Lasers in Manufacturing Conference 2021

Surface carbon enrichment of stainless steel using nanosecond pulsed laser surface alloying of a graphite based coating

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Abstract

Laser surface alloying is a promising technique for modifying and/or improving surface properties of forming tools used in the fabrication of thermoplastic composite parts. The results of a study on laser surface alloying of graphite based coatings on ferritic stainless steel using a nanosecond pulsed laser source is presented. The effect of different laser processing parameters and coating types on the laser-induced carbon diffusion in the steel are analyzed. The morphology of the processed areas was characterized using confocal microscopy and scanning electron microscopy. The atomic concentration of diffused carbon was determined using energy-dispersive X-ray spectroscopy. It was found that the surface carbon content of stainless steel can be increased substantially up to 70% in weight. Cross-sectional analysis revealed the dependence of diffusion thickness on the accumulated laser fluence, having a maximum depth of about 6.5 µm. In comparison to low and high carbon steel, and unprocessed stainless steel, laser processed samples demonstrated improved wear properties.

Keywords: Laser surface alloying; carbon enrichment; stainless steel; nanosecond laser

1. Introduction

Thermoplastic composite parts are formed using moulds made of stainless steel due to the cost effectiveness and ease of use of the material. The lifetime of these moulds, as well as forming accuracy, are severely affected by the sticking (adhesion) of polymer to the mould surface during the mould release step

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[Packham, 2002]. Such polymer-metal adhesion is circumvented typically by the use of intermediate films or release agents, which are expensive, disposable and ecologically unfriendly substances [Critchlow et al., 2006]. Recently, Chu et al. demonstrated that graphene can be successfully implemented as an intermediate film between polymer and stainless steel to achieve non-sticking behavior [Chu et al., 2020]. However, adhesion of graphene on metal surface is still challenging [Lin et al., 2016], and the upscaling of such a graphene coating process at industrial scale would be expensive. An alternate route would be to enrich stainless steel surface with carbon, preferably in its graphite form. Ferritic and austenitic stainless steels comprise over 80% of total global stainless steel usage, and are non-hardenable using conventional heat treatment techniques due to precipitation of chromium carbide at grain boundaries - known as sensitization [Kumar et al., 2004]. To circumvent the problem of decreasing corrosion resistance due to sensitization, low temperature carburizing techniques such as, Kolstering® and low-temperature colossal supersaturation (LTCSS), are widely used for increasing the surface carbon content up to a maximum of 7 wt.% [Farrel 2005, Erns et al., 2009]. Therefore, the aim of this work is to explore possible routes to graphitize the stainless steel mould surface by substantially increasing the surface carbon content using laser processing.

Surface carbon enrichment of metal and its alloy is a widely used technique for improving the mechanical and tribological properties through surface hardening [American, 1991]. Over the years, methods that matured into industrial standard can be categorized into two classes namely, low temperature treatment such as gas carburizing [Hirata et al., 2020], plasma carburizing [Michal et al., 2006], Kolstering® [Farrel 2005], and high temperature treatment by applying high energy electron beam [Losinskaya et al., 2015] or laser sources [Ion, 2005] on carbon based coatings . The solid state diffusion process involved in low temperature heat treatments is limited by the process duration and parts geometry [Hirata et al., 2020, Losinskaya et al., 2015]. Processes involving high energy sources not only overcome the aforementioned difficulties, but also provide technical and economic benefits [Ion, 2005]. From its earliest attempt in 1964, laser surface alloying has gained significant attention from the research and user community alike – resulting in material processing methods such as laser cladding, laser hardening, laser nitriding, and laser carburizing to name a few [Draper et al., 1985, Abboud et al., 2007]. By partly melting the substrate along with a thin layer of coating material or powder particles, large temperature gradient can be achieved at the solid liquid interface, which results in high quench rates and resolidification velocity [Draper et al., 1985]. Large variety of chemical compositions and microstructural states can be achieved as a result of rapid cooling and solidification rate [Laroudie et al., 1995]. The focus for laser surface alloying of steels is typically on incorporating "precious" metals into the steel matrix in order to attain extraordinary surface properties that is otherwise resource-expensive using conventional steel manufacturing techniques [Draper et al., 1985]. Laser beam carburizing of iron and steels is primarily aimed at hardness improvement using continuous-wave (cw) or long-pulsed laser sources, which suffers from the formation of cracks and gas porosity in the laser-treated layer, limited or incomplete austenisation for solid state diffusion, and secondary hardening of the non-treated area [Ji et al., 2017, Yildizli et al., 2016, Amine et al., 2014]. In contrast, short and ultrashort pulsed laser sources, with pulse durations in the femto- to nanosecond regime, can provide high peak power with low total heat input, higher heating and cooling rates, as well as formation of highly non-equilibrium structures within a relatively shallow depth, resulting in crack- and heat affected zone (HAZ) free treated layer [Gurevich et al., 2012, Hamoudi et al., 2017, Yamaguchi et al., 2017]. To the best of our knowledge, no work on (ultra) short pulsed laser surface carburization has been reported up to now.

