Enhanced mechanical behavior of a nanocrystallised stainless steel and its thermal stability

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Abstract

This paper discusses the mechanical properties of a nanocrystallised stainless steel obtained using surface mechanical attrition treatment (SMAT) and the underlying grain refinement mechanism using transmission electron microscopy (TEM). It was shown that grain refinement down to the nanometer range has the potential to significantly improve the mechanical properties of a 316L stainless steel which becomes comparable in strength to titanium alloys. Hence, promising structural applications could be considered for such a material. At the same time, the thermal stability of this nanocrystallised material was studied in the temperature range from 100 to 800 °C. The results show that the nanometer scaled microstructure is retained up to 600 °C and that a controlled annealing treatment could even lead to enhancement of both strength and ductility of this material. All these results are explained in terms of microstructural investigations, X-ray diffraction measurements, tensile and bending tests as well as microhardness measurements.

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1. Introduction

Due to its excellent corrosion resistance and its biocompatibility, austenitic 316L stainless steel is a widely used material in environments such as the petrochemical, chemical, nuclear, and food industries [1]. However, in its coarse-grained (CG) state, austenitic stainless steel possesses relatively low strength and poor wear resistance that make it unsuitable for many structural applications. It is well known that it can be strengthened by the use of hardening mechanisms but, in this case, the strengthening phenomenon is related to an overcoming of dislocations, which usually leads to the decrease of its naturally good ductility.

It is also known that a strong refinement of the grain size can lead to additional increase of strength due to the Hall–Petch relationship. So, with the emergence of methods to produce nanostructures, new routes to enhance properties of metals and alloys are arising. Among them, the recently developed surface mechanical attrition treatment (SMAT) appears as a promising technique to generate a nanocrystallised layer on the surface of metallic materials.

To date, this technique has been successfully applied in achieving surface nanocrystallization (SNC) in a variety of materials either pure metals, alloys or steels [2–5]. The grain refinement mechanism has been well investigated but little information is available on the global mechanical behavior of such nanocrystallised materials. Over the past 10 years, several processing techniques have been developed to produce bulk nanocrystalline materials such as consolidation of ultrafine powders [6], crystallization of amorphous precursors [7], ball milling and consolidation [8], severe plastic deformation (SPD) of bulk metals [9] and electrodeposition [10]. However, due to some difficulties associated to the processing cost, the sample size and the production of samples free of contamination and porosity, it is still a challenge to prepare bulk nanocrystalline materials for structural applications. Therefore, meaningful experimental data of the physical and mechanical properties of nanocrystalline materials is still very limited.

In practice, most failures of materials originate from their surface and are sensitive to their microstructure and properties. Nanocrystalline materials have been found to
exhibit many interesting properties relative to their coarse-grained (CG) counterparts such as high hardness and strength [11–13], enhanced physical properties [11–13], rapid atomic diffusion [14], improved tribological properties [15], and superplasticity at low temperature [16,17]. SMAT provides an alternative approach to effectively upgrade the global properties of engineering materials and this, without change of the chemical composition. As SMAT is simple, flexible and low cost, this technique is potentially very useful in industrial applications.

In this work, a nanocrystallised layer was synthetized at the surface of 316L stainless steel by means of SMAT. Investigations of the microstructure and the mechanical properties were performed. In particular, it is shown that the tensile yield stress, ultimate stress and microhardness of the surface nanocrystallised sample were 141, 50 and 225% higher, respectively, than those of the CG samples. The advantage of using an annealing treatment following the SMAT, in order to obtain a material with enhanced mechanical properties (high strength and ductility), is also discussed.

2. Experimental

The material used in this investigation was a 316L austenitic stainless steel with the following chemical composition (mass%): 0.019C, 17.07Cr, 11.95Ni, 2.04Mo, 1.68Mn, 0.35Si, 0.04Cu and 0.07S. The initial grain size ranged from 10 to 50 μm. To realize the surface nanocrystallization SMAT was used. Details of SMAT were reported earlier [18–20]. For the SMAT, a large quantity of hardened steel shot (3 mm diameter) was used. The treatment times ranged from 5 to 30 min. Vibration frequency was 20 kHz and the amplitude of the sonotrode was ±25 μm at room temperature.

To study the thermal stability, samples subjected to SMAT were encapsulated in a glass tube and annealed under vacuum from 100 to 800 °C for 10 min.

