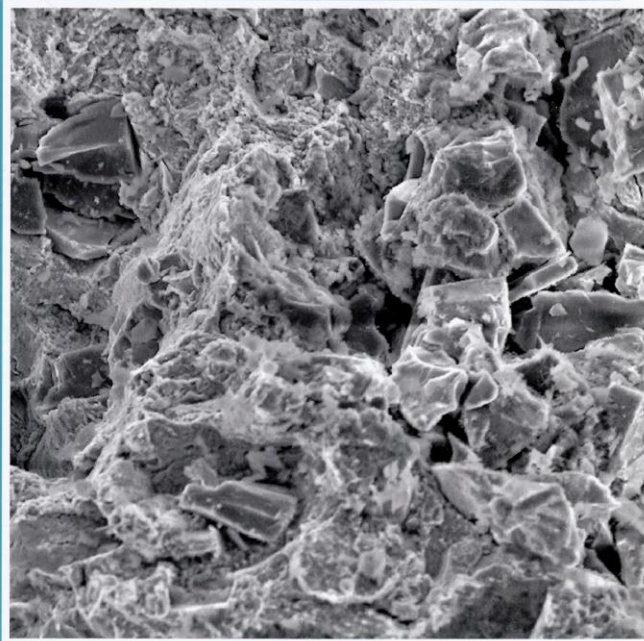


International Journal of **MATERIALS RESEARCH**

Zeitschrift für **METALLKUNDE**

10/2013



Editor:
Deutsche Gesellschaft
für Materialkunde

Co-Editors:
Société Française
de Métallurgie
et de Matériaux

Swiss Association
for Materials Science
and Technology

Managing Editors:
E. J. Mittemeijer
M. Rühle
F. O. R. Fischer

Volume 104, October 2013

www.ijmr.de

HANSER

Ihsan H. Toor^a, Bekir S. Yilbas^a, Cihan Karatas^b, Mohammed A. Hussein^a,
Mohammed N. Zafar^a

^aDept. of Mechanical Engineering, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Kingdom of Saudi Arabia

^bEngineering Faculty, Hacettepe University, Ankara, Turkey

Electrochemical investigation of the effect of different laser surface treatments on Hastelloy G alloy

In the present study, the corrosion resistance behavior of untreated and laser treated Hastelloy was examined. The electrochemical tests including potentiodynamic polarization, Tafel analysis, and linear polarization resistance were carried out in deaerated 0.5% NaCl aqueous solution at room temperature. Surface roughness was measured to correlate it with corrosion resistance properties of the materials. Surface morphology of the samples after corrosion tests was examined using scanning electron microscopy and energy dispersive X-ray spectroscopy. Results showed that laser treated surface exhibited better corrosion resistance properties as compared to untreated surface.

Keywords: Laser; Surface treatment; Hastelloy; Corrosion resistance

1. Introduction

Hastelloy has good sulfidation and oxidation resistance and excellent thermal stability at high temperatures [1]. It has low cycle fatigue resistance superior to that of most solid solution-strengthened alloys and it has a very good resistance to hot corrosion. The alloy is used to manufacture high-temperature gas path components such as turbine combustors, flame holders, liners, pressure vessels of some nuclear reactors, chemical reactors, and pipes/valves in the chemical industry.

Several surface treatment techniques are available to improve the surface properties of metallic alloys; however, laser treatment is considered to be one of the preferable techniques with improved performance as compared to conventional methods in terms of chemical cleanliness, thermal penetration, and surface profile. Considerable studies have been carried out to examine the effect of laser treatment of the Ni base alloys. Laser surface melting of austenitic Cr–Ni stainless steel was examined by Staurev et al. [2]. They observed the austenite in the melt pool with dendrite morphology and δ -ferrite in the dendrite core. The grain refinement of austenitic stainless steel through laser processing was carried out by Yamoguchi et al. [3]. They showed that fine ferrites were developed in the laser irradiated region and the grain size average of 15–19 μm was formed. Laser