In this work, we investigate the surface carbon enrichment of AISI430 stainless steel using a nanosecond pulsed laser source and graphite particle based coating. We used three different graphite coatings and irradiated the coated surface at identical laser processing conditions. The morphology and the chemical composition of the laser-treated samples are analysed to quantify the surface roughness and elemental concentration, as well as, the cross-sectional analysis are performed to measure the diffusion thickness of the carbon enriched layer. Surface properties such as wear resistance, hardness and wetting are evaluated for laser-treated samples and compared to untreated stainless steel, low carbon steel and high carbon steel.

2. Experimental

For the experiments, a nanosecond pulsed laser system (SPI redEnergy G4, wavelength = 1060 nm, pulse duration = 241 ns, $M^2 < 1.3$) was used. A galvanometer scanner system (Scanlabs IntelliScan14), equipped with an f-theta lens (f = 80 mm), translated the focused beam (beam diameter ($1/e^2$) = 40 µm) over the sample surface as shown in Fig. 1(a). The laser beam scanning velocity was varied at a constant pulse energy (25 µJ) and pulse repetition rate (80 kHz) to generate varying percentage of geometrical spot to spot overlap ranging from 96.09% to 99.97%. To create laser-treated areas, several parallel laser tracks were scanned. The line to line overlap was kept constant at 75%. At such a scanning strategy, the accumulated fluence value was used instead of nominal fluence [Mezera and Römer, 2019]. Mirror-polished AISI430 stainless steel (as used in caul sheets during a moulding process) samples were taken as target materials. For the comparison of surface functionality, mirror-polished high carbon steel grade 1.2510 and low carbon steel grade AISI 1010 was used. Colloidal graphite solution was spin-coated onto the steel samples and their surface is shown in Fig 1(b). The coating thickness was about 10 µm. Figure 2 (a) shows the result of spin coating for two different colloidal graphite solution coatings. Isopropyl alcohol (IPA) based colloidal graphite solution resulted in higher variation of coating thickness resulting in the striations (see Fig. 2(a)). This is due to the volatile nature of the alcohol solvent, which dries off before spreading uniformly over the surface. Therefore, a water-based colloidal graphite solution was introduced which resulted in better uniformity, although agglomeration of particles can be observed over the surface. The solid content in these graphite based solutions were between 18% and 20% in weight. Therefore, pure graphite powder was also used to coat the surface, by applying aluminium foil as the thickness delimiter for powders while sliding a microscope glass slide over the surface as a (modified) blade-coating process (see Fig. 2 (a)). The laser treated surfaces are shown in Fig. 2 (b), where the effect of variation in coating thickness can be observed visually as regions of high carbon diffused area (darker in colour), and low and/or no carbon diffusion (white/lighter in colour). After laser processing, the samples were cleaned with ethanol in an ultrasonic bath for 30 minutes.

