Stainless steel patterning at micrometric scale with ICP chlorinated plasma: Process optimization and understanding of etching mechanisms

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Patterning at micrometric scale of the surface of stainless steels allows providing them with new functionalities, like tribological and optical properties. In this work, we have developed a plasma etching process using an ICP reactor with a mixture of chlorine and argon for the etching of two stainless steels: 4441 austenitic steel (17.7 wt% of Cr and 14.7 wt% of Ni) and 4116N martensitic steel (14.5 wt% of Cr and 0.2 wt% of Ni).

The development of this process was carried out relying on the study of the etching of the main metals that compose these steels, namely, iron, chromium and nickel. From measurements of etching rates coupled with optical emission spectroscopy (OES) analyzes, we have shown that, in Cl_2/Ar plasma, iron presents the highest removal, followed by chromium, then nickel. We have also studied the etching rate variation of these metals and steels as a function of the substrates temperature. These studies allowed establishing some etching mechanisms involved in the etching of metallic elements. Metals and stainless steels etched samples were analyzed by X-ray photoelectron spectrometry (XPS). We have shown that in a Cl_2/Ar plasma, iron is mainly etched by a chemical process respecting an Arrhenius law. This mechanism would rely on the formation of volatile iron chlorides. In the case of chromium, ion assisted etching is required in order to desorb the non-volatile chromium chlorides formed on the surface of the material. Finally, for nickel, we observed that the etching rate decreases when the temperature increases. XPS analyzes suggest the formation of non-volatile nickel chlorides. These chlorides would be at the origin of the nickel etch rate decrease. Understanding these mechanisms led us to conclude that, in a chlorinated plasma, the blocking element in the etching of stainless steels is nickel. Indeed, 4116N stainless steel containing 0.2 wt% of Ni have an etching rate of 55 $nm.min^{-1}$ while 4441 stainless steel containning14,7 wt% of Ni have a lower etching rate (48 $nm.min^{-1}$).

On the other hand, we observed with energy-dispersive X-ray spectroscopy (EDX) the presence of chlorine rich deposits on etched stainless steels surfaces. To avoid the formation of these deposits, a sequenced process with Cl_2/Ar plasma and H_2 plasma was developed. This process allowed us to obtain a smooth etched surface as shown in fig.1. Indeed, XPS analysis on the etched surface using sequenced plasma do not reveal any metal chloride (fig.2).

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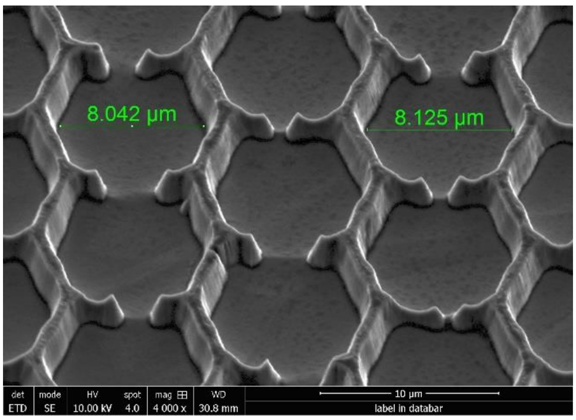

Figure 1. SEM image of 4441 stainless steel etched with sequenced plasma (Cl_2/Ar; H_2). We can observe etched patterns of 2500 nm depth.

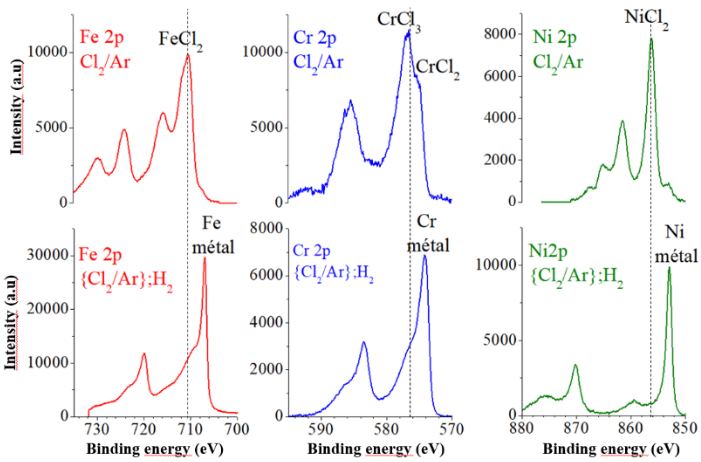

Figure 2. XPS spectra of Fe 2p, Cr 2p, Ni 2p of the surface of 4441 steel after Cl_2/Ar plasma etching (top spectra) and after sequenced {Cl_2/Ar}/{H_2} etching (bottom spectra)