MECHANICAL CHARACTARIZATION OF NITRIDE LAYERS ON NITI SUBSTRATE

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1. Introduction

The NiTi alloy is a typical shape memory material, which also demonstrate pseudo-elastic properties. These characteristics are result of a reversible martensite transformation when the material is deformed beyond its elastic limit, either by heating (SME) or by the applied load release (SE). In temperatures above the austenite starting point (As), the austenite phase (A - body centered cubic) is stable under low stresses and temperatures under the martensite starting point (Ms); under high stress conditions, the martensite phase (M - monoclinic or tetragonal) become stable. Despite the interesting features, as the low elastic modulus and high corrosion resistance, in situations where the Ni release by tribo-corrosion occurs make the NiTi alloy unsuitable for use in orthopedic devices [1-2].

The plasma immersion ion implantation (PIII) is a satisfactory technique for the NiTi surface modification, improving hardness and corrosion resistance, eventually reduction of nickel ions release in the biological environment [3].

Instrumented indentation and the analytical Oliver-Pharr methodology [4], are the most adopted methods to characterize the mechanical properties of modified surfaces . However, the phase transformations in the NiTi alloy during loading results in a coexistence of two phases with different moduli in the volume of deformation. Hence, the direct application of the Oliver-Pharr method is inadequate in such a situation. The proper study of the nitride layer formed over NiTi, ruling out the substrate influences, demands to consider the phase transition under loading, as well as the reverse transformation during unloading [5].

The objective of the work reported here was the study of mechanical properties of nitride layers formed on NiTi substrates by PIII, also considering the phase transformation induced in the bulk during indentation.

2. Experimental

The NiTi alloy was annealed at 1000 °C with subsequent water quenching at 0 ºC. The homogenized samples were submitted to PIII. The power supply applied a voltage of 8 kV with current of 10 A. The pulse width was 30 µs. The pressure of the N_2 atmosphere was kept constant at 7.3 kPa. The samples heating was attained with a hot filament adjusting the desired treatment temperatures to 600, 700 and 800 °C. To obtain substrates with similar features as those found in the nitrided samples, additional samples, not nitrided, were heat treated in a furnace, using argon atmosphere to simulate the PIII thermal conditions.

The structural changes were characterized by X-ray diffraction in the range 20°–60°, using Cu-Kα radiation. Additional grazing incidence XRD (GI-XRD) with fixed incidence angle of 2° were also carried out. The morphology of the modified surfaces was analyzed by scanning electron microscopy (SEM). The instrumented indentation was performed in two different batches:

- those samples submitted only to thermal treatment were indented using a spherical punch (R = 20 µm) under single loadings to estimate the elastic modulus; subsequently, a Berkovich indenter was employed for hardness.
- the nitrided samples were submitted to the quasi-continuous stiffness measurement (QCSM) method with a Berkovich indenter.

3. Results and Discussions

3.1 Heat Treatment

3.1.1 Structural Characterization

The diffractograms of the thermally treated samples indicated an M+A+precipitates bulk composition. There was an increase in the of $TiNi_3$ precipitate contribution as compared to the reference (only solubilized) substrate. The 600 ° C sample presented the most significant increase. In the 700-800 °C samples, there was a decrease in the $TiNi_3$ peaks in comparison with the 600 ºC case, indicating that a re-homogenization occurred at those temperatures. The Ti_2Ni compound was also identified on samples after heat treatment. It precipitated in the NiTi alloy due to stoichiometrically unbalanced Ni/Ti ratio caused by the $TiNi_3$ precipitation, which provided more available Ti atoms to nucleate new Ti-rich precipitates, as Ti_2Ni.

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3.1.2 Mechanical Properties

In instrumented indentation tests, loads were applied individually to avoid that the induced martensite from the previous loading interfered in the next cycle. The A+M+precipitates elastic modulus (*E*) was obtained by adjusting the loading curve with the Hertz equation, provided that the maximum displacement / indenter radius where lower than 0.001 [5]. The calculated values for the NiTi bulks ranged from 50-70 GPa.

To determine hardness avoiding pile-up effects during loading, the Cheng-Cheng [6] method was employed. The reference sample (NiTi just solubilized) presented the highest value (5.4 GPa). In all the heat treated samples, there was an important hardness decrease with the increasing load due to the larger induction of martensite in the volume of interaction, since the M phase presents inferior hardness than the A phase [6].

3.2 Nitrided Samples

3.2.1 Structural Characterization

The nitride layer thicknesses were 240 nm, 340 nm, and 560 nm for the treatment temperatures 600, 700 and 800 °C, respectively. The TiN compound was produced in all the nitrided surfaces, most significantly in the 800 °C treatment. Regarding the bulk precipitates, the Ti_2Ni content notably increased, in accordance with [6]. It was concluded that the temperature-modified NiTi matrices reproduced quite well the thermal conditions found in the nitriding process, inducing the precipitation of compounds of the same stoichiometry ($TiNi_3$ and Ti_2Ni) with equivalent temperature dependence. Therefore, the mechanical properties measured in the thermal treated samples do represent the bulk properties of the nitride ones, as seen next.

3.2.2Mechanical characterization

The effective elastic modulus of the nitride layers produced on TiNi, discounting the substrate effects, were inferred through the model proposed by Hay-Crawford [8]. It demands the knowledge of the substrate and the layer elastic modulus *E* and the Poisson´s ratios, as well as the layer thickness. The nitride layers formed at the three nitriding temperatures presented elastic modulus between 110 and 130 GPa.

The effective hardness of the nitride layers on NiTi substrates were calculated through the method proposed by Bhattacharya and Nix [9], using the hard layers on soft substrates equation. It demands the knowledge of the effective elastic modulus, calculated above with the Hay-Crawford method. The nitrided layers promoted a surface hardening to NiTi up to 4 times higher than the values found for the corresponding thermally treated substrates.

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4. References

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