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EFFECT OF ARGON DILUTION ON THE FORMATION OF NITRIDE/OXYNITRIDE-TYPE PHASES AND HARDENING OF BLUE-DIODE-LASER-TREATED GRADE 2 TITANIUM

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Abstract

Laser thermochemical modification of commercially pure Grade 2 titanium was investigated using a low-power blue diode laser in N_2/Ar atmospheres containing 5, 15, and 25 vol.% Ar. The treated layers were characterized by optical metallography, X-ray diffraction, and cross-sectional microhardness testing. All conditions produced a distinct modified surface region with an acicular/lamellar morphology extending to an apparent depth of approximately 70-90 µm in the examined cross sections. XRD indicated the formation of TiN-type phases with a possible Ti(O,N) contribution, together with a minor TiO_2 phase. Pronounced near-surface hardening was obtained for all gas mixtures, with maximum mean hardness values of 1303.5, 1115.4, and 1137.5 HV0.01 for 5, 15, and 25% Ar, respectively. The 5% Ar condition produced the highest peak hardness and strongest nitride-related diffraction response, whereas the 25% Ar condition exhibited a more gradual decrease in hardness with depth. The results demonstrate that the N_2/Ar ratio influences the phase constitution and hardness distribution of laser-modified Grade 2 titanium.

Keywords: laser nitriding, blue diode laser, titanium oxynitride, surface treatment, cpTi Grade 2.

INTRODUCTION

Commercially pure titanium (cp-Ti) and titanium alloys are widely used in engineering and biomedical applications because of their favorable strength-to-density ratio, corrosion resistance, chemical stability, and biocompatibility. Their corrosion resistance is largely associated with the spontaneous formation of a stable titanium oxide passive film. However, the relatively low hardness and poor tribological behavior of titanium can limit its performance under friction, contact loading, and wear, motivating the use of surface-engineering methods that improve surface properties while preserving the desirable bulk characteristics [1,2].

Nitriding is particularly attractive because titanium has a strong affinity for nitrogen and readily forms hard titanium nitride phases. Among the available techniques, laser gas nitriding enables localized rapid heating and, depending on the processing conditions, melting of a shallow surface region while nitrogen is supplied directly to the interaction zone. Nitrogen can dissolve in the titanium matrix and react during solidification to form TiN-type phases. Unlike deposited coatings, the modified layer is metallurgically integrated with the substrate, while only a localized region of the component is thermally affected [3-6]. Laser nitriding can substantially increase titanium surface hardness, with the resulting microstructure

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and hardened depth depending strongly on laser power, scanning speed, interaction time, and nitrogen supply [7-9].

The composition of the processing atmosphere is another important parameter. Nitriding in nitrogen-rich atmospheres can promote high TiN contents and very high surface hardness, but intensive nitride formation may also be accompanied by increased roughness, steep composition gradients, residual stresses, and cracking. Dilution of nitrogen with an inert gas such as Ar provides a means of controlling nitrogen availability during laser-material interaction. Previous studies have shown that N_2/Ar mixtures influence nitrogen incorporation, melt-pool behavior, TiN formation, microstructure, surface quality, and hardness distribution [4,5,10]. Increasing the Ar fraction generally reduces the nitrogen supply and may decrease nitride formation and maximum hardness while improving surface quality and reducing cracking [10]. More recent investigations of laser nitriding have also emphasized the role of nitrogen transport and redistribution in determining the depth and microstructure of the modified region [11]. The N_2/Ar ratio is therefore an important processing variable for controlling the properties of laser-nitrided titanium.

The phase constitution of laser-treated titanium may be more complex than stoichiometric TiN alone. Depending on nitrogen concentration and cooling conditions, nitrogen-containing α-Ti, non-stoichiometric TiN_x, and TiN can coexist within the modified region [5,8,11]. Oxygen must also be considered because of the strong affinity of titanium for oxygen. It may originate from the native oxide film, residual oxygen in the processing atmosphere, or oxidation of the heated surface. Consequently, TiO_2 and mixed titanium oxynitride phases may accompany nitride formation. Titanium oxynitrides, commonly represented as TiO_xN_γ or Ti(O,N), can exhibit characteristics intermediate between titanium oxides and nitrides [12]. Their identification by conventional X-ray diffraction is difficult because TiN and related Ti(O,N) structures may exhibit strongly overlapping diffraction reflections.

