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Ball milling of stainless steel scrap chips to produce nanocrystalline powder

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Abstract Nanocrystalline stainless steel powder was produced by ball milling of austenitic stainless steel scrap chips. The structural and morphological changes of samples during ball milling and after subsequent heat treatment were investigated by X-ray diffractometery, scanning electron microscopy and microhardness measurements. During ball milling the austenite in as-received chips partially transformed to the martensite phase with nanoscale size grains of ~15 nm. This structure exhibited high microhardness value of about 850 Hv which is much higher than that for original samples. The deformation-induced martensite partially transformed to austenite after annealing at 700 °C for 1 h reducing the hardness of powder particles.

Introduction

In nanocrystalline materials a significant fraction of atoms is located in the grain boundaries compared to inside the grains. Therefore, the properties of this group of materials are essentially influenced by the structure and properties of the grain boundaries. It is anticipated that nanocrystallinity could lead to a change of physical and mechanical properties [1, 2]. By decreasing the grain size it is possible to enhance both hardness and strength as well as ductility (and hence, formability) of materials simultaneously. The high volume fraction of grain boundaries increases the diffusion rate and solid solubilities. Nanocrystalline materials have been shown to have higher electrical resistivity, superior soft magnetic properties, higher chemical activity and higher thermal expansion coefficients in comparison with the corresponding coarse-grained materials [1, 2]. These characteristics along with the possibility to obtain different properties by controlling grain size have made nanocrystalline materials very attractive for potential engineering applications.

A wide variety of methods are introduced for the synthesis of nanostructured materials including; vapour deposition (chemical or physical), plasma processing, gas-condensation, electrodeposition and crystallization from the amorphous phase [1, 2]. However, it is well known that ball milling can also be applied as a solid synthesis route for production of a nanocrystalline structure [3]. Grain refinement of powders to the nanometre size is governed by the plastic deformation induced during ball milling. The intensive plastic deformation of powder particles at extremely high strain rate creates a high density of lattice defects, mainly dislocations. At the same time recovery phenomena, which are accelerated by a momentary increase in temperature of the powder particles, can take place, reducing the density of lattice defects. The progressive accumulation and interaction of dislocations lead to the refinement of grain size as well as an increase in lattice strain. The grain size decreases continuously with ball milling time until a saturation size is approached. Further refinement seems to be difficult to achieve for a fixed set of experimental

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conditions [4, 5]. The resulting powder can be subsequently consolidated by powder metallurgy techniques (HIP, HP, SPS) into bulk materials with desirable properties.

The austenitic stainless steels cannot be hardened to any great extent by heat treatment. They can, however, be considerably strengthened by cold work and/or grain refinement to the nanometre size. The scope of this work was to produce nanocrystalline austenitic stainless steel powder from the scrap chips. At the moment, scrap chips produced during machining is simply collected up, melted down and re-used. Ball milling technique may be used to produce large quantities of nanocrystalline powders from the scrap chips at low-cost relative to some other fabrication techniques.

Experimental methods

Stainless steel scrap chips with composition Fe-20.0Cr-7.03Ni-1.62Mn-0.40S-0.05C were used as starting material. Figure 1 shows morphology of as-received chips. The as-received chips were short, discontinuous and non-stringy with an average length of 2–4 mm and had a single C-shape morphology. To remove the oil, the as-received chips were cleaned by acetone before ball milling.

Ball milling experiments were carried out nominally at room temperature, using a laboratory planetary ball mill under Ar atmosphere. The milling media consisted of five 20 mm diameter balls confined in a 120 ml volume bowl. The bowl and ball materials were hardened chromium steel. In all ball milling runs the ball-to-powder weight ratio was about 10:1 and the angular velocity of the bowl and the supporting disc were approx. 400 and 235 rpm respectively. Structural changes of samples were studied by X-ray diffraction (XRD) in a Philips X'PERT MPD diffractometer using filtered CuKα radiation (λ = 0.1542 nm). The particle morphologies were investigated by scanning electron microscopy (SEM) in a Philips XL30 at an acceleration voltage of 30 kV with an energy-dispersive X-ray spectrometer (EDX) attachment. The hardness of powder particles was also determined by microhardness measurements using a Vickers indenter at a load of 10 g and dwell time of 10 s. Five indentations were made on each sample to obtain an average value of microhardness. Isothermal annealing was carried out to study the thermal behaviour of ball milled powders. Samples were sealed and then annealed at 700 °C for 1 h in a conventional tube furnace. The structural transitions occurred during annealing were determined by XRD.