cladding of austenitic stainless steel with nickel-based hard-facing alloy was examined by Kaul et al. [4]. They suggested that thin deposits with low level of impurities could be formed on the austenitic steel through controlling the laser cladding parameters. The desensitization of austenitic and duplex stainless steel using the laser surface melting technique was investigated by Cluar et al. [5]. They demonstrated that desensitization of stainless steel was possible via laser controlled melting, which was characterized by low chromium depletion and occurrence of solute segregation at the grain boundaries. Laser surface modification to improve inter-granular corrosion resistance of austenitic stainless steel was studied by Maliayan et al. [6]. Their findings revealed that laser treated surfaces resulted in improved inter-granular corrosion resistance. Laser surface re-melting of austenitic stainless steel was carried out by Bryton et al. [7]. They showed that increased laser power resulted in hardness increase at the irradiated region due to formation of dendritic and cellular-dendritic microstructures. In addition, the corrosion resistance of the laser treated surface was improved considerably. The microstructural changes and corrosion behavior of austenitic stainless steel treated by means of a laser beam was examined by Khoffallah et al. [8]. They indicated that corrosion resistance of the laser treated surface improved considerably and a shift was observed in the corrosion current and potential toward more noble values. Lutz et al. [9] studied the effect of nitriding on the corrosion resistance of the surface. They observed that the alloy surface could be efficiently nitrided using plasma immersion ion implantation and nitriding improved the corrosion resistance of the surface. High quality Hastelloy films deposited by pulsed laser ablation were studied by Zocco et al. [10]. They correlated the microstructure of the film, which was formed at the surface, with its corrosion properties.

Thermal stability of metallic nitrides produced by laser treatment was investigated by Han et al. [11]. They presented detailed information on the evolution of nitrogen concentration, phase composition and abundance, and surface hardness in terms of the annealing temperature. The reactive laser synthesis of carbides and nitrides was studied by Schaaf et al. [12]. They provided the dependence of phase formation and resulting properties in relation to the laser treatment parameters, such as laser type, pulse dura-

tion, material, and reactive gas pressure. Vignolo et al. [13] produced Hastelloy thin films using pulsed laser deposition (PLD) to analyze the influence of deposition parameters on the corrosion resistance of the resulting surface. Their results showed that the corrosion rates of the coated steel were lower than those of the uncoated substrate, which was particularly true for the thick coatings. However, the corrosion rate was much higher than that of the bulk Hastelloy thin films. Liu et al. [14] indicated that laser surface melting (LSM) could be used effectively to improve the corrosion resistance of materials. Razavi et al. [15] investigated the corrosion properties of the laser nitrided Ti-6Al-4V alloys and they reported that laser surface gas nitriding was a promising way to increase the surface hardness and wear resistance through the formation of a titanium nitride hard layer with dendritic structure at the surface. In addition, the corrosion properties of Ti-6Al-4V were reported to be strongly dependent on the surface conditions and chemical composition of the materials, which were affected by the surface treatment type and the laser processing parameters. Yilbas et al. [16] investigated laser surface treatment and corrosion properties of Inconel 617 alloy after 37000 h of usage as a transition-piece in a gas turbine engine. The electrochemical tests were conducted in 0.1 N H_2SO_4 + 0.05 N NaCl aqueous solution at room temperature. They found that the laser surface treatment improved the corrosion resistance of the alloy and a long period of operation resulted in partial degradation of the alloying elements at the surface.

Although microstructural changes of laser treated Hastelloy G alloy have been studied previously [17], the electrochemical response of the treated surface was left obscure. Consequently, in the present study, the effect of laser surface treatment of Hastelloy G on its corrosion properties was examined and results were compared with those for untreated surface. Electrochemical analysis includes potentiodynamic tests, Tafel analysis, and measurement of linear polarization resistance. The electrochemical tests were carried out in 0.5 M NaCl electrolytic solution at room temperature.

2. Experimental

A CO₂ laser (LC-ALPHAIII) with a output power of 2 kW was used to treat the workpiece. Nitrogen emerging from a conical nozzle was incorporated as an assisting gas. Laser surface treatment was repeated at different levels of laser and workpiece parameters including laser output power, scanning speed, assisting gas pressure, and focus setting of the focusing lens. Laser parameters resulting in defect-free surfaces were selected for the laser treatment process prior to the electrochemical testing. Laser treatment conditions resulting in defect free surfaces are given in Table 1.