The morphological and chemical compositional analysis were performed using a scanning electron microscope (SEM) (Jeol JSM-7200F) equipped with an Energy-dispersive X-ray spectroscopy (EDX) sensor (Oxford Instruments X-Max^N) at an accelerating voltage of 10 kV. The surface roughness was measured using a confocal laser scanning microscope (CLSM) (Keyence VK-9700), the nano-hardness was measured using a nano-indenter (Anton Paar NHT), the wetting behaviour was evaluated using an optical contact angle measuring device (DataPhysics OCA20), and the wear measurements were carried out using a tribometer (Brucker UMT 2.0).

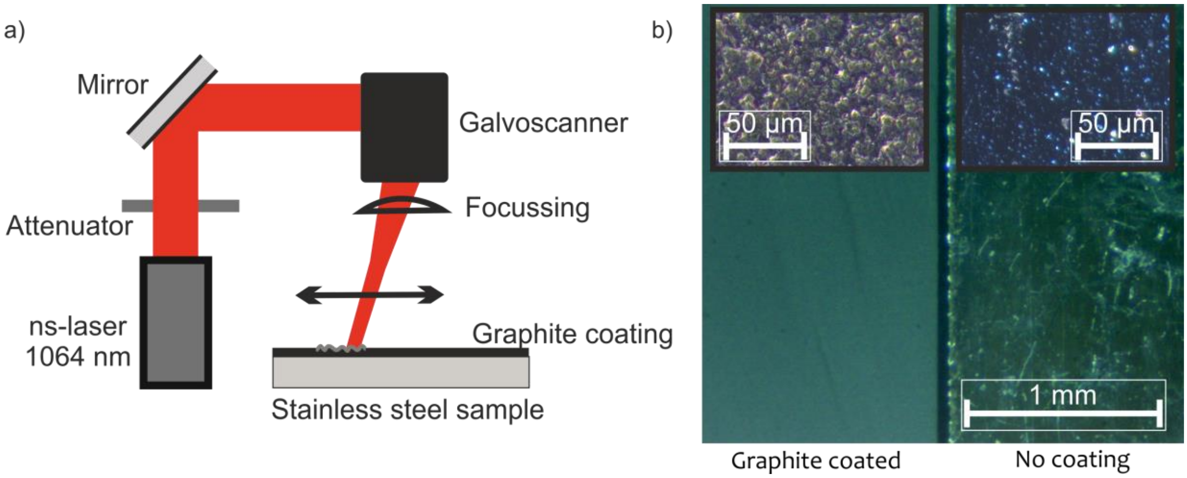

Fig. 1. (a) Schematic of laser setup. (b) Optical microscope image (brightfield) of pristine and graphite coated sample. Insets show darkfield images at a magnification of 100x.

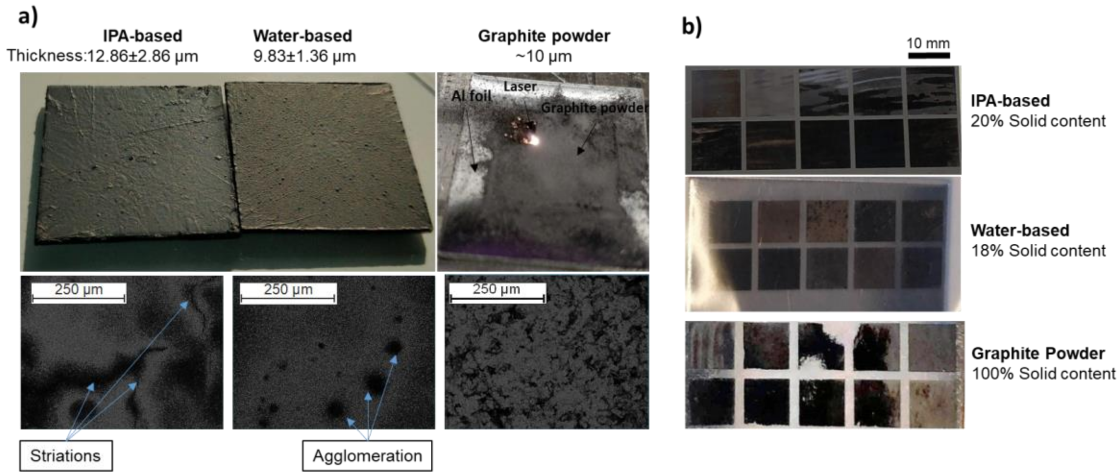

Fig. 2. (a) Stainless steel surfaces coated with graphite by spin coating (left) and powder coating (right). Lower images show the darkfield images of the coated area. (b) Impression of laser treated samples.

