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EXCIMER LASER MELTING

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MIGRATION OF CARBON IN TEMPERED MARTENSITIC STEEL DURING EXCIMER LASER MELTING.

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ABSTRACT

The migration of ion implanted ^{13}C in tempered martensitic steel (nominal composition 1.05 wt. % C, 0.2 wt. % Si, and 0.3 wt. % Mn) during excimer laser melting was examined utilizing the resonance of the $^{13}\text{C}(p,\gamma)^{14}\text{N}$ reaction at $E_p=1747.6$ keV. Depth concentration profiles after five and ten laser pulses of 1 J/cm^2 revealed deviation from random walk diffusion in a homogeneous media. This was modelled by using the solubility controlled flow of carbon in iron-carbon melt. A diffusion length of $2\sqrt{D\tau}$ 34 ± 2 nm during a period τ of the melted phase was deduced. Significant amorphous to crystalline transformation occurred during the rapid self quenching following laser melting.

INTRODUCTION

The application of energetic beams to tailor surface sensitive properties of materials has increasingly fascinated the materials research community in past two decades. Ion implantation has been shown to increase wear resistance of many metallic and ceramic materials [1,2]. Typical characteristics of this technique are fine surface finish, dimensional stability, and almost complete independence of thermodynamical restrictions. As a relatively costly treatment, ion implantation has had only limited applications despite of the unquestioned unique properties of ion implanted surfaces.

Another surface treatment method based on energetic beams is laser surface modification. Lasers can be used to melt surface and produce metastable microstructures during subsequent self quenching (laser glazing). The surface of material can also be alloyed by e.g. depositing a thin layer of desired material onto the surface and mix it with the substrate by laser melting. The applicability of different lasers in producing novel surface alloys varies greatly. Often used continuous wave (cw) CO_2 lasers have a deep penetration but a slow quenching rate. This restricts the number of obtainable metastable phases in the melted zone. The other disadvantage of CO_2 lasers is a poor absorption of infrared light in metals. Much better absorption and higher quenching rate can be obtained using excimer lasers operating in UV region. Surface roughness after excimer laser treatment is also generally significantly smaller than after a cw laser with a much deeper melting zone.

An excimer laser has been used successfully to alloy stainless steel with titanium producing beneficial mechanical properties [3]. Mixing of the ternary Fe-Ti-C system also occurs easily [4]. This system is especially interesting from a tribological point of view and is being extensively studied by different groups [5-7]. More recent studies on mixing of titanium with SiC have also been very successful promising new tools to decrease surface cracking of this material [8]. In this work we have focussed on the behavior of carbon in simple steel during excimer laser melting. This problem is important because all steels have carbon as a constituent and obtainable microstructures are greatly determined by migration of carbon. This information is also necessary if excimer lasers are to be used in carburization of steels.

PREPARATION OF SAMPLES AND MEASUREMENTS

Specimens $30\times 20\times 3\text{ mm}^3$ in size were cut from a steel bar with nominal composition 1.05 wt. % C, 0.2 wt. % Si, and 0.3 wt. % Mn. They were first austenized at 780°C for 30 min and quenched into water-10 % NaCl solution at 20°C . Subsequent tempering was carried out at 240°C for 15 min. Following to this thermal treatment samples were mechanically polished using diamond paste down to $0.3\text{ }\mu\text{m}$.

Implantation of ^{13}C was performed at the beam energy of 32 keV. The corresponding calculated range is 42 nm according to the computer code TRIM [9]. The total implanted fluence was 2×10^{17} ions/cm 2 . The implantation chamber was equipped with a liquid nitrogen cold trap and pumped with a cryopump. Base vacuum was 5×10^{-7} torr and vacuum during implantation 1×10^{-6} torr. All implantations were carried out at 0 °C.

