Effect of Simultaneous Plasma Nitriding and Aging Treatment on the Microstructure and Hardness of Maraging 300 Steel

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Abstract Simultaneous nitriding and aging heat treatment of maraging 300 steel was carried out inside a DC-pulsed plasma nitriding reactor. A single heat treatment cycle was done, as the plasma nitriding and age hardening processes occur at the same ranges of temperatures and times. Samples of maraging 300 steel, in the solution annealed and solution annealed and aged conditions, were tested. Plasma nitriding and aging, carried out at 480 °C for 3 h, increased the surface hardness up to 1140 HV, producing case depths of 50 μm since ε-Fe_3N and γ′-Fe_4N nitrides were formed in the hardened surface layer. It is observed that the microstructure of the core material remains unaltered as the typical martensite plate-like microstructure of maraging steels. The core hardness of solution annealed samples increased from 331 to 597 HV after the plasma nitriding treatment proving the possibility of nitriding and aging at the same treatment cycle. The pre-aged samples

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did not show any overaging or martensite reversion to austenite after the simultaneous plasma nitriding and aging treatments, that could be showed by the core hardness of 620 HV and can be related to the time of total aging exposure of 6 h, including pre-aging and plasma nitriding.

Keywords Maraging steel · Plasma nitriding · Case depth · Microstructure · Hardness

1 Introduction

Maraging refers to the aging of martensite, a hard microstructure commonly found in steels. Martensite is easily obtained in these steels owing to the high nickel content. The only transformation that occurs at ordinary cooling rates is martensite formation. The martensite without carbon is quite soft, but heavily dislocated. These steels are based on the Fe–Ni binary alloy with additions of various alloying elements such as cobalt, molybdenum, titanium and aluminum. Hardening and strengthening of these steels are subsequently produced by heat treating (aging), caused by precipitation of extremely fine, coherent intermetallic compounds such as Ni_3X (X = Ti, Mo) [1–3]. Maraging 18 %Ni grades are denoted by numbers such as 200, 250, 300 or 350, the number specifying the level of the yield strength in ksi that can be obtained in the steel with appropriate heat treatments [2]. Its high strength to weight ratio, good weldability, and easy machinability in the solution annealed condition and dimensional stability during aging make this material an ideal choice for critical applications in aerospace industries, such as rocket motor casing [1–3]. It has been reported that depending upon the aging duration, the steel undergoes systematic characteristic microstructural changes. The early aging period is characterized by recovery of martensitic structure and hardening due to precipitation of hexagonal the intermetallic precipitates, that takes place rapidly due to fast diffusion of titanium atoms [4–6]. The intermediate aging period is characterized by reversion of austenite accompanied by precipitation of hexagonal Fe_2Mo intermetallic phase. These two processes, occurring at the intermediate aging period, affect hardening in the opposite manner; thus, overall hardening levels off after reaching a maximum [4]. A decrease in hardening, observed during longer aging durations, is attributed essentially to the formation of reverted austenite and precipitate coarsening. The amount of reverted austenite has been reported to increase with an increase in aging temperature and time [1, 2]. Maraging 300 steels are normally subjected to solution annealing at 820 °C for 1 h followed by aging at 480 °C for 3 h. This heat treatment results in the best combination of mechanical properties, i.e., ultrahigh strength coupled with good fracture toughness due to precipitation of intermetallic phases in low-carbon soft martensitic matrix. Additional time exposure at this aging temperature does not improve the hardness substantially, and after

10–15 h of exposure, it has observed a decrease in the hardness due to the reasons described before [3].

There are some specific demands that requires high strength and good wear resistance, such as slat track, high speed gear and torsion shaft for aeronautical components [7]. Nitriding is a surface treatment process involving the introduction of nitrogen into the surface of steel, which produces a modified layer with excellent properties such as high hardness, good wear and corrosion resistance [8, 9]. However, conventional nitriding of this steel is usually carried out at high temperature for a long time, which is beyond the aging temperature and time of 18Ni maraging steel and would result in the overaging and reversion of martensite to austenite of the core. Maraging steel possesses high strength, and good wear resistance can be achieved by plasma nitriding, that can be carried out at the same temperature or lower than the aging temperature, avoiding the overaging or reversion of martensite to austenite of the core [10].