The workpieces were cut from Hastelloy G sheets with 2.0 mm thickness. The workpiece size was kept as

$10 \times 20 \times 2$ (width \times length \times thickness) mm³. Micrographs of the laser treated surfaces were obtained using Jeol 6460 scanning electron microscope (SEM) and elemental composition of the laser treated layer was determined from the energy dispersive X-ray spectroscopy (EDS). The surface roughness measurement was carried out using Mitutoyo SurfTest (SJ-301) equipment.

Corrosion tests (potentiodynamic polarization, linear polarization, Tafel behavior etc.) on laser treated and untreated surfaces were carried out in a three electrode cell, which was composed of a specimen as a working electrode, a Pt wire as a counter electrode, and a saturated calomel reference electrode (SCE). The specimens were degreased in benzene, cleaned ultrasonically, and subsequently washed with distilled water prior to electrochemical tests. The investigations were carried out with an exposed working electrode area of 0.07 cm² in 0.5 M NaCl solution at room temperature in PCI4/750 Gamry potentiostat and repeated several times to ensure the reproducibility of the data. Potentiodynamic polarization experiments were performed at a scan rate of 0.5 mV s⁻¹ and DC105 corrosion software was used to analyze the Tafel region. The open-circuit potential (OCP) measurements were carried out on freshly cleaned samples and maintained for up to 1800 s.

3. Results and discussion

Electrochemical response of the laser treated Hastelloy G alloy surfaces was examined. Metallurgical and morphological characterization of the treated layer was realized incorporating SEM and EDS prior to and after the corrosion tests.

Figure 1 shows SEM micrographs of the top surface of the laser treated region. The regular laser tracks were formed during the laser scanning process and no large scale surface defects are formed at the surface. Therefore, laser overheating at the surface, giving rise to the surface evaporation, is avoided during the laser processing. SEM micrograph reveals that fine grains are formed at the surface due to the high cooling rates. Figure 2 shows cross-sections of the laser treated layer. The depth of the laser treated layer extends almost uniformly below the surface and fine grains with dense regions are formed in the surface region. At some depth below the surface, cellular dendrites are formed. This is attributed to rapid solidification of the liquid phase at the interface. The non-uniform cooling results in anisotropy of the growth rate of the cells below the surface while altering the cell size in this region. Moreover, fine grooves in between the cells occur because of the segregations at the grain boundaries at high cooling rates. However, the segregation decreases at low cooling rates. The EDS data for the laser treated layer is given in Table 2. The elemental composition of the laser treated surface remained the same after the laser treatment process; however, the presence of nitrogen indicates the creation of nitride

Table 1. Laser heating conditions used in the experiment.

Scanning Speed (cm s ⁻¹)	Power (W)	Frequency (Hz)	Nozzle Gap (mm)	Nozzle Diameter (mm)	Focus setting (mm)	N ₂ Pressure (kPa)
10	120	1500	1.5	1.5	127	600

compounds at the treated surface. This is because of the use of nitrogen at high pressure during the treatment process.

Table 3 summarizes the results of potentiodynamic polarization while Fig. 3 shows potentiodynamic polarization response of the specimens in 0.5 M NaCl solution. The corrosion potential (E_{corr}) was found to be -320 mV for laser treated surface. The pitting potential of the laser treated sample was found to be 837.3 mV_{SCE} and that of the untreated one was 345 mV_{SCE}. Passive current density (i_p) as well as corrosion current density of laser treated surface was less than those for the untreated surface, which suggests a stable passive film (lower corrosion rate) on the former compared to the as-received surface. Passive current density on the untreated surface showed a continuous increase along with localized breakdown/repassivation phenomenon, which is related with unstable films (metastable pitting). Table 4 summarizes the results of Tafel analysis and it is clear that the corrosion rate of laser treated surface decreased significantly as compared to untreated surface. The results presented showed that the laser treated specimen has exhibited the better corrosion resistance in terms of high E_{pit} , lower i_{corr} , and lower i_p as compared with the