3. Result & Discussion

3.1. Morphology and chemical composition

Figure 3 (top row) shows the confocal images of the laser irradiated surfaces processed at different scanning velocities. As can be observed, the roughness of the sample increases with decreasing scanning velocity. This can be attributed to the accumulated fluence, which is higher at lower scanning velocity. Therefore, the sample is heated to a higher temperature at lower scanning velocity and surface structures exhibit hydrodynamic instabilities. At higher beam scanning velocity, the surface appears to be covered with carbon inhomogeneously, as can be observed in the upper rightmost image in Fig. 3 as whitish spots/bands. SEM micrographs of the laser irradiated surfaces are also shown in Fig. 3 (bottom row). The cooling rate of the sample during processing depends on the accumulated fluence. Consequently, different phases and microstructures are formed at different scanning speed, being affected by the heating and cooling rates.

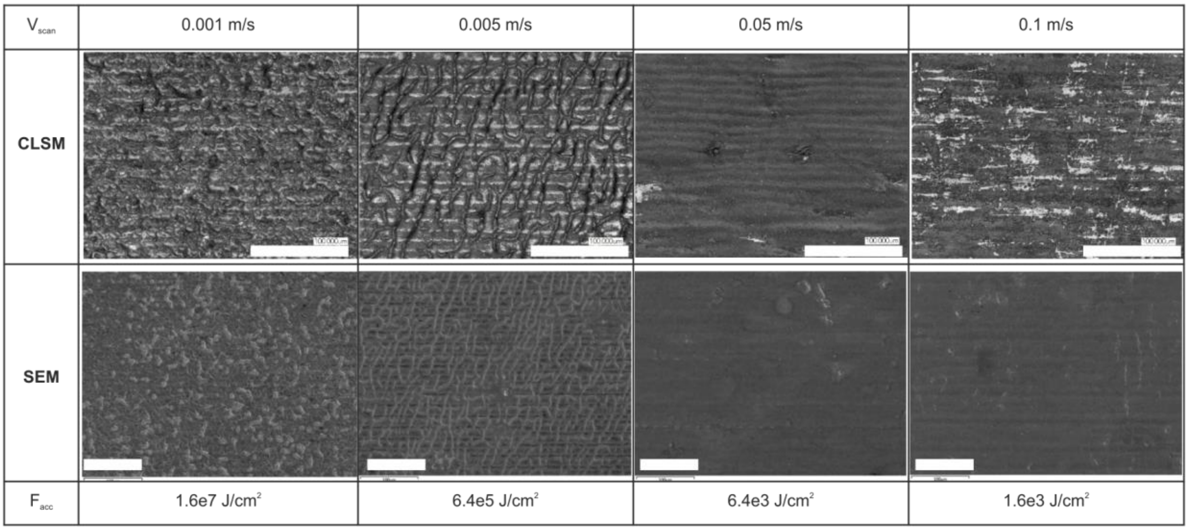

Fig. 3. Confocal (CLSM) and SEM micrographs of laser irradiated graphite coated surface at different beam scanning velocity and accumulated fluence. All images are in same scale. Scale bar denotes 100 µm.