Transmission electron microscopy (TEM) observations were performed using a JEOL 2010 microscope operating at 200 kV. The TEM samples were prepared by mechanically polishing the stainless steel disks down to a thickness of about 30 μm and then by dimple grinding down to a thickness of about 10 μm. Further thinning to reach a thickness of electron transparency was carried out using ion beam milling. In-plane TEM samples were prepared for different depths beneath the surface of samples subjected to SMAT. They were obtained first by polishing the corresponding surface layer and then by mechanically polishing the sample from untreated side until the sample thickness reaches about 30 μm.

X-ray diffraction (XRD) analysis of the surface layer in the sample subjected to SAMT was carried out on a Rigaku D/max X-ray diffractometer (12 kW) with Cu Kα radiation. Small angular steps of 2θ = 0.02° and a counting time of 20 s were used to measure the width of diffraction peak in the step-scanning mode. A standard SiO2 sample was employed to calibrate the instrument and the average grain size was calculated from line broadening of Bragg diffraction peaks using the Scherrer and Wilson method [21].

Mechanical properties were studied at room temperature by different methods on the samples subjected to SMAT before and after annealing.

The variation of hardness with depth was measured on a cross-sectional sample using a Nano Indenter XP™ fitted with a Berkovich diamond. The maximum load for the experiments was 20 mN, and the distance between any two neighboring indentations was at least 10 μm. Tensile tests were carried out using a computerized testing machine on untreated and both side treated samples having a cross-section of 5 mm × 1 mm or 5 mm × 0.5 mm. A displacement rate of 2 mm min⁻¹ was used for all the tests.

For bending tests, rectangularly shaped samples with dimensions of 100 mm × 15 mm × 1 mm were subjected to SMAT during 15 min on both sides.

3. Results and discussion

3.1. Microstructural characterization

3.1.1. TEM study

Fig. 1 corresponds to a TEM observation of the top surface layer of a stainless steel subjected to SMAT. Nanograins with highly random crystallographic orientation are clearly evident. Averaging over several electron micrographs yielded a mean grain size of approximately 20 nm. This result is close to the values estimated from X-ray diffraction using the Scherrer and Wilson method. This nanograin morphology is quite similar to those formed with other SPD processes [9,22]. From the corresponding selected area electron diffraction (SAED) pattern,
Fig. 2. Bright field image of ultrafine grains with twins.

one can see that the diffraction rings belong to both austenite and martensite phases. At higher magnification, Fig. 2 shows the aspect of one particular nano-sized grain. The grain boundary is well defined. A high density of stacking faults induced by deformation is observed within the grain. Similar nanocrystallites with comparable stacking fault structures were recently observed after SMAT of pure cobalt [23].

In order to clarify the process leading to the nanoscale grain in the top surface layer, the microstructure in the surface layer at different stages of straining was investigated. As the strain generated in the surface layer is non-uniform and presents a gradient distribution, the microstructure observation at various depths beneath the surface can, therefore, provide information on grain refinement mechanisms.

Fig. 3, taken at about 200 μm depth from the surface, reveals the presence of unidirectional parallel mechanical twins that lead to the formation of a twin-matrix alternative lamellar structure. A high density of dislocations can also be observed inside the twins and close to their boundaries. An arrangement of these dislocations leads to the formation of walls inside the microtwins while others are arranged into planar arrays which are particularly characteristic of material with low stacking fault energy (SFE) [24] under plastic deformation. Twinning is an additional deformation process that competes with dislocation activities as the strain increases. At 50 μm below the surface, to sustain the higher strain induced by peening, twin–twin intersections occurred. Fig. 4 shows a typical intersection of twins in the subsurface layer. The SAED is typical of superposition of two sets of twins. This phenomenon is supposed to be the origin of the process which generates nano-grains. Probably favored by the multidirectional repetitive loading, different twin systems are activated and as shown in Fig. 4, this may lead to them crossing each other. The initial coarse grains are, therefore, gradually subdivided into tiny parts bordered by large angle boundaries. Further increase of strain (close to the surface layer) causes the formation of nanometer thick mechanical twins that generate nanometer sized parts so that a refined structure starts to be

Fig. 3. TEM micrograph of the microstructure of the subsurface layer at about 200 μm deep from the treated surface.