untreated sample surfaces. These improvements in pitting potential and passive current density, along with more noble corrosion potential can be related to the dissolution of carbides, inclusions, and precipitates during the laser treatment, which were initially present in the untreated material. In addition, fine and homogeneous structures formed at the surface after laser treatment process decreased the possible pitting sites substantially, which ultimately increased the pitting potential, decreased the passive current density as well as decreased the overall corrosion rate of the laser treated surface. The presence of nitrogen also improved the corrosion properties of the laser treated surface. It was discussed previously that nitrogen in stainless steels and other alloys has a significant effect on the improvement of the overall corrosion resistance. This improvement was attributed to the modifications in the properties of the passive films caused by nitrogen [18]. It was also reported that nitrogen could improve the resistance to pitting corrosion of stainless steels by preferential enrichment at the film/metal interface through anodic segregation, so that the passivity was improved with subsequent retardation of metal dissolution [19].

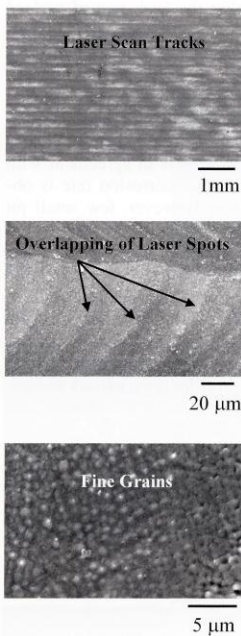


Fig. 1. SEM micrographs of laser treated surface.

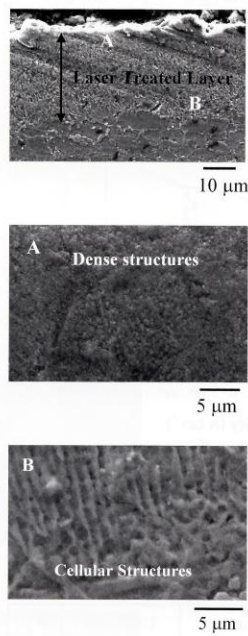


Fig. 2. Cross-section of laser treated layer.

Table 2. Chemical composition Hastelloy G (wt.%).

Element	C	Ta	Cr	Fe	N	Co	Mg	Cu	Ni
Untreated Surface	0.1	1.1	17.0	20	0.0	2.5	1.0	1.5	Balance
Laser Treated Surface	0.1	1.3	15.5	17	4.2	2.5	0.5	1.5	Balance

The findings are further complemented by experiments such as linear polarization resistance and current decay curves. Linear polarization resistance (R_p) is widely used to characterize the material's resistance to polarizing and thus can determine the protectiveness of film on material surface. The higher the polarization resistance the lower is the corrosion current density, i.e. corrosion rate. This method can be used to check the polarization resistance, i.e. corrosion rate of coating, or any other surface treatment. The polarization resistance of the laser treated surface is found to be 8.46 ohm as compared to 4.76 ohm for the untreated surface. This trend is similar to the one observed based on corrosion current density calculation by Tafel analysis, which shows that corrosion current of 0.0624 nA for the laser treated surface and 0.512 nA for the untreated surface. This suggests that the laser treated surface has the highest corrosion resistance properties as compared to untreated surface. A higher value of R_p (8.46 ohm) for laser treated

surface means that after laser treatment, the alloy surface becomes less active owing to more homogeneous and uniform surface structure. These results are in good agreement with those discussed previously on potentiodynamic polarization, where the laser treated specimen shows higher pitting potential values.

In order to confirm the positive electrochemical effect on the laser treated surface, current decay curves were measured for one hour in 0.5 M NaCl solution at room temperature. A constant potential of 200 mV_{SCE} was applied in these measurement to examine the passive film stability. The potential of 200 mV was selected because at this potential both the samples are in a stable passive region. Results presented in Fig. 4 show significant decrease in current density for laser treated surface as compared to untreated surface. This finding, again, complements the results obtained from linear polarization resistance as well as potentiodynamic experiments while suggesting that the passive film on laser treated surface is more stable as compared to the untreated sample.

