SURFACE CEMENTATION OF ALUMINUM ALLOYS BY EXCIMER LASER INDUCED PLASMA

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Abstract

The excimer laser cementation process reported is developed to enhance the mechanical and chemical properties of aluminum alloys. An excimer laser beam is focused onto the alloy surface in a cell containing 1 bar nitrogen and propylene gas. A vapor plasma expands from the surface and shock wave dissociates and ionizes the ambient gas then nitrogen and carbon from plasma in contact with the surface penetrates in depth.

1. Introduction

The excimer laser cementation process proposed in this study is a surface treatment leading to the enhancement of the mechanical properties of AlSi₃Mg₀.₃ alloy. The use of aluminum alloys in the automotive industry is of great interest mainly because of their low density, corrosion resistance and good workability. The motor weight can be reduced by replacing usual materials such as iron-steel by light alloys treated to increase their wear resistance. Ceramic materials generally exhibit great strength, resistance to wear and oxidation.

The use of laser beams allows surface treatment to be preferentially located at the parts strongly exposed to wear and friction. During the laser treatment the surface undergoes a transformation leading to an increase in hardness without changing the dimensions of the piece; thus post machining after treatment is avoided. Moreover, it is an environment friendly process with no pollution by chemical solvent or emanation.

The nitriding of light alloy have been studied previously in our laboratory [1, 2, 3]. The nitriding laser process has been widely studied by P. Schaan et al [4, 5, 6, 7] in the case of steel substrates. The present work is more concerned by the study of the carburizing of aluminum by laser induced plasma treatment.

The excimer laser beam is focused onto the surface of a sample located in a cell containing a propylene or methane atmosphere (1 bar). At each pulse, the laser-surface interaction leads to metal heating and vaporization. The vapor plasma induced by laser beam interaction with the target expands against the ambient gas and is several mm high. At the plasma front a shock wave develops exciting the gas, thus the plasma plume on the target surface is composed of vapor and gas species. During the plasma time duration the target surface in is liquid phase and gas species can diffuse in. From the plasma temporal spectroscopy study [1] it can be seen that this plasma recombination phase lasts several µs. A ceramic layer with several µm in thickness (corresponding to the liquid pool depth) is obtained and grows as a function of the laser pulse number.
2. Experimental set-up

Surface treatment is achieved on AlSi₂Mg₀.₃ aluminum alloy (7 % Silicon and 0.3 % Magnesium). The samples that are 1×1 cm² width × 2 mm thick are placed in a cell at a vacuum near 10⁻⁵ mbar, to limit oxygen contamination. Then the cell is filled with 1 bar of treatment gas (propylene or methane). The laser beam (Lambda Physik, Compex 205, KrF excimer, λ = 248 nm, τ = 25 ns, ν = 40 Hz) goes across an optical homogenization system and is focused into the cell onto the sample. The experimental device is presented in Fig. 1. The energy density on the sample surface is chosen to be 2.4 J/cm², slightly over the energy density needed for the plasma formation (plasma threshold, about 2 J/cm²) but not too high to avoid an increase in sample surface roughness.

Fig. 1. Experimental set up.

The rectangular laser spot on the surface is about 6 mm² in section, in order to obtain a large treated area, thanks to a crossed motorized X-Y sample holder, the aluminum surface may be moved in front of the laser beam to achieve a complete surface treatment.

The laser beam interaction with the target induces two phenomena, firstly a crater formation due to the plasma piston effect [5, 6, 7], secondly an heterogeneous radial profile of gas species diffused into the surface [2, 5]. When the laser beam scans the target, the crater formation induces a large roughness on the surface, moreover the concentration of carbon is heterogeneous in the ceramic layer. Previous works have shown that the scan of the laser beam on the target must be done with an overlapping of the laser spots [2, 3]. By using a laser impact overlapping of 90 %, the layer chemical composition becomes homogeneous and the roughness is drastically decreased from 3 μm to 0.5 μm.
After treatment, samples are analyzed by different techniques to evidence the composition (nuclear analysis) and the crystalline phases (X-ray diffraction) of the layer. It is necessary to use different complementary techniques to obtain sufficient informations describing the layer. The Rutherford Backscattering Spectroscopy (RBS) technique leads to Al, C and O chemical species concentration profiles on 1.5μm thick. These analyses have been achieved with a 2 MeV He⁺ beam. The spectra obtained are analyzed by RUMP (Rutherford Universal Manipulation Program) [8] by dividing the sample into a superposition of several layers with different thickness and compositions. Unfortunately the carbon signal in RBS is very weak and it is difficult to obtain a significant interpretation. Nuclear Reaction Analysis (NRA) is used to quantify the absolute C contents in the target through the $^{12}$C(d,p)$^{13}$C nuclear reactions with a 1 MeV deuteron beam.