In the present investigation, a combined plasma nitriding and aging at 480 °C for 3 h treatment of a maraging 300 steel was studied. Specially focusing on the possibility of increasing the hardness of the core by aging, at the same time that hard surface layers were created during the thermo-chemical treatment, were kinetic and microstructure control can easily be done, improving the resistance and decreasing the cost of production of the material. Microstructural changes were evaluated by of optical microscope (OM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Hardness and case depth were evaluated and explained with the help of microstructural observations.

2 Experimental Procedure

The samples were solution annealed at 820 °C for 1 h. The chemical composition of the maraging 300 steel solution annealed is shown in Table 1. Some of the samples were subjected to an additional age hardening treatment at 480 °C for 3 h. The samples in both conditions were nitrided in the furnace under vacuum. Plasma was obtained by passing the gas mixture of H_2 and N_2 gases in the ratio of 3:1 under vacuum. Plasma nitriding was carried out at 480 °C for 3 h for both conditions.

Microstructural examination was carried out on Carl Zeiss H-PL optical microscope. Cross sections from nitrided and un-nitrided samples were ground, polished (final polishing step: 1 μm diamond suspension) and etched using $FeCl_3$ 10 % (5 g $FeCl_3$ in 45 mL of water) at room temperature for about 2 s.

Phases present in the un-nitrided and formed in the nitrided samples were characterized by XRD on a Panalytical X′ Pert Powder diffractometer using Cu–K_α

Table 1 Chemical composition (wt%) of the maraging 300 steel studied

Element	Ni	Co	Mo	Ti	Al	C	S	P	Si	Mn	Fe
wt%	19.00	9.37	4.94	0.63	0.08	0.008	0.002	0.004	0.06	0.01	Balance

radiation, λ = 0.1542 nm, in conventional θ/2θ Bragg-Brentano symmetric geometry. The diffraction angle range (30° < 2θ < 90°) was scanned in steps of 0.0170° with a counting time of 15.24 s per step. For the identification of the phases, based on the positions of the diffraction peaks, data of the HighScore database were used.

Energy dispersive spectroscopy (EDS) analyses, to measure the nitrogen profile in the surface after nitriding were performed by means of an x-act SDD spectrometer incorporated with scanning electron microscope (SEM) model VEGA 3/ TESCAN.

Hardness from the surface, profile and core was measured using Vickers hardness tester (FutureTech FM-700) with a load of 100 gF and a dwell time of 9 s. Hardness values were measured at five places for each sample. The core hardness before and after plasma nitriding treatment was measured for previously solution annealed and solution annealed and aged samples in order to compare the behavior of the core when exposed to the thermal cycle during the plasma nitriding treatment.

3 Results and Discussions

Optical micrographs of un-nitrided and plasma nitrided samples are shown in Fig. 1. The nitriding behavior is the same for samples with starting microstructure on the solution annealed and aged state. These micrographs show a uniform and

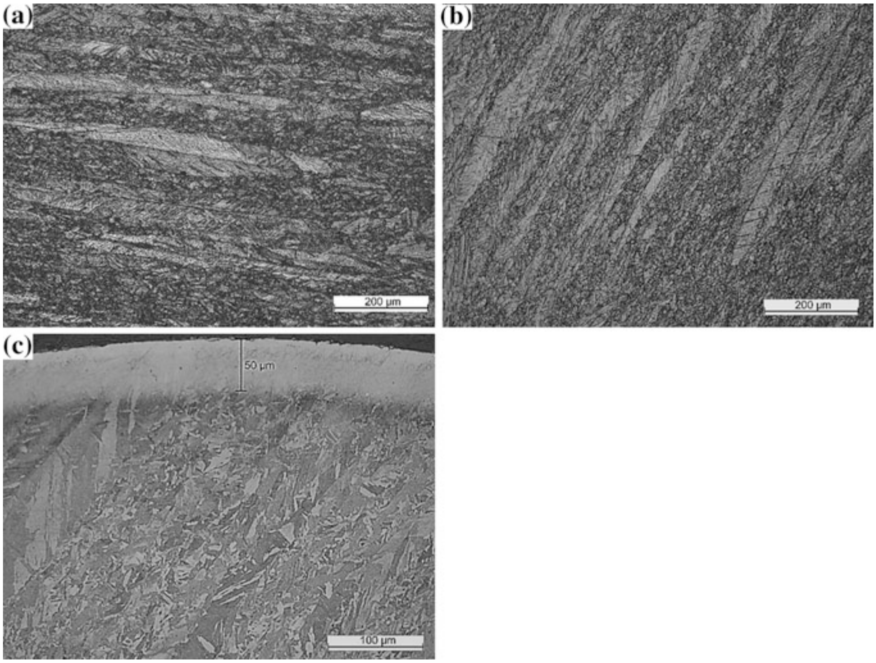


Fig. 1 Optical micrographs of maraging 300 **a** solution annealed, **b** solution annealed and aged, **c** solution annealed and plasma nitrided and **d** solution annealed, aged and plasma nitrided