After the corrosion experiments (potentiodynamic polarization), SEM was conducted over a large area at the surface to investigate and compare the surface degradation of treated surfaces and correlate those with electrochemical tests. It is clear from Fig. 5 that the laser treated surface has fewer pit sites as compared to the untreated surface. Since polarization scans are stopped as soon as there is a significant increase in current, no deep pit sites are expected to form at the surface. The initiation of pit sites is evident from SEM micrographs and pits are randomly distributed at the surface. Elongated large pit sites are clearly seen on the untreated surfaces. This is in agreement with the Tafel results, in which a higher corrosion rate is observed for the untreated surface. However, few small pit sites are observed on the laser treated surface. The pits are shallow and no micro-cracks emanate from the pit sites. This is attributed to the formation of nitride species and fine grains formed at the surface region, which act as a self protective layer at the surface and, thus, improve the corrosion resistance of the laser treated surface.

The surface roughness measurement was carried out to compare the roughness pattern of the laser treated and untreated surfaces and to correlate the surface roughness data

Table 3. Results of electrochemical tests for laser treated and untreated samples in 0.5 M NaCl solution.

	E_{corr} (mV _{SCE})	E_{Pit} (mV _{SCE})
Laser Treated Surface	-320	837.3
Untreated Surface	-338	345

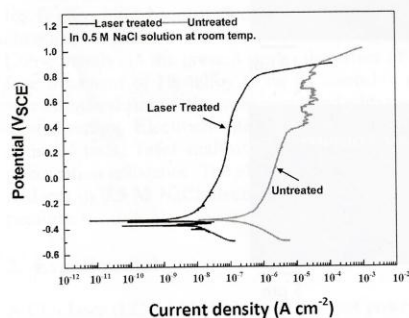


Fig. 3. Potentiodynamic polarization response of two specimens in 0.5 M NaCl solution. Polarization experiments were repeated three times and based on the repeatability of the experimental data, the estimated error was within 4%.

Table 4. Result from Tafel slopes and polarization resistance using LPR method.

	Laser Treated	Untreated
β_a (V/decade)	0.0504	0.1024
B_c (V/decade)	0.0167	0.0557
I_{corr} (nA)	0.0624	0.512
E_{corr} (V)	-0.0998	-0.192
Corrosion rate (mpy)	3.90×10^{-4}	3.202×10^{-3}
Polarization resistance (R_p) (ohm)	8.46	4.7

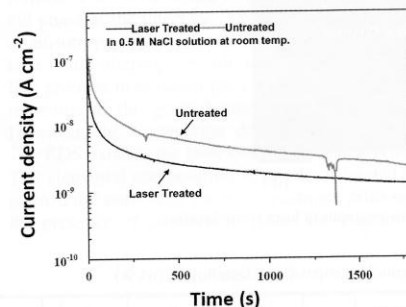


Fig. 4. Current decay curves at an applied potential of 200 mV_{SCE} in 0.5 M NaCl solution. The constant potential experiments were repeated three times and based on the repeatability of the experimental data, the estimated error was within 6%.

with the corrosion behavior of the surfaces. It is well documented that corrosion properties of the materials are seriously affected by their surface roughness profile, because surface roughness affects the ability of pits or corrosion initiation sites to form on the metal surface. Various researchers [20–22] have examined this effect for stainless steel alloys and found that a fine surface had higher corrosion resistance, as the ability of pitting to occur/corrosion initiation sites to form was reduced on the smooth surfaces. In other words, an increase in surface roughness increased the possibility of pitting corrosion. It is clear that surface defects contribute to the formation of corrosion initiation sites. In addition, for rough surfaces, the time of contact (diffusion) of corrosion causing species, such as chloride ions, increases. This, in turn increases the corrosion rate by decreasing the re-passivation ability of the surface and so there are more pit sites forming at the surface. In the present study the average roughness (R_a) of the laser treated surface was found to be $0.63 \mu\text{m}$, as compared to that of the un-

treated surface ($0.755 \mu\text{m}$). It is evident from these values that laser treated surface is relatively smoother than the untreated surface, which ultimately reduces the corrosion initiation sites, i.e. leads to improved corrosion resistance of laser treated surface, which is discussed in the earlier paragraph.