The roughness values of the laser irradiated surfaces as function of the accumulated fluence are plotted in Fig. 4(a). In general, decreasing the scanning velocity increases the surface roughness due to higher overlap, which leads to a high temperature thermal process [Campanelli et al., 2007]. However, for higher scanning velocity, i.e. lower F_{acc}, the roughness value is close to the untreated surface as can also be observed in Fig. 3 and Fig. 4(a). The chemical composition (only carbon in wt%) of the laser irradiated surfaces are shown in Fig. 4(b). The carbon content at the pristine AISI 430 surface (reference) was 1.9 wt%, which is higher than the specified value of <0.08 wt% possibly due to adventitious carbon and adsorption of graphite coating layer. As can be observed from Fig. 4 (b), the carbon content on the surface initially increases up to 68%, and then gradually drops with increasing accumulated fluence. In this work, the accumulated fluence for which the surface carbon content is found to be highest is termed as optimal fluence. Increase in carbon content is associated with a decrease in oxygen as well as iron content. Therefore, the surface appears to be coated with carbon atoms.

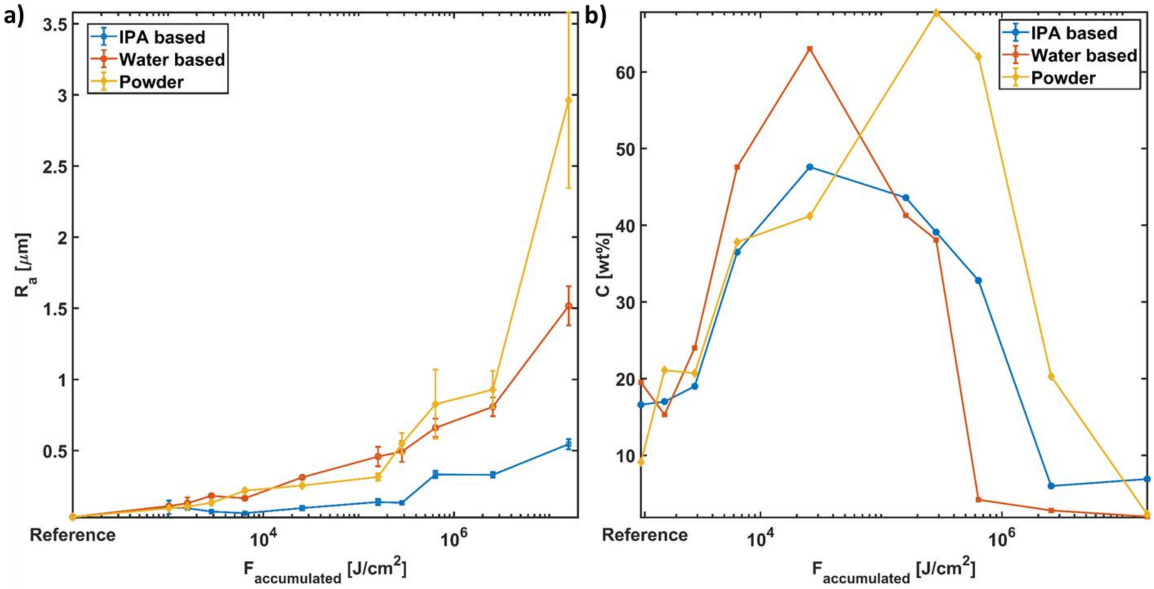

Fig. 4. (a) Surface roughness as a function of accumulated fluence, (b) carbon content of laser irradiated surfaces as a function of accumulated fluence. Lines are a guide to the eye.

To investigate the diffusion depth of carbon enrichment, cross-sectional analysis of the laser treated samples was performed. As shown in Fig. 5, the diffusion of carbon layer can reach up to 6.6 µm into the material, perceptible in the shade difference and interrupted steel grain structures. It was found that the diffusion depth depends on the accumulated fluence. If the accumulated fluence is either lower, or higher than the optimal value (F_{acc} = 2.56e4 J/cm^2, shown by the dotted black line in Fig. 7(a)), the diffusion depth becomes shallower. However, the diffusion thickness along the processed area is not uniform, which may be attributed to the non-uniform thickness of the graphite coating applied to the surface of the sample.