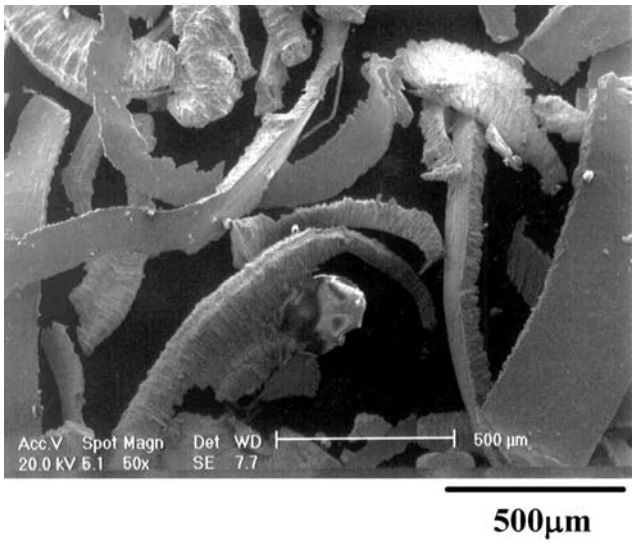

Fig. 1 SEM image of as-received chips

Results and discussion

Ball milling behaviour

The XRD traces presented in Fig. 2 show the structural changes of samples during ball milling process. The

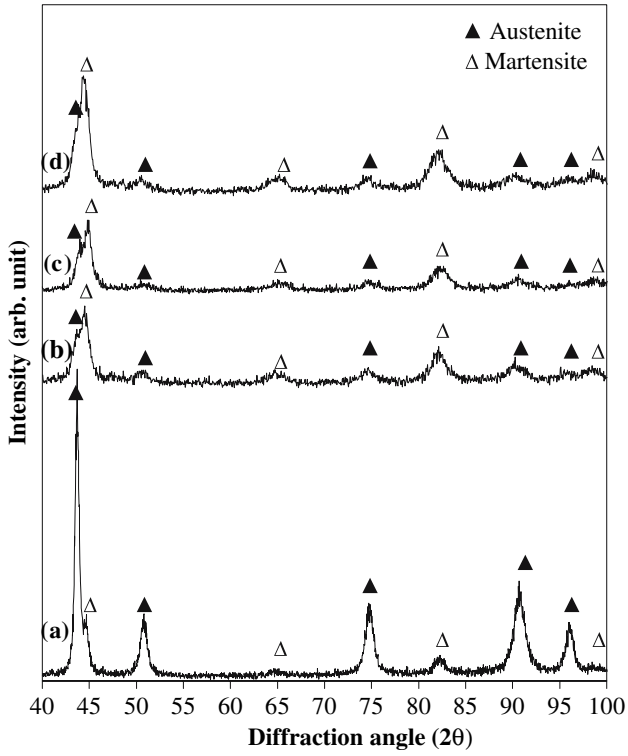

Fig. 2 XRD traces of (**a**) as-received chips and ball milled powders for (**b**) 25 h, (**c**) 50 h and (**d**) 100 h

as-received chips had a dual-phase structure consisting of austenite and martensite phases. Austenite appeared to be the predominant phase in the as-received chips. As-seen in Fig. 2b after 25 h of ball milling the intensity of diffraction peaks of austenite decreased significantly, and instead, the diffraction peaks of martensite became more pronounced suggesting a remarkable increase in fraction of martensite phase with ball milling process. Increasing ball milling time to 50 h and then 100 h only led to a slight increase in fraction of martensite. The austenite did not completely transform to the martensite structure even after 100 h of ball milling time. In fact the austenitic stainless steels are classified into two groups according to the stability of the austenite in the microstructure: stable austenitic and metastable austenitic stainless steels [6]. The structure of the metastable austenitic stainless steel is transformed to some degree by cold working so that a mixed martensitic-austenitic structure is developed [6]. It is worth nothing that, in contrast to the as-received chips, the ball milled powders exhibited a very strong ferromagnetic behaviour as a result of a high fraction of martensite in the ball milled sample.