4. Conclusions

The electrochemical response of laser treated Hastelloy G surface was investigated. Electrochemical tests were carried out in deaerated 0.5% NaCl aqueous solution at room temperature. Microstructural characterization of the different treated samples was carried out using scanning electron microscopy. It was found that the laser treated layer extends uniformly below the surface. Fine grains formed at the surface because of the high cooling rates and nitride compounds. Although high cooling rates generate high thermal stress at the surface region, no cracks or crack networks were observed. Closer examination of the laser scanning tracks reveals that the overlapping ratio of the laser spots is on the order of 65%, which produces a continuous melting at the surface. The dense structures formed at the surface consisted of fine grains and as the depth below surface increased in the laser treated layer, a cellular structure formed. Grooves between the cells formed due to the segre-

Table 5. Surface roughness of the treated samples.

	Laser Treated	Untreated
R_a (μm)	0.63	0.755

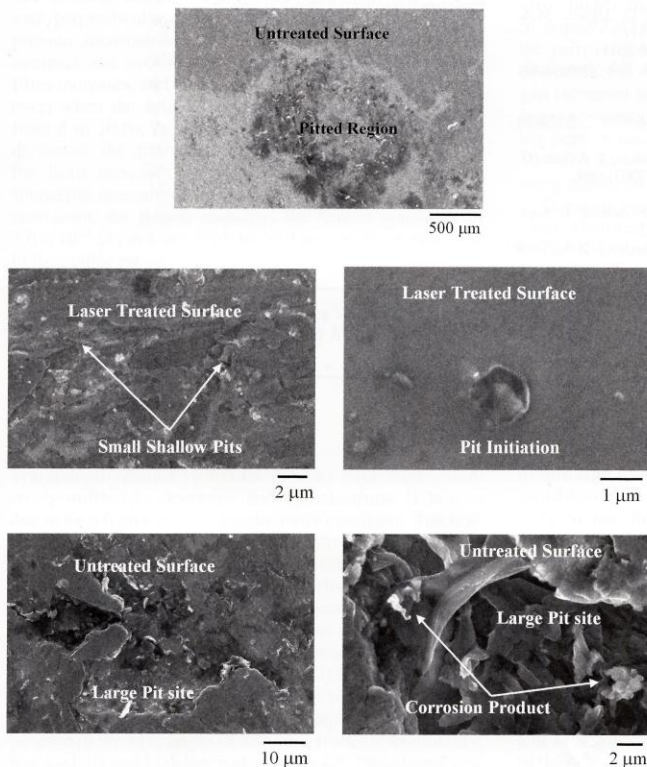


Fig. 5. SEM micrographs of pit sites at laser treated and untreated surfaces.

gation at the grain boundaries and the cell size varied because of non-uniform cooling in this region. Electrochemical test results revealed that laser treatment improves the corrosion resistance of the alloy significantly. The pit sites formed at the surface are shallow and randomly scattered. Few small pit sites were observed at the surface of the treated samples; however, elongated large pits formed at the surface. The formation of fine grains and low surface roughness contributed to the improved corrosion resistance of the laser treated surfaces.

The authors acknowledge the support of King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia for this work.