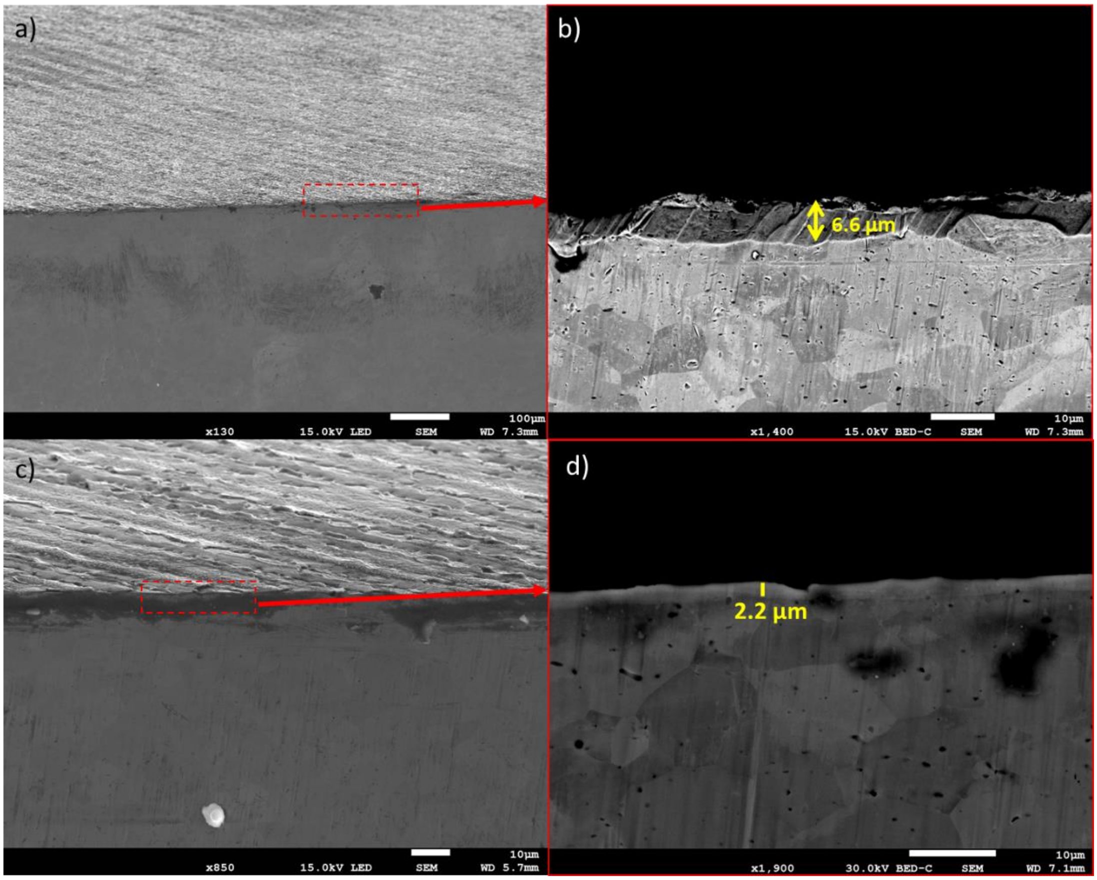

Fig. 5. SEM micrograph of the cross-section of laser-induced carbon enriched stainless steel samples with surface carbon content of (a)-(b) 47 wt% and (c)-(d) 19 wt%, processed at F_{acc} = 2.56e4 J/cm^2 and 2.85e3 J/cm^2 respectively. The scale bar is 10 µm.

3.2. Surface functionality tests

Since enrichment of carbon over the surface increases the hardness of the material [Laroudie et al., 1995], therefore, nano-indentation was performed to identify the hardness characteristics of the laser treated samples. The samples were investigated for a load of 15 mN, applied for 5 seconds. As can be observed in Fig. 6(a), the hardness values increases in all cases, at least by a factor of 2. However, the spread in the indentation hardness values increases as the roughness of the samples increases with increasing accumulated fluence. Figure 6(b) shows the results of scratch testing of untreated stainless steel (SS), laser treated stainless steel samples with corresponding surface carbon content (CC), high carbon steel (HCS) and low carbon steel (LCS), performed at 20 N load for 1000 strokes over a stroke length of 6 mm. The coefficient of friction (COF) is similar for untreated samples (SS, HCS, and LCS). However, COF reduces with increasing surface carbon content, and shows a significant reduction (75%) in dry condition (i.e. no lubrication) for the laser treated sample with 63 wt% surface carbon content. This is also reflected in the width and depth of the wear track (see Fig. 6(b)). One of the possible causes could be that the embedded graphite particles acts as lubrication and results in a reduction in the coefficient of friction [Mandal et al., 2020].