Ball milling is often associated with the broadening of the crystalline diffraction peaks as a result of refinement of crystallite size as well as accumulation of internal strain. The crystallite size and internal strain of austenite and martensite were calculated by analyzing the X-ray diffraction peak broadening after correcting for instrumental broadening. The approach of Williamson and Hall was used to separate the two effects of crystallite size and strain [7].

$$\beta \cos\theta = \frac{K\lambda}{D} + 2A\sqrt{\langle \varepsilon^2 \rangle} \sin\theta \qquad (1)$$

Where θ is the Bragg diffraction angle, D is the crystallite size, ε is the average internal strain, λ is the wavelength of the radiation used, β is the diffraction peak width at half-maximum intensity, K is the Scherrer constant (0.91) and A is a coefficient which depends on the distribution of strain; it is near to unity for dislocations. Both austenite and deformation-induced martensite achieved a nanocrystalline structure after 25 h of ball milling time. The average grain size of the austenite and martensite was about 10 nm and 15 nm respectively. The average internal strain in the austenite and martensite was about 1% and 1.4 % respectively. The grain size as well as internal strain appeared not to change significantly after longer ball milling times.

SEM micrographs of the samples after 50 h and 100 h of ball milling times are shown in Fig. 3a-c. The original chips changed to the spherical powders with a narrow size distribution and a mean size of 300 μm after 50 h of ball milling time. As ball milling time increased the powder particles decreased in size so that the final product after 100 h of ball milling, Fig. 3b, had a mean size of 60 μm. A higher magnification SEM micrograph of the particle surface, after 100 h of ball milling time, is shown in Fig. 3c. The surface characteristics of powder particles suggest that the fracturing of the scrap chips predominates over

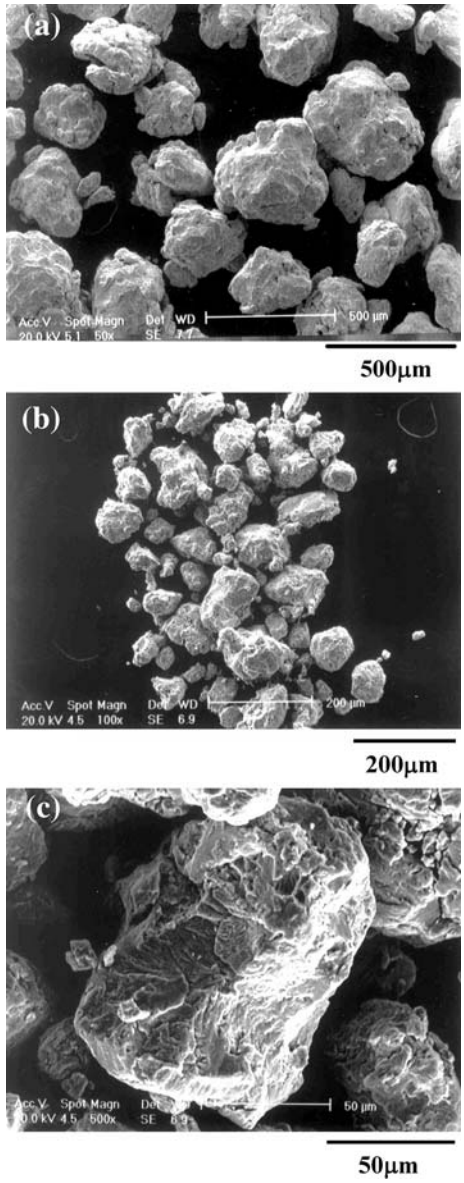

Fig. 3 SEM images of powder particles after (**a**) 50 h, (**b**) and (**c**) 100 h of ball milling times

the cold welding process even at long ball milling times.

Thermal stability

Nanocrystalline structures, whichever way they are prepared, are metastable. Consequently, on subsequent heating, a nanocrystalline structure will lower its free energy by diminishing the grain boundary area. Figure 4 shows the XRD traces of powder particles as-ball milled for 100 h and after subsequent isothermal annealing at 700 °C for 1 h. Isothermal annealing resulted in partial transformation of martensite to the austenite. The austenite and martensite crystallites after annealing had a size of 53 nm and 22 nm respectively. These values are much larger than those observed before annealing. It is of interest to note that coarsening of the crystallite size of austenite is much faster than that of deformation induced martensite. Accordingly, the average internal strain in the austenite and martensite after annealing reduced to 0.5% and 0.3% respectively. The annealed powders still continued to have a strong ferromagnetic behaviour suggesting that there is still a significant fraction of martensite, remaining from incomplete martensite-to-austenite transformation, in the sample after annealing. The microhardness measurements provided further support for presence of martensite in the annealed structure.