Laser melting was carried out using an excimer laser operating at a wavelength of 248 nm. The energy density per pulse was 1 J/cm 2 . The sample was moved at a constant speed in such a way that either five or ten pulses overlapped with the total energy deposition 5 and 10 J/cm 2 , respectively. The repetition rate of pulses was 1 Hz, which was long enough to allow complete cooling of the sample to ambient temperature between separate pulses. The pulse length was 25 ns. The average melt depth and cooling rate can be estimated from a 1-D thermal conduction model [3]. For these conditions, the melt depth was approximately 0.5 μm , the duration of melt 50 ns, and the initial cooling rate 1.5×10^{10} K/s.

Depth concentration profiles of implanted ^{13}C were determined utilizing the resonance of the $^{13}\text{C}(p,\gamma)^{14}\text{N}$ reaction at $E_p=1747.6$ keV [10]. Because the width of this resonance is 70 eV, the depth resolution was determined by the energy resolution 1.6 keV of the accelerator at the energy involved. The depth resolution was 20 nm at the surface. The γ -rays of energy of 9.170 MeV were detected with a NaI(Tl) detector 12.7×10.2 cm 2 in size.

Microstructure of the samples was examined with a transmission electron microscope (TEM). The samples were made by thinning electrolytically from the unimplanted side.

RESULTS

Shown in Fig. 1 are the measured concentration distributions of implanted ^{13}C in the as-implanted case and after laser melting with 5 and 10 pulses. Considerable diffusion of carbon can be observed as broadened profiles. However, an abrupt change in the slope of the distributions of the laser treated samples at a depth of approximately 120 nm suggests a deviation from normal random walk diffusion. This situation resembles solid state diffusion in samples with an implanted concentration above the solubility limit of the species involved [11]. Diffusion in these cases can be expressed by a model of solubility controlled flow. The solution of Fick's second equation with the boundary condition $C(x_0,t)=C_0$ yields

$$C(x,t)=C_0 \operatorname{erfc} \left(\frac{x-x_0}{\sqrt{4Dt}} \right) \quad (1)$$

where $\operatorname{erfc}(z)$ is the complementary error function and x_0 is the depth of the abrupt change in the slope of the concentration profile. D is the diffusion coefficient and t the diffusion time.

Fig. 1. Concentration profiles of ^{13}C before and after laser treatments.

Fig. 2. Comparison of the measured and fitted concentration profiles.

The above model was applied to the present case on the basis of the shape of the depth distributions of ^{13}C . The values of $x_0=120$ nm and $C_0=15$ at. % were used. In Fig. 2 the curves fitted into the tail parts of the distributions of Fig. 1 according to the formula (1) are shown together with the measured values. The excellent agreement can be observed. Diffusion lengths $2\sqrt{Dt}$ of 41 and 51 nm were deduced corresponding to 5 and 10 pulses. The diffusion lengths $2\sqrt{Dt}$ per melted period τ can be calculated using the identity $t=n\tau$ where n is the number of pulses. Values of 36 and 32 nm were obtained in the cases of 5 and 10 pulses, respectively.

Microstructures of the samples changed drastically during ion beam and laser treatments. The initial microstructure was typical high carbon steels tempered at relatively low temperatures. The structure consists of bcc martensite with precipitated hcp ϵ -carbide. This is illustrated in Fig. 3 where both bright field images and electron diffraction patterns can be seen. Some retained carbides can also be detected indicating an incomplete austenizing treatment. The bright field image of the substrate reveals a typical morphology of tempered martensite with twinning in martensite laths. Retained carbides are visible as spheroidal inclusions. After carbon implantation the microstructure was still crystalline, the diffraction pattern consisting mainly of ϵ -carbide reflections. The morphology of martensite phase had completely disappeared and remarkable refinement of the microstructure occurred. A detailed description of the microstructure of carbon implanted tempered martensite will be given in a forthcoming paper.

