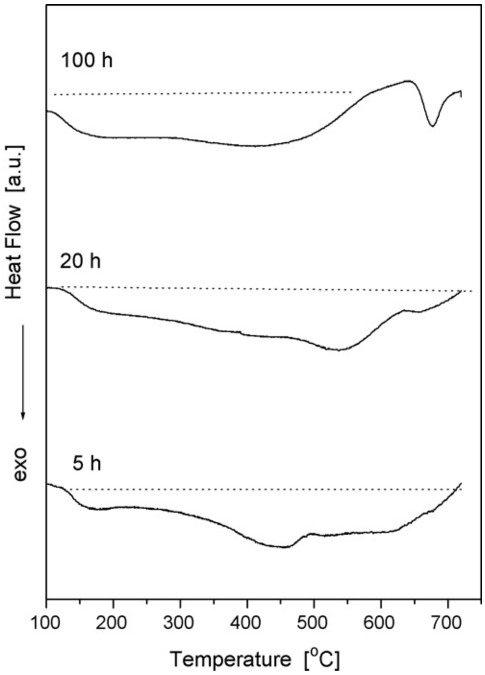

Fig. 3. DSC curves registered for selected ball milled samples.

The DSC curves recorded during heating of selected samples up to 720 °C are presented in Fig. 3. All curves reveal exothermic effects in the broad temperature range. Only for the sample ball milled for 100 h more distinct peak is visible at 670 °C. The total heat evolved changes from 20 to 40 J/g, depending on milling times.

The Mössbauer spectrum of the starting powder consists of the paramagnetic component characteristic for the austenitic phase (Fig. 4). The quadrupole doublet observed at the centre of the spectrum is characterised by a small quadrupole splitting of 0.18 mm/s and isomer shift of −0.10 mm/s. After already 1 h of milling a magnetic six-line component appears in the spectrum. This sextet with characteristic broad lines and hyperfine field of 26.8 T is related to the martensite phase transformed from the austenite during the milling process. The results of Mössbauer analysis are collected in Table 1.

The results of magnetization measurements as a function of milling time and temparature are shown in Fig. 5. All the milled samples exhibit the strong ferromagnetic ordering with Curie temperature exceeding 835 K, depending on milling time. The temperature variation of magnetization shows approximately linear decrease up to about 700 K, which is followed by the faster one at higher temperatures.

The changes of martensite fraction in the structure of steel with milling time, determined by three different techniques (XRD, Mössbauer spectroscopy and magnetization measurements) are shown in Fig. 6. All curves exhibit the same character. As determined from XRD measurements, the maximum content of martensite (55%) is observed after relatively short milling time, i.e. 2 h. For longer milling times a decrease of martensite

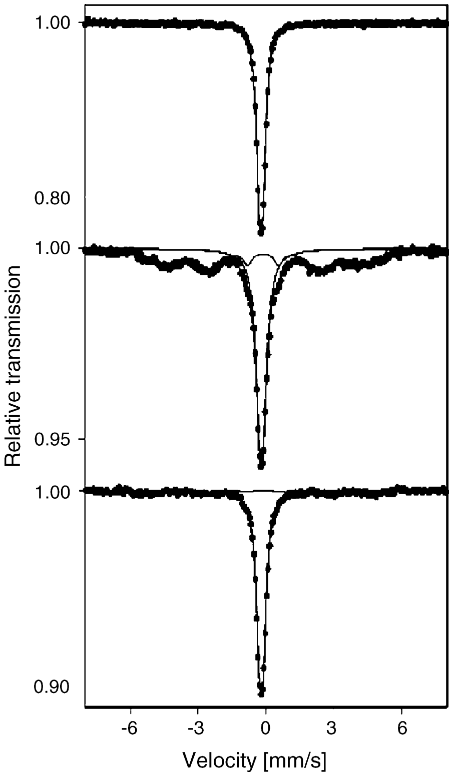

Fig. 4. Mössbauer spectra collected for the samples (from the top): before milling, after 100 h of milling and after 100 h of milling followed by heating in the DSC.

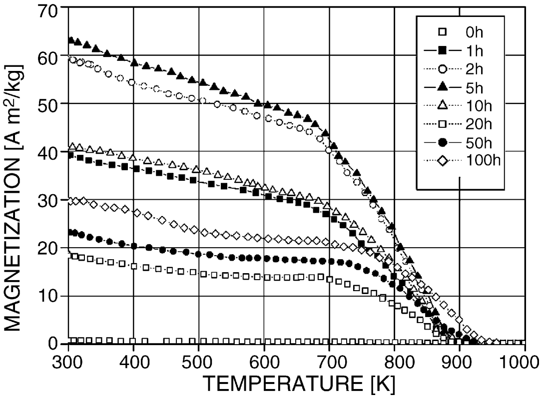

Fig. 5. Magnetization vs. temperature for the samples after all milling times.

