Excimer laser surface remelting processes of metallic materials

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ABSTRACT

Physical and chemical transformations induced upon metallic materials such as aluminum alloys and steels under KrF excimer laser radiation have been studied in order to improve their mechanical and physical-chemical properties. The laser treatment leads, after laser surface remelting (LSR) process, to important changes in the topography, structure, phases and elements composition resulting in different hardness, wear properties and corrosion resistance. Up to now, the use of excimer lasers for industrial applications remains marginal in spite of the interest related to the short wavelength (better energetic coupling) and the reduced thermal effects in the bulk material. This paper concerns mainly the corrosion resistance improvement of metallic alloys irradiated at 248 nm. Electrochemical tests have revealed a significant change in the corrosion properties mainly due to chemical composition and structural modifications.

1. INTRODUCTION

The advent of excimer lasers with interesting energy level, good reliability and better beam quality has allowed to consider an important development of the short wavelength, short pulse duration surface treatment. Effectively, the ultraviolet light can be coupled very efficiently to the surface of metallic or ceramic samples compared with IR and visible radiations (CO₂, Nd:YAG, Copper vapor laser,...); furthermore, taking into account their short pulse duration, the heat penetration depth is not very large and the quench rate is very high (10 ⁹ K/s). This quenching effect of the material may lead to a rapid solidification rates producing fine microstructures and changes of phases. This type of process (Laser Surface Remelting LSR) has got some potential applications in automotive industry with the possibility of improving the tribological behaviour of some components (smoothing and hardening of camshaft, crankshaft and gear wheels) or ablating deformation layer on cast iron component occuring during the mechanical preparation. The open spheroidal or lamellar graphite act as an oil reservoir creating an autolubrificated film, minimizing the oil usage and improving the functioning of the motor¹⁻². As well, improvement of the high temperature resistance on austenitic steel valves after smoothing and remelting processes has been demonstrated. In aerospace industry, the increase of wear resistance, fatigue behaviour and corrosion resistance of lightweight parts by changing hardness, roughness, residual stresses and chemical composition is of the greatest importance. In medicine, it is possible to prolonge the medical prostheses life such as hip joints, pins and other implants which can corrode inside the body. At present, stainless steel prostheses are implanted with ions to delay the corrosive process and reduce friction. It is cheaper to use the excimer LSR technique³.

To this present day, the use of the excimer lasers for industrial applications has given rise to a great deal of research programs and some interesting results have been obtained in United States and Europe. We started in Marseille at the beginning of the nineties such a research program both for a better understanding of the basic mechanisms which are involved in the laser-matter interaction phenomena and for underline the possible improvements of the mechanical and chemical properties of metallic materials ⁴⁻⁵. These modifications concern mainly the topography (roughness and smoothness), the hardness, the structure, the residual stresses and the chemical composition of the near-surface region, and induce changes in the lifetime of these materials (wear, fatigue, corrosion and so on). We focuse this paper on aluminum alloys (2017 A and 6000 type) and steel alloys (304 L, 434 L, 35 NCD 16) irradiated by KrF excimer lasers (20 ns, 0.5-10 J/cm2) in air, argon,

nitrogen or helium. The results have been obtained through analysis by means of scanning electron microscopy, energy dispersive spectroscopy, coupled and low-incidence angle X-ray diffraction, microhardness tester and electrochemical test equipment.

Of course, the absorptivity of metals depends on the intrinsic properties of the material and the surface quality (roughness, defects, impurities, oxide layers,...) and the temperature but also on the wavelength and the polarization of the beam. The incident intensity impinging the surface and the surrounding gas (nature and pressure) can also change the thermal coupling and then, the efficiency of the surface processing. For instance, here are some absorptivity values concerning three wavelengths 10.6 μ m, 1.06 μ m and 0.25 μ m at room temperature for Fe (0.05; 0.4; 0.6), Ti (0.05; 0.45; 0.65) and Al (0.03; 0.20; 0.25). In fact, for the aluminum, the inevitable alumina layer formed onto the surface is a better absorber (0.6) than pure theoretical aluminum. Furthermore, the energy of UV photons is high (5eV for 248 nm compared with 1 eV for 1.06 μ m and 0.12 eV for 10.6 μ m). The energy is absorbed by electron excitations which are thermalized very quickly (picoseconde), so that below the vaporization threshold, a purely thermal effect on the surface is obtained. The absorption skin depth $\delta = (K_{ext})^{-1} = \lambda/4\pi n_2$ (Kext extinction coefficient; I = I_o e^{-Kext x}; n₂ imaginary part of the refractive index) in most of metallic materials is about 5-30 nm.