The global crystalline quality and the nature of the phases grown in the layer are carried out by X-ray diffraction in the grazing incidence (GIXD) in order to obtain insights on the evolution of layer structure as a function of the depth.

3. Experimental results

Role of the plasma

As mentioned above, it has been determined that the laser density threshold for plasma creation in metallic vapor with methane or propylene is 2 J/cm². Two targets have been irradiated by 1000 laser pulses in 1 bar methane pressure at two different laser fluences, the one below (1.75 J/cm²) and the other over (2.7 J/cm²) the plasma threshold.

The RBS signal of the first sample is similar to those of untreated sample. No gas species has diffused in the target. Conversely with a laser fluence of 2.7 J/cm² the RBS signal is clearly different. The surface layer of the target contains carbon and oxygen in addition to substrate elements. Thus it appears that the plasma formation is needed to obtain the diffusion of carbon gas species in aluminum. Indeed the CH₄ molecules of the ambient gas are dissociated at the vapor plasma front. These collisions are responsible of the production of carbon atoms.

Oxygen contamination

The cell containing the sample can be evacuated to $10^{-5}$ mbar before fulfilling with methane. At this residual pressure of $10^{-5}$ mbar a lot of water remains adsorbed on the cell walls and contaminates the ambient gas and the target. It has been shown that a residual pressure of $10^{-7}$ mbar is needed [9] to obtain a limited oxygen contamination (<5%) of the target after treatment.

A previous work [2] has shown that the diffused oxygen is located at the top (200 nm thick) of the ceramic layer (3 μm thick). This oxygen does not lead to oxide formation but seems to be inserted in the ceramic lattice. This layer can be considered as a diffusion barrier for corrosion. It has also been shown in previous studies [3] that a soft laser ablation of this contaminated layer does not have significant effect on the tribological behaviour of the treated surface.

Carbon detection

The RBS carbon signal is very weak in comparison with those of other elements. This is due to the low weight of the carbon atom that induces a low backscattering energy of the He⁺ and a low backscattering cross section. Thus the carbon signal is embedded in the noise one.

In order to improve the carbon detection in the layer, another nuclear technique the Nuclear Reaction Analysis (NRA) has been achieved with the $^{12}$C(d,p)$^{13}$C reaction allowing a more
visible carbon signal. As no standard sample is available to quantify carbon concentration, only relative data can be given. All the carbon concentration results presented in the following parts have been obtained using this analysis reaction.

Figure 2: NRA spectra Carbon dosage with $^{12}$C(d,p)$^{13}$C reaction, influence of the treatment gas.

Gas nature
The ambient gas is a key parameter on the ceramic layer growth as it produces the carbon species diffusing in the layer.

Two kind of gases have been used for experiment, methane CH$_4$ and propylene C$_3$H$_6$. It appears that propylene decomposition in plasma phase produces three times more carbon in the layer than methane. Fig.2 shows NRA results obtained for two samples treated in CH$_4$ with respectively 400 and 1200 laser pulses and on another sample treated in C$_3$H$_6$ with 400 laser pulses. Both signals for CH$_4$, 1200 pulses and C$_3$H$_6$, 400 pulses are similar, showing the same concentration of carbon in the layer. The signal for CH$_4$, 400 pulses exhibits a carbon concentration that is the third of the previous one, the carbon concentration in the layer is directly proportional to the number of laser pulse number.

From these results, it is also deduced that the carbon-containing layer is thicker than 2 µm for an irradiation with 400 laser pulses. Consequently the use of C$_3$H$_6$ leading to the best carbon diffusion phenomenon is more convenient to limit the number of laser pulse. Indeed it is important to reduce the treatment duration and to avoid a too high increase of the roughness on the layer surface.