Fig. 4. TEM image of the microstructure at the depth of 50 μm in the sample subjected to SMAT, illustrating twin–twin intersections.
formed into the nanometer scale. At the same time, a martensite transformation takes place through a strain-induced process [5,23]. At a certain strain level, in order to minimize the total system energy at the start point of the formation of the randomly oriented nano-sized grains from the refined structure, the grain boundaries may slide and/or the grains may rotate. This postulate for the possible process is based on previous studies which showed that, beyond a certain nanometer scale, classical dislocation activities no longer exist and accommodation of the plastic deformation is replaced by grain rotation and grain boundary sliding [25–27]. So, in 316L austenitic stainless steel, as in materials of low SFE, a configuration including twin–twinn intersections and mechanical twins, as well as dislocation arrays is primordial in order to develop a nanocrystallised layer. This is in good agreement with the results of other studies dealing with cold deformation of austenitic steels [5,28–30].

3.1.2. X-ray study

Fig. 5 shows X-ray diffraction profiles of the as-annealed state and the samples subjected to SMAT. Inset is the volume fraction of martensite (\(V_m\)) calculated at different annealing temperatures. It can be found that the annealed sample consists of austenite (f.c.c) while the as-treated one contains both the \(\gamma\) austenite phase and the \(\alpha^\prime\) martensite phase (b.c.c). Contrary to the findings for the SMAT of the AISI 304 stainless steel [5] (where the top surface layer becomes fully martensite) here, a martensitic transformation took place and led to a mixed structure, combining these two cubic phases. It has to be noted that the strain-induced martensitic transformation has been well studied in stainless steels [31–34]. It is interesting to note, that this kind of phase develops through the SMAT of the 316L stainless steel. Usually, in 316L stainless steel, the \(\gamma\) phase is more stable because of the presence of molybdenum and it is not prone to martensite formation. For instance, this material maintains its initial austenitic structure upon cold rolling whereas a 304L stainless steel, less stable, develops a martensitic transformation [35].

By means of successive electrolytical etchings, the treated surface was removed layer by layer, so that the structure evolution along the depth from the treated surface could be determined using XRD analyses. It was, therefore, shown that the hard martensite phase is present to a depth of about 150 \(\mu\)m from the top treated surface.

From the top surface layer, evident broadening of Bragg diffraction peaks was seen due to a grain refinement and/or an increase in the atomic level lattice strain. The average grain size of the samples subjected to SMAT was calculated to be about 12 \(\mathrm{nm}\) for the austenitic phase and 8 \(\mathrm{nm}\) for the martensite phase. The microstrain was negligible. As the depth increases, the XRD peak broadening reduces indicating that grain sizes gradually rises (not shown in the figure). In accordance with the 304L stainless steel subjected to SMAT where nearly 100% volume of martensite phase is produced at the top surface, the martensite phase is only formed at intersections of twins induced by plastic deformation. So, with an increase of the depth from the top surface, strain amplitude and strain rate decrease accompanied by a significant reduction of the martensitic transformation and even a disappearance of the latter. In the same way, the grain size rises as the depth increases.

Furthermore, with an increasing annealing treatment temperature, the peaks belonging to the martensite phase tend to increase indicating a higher proportion of martensite. The volume fraction of martensite was deduced from

\[
V_m = \frac{1/n \sum_{j=1}^{n} I_j/R_j}{1/n \sum_{j=1}^{n} I_j/R_j + 1/n \sum_{j=1}^{n} I_j/R_{\alpha}}
\]  

(1)

where \(n\), \(I\) and \(R\) represent the number of peaks of the phase used in calculation, the integrated intensity for reflecting plane and the material scattering factor, respectively. \(R\) is given by:

\[
R = \frac{1}{\nu} \left( |F|^2 \left( \frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \right) \right) e^{-2M}
\]  

(2)

with \(\nu\) the volume of the unit cell, \(F\) the structure factor and \(e^{-2M}\) being a temperature factor. Using the 2 0 0, 2 1 1, 2 2 0 reflections for martensite and the 2 0 0, 2 2 0, 3 1 1 reflections for austenite, \(V_m\) was determined to be about 15% just after SMAT and it reached a maximum value of 25% after annealing at 500 °C.