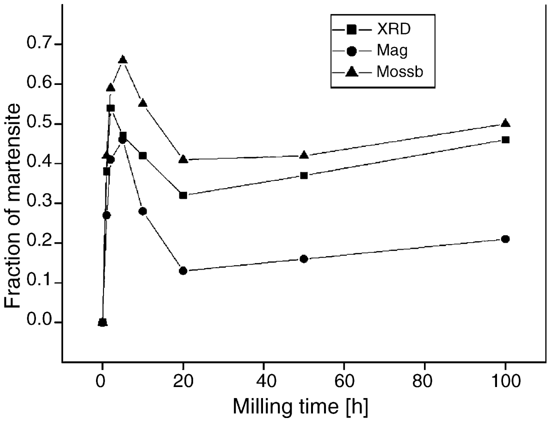

Fig. 6. Dependence of martensite fraction in the structure of steel on milling time, determined by three different techniques.

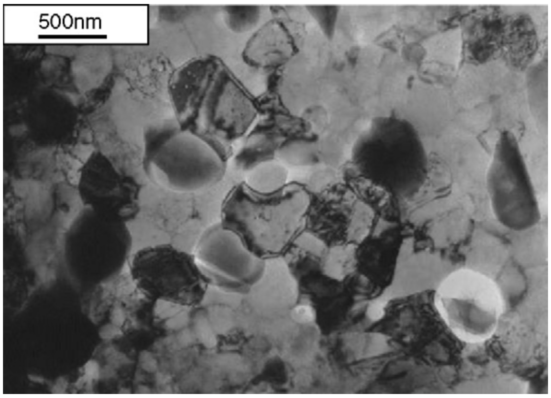

Fig. 7. TEM micrograph (bright field) of the compacted sample after pulse current sintering.

fraction down to 32% is observed, followed by an increase up to 46% after 100 h of processing.

The powders ball milled for 100 h were subjected to pulse current sintering. A fully dense sample was obtained. The XRD pattern of this sample reveals the diffraction lines belonging to austenite phase mainly. However, the traces of ferrite lines are also visible.

The microstructure of fully dense sample after pulse current sintering observed in TEM is presented in Fig. 7. The grains of austenite, some of them deformed, with sizes in the range 150–300 nm are visible. The microhardness of the compacted sample was 400 $HV_{0.3}$.

Table 1

Hyperfine parameters (QS, quadrupole splitting; H_{hf}, hyperfine field; IS, isomer shift; A, relative content) of the phases observed in the 316L steel powders determined from the Mössbauer spectra

Sample	Austenite			Martensite		
	QS (mm/s)	IS (mm/s)	A (%)	H_{hf} (T)	IS (mm/s)	A (%)
Powder before milling	0.18	−0.10	100	–	–	–
After 100 h of milling	0.18	−0.08	50	26.8	−0.01	50
After milling and heating up to 720 °C in the DSC	0.18	−0.09	92	30.5	−0.02	8

4. Discussion

Ball milling of 316L austenitic steel powders results in partial transformation of austenite into martensite phase, as confirm XRD, Mössbauer spectroscopy and magnetization measurements. The fraction of martensite increases rapidly, reaching the maximum after short milling time (2–5 h). Prolongation of processing leads initially to a decrease of martensite content in the structure, followed by a slight increase after final milling time (100 h). A significant agreement between all experimental techniques applied for martensite fraction determination is observed. The character of the observed changes is the same, however, the results obtained from the magnetization measurements show lower values of martensite fraction than obtained from other methods. Such a result can arise from the decrease of measured magnetization due to the localization of defects at the grains surface.

The strain induced transformation of austenite into martensite upon ball milling of 304 austenitic steel was reported by Huang et al. [5]. The fraction of martensite determined from magnetization measurements reached 90%, however, another type of ball mill was employed for experiment. It was not possible to obtain 100% martensite in powders, probably due to the stabilisation of the austenite by the small crystallite size and by the residual stresses generated during milling. Similarly, the slight decrease of martensite contribution in the structure was observed by Huang after longer milling times. Such a behaviour can be explained by a partial reversal to the austenitic phase due to local particle temperature increase during milling, sufficient for reversion from martensite to austenite.

The results of magnetization measurements are very similar to the ones obtained by Huang et al. [5], where suppression of magnetization above 750 K was observed in 304 austenitic stainless steel powders and was ascribed to the reversal martensite to austenite transition.

A weak correlation between the total heat evolved during heating the samples in the DSC and the fraction of martensite is observed. It is assumed that the registered broad exothermic effects at the DSC curves are attributed to strain decrease and crystallite size increase. However, the transformation of martensite into austenite also takes place during heating the ball milled samples. The fraction of martensite in the sample after 100 h of milling followed by heating in the DSC up to 720 °C decreases down to 8%, comparing to 50% after ball milling, as determined from Mössbauer spectroscopy measurements.

5. Conclusions

Ball milling of 316L austenitic steel powders resulted in the two-phase nanocrystalline structure consisting of austenite and martensite. The fraction of both phases in the structure of steel depended on milling time. The maximum content of martensite, estimated from Mössbauer spectroscopy measurements, reached 66% and was observed after short processing time. The decrease of its contribution after prolonged milling was explained by stabilization of nanocrystalline austenite and residual stresses. Pulse current sintering technique allowed obtaining fully dense samples exhibiting austenitic structure characterized by grain size in the range of 150–300 nm.

Acknowledgement

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