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Influence of temperature in arc-activated plasma nitriding of maraging steel in solution annealed and aged conditions

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ABSTRACT

Maraging alloys are a group of high performance steels that combine high strength and good fracture toughness. Their excellent combination of properties is due to their microstructure, formed by nanometer-sized intermetallic precipitates embedded in a ductile martensite matrix. Their hardening treatments consist of aging processes that are compatible with thermochemical treatments such as nitriding or nitrocarburizing.
An arc-activated plasma nitriding technique has been used in this study to investigate the effect of simultaneous aging and ion nitriding of maraging steel grade 300 at temperatures from 450 °C to 510 °C. The paper compares the results obtained for solution annealed and aged hardened samples in order to verify the compatibility of both processes, aging and nitriding.
Chemical composition and micro-hardness profiling, glancing incidence X-ray diffraction (GIXRD), metallographic tests, corrosion studies and wear resistance tests were carried out. The results demonstrate the feasibility of arc-activated ion nitriding to achieve significant improvements of the surface properties of maraging steels and to merge together thermochemical and aging processes, thus reducing their processing time and energy consumption.

1. Introduction

Maraging steels are a kind of alloys belonging to ultra-high strength steels that present an excellent strength to toughness ratio, good machinability and weldability and ease of heat treatment [1–4]. The most extended maraging alloys are those containing 18% of nickel and high cobalt levels. Alloys with high titanium and molybdenum contents combine strength values up to 2400 MPa with fracture toughness (K_{IC}) around 70 $MPa \cdot m^{1/2}$ [2].

Hardening treatment of maraging steel consists of a solution annealing step aiming to get a homogeneous martensitic matrix followed by an aging process at around 500 °C during 1–4 h. The mechanical properties are achieved by precipitation of nanometer-sized intermetallic compounds during the aging stage. Ni_3Ti is formed during the first steps – usually expressed as $(Ni,Fe,Co)_3(Ti,Mo)$ – followed by Fe_2Mo – $(Fe,Co,Ni)_2(Ti,Mo)$ – and Fe_7Mo_6. Some important advantages of maraging steels with respect to other steels are the already abovementioned great resistance to crack propagation and dimension stability during aging treatment, due to their good thermal conductivity. The exceptional properties of maraging steels make them to be considered as strategic materials, although the costly alloy elements that are used in their production explain why they are only used for added value applications. Moreover, maraging alloys present some other limitations, especially their low wear resistance compared to conventional tool steels due to the absence of carbides, as carbon content is below 0.03 wt.%.

Surface properties of maraging steels can be improved through the utilization of thermochemical treatments [5–8] and the compatibility of temperature and time can be exploited to make simultaneous aging and nitriding. In particular, plasma assisted nitriding has become one of the most interesting techniques for these materials. Conventional processes such as gas nitriding are usually applied at 500–550 °C, which can affect the mechanical properties of the alloys due to overaging [1,2]. On the contrary, plasma assisted nitriding can be carried out at temperatures lower than 500 °C with good efficiency, avoiding overaging inconveniences and showing good effectiveness for increasing wear resistance, surface hardness and corrosion resistance [6,9–13].

In this study, a plasma assisted nitriding technique was carried out in a conventional PVD reactor. It is based on the generation of a cathodic arc, similar to that of PVD coating processes, to enhance the ionization of the plasma. N_2–Ar gases are used as precursors during ion nitriding. The application of the glow discharge is produced by a medium–high current on the metallic cathodes usually employed for the deposition of PVD films. A secondary anode is used as an electron collector in the chamber to increase the ionization of the plasma. Resistive heaters installed at the walls of the reactor allow an accurate control of the nitriding temperature and therefore, of the aging treatment. In this

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Table 1
Chemical composition of the main elements in the alloy (wt.%).

Element	GDOES	Specified
C	0.008	<0.03
Ni	17.31	17–19
Co	9.05	8.5–9.5
Mo	4.90	4.7–5.2
Ti	0.66	0.6–0.7
Al	0.11	<0.15
Fe	Balance	Balance

Table 2
Experimental parameters of the processes.

Process temperature (°C)	Intensities at heater (A)	Bias (V)	Time (min)	Ar/N_2 mass flow rate	Total pressure (mbar)
450	50	−600	90	3:1	1×10^{-2}
475	150	−600	90	3:1	1×10^{-2}
500	350	−600	90	3:1	1×10^{-2}
515	450	−600	90	3:1	1×10^{-2}

work, temperatures of 450 °C, 475 °C, 500 °C and 515 °C during 90 min have been used to investigate the effect of nitriding on maraging steel specimens in annealed condition and also on specimens subjected to prior aging treatment, with special attention to hardness, wear and corrosion resistance.