Laser-source characteristics additionally affect the thermal interaction with titanium. Laser nitriding of titanium has been demonstrated using CO_2, Nd:YAG, fibre, and high-power near-infrared diode laser systems [9,13,14]. Direct diode lasers offer compactness and high electrical efficiency, and near-infrared diode systems have been successfully applied to Ti/TiN surface modification. More recently, blue diode lasers operating near 450 nm have emerged as an alternative for materials processing. Low-power 450 nm diode arrays have demonstrated sufficient energy coupling for processing Ti-6Al-4V, indicating the potential of short-wavelength diode sources for localized modification of titanium at comparatively low optical power [15].

Against this background, the present work investigates the thermochemical surface modification of commercially pure Grade 2 titanium using a low-power blue diode laser under controlled N_2/Ar atmospheres. Three gas mixtures containing 5, 15, and 25 vol.% Ar were studied while maintaining constant laser power, scanning speed, and total gas flow. The influence of Ar dilution was evaluated by cross-sectional metallography, X-ray diffraction, and microhardness profiling, with particular attention to the near-surface microstructure, nitride/oxynitride-type and oxide phase formation, and the magnitude and depth distribution of hardening.

EXPOSITION

Experiment and characterization

Commercially pure Grade 2 titanium was cut from a 16 mm diameter rod into 5 mm thick discs. Its nominal chemical composition was Ti balance (≥98.9 wt.%), with maximum contents of 0.30 wt.% Fe, 0.25 wt.% O, 0.08 wt.% C, 0.03 wt.% N, and 0.015 wt.% H. The treated surfaces were ground, polished to a mirror finish, and degreased with acetone. Thermochemical treatment was carried out using a Falcon

blue diode laser with a nominal wavelength of 450 nm and a maximum optical output of 22 W. The laser power was set to 11 W, with a nominal spot size of 80 × 100 μm and a scanning speed of 1000 mm min^{-1}, corresponding to a linear energy input of 0.66 J mm^{-1}. Each track was produced in a single pass. A custom nozzle supplied a total gas flow of 30 L min^{-1}. Three N_2/Ar gas mixtures were investigated: 95/5, 85/15, and 75/25 vol.%.

For metallographic examination, transverse sections were prepared using a DTQ-5 low-speed cutting machine, mounted in resin, ground to P800, and polished with 1 μm diamond suspension. The specimens were etched using an HF/HNO_3/distilled water solution in a 5:15:85 volume ratio. The resulting microstructures were examined at 50× magnification using an LM-308 upright metallurgical microscope equipped with a DGT-SRT200A digital camera.

Surface phase analysis was performed using a TDM-10 diffractometer with Cu Kα radiation in coupled 2θ mode. Diffraction patterns were recorded over the range 20-90° using a step size of 0.1° and evaluated with X'Pert HighScore Plus software.

Cross-sectional microhardness profiles were obtained using an HV-1000 semi-automatic tester with a load of 0.01 kgf (HV0.01) and a dwell time of 10 s. Indentations were made at nominal depths from 5 to 75 μm below the treated surface. Three measurements were performed at each depth for each treatment condition. The results are presented as mean values, while the corresponding minimum and maximum values are shown as asymmetric error bars.

Microstructure

Figure 1 shows the cross-sectional microstructures of the laser-treated Grade 2 titanium obtained with 5, 15, and 25 vol.% Ar in the N_2/Ar processing atmosphere. In all three cases, a distinct surface-modified region is observed adjacent to the treated surface, clearly differentiated from the underlying substrate. The bulk material retains the characteristic equiaxed grain structure of commercially pure titanium, whereas the laser-affected region exhibits a substantially finer, predominantly acicular/lamellar morphology.