Taking into account the thermal diffusivity κ and the classical pulse duration τ , the thermal affected depth $(4\kappa\tau)^{\frac{1}{2}}$ is always greater than δ and then much of the incident energy is deposited in a near-surface region. In this case, the depth of penetration of the heat (some μ m for metals, some 100 nm for ceramics) is not very large and we can consider than the bulk material and then its main properties have not been modified (no distortion, no mechanical or thermal damage).

2. LASER MATTER INTERACTION PHENOMENA

Generally speaking, during the sample irradiation at low and medium intensities, the interaction phenomena and the resulting effects on the material depend on different parameters listed as follows : firstly, the parameters related to the laser source and to the experimental conditions (wavelength of the radiation, polarization, pulse duration, intensity and fluence, size of the interaction zone, incidence angle, nature and pressure of the surrounding gas) ; secondly, the parameters related to the material itself (nature, microstructure, topography, chemical composition, cleanness,...). When the laser beam impinges the sample, we generally observe during the first moment of the interaction, reflection and scattering of the energy due to optical properties of the material. The relative importance of the specular reflected light and the scattered one depends on the surface conditions. An other part of the energy is absorbed leading to the heating, melting and vaporization of the irradiated sample. At higher intensity, the vapor can be more or less ionized, electrons are accelerated due to inverse bremsstrahlung absorption process, they ionize again the metallic atoms and so on ; a cascade ionization occurs and leads to the formation of an absorbing plasma. This one can be beneficial or detrimental to the beam coupling. At intensities just above plasma ignition, the plasma generated close to the surface can help for the coupling through re-irradiation process. At higher intensity, it can block the incident energy thus reducing beam coupling. The hydrodynamical regimes induce in these conditions (laser supported absorption wave, blast wave) as well the mechanical effects due to pressure recoil (up to 0.2 GPa) were studied in details 6 .

The main objectives of these studies was to observe the possible structural modifications and chemical composition changes of some metallic alloys treated using excimer laser. These modifications concern mainly the topography (roughness and smoothness), the hardness, the structure, the residual stresses and the chemical composition of the near-surface region, and induce changes in the lifetime of these materials (wear, fatigue, corrosion and so on). Of course, it is possible to get a material with adequate strength as well as high resistance to corrosion and oxidation at high temperature, applying an additional material to the base one. Coatings as Cr, Ni, Zn, Al, Cu and so on or non-metallic materials as paint, varnish, rubber, plastic can provide a satisfactory barrier between metal and its environment. Several methods exist to apply such coatings 7 , electrodeposition, vapor deposition, plasma spraying, alloying or cladding using laser techniques. But some limitations of these techniques are : poor adherence, high porosity and roughness, uneven surface. To avoid all these problems, we discuss in this paper the excimer laser "one-step treatment" method.

3. EXPERIMENTAL CONDITIONS - CORROSION

Experiments were carried out using KrF excimer laser device able to deliver up to 100 watts average power, 200 Hz, 20 ns. For our experiments, lasers were configured with stable optical resonator allowing with adequate focusing optics to choose the irradiation conditions within a range of fluence/intensity ($0.5-10 \text{ J/cm}^2$; 25-500 MW/cm²) with a rather good intensity distribution in the spot. Different nature and pressure surrounding gases such as air, nitrogen, argon, helium have been tested in order to study the dynamics of vapor/plasma induced in front of the surface and then optimize the process.

The metallic samples investigated were low alloy steel (35 NCD16 0.36 % C, 0.28 % Si, 0.48 % Mn, 3.9 % Ni, 1.7 % Cr, 0.3 % Mo, 93 % Fe), stainless steel (304 L <0.03 % C, 0.7 % Si, 2 % Mn, 9.5 % Ni, 18 % Cr, 70% Fe [Z2CN18 -10],

aluminum alloys (2017 A/AU4G 4 % Cu, 1.5 % Mg, 0.6 % Mn 93 % Al; 6000 series 0.29 % Mg, 1.15 % Si, 94 8 % Al). They have been mechanically worked in order to get large initial roughness (as received samples) and carefully cleaned before treatment (acetone). For each treatment, the experimental parameters (number of pulses, repetition rate and fluence) were varied.