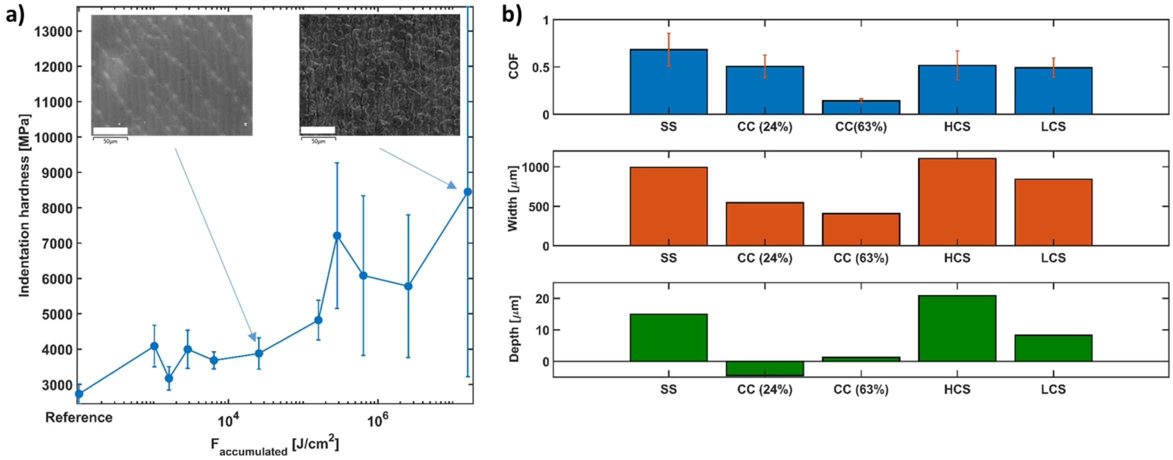

Fig. 6. (a) Indentation hardness of laser treated graphite coated samples, insets show the SEM micrograph of representative surfaces with scale bar indicating 50 µm. (b) Coefficient of friction, as well as, the width and depth of wear tracks of laser treated samples (CC) in comparison to untreated stainless steel (SS), high and low carbon steel samples (HCS and LCS).

To investigate the wetting behaviour of the untreated, graphite coated and laser treated samples, optical contact angle (OCA) for deionized water was measured at room temperature and at 21% humidity. As can be observed in Fig. 7(a), the trend in OCA for laser treated samples depends on the surface roughness of the sample, which is in accordance with literature [Prajitno et al., 2016]. The green and blue squares within the red dash-dotted rectangle represent the contact angle of HCS and LCS samples. The graphite coated stainless steel samples show more hydrophobicity than the uncoated samples, although the subsequent laser treatment of the graphite coated steel induces even more hydrophobicity. Interestingly, in comparison to untreated stainless steel samples, the carbon enriched samples with comparable surface roughness exhibits hydrophilicity. A similar static contact angle measurement was also performed for hexadecane, where the contact angle lies within 8° to 12° for all samples. Figure 7(b) shows a range of surface patterns to demonstrate the flexibility of the technique, i.e. possibilities of local carbon enrichment in different shapes and sizes, which is not possible using conventional cw and long-pulsed laser carburizing techniques.

