

Laser surface melting of mild steel with submicronic titanium carbide powders

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Surface alloys are of great interest for improving the mechanical and/or chemical properties of the near-surface region of metallic materials. A new method is described to produce surface alloys under laser irradiation using submicronic powders suspended in a polymeric mixture. By this process, Fe–TiC composite surface alloys were achieved on mild steel; they exhibited increased hardness, the value of which may be varied by controlling the TiC fraction incorporated.

1. Introduction

The use of laser melting allows the near-surface region of metals to be modified by addition of foreign material. Such modifications can lead either to an alloyed surface layer (solid solution or biphased structure) or to a surface composite where the foreign material precipitates within the metallic matrix of the substrate. This latter structure, appearing when the solubility of the foreign material is low, is frequently observed in the case of carbide or nitride additions into metals. It can afford improved hardness and wear resistance to the base metal [1], depending on the volume fraction incorporated. As an example, in automotive internal combustion engine pistons, where enhanced wear resistance and desirable frictional properties are needed, a dispersion of silicon carbide in the aluminium matrix is gradually being adopted in the place of unreinforced alloy [2]. Among other composites of this type already studied and reported in the literature are Co/WC–TiC and Ni–TiC [3].

In the manufacture of cutting tools where the tool bits are welded to the holder, the cutting heads are always made of hard materials such as carbides or nitrides. These materials are brittle with a low toughness, and their ability to withstand mechanical shocks is mediocre. To combat such undesirable properties, they are welded to another material of high ductility and toughness which absorbs the shock during working. Accordingly, if these hard materials, such as titanium, tungsten or molybdenum carbides, could be directly incorporated into the matrix of a ductile material, their technological importance should increase further.

Different methods of preparation of such composites have been reported: precipitation from Fe–Ti–C melt of appropriate composition [4]; sintering of TiC powders with iron [5]; chemical vapour deposition of TiC [6]; or laser mixing of evaporated films of Fe–Ti–C [7]. Of particular importance in this area of study is the work of Ayers *et al.* [8] who used a particle injection method. This method was justified by the large difference between the volume mass of titanium carbide and that of stainless steel: titanium carbide being less dense than stainless steel, these authors claimed that without injection, it will simply float on top of the melt pool unless entering it with sufficient velocity. Unfortunately, by this method the Fe–TiC composites obtained were never crack-free. More recently, Ceri *et al.* [9] and Ariely *et al.* [10] have produced carbide-reinforced layers by the TiC laser-injection technique. In contrast to Ayers *et al.* [8], the coating was defect-free.

Kim *et al.* [11] have studied Fe–TiN materials prepared from a slurry of TiN particles in propyl alcohol, deposited onto iron and irradiated under different power densities with argon or nitrogen as shielding gas. The authors claimed that a fraction of the TiN decomposed to titanium and nitrogen under argon atmosphere, whereas no decomposition occurred under nitrogen.

In the present study, Fe–TiC crack-free surface composites were prepared on mild steel by a new and original method: laser irradiation of a mixture of submicronic TiC particles and polyethyleneglycol deposited on the metallic substrate. The influence of the laser power, translation speed and surface coverage by

the titanium carbide particles on the microhardness and morphology of the resulting surface layer are discussed.

2. Experimental procedure

Various quantities of submicronic particles of titanium carbide supplied by Societe Cerex, Annemasse, France and polyethylene glycol (PEG, M_w 2000) obtained from Sigma-Aldrich, St Quentin Fallavier, France, were mixed. They were brought to a pasty state by heating the mixture to the melting point of the polymer ($T_m = 70^\circ\text{C}$). The paste was applied onto the surface of an iron block by brushing, and left to dry in air. Different thicknesses were prepared ranging from 50 to 150 μm . The corresponding surface coverages by TiC ranged respectively from 0.13 to 9.2 mg cm^{-2} .