continues case hardened nitrided layer and the typical martensite plate-like microstructure of maraging steels can be seen in the un-nitrided core [1–3]. The thickness of 50 μm was found in the nitrided layer for all nitrided samples. In the light optical micrographs (Fig. 1), no difference in the microstructure of the un-nitrided core of the age-hardened sample can be observed as compared to that of the only solution annealed sample. No hints of austenite can be seen in the micrographs, which is compatible with the XRD phase analysis discussed below (Fig. 2).

XRD patterns obtained from the surface of un-nitrided and plasma nitrided samples are shown in Fig. 2. The un-nitrided samples exhibit diffraction peaks only due to the martensitic phase α′-Fe. The presence of intermetallic precipitates in the aged sample is not revealed by separate reflections in the aged's X-ray diffraction patterns, likely due to the coherent nature of these precipitates [10, 11]. After plasma nitriding, α′-Fe peaks disappeared or are overlapped, giving place to peaks indexed as ε-Fe_3N and γ′-Fe_4N nitrides, corresponding to the compound layer.

Figure 3 shows concentration depth profile of nitrogen measured by energy dispersive spectroscopy (EDS) on the samples plasma nitrided. The composition of the outer layer reached to around 7 wt% nitrogen for both conditions. These compositions agree very well with ε and γ′ nitrides, respectively [11]. The data demonstrates a gradual decrease of the nitrogen concentration when moving from the compound layer toward the substrate, and about 50 μm from the top surface, the

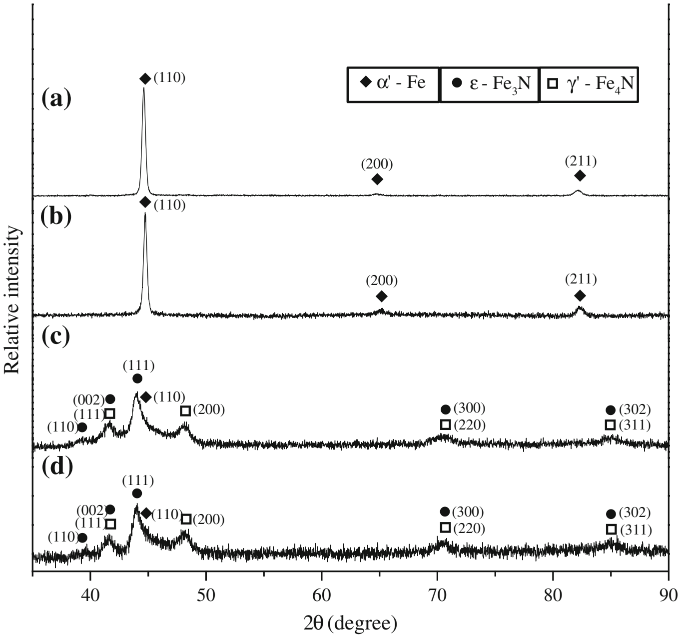
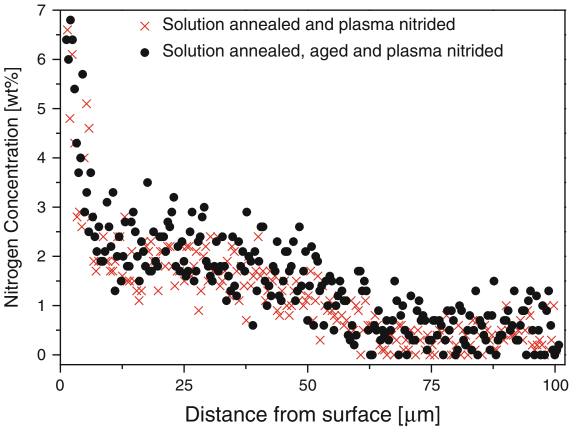


Fig. 2 X-ray diffraction pattern of **a** solution annealed, **b** solution annealed and aged, **c** solution annealed and plasma nitrided and **d** solution annealed, aged and plasma nitrided

Fig. 3 EDS depth profile of nitrogen analyzed from solution annealed and plasma nitrided and solution annealed, aged and plasma nitrided



nitrogen concentration starts decrease to zero, confirming the information of nitride layer thickness observed by optical micrograph.