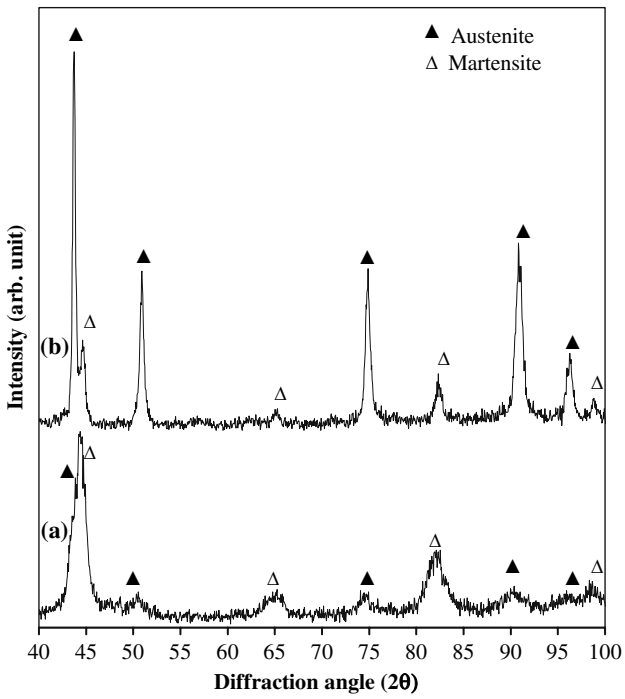

Fig. 4 XRD traces of powder particles (**a**) as-ball milled for 100 h and (**b**) after subsequent annealing at 700 °C for 1 h

Hardness measurements

The dependence of hardness on the microstructure of a material makes it a useful tool to study the microstructural changes occurring during ball milling process. The average value of microhardness of samples is shown in Fig. 5. The as-received chips had a microhardness value of 460 Hv. As seen ball milling led to a drastical increase in hardness values of the sample so that after 50 h and then 100 h of ball milling time the powder particles achieved a value of microhardness of 820 Hv and 850 Hv respectively. This is mainly caused by the formation of nanosized martensite phase. After annealing the value of microhardness for as-received chips reduced to 374 Hv while that for the ball milled powder reduced to 630 Hv and 710 Hv respectively. This decrease in hardness value is due to the transformation of martensite to austenite, in consistent with the XRD results, and grain growth process as well as annihilation of lattice defects during heat treatment.

Conclusions

Ball milling behaviour of austenitic stainless steel chips was studied. The results showed that ball milling led to the formation of nanoscale size martensite phase. The powder particles after ball milling had a dual structure consisting of austenite and martensite phases with a microhardness value twice greater than that of the original chips. The deformation-induced martensite did not completely transform to the austenite during

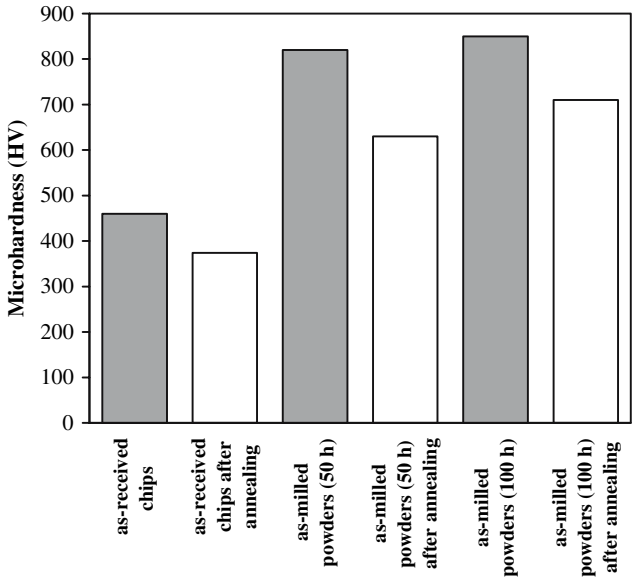

Fig. 5 Average value of microhardness of samples

annealing. These results show that ball milling technique can be readily used to produce nanocrystalline stainless steel powders from the of scrap chips.

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