References

- [1] M.D. Rowe, V.R. Ishwar, D.L. Klarstrom: ASME J. Eng. Gas Turbines Power 128 (2006) 354. DOI:10.1115/1.2056527
- [2] D. Stavrev, T. Dikova, V. Shtarbakov, M. Milkov: Adv. Mater. Res. 264–265 (2011) 1287. DOI:10.4028/www.scientific.net/AMR.264–265.1287
- [3] T. Yamaguchi, N. Imamura, M. Katoh, K. Nishio: Quarterly J. Japan Welding Soc. 27 (2009) 270. DOI:10.2207/qjw.27.270
- [4] R. Kaul, P. Ganesh, S.K. Albert, A. Jaiswal, N.P. Lalla, A. Gupta, C.P. Paul, A.K. Nath: Surf. Eng. 19 (2003) 269–273. DOI:10.1179/026708403322499182
- [5] R. Kaul, N. Parvathavarthini, P. Ganesh, S.V. Mulki, I. Samajdar, R.K. Dayal, L.M. Kukreja: Welding Journal (Miami, Fla) 88 (2009) 233 s.
- [6] S. Mahajan, V. Kain, P. Ganesh, R. Kaul, A.K. Nath, R.C. Prasad: Int. Corrosion Conf. Series 1 (2007) 071911.
- [7] T.Z. Brytan, M. Bonek, L.A. Dobrzanski, D. Ugues, M.A. Grande: Mater. Sci. Forum 654–656 (2010) 2511. DOI:10.4028/www.scientific.net/MSF.654-656.2511
- [8] I.Y. Khalafallah, M.N. Rahoma, J.H. Abboud, K.Y. Benyounis: Opt. Laser Technol. 43 (2011) 806. DOI:10.1016/j.optlastec.2010.11.006
- [9] J. Lutz, A. Lehmann, S. Mandl: Surf. Coat. Technol. 202 (2008) 3747. DOI:10.1016/j.surfcoat.2008.01.020
- [10] A. Zocco, A. Perrone, M.F. Vignolo, S. Duhalde, I. Avram, C. Morales, T. Perez: Appl. Surf. Sci. 208–209 (2003) 669. DOI:10.1016/S0169-4332(02)01423-X
- [11] M. Han, E. Carpena, F. Landry, K.P. Lieb, P. Schaaf: J. Appl. Phys. 89 (2001) 4619. DOI:10.1063/1.1343522
- [12] P. Schaaf, M. Kahle, E. Carpena: Surf. Coat. Technol. 200 (2005) 608. DOI:10.1016/j.surfcoat.2005.01.028
- [13] M.F. Vignolo, I. Avram, S. Duhalde, C. Morales, T. Pérez, L. Cultrera, A. Perrone, A. Zocco: Appl. Surf. Sci. 197–198 (2002) 343. DOI:10.1016/S0169-4332(02)00421-X
- [14] Z. Liu, H. Liu, F. Viejo, Z. Aburas, M. Rakhes: Proc. Inst. Mech. Eng. C, J. Mech. Eng. Sci. 224 (2010) 1073. DOI:10.1243/09544062JMES1858
- [15] R.S. Razavi, G.R. Gordani, H.C. Man: Anti-Corros. Methods Mater. 58/3 (2011) 140–154. DOI:10.1108/00035591111130523
- [16] B.S. Yilbas, M. Khaled, M.A. Gondal: Opt. Laser Eng. 36 (2001) 269. DOI:10.1016/S0143-8166(01)00050-1
- [17] B.S. Yilbas, S.S. Akhtar, C. Karatas: Surf. Interface Anal. 44 (2011) 352. DOI:10.1002/sia.3811
- [18] R.F.A. Jargelius-Pettersson: Corros. Sci. 41 (1999) 1639. DOI:10.1016/S0010-938X(99)00013-X
- [19] R.D. Willenbruch, C.R. Clayton, M. Oversluizen, D. Kim, Y. Lu: Corros. Sci. 31 (1990) 179. DOI:10.1016/0010-938X(90)90106-F
- [20] H.-Y. Ha, H.-J. Jang, H.-S. Kwon, S.-J. Kim: Corros. Sci. 51 (2009) 48. DOI:10.1016/j.corsci.2008.10.017
- [21] N.J. Laycock, J.S. Noh, S.P. White, D.P. Krouse: Corros. Sci. 47 (2005) 3140. DOI:10.1016/j.corsci.2005.07.003
- [22] G.T. Burstein, S.P. Vines: J. Electrochem. Soc. 148 (2001) B504. DOI:10.1149/1.1378291

(Received November 29, 2012; accepted March 25, 2013; online since May 2, 2013)

Bibliography

DOI 10.3139/146.110947
Int. J. Mater. Res. (formerly Z. Metallkd.)
104 (2013) 10; page 1007–1012
© Carl Hanser Verlag GmbH & Co. KG
ISSN 1862-5282

Correspondence address

Professor Bekir Sami Yilbas
King Fahd University of Petroleum and Minerals
Dhahran 31261
Saudi Arabia
Tel.: +966 3 860 4481
Fax: +966 3 860 2949
E-mail: bsyilbas@kfupm.edu.sa

You will find the article and additional material by entering the document number **MK110947** on our website at www.ijmr.de