The test equipment was a Tacussel Electronique potentiostat, a pilote generator (-750 mV to 2 V), a corrosion cell constituted with the working electrode, platinised titanium auxiliary electrode and the saturated calomel reference electrode.

Corrosion phenomenon which can be defined as the deterioration or destruction of a material because of chemical reaction with its environment can be divided into two main types :

* the chemical corrosion, for instance the dry corrosion in high temperature oxidizing atmosphere.

* the electrochemical corrosion in marine medium and acid medium for instance. This one concerns this paper. The electrochemical nature of corrosion can be divided into two reactions, these are oxidation or anodic reaction (production of electrons) and reduction or cathodic reaction(consumption of electrons). These two reactions must occur simultaneoulsy onto the metal surface and, during the metallic corrosion, the rate of oxidation equals the rate of reduction.

there is an example applied to iron immersed in sea water. The corrosion reaction can be written as

$Fe \rightarrow Fe^{2+} + 2e^{-}$	(oxidation)
$2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{H}_2$	(proton reduction)
$O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^-$	(reduction dissolved oxygen)
bloride found in sea water does not participate in the reaction and thus th	

The sodium chloride found in sea water does not participate in the reaction and thus the overall reaction is found by adding the partial reactions to give.

2 Fe + 2 H₂O + O₂ \rightarrow Fe²⁺ + 4 OH⁻ \rightarrow 2 Fe(OH)₂ 2 Fe(OH)₂ + H₂O + 1/2 O₂ \rightarrow 2 Fe (OH)₃

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The ferrous hydroxide precipitates from the solution, is instable and is oxidized to the ferric salt.

Passivation can be described as the loss of chemical reactivity during corrosion process and the formation of a passive layer (sometimes oxide layer on the surface which inhibits further corrosion when formed). The differing forms of corrosion can be classified by the visual appearance of the corroded metal. The main types of corrosion which are of interest for this study can be listed as : - uniform or general attack ; - galvanic or two metal corrosion ; - crevice corrosion ; - pitting corrosion ; let us briefly discuss the pitting corrosion.

Pitting is a localized attack which can result in relatively small holes on a metal surface (diameter \leq depth) sometimes isolated or so close together to give the appearance of a rough surface. This along with being an intense localized form of corrosion makes pitting corrosion a particularly frequent cause of failure. The beginning of a pit occurs when the rate of metal dissolution is momentarily high (due to surface scratch), interstice, dislocation, compositional heterogeneity like inclusion, segregate or precipitate, or a random variation in the solution composition. Rapid dissolution of metal M within the pit and no much oxygen reduction tends to produce an excess of positive charge in this area, resulting in migration of chloride cations to maintain electroneutrality. The process is accelerated as hydrogen and chloride ions stimulate the dissolution of most metals and alloys and the entire process accelerates with time.

Similar to the effect in crevice corrosion, there is little oxygen in the pit ; therefore no oxygen reduction occurs within the pit but instead occurs on the surface adjacent to the pit. This O_2 reduction causes the surface to be cathodic with respect to the pit and hence tends to suppress corrosion on the surface. So the pits cathodically protect the rest of the metal.

4. RESULTS AND DISCUSSION

For the 35NCD16 steel, it is interesting to notice that after irradiation and exposure to the ambient sea atmosphere for a period of 1 month, examination of the sample showed a difference in the corrosion which had occured on the treated area compared with the untreated one. The untreated surface had clearly experienced a higher level of corrosion than the laser melted zones (kept their shiny brightness). A 35NCD16 sample immersed in 1 M NaCl 25° C was melted using an energy density of 1.7 (40 shots per unit area), 2.4 (32 shots) and 4.1 J/cm2 (50 shots) through a cylindrical lens. We notice an 20 % improvement in the corrosion resistance (Fig.1) from -360 mV to -270 mV probably due to a refining of the grains. Cross sections of the samples showed that the depth of the melted zone is less than 3 μ m. Average grains size (some μ m at the initial stage) decreases up to 100 nm after treatment (10-30 nm into 0.05 μ m depth). The hardness increases due to the microstructure change.

35NCD16 steel



Figure 1 : Plot of Ecorr for laser treated and untreated 35NCD16 ; aerated 1 M NaCl solution.

The behavior after irradiation of the 304L stainless steel is presented in the figures 2 and 3. The main observation we can draw is that the resistance of this metal to pitting corrosion decreases considerably after the processing. Two series of experiments have been carried out with small different procedures. The figure 2 represents the pitting potential evolution as a function of number of pulses per unit area. The lowest value of the potential is obtained when the energy density and the number of pulses increase. In this case the pitting potential decreases from +144 mV in the virgin zone to -196 mV in the irradiated one.

