Influence of surface mechanical attrition treatment on the oxidation behavior of 316L stainless steel at 750°C

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Abstract. In this paper, the effects of Surface Mechanical Attrition Treatment on the high-temperature oxidation of AISI 316L austenitic stainless steel are investigated. Samples treated with different conditions were oxidized at 750°C in order to study the effect of this type of nanocrystallisation on the oxidation resistance of the alloy concerned. X-ray diffraction and in-situ Raman spectroscopy were used to identify the oxides formed at the surface. The results indicate the presence of hematite, magnetite and chromium oxides. Experimental results obtained by Raman spectroscopy were also used to study the stress evolution in Cr2O3 films during isothermal conditions.

1. Introduction
Surface Mechanical Attrition Treatment (SMAT) is a recent process that enables to nanocrystallise the surface of metallic alloys. It can enhance the mechanical properties of the treated material by inducing a grain refinement down to the nanometer scale in the top surface layer. This nanocrystallisation process leads to different effects that were successively studied on several metallic materials such as increase of the surface hardness, enhancement of wear resistance, fatigue properties [1] [2] or the coupling with nitriding process [3]. Recently, some investigations have been performed on these effects; most of them mainly focus on the surface morphologies and tribological properties [4]. It can be expected that SMAT could affect the oxidation resistance. Indeed, due to the induced grain refinement, an increase of the grain boundary fraction, from the core to the top surface of the sample, can modify the diffusion mechanisms. It is now well established that the surface reactivity can be modified by nanocrystallisation treatment [5]. Moreover, the presence of residual stresses in thermal oxide layers during the isothermal oxidation process may influence the protective properties of the oxide layers. In the present work, the effects of SMAT on the oxidation behavior of a 316L stainless steel are specifically investigated at 750°C. This stainless steel is widely used in various sectors of industry due to its high mechanical strength and generally good oxidation resistance at high temperature [6]. In the first section of the present paper, the oxidation mechanisms occurring in metal/oxide systems and phase evolution are investigated using thermogravimetric analyses, X-ray diffraction and in-situ Raman spectroscopy measurements. The latter technique is also used to evaluate experimentally the residual stresses in Cr2O3 films, thus allowing the determination of growth stresses. Finally,
the mechanisms involved are analysed in order to understand how SMAT may affect the oxidation resistance of 316L stainless steel.

2. Material and surface treatment and oxidation

3 mm thick AISI 316L samples were cut from 35 mm diameter bars and SMATed with the nanocrystallisation process SMAT. Fig. 1 shows a simple geometrical representation of the process. During the treatment, spherical 100Cr6 balls are set in motion by a high frequency (20 kHz) ultrasonic generator. Random shot impacts at the sample surface generate severe plastic deformations so that a superficial nanocrystalline layer is formed [7]. This process takes place in air at room temperature, during 20 minutes on each side of the surface sample (symmetric treatment). Suitable SMAT parameters such as processing time and shot size (3 mm) were chosen, based on previous experiments [8]. An intermediary mechanical polishing step is carried out after SMAT and before oxidation to remove a thin superficial layer of 3±0.3µm [3]. Moreover, after nanocrystallisation treatment, oxidation under different temperatures has been investigated. However, this paper only focuses on the case performed at 750°C in ambient air during an oxidation time of 20 h. This temperature was chosen and carefully investigated according to common solicitations of 316L, but also to keep benefits of the SMAT technique. Indeed, if oxidation temperature becomes too high (> 750°C), grain growth can occur and lead to the disappearance of nanocrystals [9].

![Figure 1 Geometrical representation of the SMAT process](image)

3. SMAT chemical effects on oxidation resistance at 750°C

3.1. Experimental techniques

Oxidation of the 316L stainless steel has been studied using several techniques. First, the problem has been considered from a chemical and macroscopic point of view. A classical thermogravimetric analysis in a Setaram TGA 92 thermobalance has thus been used. Samples were heated at 50°C/min up to the desired oxidation temperature of 750°C. The selected temperature is supposed to be stable after 15 min within the range ±0.1°C. The in-situ characterization of the oxide scales was carried out in a high temperature chamber adapted on a high resolution XY Raman spectrometer equipped with a CCD detector. Its wavenumber precision Δυ Raman is equal to 0.1 cm⁻¹. The stimulation source is a helium–neon laser (λ =...
632.817 nm). The crystal structure was also analysed by X-ray diffraction (XRD) with a Seifert PTS-3000 X-ray diffractometer using CuKα radiation and Bragg–Brentano conditions, directly on the sample surface.

3.2. Kinetics results
The weight change curves (per unit of surface) as a function of the oxidation time are shown in Fig. 2, for both SMATed (blue line) and untreated (red line) specimens. For untreated samples, two stages are observed: it starts with a paralinear stage (with a parabolic rate constant $k_{MP} = 7.26 \times 10^{-10} \text{ kg m}^2 \text{s}^{-1}$), then after a breakaway, the regime becomes linear with a slope of $9.82 \times 10^{-8} \text{ kg m}^2 \text{s}^{-1}$. On the other side, the curve of the SMATed 316L presents two paralinear stages, with an evolution of the parabolic rate constant from $k_{MP} = 34.2 \times 10^{-10} \text{ kg m}^2 \text{s}^{-1}$ to $k_{MP} = 3.26 \times 10^{-10} \text{ kg m}^2 \text{s}^{-1}$. Consequently, and regardless to the chosen data processing method, experiments show that SMAT may lead to a decrease in the degradation of 316L materials during high temperature oxidation at 750°C after 20 h.