3.2. Mechanical properties and strengthening mechanisms

3.2.1. Microhardness

Fig. 6 shows the microhardness of the surface nanocrystallised stainless steel with the corresponding depth for two different treatment conditions. The scatter of the measured values is represented with error bar and does not exceed 5%. A first experiment was realized with a high vibration amplitude (50 \(\mu\)m) of the sonotrode and another one with a low vibration amplitude (25 \(\mu\)m) chosen during the SMAT.

The points near the surface indicate that there is no appreciable difference in hardness between the two tested conditions at the top treated surface, probably caused by a saturation effect (stabilized grain size). However, when the treatment is more
severe, the nanocrystallised hardened layer is thicker. This can be explained by a higher strain rate supported by the material in such a case. As the distance below the treated surface increases, the microhardness gradually decreases to reach the microhardness of the matrix (2.5 GPa). So, the large reduction in grain size is reflected in the significant increase of the hardness value by a factor of more than two. The high hardness value can also be explained by the presence of martensite at the top surface.

With regard to the well-established Hall–Petch equation, that relates the hardness of a material, $H_v$, to the grain size, $d$, through the expression

$$H_v = H_o + K_h \sqrt{d}$$  \hspace{1cm} (3)

where $H_o$ and $K_h$ are appropriate constants, and assuming the validity of the empirical relationship

$$H_v = 3\sigma_y$$  \hspace{1cm} (4)

(where $\sigma_y$ is the tensile stress) the tensile stress can be expressed as a function of the grain size as follows:

$$\sigma_y = \sigma_o + \frac{K_y}{\sqrt{d}}$$  \hspace{1cm} (5)

where $\sigma_o$ is the friction stress and $K_y$ is a yield constant. Thus, a high tensile stress of the treated surface layer can be expected. Taking into account the expression (3), the grain size distribution along the depth was determined so that the mechanical features of the transformed layer could be revealed. It was established that the nanocrystallised layer (grain size less than 100 nm) had a yield stress varying from 1400 to 1800 MPa. These calculated values have been confirmed recently by experimental work [36] indicating that even if some studies have revealed material softening [37,38] with decreasing grain size, here the Hall–Petch relation is adequate to describe the behavior of the nanocrystallised layer, especially because of the fully dense and the porosity-free nature of the nanocrystallised material. Then, as the depth increases, the yield stress gradually decreases along a transition layer to finally reach the value of the bulk. Thus, after SMAT, the surface layer exhibits advanced mechanical properties with a very high strength, higher than any kind of Ti alloys. Combined with the transition layer, it may contribute to the overall increase of the mechanical properties of the treated sample. It should be noted that an enhanced role of small grain size in the formation of high strength state materials was also revealed elsewhere [9,39,40].

### 3.2.2. Tensile and bending properties

Tensile stress–strain curves of surface nanocrystallised stainless steel are shown in Fig. 7 for different SMAT time conditions. For comparison, the curve of an annealed coarse-grained sample with the same geometry as the samples subjected to SMAT is also plotted. Compared with the coarse-grained state, the surface nanocrystallised samples processed by SMAT are characterized by two significant features: firstly, by significantly high values of yield stress and ultimate stress, and, secondly, by less pronounced strain hardening. The latter is obviously caused by change in the deformation behavior of nc stainless steel in which grain boundary sliding may occur [41,42]. With a treatment time of 30 min, the yield and ultimate stresses were increased by 141 and 30%, respectively, compared to the coarse-grain counterpart. These higher stress values of the nanocrystallised stainless steel are explained by the high performance of the nanocrystallised layer which sustains an important part of the loading during the deformation and contributes to the overall improvement of the properties of the bulk treated sample. This conclusion agrees with the results of recent work [36], in which tensile tests were performed on miniaturized specimens and where rather high strength in the nanocrystalline layer was revealed. It is worth noticing that the thicker the nanocrystalline layer is, the better the performances are.

To evaluate the influence of the nanocrystalline layer and because of its rather low thickness (several tens of microns), which causes difficulties for direct mechanical measurements, bending tests were performed (see Fig. 8). These bending tests
were carried out on treated and untreated specimens, all with the same geometry. The bending load–displacement curve in Fig. 8 shows that higher bending load can be achieved due to the presence of the nanocrystallised layer in comparison with the non-treated material. This result is in good agreement with those observed by Popov et al. on ultrafine grain/nanocrystalline materials prepared with processes including severe plastic deformation [43]. SMAT is thus a promising treatment to strengthen materials.

