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# THE USE OF HYDROGEN IN PLASMA DIFFUSION PROCESSSES

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Hydrogen is a versatile chemical agent which is widely used in plasma surface engineering. For example, the addition of hydrogen in plasma nitriding increases the nitrogen ionization and controls the nitrogen chemical potential. Moreover, hydrogen is added for cleaning purposes due to its chemical reduction properties. Thus, atomic hydrogen ions are reactive species leading to control the surface oxide content in ferrous alloys under plasma treatments. Indeed, hydrogen increases the reduction potential of the gas mixture in the plasma, decreasing the oxygen content in ion nitriding of austenitic stainless steels.
In this work, we study the effect of hydrogen on plasma post-oxidation, following pulsed plasma nitriding of AISI 1045. By X-ray diffraction in conventional and glancing angle geometries, one can conclude that hydrogen controls the formation of hematite and magnetite. It is well known that the hematite phase (alpha-$Fe_2O_3$) is porous and brittle, while the magnetite phase ($Fe_3O_4$) is compact and homogenous, two important technical characteristics for corrosion resistance and low friction coefficient. At hydrogen content of 25 % in the oxidation mixture, a pure magnetite phase is obtained. As a complementary characterization tool, X-ray photoelectron spectroscopy also indicates the effect of hydrogen where it avoids the formation of a characteristic satellite peak for Fe(III) that corresponds to hematite. Scanning electron microscopy and atomic force microscopy show a homogenous oxide layer in cross-section and low surface roughness at high hydrogen content, respectively. The Rietveld refinement method is used in order to quantify the crystalline phases in nitrided and oxidized layers as a function of hydrogen content. By using thermodynamical calculations, we estimate the change of Gibbs free energy for reduction from hematite to magnetite at 500ºC in two different routes assuming either molecular or atomic hydrogen as chemical agents. The presence of atomic hydrogen is mandatory to render spontaneous the reduction of Fe(III) in hematite to Fe(II) in magnetite. Finally, the oxide layer thickness evolution as a function of time and temperature process is also shown.

**Keywords**
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