The hardening effect was evaluated by surface hardness and hardening profiles. Considering the starting core hardness for solution annealed condition as 331 HV and for aged condition as 604 HV, Table 2 shows that the surface hardness increases for both conditions and the presence of the compound layer is responsible for an additional hardening effect, achieving a hardness up to 1140 HV. Figure 4 shows the hardness profile after the plasma nitriding for both conditions. The continuous decrease of hardness from surface to the core of the sample suggests the presence of a diffusion zone in which precipitates of nitrides of iron and other metals were formed at the grain boundaries as well as within the grains. These precipitates distort the lattice and pin crystal dislocations and thereby increase the hardness of the surface layer of the ion-nitrided samples [10].

The possibility to use the plasma technology for a simultaneous aging and nitriding treatments is dependent of the core hardness response. Core hardness attained after the plasma nitriding treatments are shown in Table 3. Considering the starting core hardness, the treatment was effective to increase the core hardness for the solution annealed sample from 331 HV up to 597 HV, proving that the simultaneous aging and nitriding treatments are possible to be done. On the other hand, the aged sample retain the core hardness after the treatment avoiding the overaging process and reversion of martensite to austenite for the tested cycle,

Table 2 Surface hardness values of un-nitrided and plasma nitrided samples

	Solution annealed	Solution annealed and aged	Solution annealed and plasma nitrided	Solution annealed, aged and plasma nitrided
Surface hardness (HV)	331 ± 5	604 ± 18	1010 ± 6	1140 ± 4

Fig. 4 Hardness profiles for samples plasma nitrided

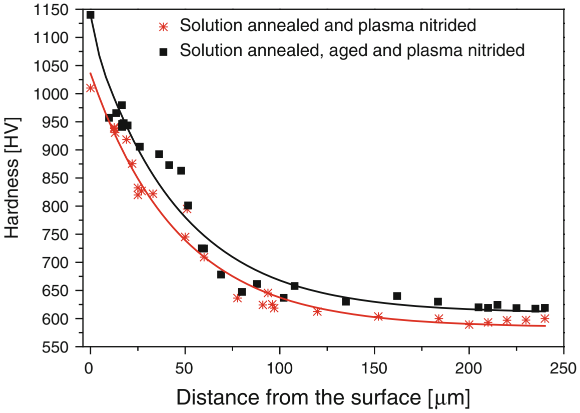


Table 3 Core hardness values of un-nitrided and plasma nitrided samples

	Solution annealed	Solution annealed and aged	Solution annealed and plasma nitrided	Solution annealed, aged and plasma nitrided
Core hardness (HV)	331 ± 5	604 ± 18	597 ± 2	620 ± 3

showing that the use of additional heating during the nitriding process affect slightly the hardness, increasing the core hardness up to 620 HV. This fact is related to the precipitation growth. The increase in the strength and hardness of maraging steels is a function of the precipitate fraction and size. The growth of the precipitate and the increase in the precipitation fraction is a function of time and temperature, and at 480 °C the aging of maraging 300 is rapid and intense [1]. In the solution annealed, aged and plasma nitrided sample, after 6 h of aging (3 h of aging plus 3 h of plasma nitriding), the precipitate remains distributed in the matrix as an extremely dense dispersion, and its average diameter can be slightly grown from the previous aging treatment. In the case of 2000 MPa grade cobalt-free maraging steel, after aging for 6 h, the Ni_3Ti average diameter has grown to about 4–5 nm when compared to 3–4 nm after aging for 3 h [1]. Therefore, the core hardness increasing around 4 % only does not justify the additional costs related to 3 h of heating.

4 Conclusions

In the present investigation, maraging steel (300 Grade) solution annealed and aged was plasma nitrided at 480 °C for 3 h. An uniform and continues case hardened nitrided layer and the typical martensite plate-like microstructure of maraging steels can be seen in the un-nitrided core. The iron nitride formed in the hardened surface layer is ε-Fe_3N and γ′-Fe_4N with a case depth of 50 μm and these nitrides improve the surface hardness of maraging 300 steel substantially achieving a hardness up to 1140 HV. After plasma nitriding, core hardness of solution annealed samples increased up to the levels expected after aging. When solution annealed and aged samples are nitrided no decrease in core hardness can be observed. These results prove that simultaneous aging and nitriding treatments may be done using a single cycle thermochemical treatment on the DC-plasma nitriding reactor using the low temperature of 480 °C.

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