During laser melting significant crystalline to amorphous transformation occurred as can be seen in Fig. 3 where the diffraction pattern and microstructure of carbon implanted steel after 5 shots are shown. Instead of sharp well-defined diffraction rings of the substrate or carbon implanted sample the diffraction pattern of the laser melted samples consists of diffuse rings indicating existence of an amorphous phase. Some TEM samples revealed also crystalline diffraction especially after 10 pulses. However, it is impossible to determine what area of the implanted zone those samples were from.

DISCUSSION

Analysis of the measured concentration profiles of the samples treated 5 and 10 times yielded diffusion lengths per the melted period τ 36 and 32 nm, respectively. These values can be considered identical within error limits. The differences may be caused by pulse energy variation as well as changes in absorption properties of the surface as a function of the number of pulses. Thus the average value is 34 ± 2 nm. Using the estimated duration of the melted period $\tau=50$ ns, the diffusion coefficient D can be calculated. The value obtained $5 \times 10^{-5} \text{ cm}^2/\text{s}$, is in good agreement with the published value of the diffusion coefficient of carbon in iron $6\text{--}7 \times 10^{-5} \text{ cm}^2/\text{s}$, at 1550°C [12]. The high value of a diffusion coefficient indicates that diffusion of carbon has definitely occurred in liquid state. The diffusivity of carbon in solid state is orders of the magnitudes lower and can be ignored in the analysis.

The most interesting feature of the concentration profiles of ^{13}C is the deviation from the random walk diffusion. The shape of the depth distributions after 5 and 10 pulses are very much

Fig 3. Transmission electron diffraction patterns and micrographs of the untreated substrate and the carbon implanted, laser melted sample.

similar to those found in solid state diffusion of solvents in samples implanted above the solubility limit, e.g. nitrogen in 304 stainless steel [13]. The interpretation of the model of solubility controlled flow in the solid state case is as follows. In the area $x < x_0$ (formula 1) the solubility limit is exceeded and precipitates and a solid solution are in thermodynamic equilibrium. This means that at a constant temperature, the compositions of the precipitates and solid solution are constant. Only solute atoms able to diffuse are in the solution. In solubility controlled flow the diffusion of solutes into the region $x > x_0$ occurs as precipitates in the two phase region ($x < x_0$) dissolve.

Solubility controlled flow of carbon in laser melted steel could result from the undissolved solid phase in the melted zone. Diffraction patterns did not reveal any significant crystalline phases; only an amorphous microstructure was observed, particularly in the sample treated with 5 pulses. Since the concentration of carbon in steel before implantation was 4.5 at. %, the total concentration of carbon at the abrupt change in the slope of the distribution profiles is 19.5 at. %. This corresponds to the carbon solubility (in equilibrium with graphite) in liquid iron at 1427 °C [14]. This temperature is in fair agreement with that suggested by the deduced diffusion

coefficient, 1550 °C. Solubility controlled flow is evidently caused by the solubility of carbon in liquid iron, although graphite was not detected in TEM studies.

Amorphization of the iron-carbon system is difficult. For example carbon implantation into iron at room temperature up to 50 at.% was found to produce hexagonal ϵ -carbide precipitates in iron matrix [15]. At higher concentrations of carbon an amorphous phase was also observed, though complete amorphization was never obtained. This was explained by the formation of the relatively simple and radiation resistant ϵ -carbide instead of the amorphous phase. Only at high concentrations, when the accommodation of carbon in ϵ -carbide becomes impossible the amorphous phase was expected and verified. These results are consistent with those obtained in this work. The maximum carbon concentration in our samples was about 50 at. % (implanted ^{13}C plus carbon in steel substrate). The microstructure of implanted samples mainly consisted of ϵ -carbide precipitates and bcc martensite. It is interesting to note that although ϵ -carbides were involved in our samples already before implantation, no significant growth of these precipitates was found after implantation. The nucleation of new precipitates also in this case is remarkable.