The figure 3 gives the pitting potential versus fluence for a given number of laser shots per unit area (50-100). We note a drastically decrease of the potential from +200 mV (virgin material) to zero in the irradiated zone with two kinds of treatment (scanning mode or mosaic mode treatment).

We can give some possible explanations of this behavior. The FCC austenitic material has the ability to form a protective passive film. After irradiation, we observed some topography discontinuities of the surface due to the creation of microcraters around inclusions. Then, the inclusion-metal boundary becomes the preferential site for the initiation of pitting corrosion especially with chloride ions in the reactive medium. Furthermore, the irradiation at a certain fluence can destroy the chromium oxide protective layer.

The topography discontinuities due to the overlap can also play an important role in the experimental results. Recent results showed that the pitting occurred mainly on overlap regions.

We did not confirm the Jervis' results concerning the increase of the Cr concentration in the oxide layer close to the surface due to repeated melt – resolidification cycles. In his investigations, Auger electron spectroscopy shown that the Cr/Fe ration can increase by a factor 6 with 1 to 20 pulses at 1 J/cm². A thicker chromium rich oxide layer was formed and identified by a gold colored film and then, the pitting corrosion resistance was increased.

Some interesting results were obtained on a two phases ferritic and autenitic steel (434 L stainless steel). These two phases Fe $_{\alpha}$ and Fe $_{\gamma}$ coexist in the original material. At higher fluence, the α phase is totally removed giving finally a characteristically FCC austenitic material (equivalent to 304 L SS). That means that it is possible to change the corrosion resistance behavior of a cheaper steel depending, of course, on the laser irradiation conditions but, mainly, on the structural conditions of the material.



Figure 2 : Pitting potential for 304 L stainless steel samples as a function of number of pulses for two different irradiation conditions at 248 nm

Stainless steel 304L (ref ENH)



Figure 3 : Pitting potential as a function of the incident fluence (number of shots : 50-100)

The case of aluminum alloys is certainly the most interesting when looking at the corrosion resistance (Fig. 4-5-6). Electro chemicals tests (NaCl 1M 25°C) revealed that the pitting potential of this alloy is enhanced depending on the fluence values and number of pulses. Generally speaking, for these experimental conditions, the melt depth is very small (<10 μ m) this leads to an extremely high cooling rates (10⁹ – 10¹⁰ K/s) resulting in the formation of more refined microstructures (50 nm) where the precipitates melted during the process do not have time to reform and stay in soluble solution with the surface layer. In Aluminum Alloy 2017 A for example, pitting can begin at copper precipitates where the oxide layer is not thick enough to protect the surface.

The excimer LSR process could reduce the size of these precipitates; there would be not possible anodic sites and a more uniform oxide layer would exist on the surface. Then, low-incidence angle X-ray diffraction analysis revealed a change of the FCC α phase and θ phase Al₂Cu (Fig. 6). The dissolution of khatyrkite Al₂Cu phase, eventually Al₂CuMg in the matrix leads to redistribution of the copper atoms within the melted layer. Other explanations can be given from the X-Ray diffraction analysis : the characteristic peaks of the aluminum are shifted after treatment corresponding to a decrease of the

crystalline parameters and the relative intensities change explaining a preferential orientation of the crystalline planes near by the extreme surface.

Let us precise that the dissolution of Al₂Cu precipitate induces a slight decrease in hardness Vickers (150 \rightarrow 140 HV100).



Figure 4 : Pitting potential evolution for Series 2000 and 6000 Aluminum alloys



Figure 5 : Pitting potential for 2017A aluminum alloy for different irradiation conditions (OL=overlap).



Figure 6 : Low-incidence angle X-Ray diffraction diagrams for 2017A Aluminum alloy

5. CONCLUSION.

Experiments presented in this paper showed that it is possible to improve some metal properties by excimer laser surface remelting (LSR) choosing appropriate irradiation conditions. This kind of "one-step treatment" can lead to important modifications of topography, structures, hardness, residual stresses, near-surface chemical composition which have significant influence on electrochemical corrosion resistance. In the case of more resistant corrosion materials (stainless steel), the laser treatment at relatively high fluence destroys the passivation layer which protects the surface ; then, the corrosion resistance is reduced. The most important improvement was obtained for series 2000 and 6000 Aluminum alloys.

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