Crystalline phase detection
The X ray diffraction analysis technique has been used to identify crystalline phases present in the irradiated samples (CH$_4$, 1200 pulses). The diffraction spectra have been performed using different grazing incidence angles of the X ray source on the target surface. This
technique allows to obtain the depth evolution of the crystalline phases in the layer as a function of the depth. Diffractograms evidence the presence of aluminum carbide (Al₄C₃) at the sample surface with no aluminum oxide phase. It appears from the comparison between spectra obtained at different incidence angles that the carbide peak area is kept similar, revealing a constant crystalline composition of the layer over 1.5 μm.

Surface state
The roughness distribution on the surface depends on the way to scan the laser beam on the target. Two different scans, linear and diagonal, are compared. All the samples are treated with propylene, a laser fluence of 2.4 J/cm², 300 laser pulses per square centimeter, and an overlapping of 90%. Each laser impact induces ridges on its edges. For a treatment with 300 laser pulses per square centimeter and any overlapping of impacts, the ridges are several μm high and the mean roughness of the sample is 3 μm. The overlapping of the laser impacts leads to a diminishing of this roughness. Indeed the ridge height is limited by the following overlapping impact that smashes the ridge. With a linear treatment the upper ridge of each impact is never overlapped, leading to a longitudinal roughness (0.56 μm) larger than the lateral one (0.38 μm) this phenomenon is avoided using a diagonal scan (0.32μm and 0.38μm for lateral and longitudinal roughnesses). The roughness has been measured with a roughness-measuring device of accuracy class 1 (HOMMEL Tester T500).
NRA analyses for these two samples show that carbon concentration keeps similar in both, thus the scan mode does not influence the carbon content in the layer.

Fretting test
Fretting tests have been performed using untreated and treated samples. These friction tests are characterized by the very small amplitude of the displacement imposed between the two contacting surfaces, generally in the micrometer range [10]. In this study, the following testing conditions were chosen: plane aluminum samples rubbing against a reference cylinder (Ø = 20 mm, length = 1cm) made of 100Cr6 bearing steel; applied normal load of Fn = 20 daN; fretting amplitude D = ± 10 μm; frequency f = 5Hz. During the fretting test, the tangential force (Ft) is continuously recorded as a function of the imposed displacement D and of the number of cycles N. When gross slip occurs in the contact, a friction coefficient μ may be defined as the ratio of Ft over Fn. The evolution of this friction coefficient versus the number of cycles shows that the friction coefficient tends to drastically climb up to a maximum value before slowly decreasing to reach a stable state value. The maximum value of μ and the critical time needed to reach it strongly depend on the laser treatment conditions. For the untreated aluminum alloys, the peak of the μ value occurs very quickly and it may reach values as high as 1.4. This behavior has been related to the very high plastic deformation occurring in the ductile subsurface mainly located at the contact ends [11,12]. It creates front ripples, which induce frictional resistance and drastically increase the friction coefficient. As plastic deformation is accumulated, the material undergoes structural transformation leading to the formation of a Tribologically Transformed Structure (TTS) being nanocrystalline, very hard and brittle which will generate particles by microcracking [12].
Depending on the laser treatment parameters, the occurrence of the plastic deformation peak is delayed and the reached maximal value decreased. Two phenomena may contribute to this effect [11]: the carbide layer having some solid lubricant properties modifies the stress field in the contact, this modification reducing and/or delaying the plastic deformation; the carbon diffusion layer exhibits enhanced mechanical properties that limits the plastic deformation
phenomenon and the associated peak effect. Both explanations are in agreement with the observed results, i.e. the highest the carbon content is, the highest the peak delay and reduction is. Nanohardness depth profiles will be performed to check the second hypothesis.

4. Conclusion

The efficiency of the cementation of aluminum by excimer laser has been demonstrated and the improvement of tribological properties of the target. By means of the plasma induced by laser interaction with target, carbon species have been incorporated in aluminum, creating a carbide layer on the surface. The diagonal treatment in propylene atmosphere with a laser fluence of 2.4 J/cm², and 300 laser pulses leads to the formation of a Al₄C₁ layer with a thickness of 2 μm and a surface roughness lower than 0.4μm. This carbide layer increases the wear resistance of the surface as deduced from fretting tribological tests.

References