Amorphous Fe-C alloys can be produced by splat cooling [16] or using a continuous wave CO_2 laser [17]. In the work performed with a CO_2 laser the estimated average cooling rate was 10^5 K/s. Theoretical calculations on the Fe-C system suggest that the minimum cooling rate for glassy alloy formation is of the order of 10^9 K/s [18]. At least in part for that reason complete amorphization was not found in glazing of $\text{Fe}_{82}\text{C}_{18}$ alloy with a CO_2 laser. The quenching rate in the case of an excimer laser is higher, in our case about 1.5×10^{10} K/s. This exceeds the critical cooling rate for amorphous phase production. Accordingly, a complete amorphization was found as a result of excimer laser melting. This was probably also promoted in part by higher carbon concentration in our case.

A formation of ϵ -carbide competes with amorphization during implantation as pointed out in ref. [15]. This keeps the level of supersaturation low. During laser melting and subsequent rapid self-quench the concentration of carbon atoms in solution is much higher and presumably much higher degree of supersaturation is possible.

CONCLUSION

The diffusion and solubility controlled flow of carbon during laser melting of tempered martensitic steel were observed and found to be consistent with liquid state diffusion and the solubility of carbon in the Fe-C melt. Transformation of the microstructure from typical tempered martensitic to a refined, ϵ -carbide rich phase during carbon implantation and then to an amorphous phase during subsequent laser processing occurred.

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REFERENCES

1. J.K. Hirvonen, in *Ion Implantation and Ion Beam Processing of Materials*, edited by G.K. Hubler, O.W. Holland, C.R. Clayton, and C.W. White (North-Holland, New York, 1984), p. 621.
2. M. Nastasi, R. Kossowsky, J-P. Hirvonen, and N. Elliot, *J. Mat. Res.* 3, 1127 (1988).
3. T.R. Jervis, J-P. Hirvonen, M. Nastasi, *J. Mat. Res.* 3, 104 (1988).
4. J-P. Hirvonen, M. Nastasi, T.R. Jervis, J.R. Tesmer, and T.G. Zoco, *Mat. Res. Soc. Symp. Proc.* 140, 183 (1989).
5. D.M. Follstaedt, J.A. Knapp, and L.E. Pope *Mat. Res. Soc. Symp. Proc.* 140, 133 (1989).
6. I.L. Singer and R.A. Jeffries, *Appl. Phys. Lett.* 43, 925 (1983).
7. J-P. Hirvonen, M. Nastasi, T.R. Jervis, J.R. Tesmer, and T.G. Zocco, in *Proceedings of the 5th International Congress on Tribology, EUROTRIP'89*, edited by K. Holmberg and I. Nieminen (Finnish Society for Tribology, Espoo, Finland 1989) pp.172-177.

8. T.R. Jervis, J-P. Hirvonen, M. Nastasi, and M. Cohen, presented at the 1989 MRS Fall Meeting, Boston, MA, 1989 (to be published).
9. J.F. Ziegler, J.P. Biersack, and U Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 1985).
10. G. Deconninck, *Introduction to Radioanalytical Physics* (Akademiai Kiado, Budapest 1978) p.229.
11. S.M. Myers and R.A. Langley, J. Appl. Phys. **46**, 1034 (1975).
12. E. Fromm and E. Gebhardt, *Gase und Kohlenstoff in Metallen* (Springer Verlag, Berlin, 1976) p. 580.
13. J-P. Hirvonen and A. Anttila, Appl. Phys. Lett. **46**, 835 (1985).
14. E. Fromm and E. Gebhardt, *Gase und Kohlenstoff in Metallen* (Springer Verlag, Berlin, 1976) p. 579.
15. D.M. Follstaedt and J.A. Knapp, Mat. Res. Soc. Symp. Proc. **51**, 473 (1986).
16. J.R. Sare, Scripta Met. **9**, 607 (1976).
17. C. Antonione, L. Battezzati, G. Riontino, and C. Turco, Mat. Res. Soc. Symp. Proc. **28**, 105 (1984).
18. P.G. Roswell and G.A. Chadwick, J. Mat. Sci. **11**, 2287 (1976).