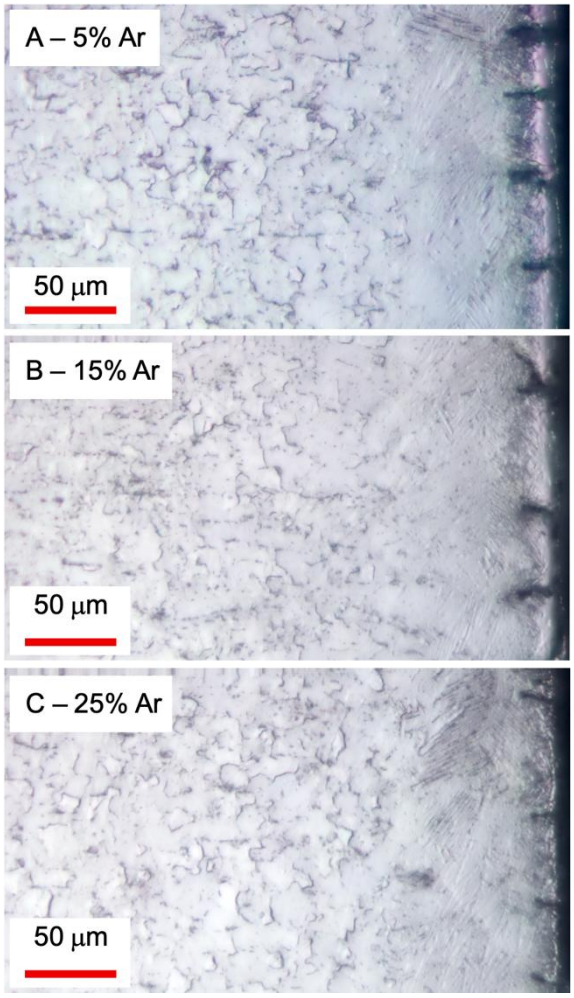


Fig. 1. *Optical micrographs of cross sections after laser treatment in N_2/Ar containing (A) 5%, (B) 15%, and (C) 25% Ar;*

Based on the representative cross-sectional micrographs, the modified zones extended to an approximate depth of 70-90 μm. Their transition to the unaffected substrate is relatively gradual rather than being defined by a sharp planar interface. This morphology is consistent with the steep thermal gradients and rapid heating and cooling associated with laser processing. The elongated features within the near-surface region are preferentially oriented toward the treated surface, indicating directional microstructural development during the thermochemical treatment. Phase

identification cannot, however, be established from the metallographic observations alone and is considered together with the XRD results.

Comparison of Fig. 1A-C shows that all three N_2/Ar mixtures produced a continuous modified region of broadly comparable depth. Some differences in the morphology and apparent extent of the affected zone can be observed, with the 25% Ar condition showing a relatively well-developed acicular region, but the optical micrographs do not indicate a pronounced change in layer depth with increasing Ar content. Thus, within the investigated range, variation of the N_2/Ar ratio appears to influence the detailed morphology of the laser-modified zone more strongly than its overall penetration depth.

Phase composition

Figure 2 shows the XRD patterns of the laser-treated surfaces obtained with 5, 15, and 25 vol.% Ar. All specimens exhibit strong reflections from the titanium substrate together with additional peaks associated with reaction products formed during laser thermochemical treatment. The reflections at approximately 37.2° and 43.1° 2θ are consistent with TiN-type phases and indicate nitrogen incorporation into the modified surface layer.

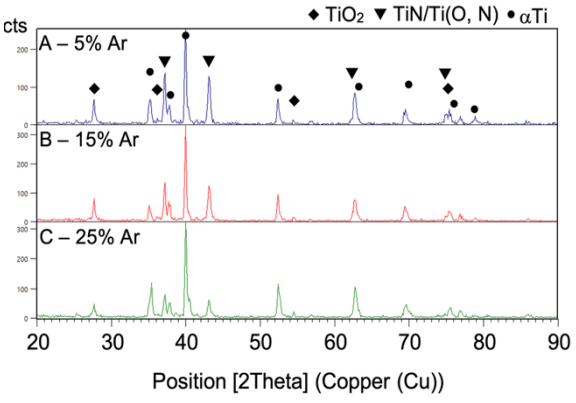


Fig. 2. *X-ray diffraction patterns of Grade 2 titanium after laser thermochemical treatment in N_2/Ar atmospheres containing 5, 15, and 25 vol.% Ar.*

An additional reflection at approximately 27.7° is present in all three patterns. This peak, together with weaker reflections near 36.2° and 54.4°, is consistent with the presence of rutile TiO_2. The occurrence of oxide phases despite the use of N_2/Ar processing atmospheres may be related to oxygen originating from the initial native oxide film, residual oxygen in the processing environment, and/or oxidation of the heated surface during or after laser treatment.