To investigate the effect of laser-produced carbon enriched surfaces on adhesion of the polymers (PA6 and PEKK), a binary test described by Feinaeugle et al. was performed [Feinaeugle et al., 2019]. The laser treated samples were found to stick to the thermoplastic polymer qualitatively in similar fashion as non-treated ones. We assume that the laser treated surface does not exhibit purely graphitic surface. We speculate that the thermoplastic resin of the colloidal graphite is decomposed by the absorbed laser energy, then the decomposition product like amorphous carbon gets deposited on the surface, and finally gets diffused within the material along with the graphite particles. Further studies need to be performed to determine the type of carbon allotropes at the processed surface. Moreover, the phases of diffused carbon need to be analysed using X-ray diffraction (XRD) analysis to explain the high surface carbon content. Finally, sophisticated adhesion tests need to be performed, because binary tests only result in a qualitative validation of adhesion of polymer on steel surfaces, without providing any indication about the adhesion force at the polymer-metal interface.

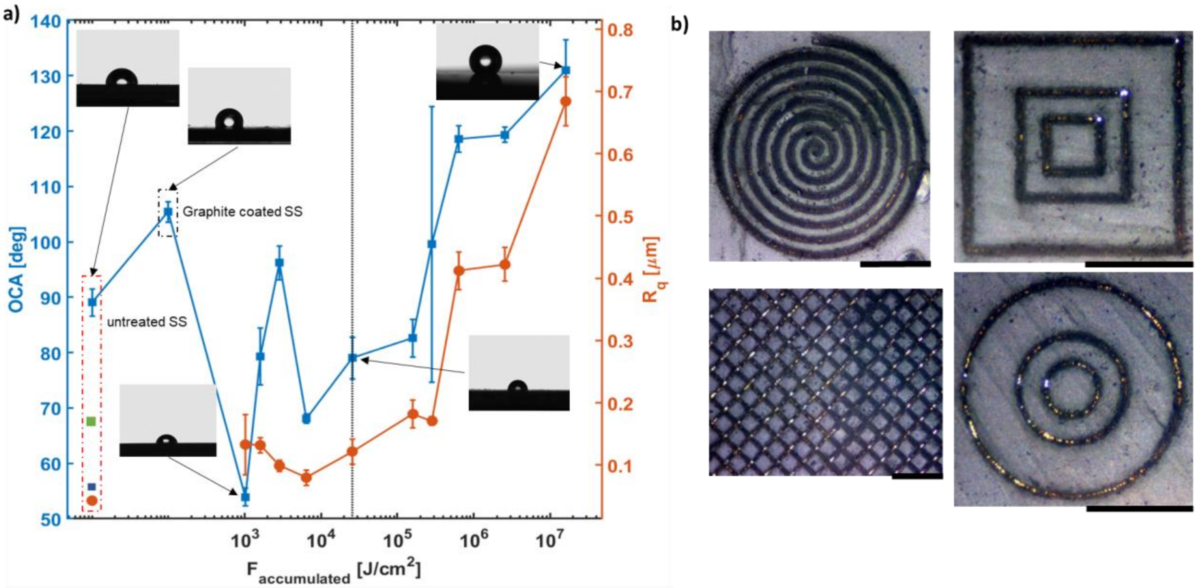

Fig. 7. (a) Contact angle and RMS roughness of the untreated, coated and laser treated samples (b) application possibility of proposed method in different size and shape. Scale bar denotes 1 mm.

4. Conclusion

We presented a novel technique for enriching the surface carbon content of ferritic stainless steel using a nanosecond pulsed laser source and graphite based coatings. Surface carbon content was found to be a function of accumulated fluence, and at an optimum fluence value, carbon content was found to be higher than 50%, with a diffusion depth up to 6.6 µm. The laser-treated samples exhibit 75% reduction in friction in dry conditions, and a two-fold increase in hardness. Adhesion tests need to be followed-up by sophisticated experimentation, and warrants further investigation by Raman spectroscopy and XRD to explain such high carbon enrichment. Nevertheless, the proposed techniques opens up possibility for designing steel surfaces with alternating areas of high and low carbon concentrations in different sizes and shapes, which may find applications in wear-prone parts of a component.

Acknowledgements

The authors would like to acknowledge funding from their institute's program 'Top Technology Twente: Connecting Industry'. We would like to thank L. Chu, W.J.B. Grouve, M.B. de Rooij, S.B. Zaman, E.G. de Vries and R.J. Meijer of University of Twente for their input through scientific discussions and technical assistance.

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