This ion nitriding also allows the development of duplex treatments where the nitriding may be followed by a PVD deposition.

2. Experimental

Grade 300 annealed and aged maraging steels were used in this work. Specimens in the annealed condition were denoted as "S" (=solubilized), whereas aged samples were labeled with a "T" (=thermal treated). Table 1 gathers the nominal chemical composition for grade 300 and that averaged on various specimens after a chemical analysis using Glow Discharge Optical Emission Spectroscopy (GDOES). A number of samples of this alloy were prepared in the form of mirror polished discs of 5 mm thick and 35 mm in diameter. The average hardness of the substrates in the annealing condition before plasma nitriding was 30 HRc and 52–53 HRc for the age hardened specimens.

2.1. Arc activated plasma nitriding technique

The treatment presented here consists of an arc-activated plasma nitriding technique [14]. The schematic diagram of the arrangement is shown in Fig. 1. The processes were carried out in a commercial PVD equipment (METAPLAS IONON MZR 323). The capacity of the vacuum chamber is 400 mm × 400 mm × 500 mm. The procedure starts with the use of heating resistances and the final cleaning of the samples with the assistance of argon ion bombardment at 400 °C.

For the arc-activated plasma nitriding, three chromium cathodes were used. In the treatment, a current of 85 A is applied to the metal cathodes to get a discharge. At the other side of the chamber, a separated secondary anode is polarized to act as an electron collector, gathering the electrons resulting from the cathodic arc electronic thermal emission and those generated in the glow-discharge. Opposite to the cathodes, a shield is placed so the generated vapor stream is blocked and does not reach the specimens. Thanks to this arrangement, only electrons can cross the chamber, which increases the ionization of the gases during their path to the secondary anode.

Table 2 summarizes the experimental parameters utilized in this study. Ohmic currents varied from 50 A to 450 A. Samples were biased

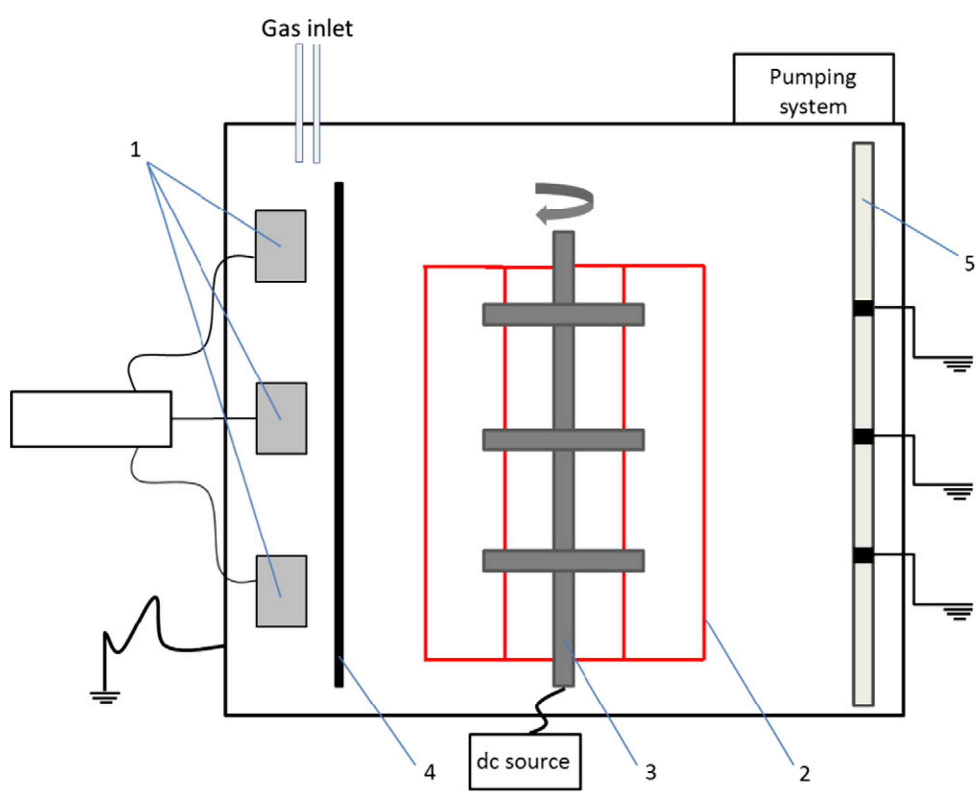

Fig. 1. Scheme of the PVD equipment used for the nitriding process: 1, arc cathodes; 2, heating resistance; 3, substrate holder assembly; 4, cathode shield; 5, electron collector (secondary anode).