3.3. Thermal stability

In order to study the thermal stability, stainless steel samples subjected to SMAT were annealed from 100 to 800 °C for 10 min. The evolution of mechanical properties with annealing temperature are shown in Fig. 9. The thermal stability is an important issue for structural applications.

As shown in Fig. 9, the yield and ultimate stresses of both the nanocrystallised layer and the bulk treated material are stable at temperatures up to 600 °C which is remarkable. Annealing at temperatures between 300 and 500 °C is particularly beneficial since it improves both ductility and strength. Annealing at 300 °C causes an increase in σu above the as-processed condition. An analogous increase in strength characteristics was observed after annealing of ultrafine/nanocrystalline grain materials prepared by SPD [44]. Evidently the structural changes are connected with the redistribution of dislocations and formation of a more ordered structure. As seen in Fig. 1, the grain boundary contours in the nanocrystalline layer present some extinction (poorly defined) and these appear to be mostly curved and wavy; they are characteristic of a structure with a high density of defects [9]. Also, the subsurface exhibits a layer with very high dislocation densities in the matrix and between the mechanical twins. All these defects induced by the elongation of the surface during SMAT are associated with the formation of compressive residual stresses in the surface layer. In reference to [9,44], annealing treatment reduces the internal stress by annihilation of these dislocations. This phenomenon, coupled with a grain size increase, can also explain why the elongation to failure increases with the annealing temperature, especially for temperatures higher than 600 °C. At the same time, some defects migrate from the interior to the grain boundaries so that strength of the material increases.

Fig. 10 shows the variation of the average grain size in the top surface layer (about 5 μm thick) with the annealing temperature derived from XRD analysis. A significant increment in grain size onsets at about 600 °C, below which a slight increase in grain size was noticed, from 12 nm in the as-treated sample to about 17 nm at 500 °C. Additionally, preliminary observation by TEM [45] has shown that after annealing treatment conducted at 500 °C for 2 h an almost identical microstructure was seen as in the as-treated sample. When the sample was annealed at 700 °C for 2 h, an obvious abnormal grain growth occurs, resulting in the formation of rather larger grains (>50 nm in size) with poorly defined grain boundaries. An increase in grain size could explain why annealing at temperatures higher than 600 °C causes σu to decrease. In order to determine the thermal stability of the nanocrystallised layer, the microhardness was also measured on
the top surface layer after the various annealing treatments. No obvious decrease was observed for the chosen range of temperature, except around 400 °C where a slight decrease can be observed, probably due to a relaxation structure. Thus, nanostructures processed by SMAT exhibit high thermal stability up to 600 °C. Comparable results were obtained by Nikitin et al. [46] on the thermal stability of a nanocrystalline surface layer generated by deep rolling of AISI 304 austenitic steel. They showed that this superficial nanostructure is stable during short annealing up to 600 °C for up to 30 min annealing time. Origin of the dependance of ductility and strength on the temperature of post-annealing is caused apparently by structural changes. A possible explanation of the increase of the strength after annealing may be recovery.

4. Conclusion

- Analogous to the grain refinement mechanism during plastic deformation of bulk metals, formation of nanostructures from the coarse-grained polycrystals in the surface layer upon SMAT involves various dislocation activities and development of grain boundaries. In 316L stainless steel, a material with low SFE, plastic deformation change from dislocation slip to mechanical twinning and twin–twin intersections appears to be the main point enabling the nanocrystallised surface layer to be formed as observed in [5]. A deformation-induced martensite was also observed.

- Composed of ultrafine grains (<50 nm), the nanocrystallised surface layer exhibits very high tensile yield stress of 1500 MPa that is about five times higher than that of the coarse-grained counterpart as well as a high microhardness of 4.5 GPa. Because most failures of materials occur on surfaces, this nanocrystallised surface layer effectively enhances the global behavior of the studied material. As a future step, it is reasonable to propose that the generation of a nanocrystallised surface layer could improve material performance in terms of fatigue and wear resistance. As a surface treatment, SMAT also offers an alternative technique to bulk nanocrystallised materials which are time consuming and cost expensive to produce.

- The nanocrystalline layer is stable during annealing treatment up to 600 °C. During annealing, in the range of 300 to 500 °C, the high dislocation densities introduced in the subsurface layer rearrange and annihilate through a recovery process which leads to enhancement of both strength and ductility compared to an as-nanocrystallised state.

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