A possible titanium oxynitride contribution should also be considered. Partial substitution of nitrogen by oxygen in the TiN-type lattice can produce TiO_xN_γ phases retaining a cubic structure similar to TiN. Consequently, the reflections around 37.2° and 43.1° may contain overlapping contributions from titanium nitride and titanium oxynitride.

With increasing Ar content, the relative intensities of the reflections near 37.2° and 43.1° decrease, particularly for the 25% Ar condition, while the titanium substrate reflections become more pronounced. This suggests a reduced degree of nitrogen incorporation as the nitrogen fraction in the processing atmosphere decreases. Overall, the XRD results indicate a multiphase surface region containing the titanium substrate, TiN-type phases with a possible Ti(O,N) contribution, and a minor titanium oxide phase.

Microhardness

All laser-treated specimens exhibited pronounced near-surface hardening (Fig. 3). At a depth of 5 µm, the mean hardness values were 1303.5, 1115.4, and 1137.5 HV0.01 for 5, 15, and 25% Ar, respectively, corresponding to approximately 4.9, 4.2, and 4.3 times the nominal substrate hardness of 265 HV. The 5% Ar condition exhibited the highest hardness within the first 25 µm, followed by a rapid decrease to approximately 358 HV at 35 µm. In comparison, the 25% Ar condition maintained values of about 409, 401, and 350 HV at depths of 35, 45, and 55 µm, respectively. The 15% Ar profile showed an isolated increase to 343 HV at 65 µm. At 75 µm, all specimens approached the substrate

hardness range, with values of approximately 267-290 HV.

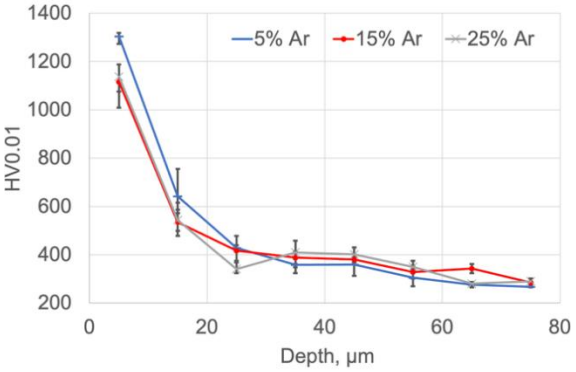


Fig. 3. *Cross-sectional microhardness profiles of cpTi Grade 2 after laser thermochemical treatment in N_2/Ar atmospheres containing 5, 15, and 25 vol.% Ar.*

The pronounced surface hardening is consistent with the formation of TiN-type phases and the possible contribution of Ti(O,N), as suggested by the XRD results, together with the modified near-surface region observed metallographically. The highest surface hardness obtained with 5% Ar agrees with the stronger nitride-related diffraction contribution under the nitrogen-richer atmosphere. Increasing the Ar fraction reduced the maximum hardness, while the 25% Ar condition exhibited a comparatively more gradual decrease in hardness with depth. The wider min-max ranges close to the surface indicate greater local hardness variation within the strongly modified region, whereas the scatter decreases with increasing depth as the hardness approaches that of the untreated substrate.

CONCLUSION

Laser thermochemical treatment of cp-Ti Grade 2 in N_2/Ar atmospheres produced a distinct modified surface region with pronounced near-surface hardening. Optical microscopy revealed an acicular/lamellar near-surface microstructure extending to an apparent depth of approximately 70-90 µm in the examined cross sections, while XRD indicated TiN-type phase formation with a possible Ti(O,N) contribution, together with a minor TiO_2 phase.

The gas composition influenced the phase response and hardness distribution. The nitrogen-richest condition, containing 5% Ar, produced the highest surface hardness of about 1300 HV0.01, nearly five times that of untreated Grade 2 titanium, and showed the strongest nitride-related diffraction contribution. Increasing the Ar content reduced the peak hardness, although the 25% Ar condition maintained elevated hardness over a somewhat greater subsurface depth. At 75 µm, the hardness of all specimens approached the substrate range. Overall, the results show that the N_2/Ar ratio can be used to modify the balance between maximum surface hardness and the depth distribution of the hardened layer during low-power diode-laser treatment.

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