![Figure 2 Mass change of untreated and SMATed 316L, during isothermal oxidation at 750°C in air.](image)

3.3. Nature of the oxides
In order to complete the previous experimental observations, the composition of the oxide layer was also studied. Fig. 3 represents XRD analyses in the conventional θ–2θ mode, for the SMATed and untreated specimens after oxidation process. Two indexed Raman spectra are also presented in Fig. 4, which only correspond to an illustration of the phases actually present within the oxide layer (at particular instants of the measurement, i.e. after 2h and 20h).
Fig. 4 shows differences between Raman spectra of SMATed and untreated samples. SMAT can lead to microstructural effects that can explain these differences. For short oxidation periods (2h), the only oxide observed is Fe$_2$O$_3$, for both specimens. For longer exposure times (20h), different oxides are found such as Fe$_2$O$_3$, Fe$_3$O$_4$ and Cr$_2$O$_3$, for both specimens. The presence of NiFe$_2$O$_4$ and significant peaks of Cr$_2$O$_3$ can also be identified in the SMATed sample. It can also be observed on the X-ray diffractogram of Fig.3 (corresponding to ambient measurement after 20 h oxidation) that the oxide layer formed on the SMATed and oxidised specimen is mainly constituted of chromium oxide, and magnetite. As for the oxidised untreated samples, they present a great amount of hematite and smaller amount of chromium oxide and magnetite. Analysing quantitatively the diffractograms with Maud program [10], it was possible to a better treatment of the XRD measurements and to extract the percentages of oxides. The oxide layer formed in the analyzed zone of the untreated sample contains 76% Fe$_2$O$_3$, 18% Fe$_3$O$_4$, 5% Cr$_2$O$_3$ (vol. %) while the oxide layer of the SMATed sample contains 60% Cr$_2$O$_3$, 40% Fe$_2$O$_4$. These results confirm the protective character of chromium oxide reflecting a better oxidation resistance of the SMATed sample. The selective oxidation of chromium could be correlated with the formation of the fine-grain structure on
the surface region of the SMATed sample. In the next part, this work will focus on the stress
evolution with oxidation time related to the oxidation kinetics.

4. SMAT mechanical effects on oxidation resistance at 750°C
Deformations have been measured using a micro-Raman spectrometer previously described.
Three peaks from the chromium oxide layer are specifically investigated in each Raman
spectrum, corresponding to the following three vibrations modes; two Bg and one Ag [11]. In
Fig. 4, these three peaks are indexed according to their wavenumber at room temperature.
The experimental stresses within the global oxide films are studied through the
determination of stresses in the Cr₂O₃ phase. Thus, by using a pseudo-Voigt fitting (with Lab-
Spec software), the corresponding wavenumber \( \nu \) is deduced as a function of the oxidation
time. Besides, in order to calibrate this methodology, the stress-free state is required. The
stress-free wavenumber evolution with temperature for the considered modes of chromium
oxide has been obtained for different temperatures in the literature [11]. The corresponding
stress-free reference spectrum at 750°C is deduced. At this working temperature, it is possible
to determine the stress in the constrained oxide from the variation of the wavenumber with
respect to this reference. The variation \( \Delta \nu \) for each mode is used to deduce the
corresponding stress \( \sigma \) (with \( \Delta \nu = \nu(T,\sigma) - \nu(T,0) \) where \( \nu(T,\sigma) \) and \( \nu(T,0) \) are,
respectively, the wavenumbers for stressed and unstressed oxides at the working temperature
T). According to Mougin [12], the following stress dependency of the \( \Delta \nu \) wavenumber was
calculated for the peak at 551 cm⁻¹:

![Figure 4 Intensity versus wavenumber. Raman spectra of untreated and
SMATed specimens, for two different times (2 h and 10 h).](image)
\[ \Delta \sigma_{ox} = -0.307 \Delta \nu \pm 120 \text{MPa} \] \hspace{1cm} (1)

Where \( \sigma_{ox} \) is expressed in GPa and \( \Delta \nu \) in cm\(^{-1}\).

Stress evolutions for untreated and SMATed samples are presented in Fig. 6.

At the beginning, the system is spontaneously able to generate increasing compressive stress in the oxide film during its growth. In a second stage, the absolute value of stress decreases because of relaxation phenomena. The shape of these curves is in agreement with previous experimental results obtained during isothermal oxidation of other metal/oxide systems, e.g. \( \text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4/\text{Fe} \) [15], or \( \text{Cr}_2\text{O}_3/\text{NiCr}_30 \) [14]. Span of both presented curves is similar with minimum values around -2 GPa and relaxation time values around 3h. After relaxation (for long oxidation times), the stress reached in the oxide film is smaller for SMATed samples, which means higher amplitude of relaxation in this case in the chromium phase.

5. Conclusion
In the present work, different experiments have been performed on nanocrystallised 316L stainless steel. High temperature oxidation of this alloy has been studied with both macroscopic and mesoscopic experiments. Specific mass gain measurements after 20 h oxidation at 750°C indicated that the mass gain of the SMATed 316L material was significantly lower than that of the untreated material, in correlation with the increase of chromina volume fraction formed within the oxide layer at 750°C. For all studied samples, XRD and Raman spectroscopy results revealed the presence of three main oxide phases: \( \text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4 \) and \( \text{Cr}_2\text{O}_3 \), which are present in the protective oxide layer. The oxide composition changed after SMAT, from Fe rich oxide to Cr rich oxide which can explain the better oxidation resistance of SMATed sample compared to the untreated one. The selective oxidation of chromium should be correlated with the formation of the fine-grain structure on the surface region of the SMATed sample. In-situ Raman measurements have been analysed and show the oxide stress evolution as a function of oxidation time, taking into account the calibration dependence of wavenumbers with temperature.
6. **Acknowledgements**

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7. **References**

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