The samples were then placed on a computer controlled x - y translation stage for laser treatment. The Nd^{3+} : YAG laser employed could deliver a maximum power of 300 W and the beam was guided by an optical fibre to give a spot diameter of about 950 μm . The surface layers were produced with power densities ranging from 1 to $4 \times 10^8 \text{ W m}^{-2}$, translation speeds varying from 3 to 30 mm s^{-1} and different overlapping fractions between 30 and 70%. They were characterised by X-ray diffraction (XRD) analyses, scanning electron microscopy (SEM), electron microprobe analysis (EPMA), energy-dispersive spectroscopy (EDX) and microhardness testing.

3. Results and discussion

3.1. Nature of the formed products

XRD analysis of all surface composites showed the presence of two phases: α -Fe (ferrite or martensite), and the carbide TiC. As no iron concentration measurements could be made, the formula "TiC" will be used in the following, without any signification concerning the absence or presence of dissolved iron.

3.2. Thickness of the Fe-TiC layer

The thickness of the composite layer achieved at constant scanning rate increased with the laser power between 120 and 200 W. At constant power, the actual thickness increased with the value of the surface coverage by TiC as shown in Table 1. This phenomenon is a result of better light absorption by surfaces covered with more TiC.

3.3. Hardness and morphology

Systematic alloying and post-treatment examinations were made with increasing surface coverage of the steel by TiC. Both hardness and morphology were shown to depend largely on this parameter. The results obtained with two different values of the surface coverage (2 and 9.2 mg cm^{-2}) are discussed below.

3.3.1. Surface coverage of 2 mg cm^{-2}

Microhardness measurements as a function of depth

TABLE I Measured thickness of Fe-TiC surface layer for two different values of the surface coverage ($P = 175 \text{ W}$, $V = 3 \text{ mm s}^{-1}$)

Surface coverage by TiC (mg cm^{-2})	Thickness of the Fe-TiC composite layer (μm)
2	100
9.2	200

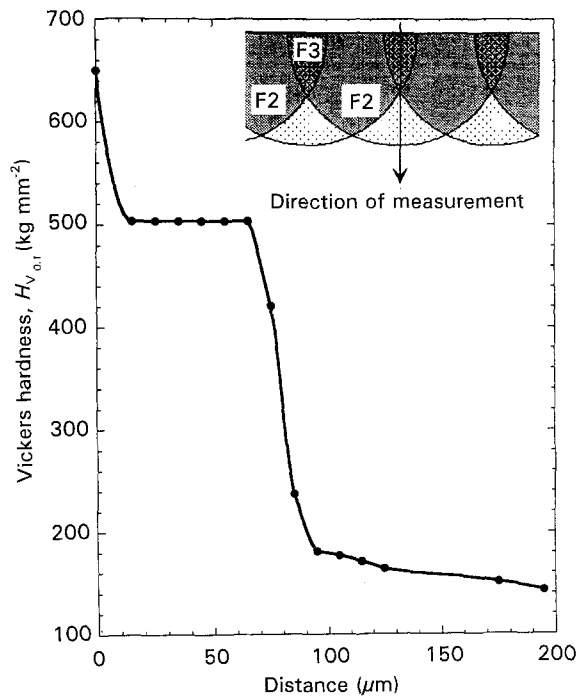


Figure 1 Vickers microhardness measured at the centre of the laser pass as a function of depth on a transverse section. Surface coverage, 2 mg cm^{-2} ; laser power, 175 W; scan rate, 3 mm s^{-1} .

were carried out on polished cross sections of the surface composites with a Vickers indenter at a load of 100 gf. The results are shown in Fig. 1, which shows that the hardness is maximum near the surface, suggesting an enrichment in carbide or a slight contamination by oxygen. Except this near-surface region, a constant hardness was measured throughout the melted layer, indicating a good homogeneity in composition and microstructure. The hardness then diminishes sharply to the value of the heat-affected zone and gradually decreases to the value of the substrate.

Fig. 2 shows that the hardness is roughly inversely proportional to the power. An increase in power at constant scan rate signifies an increase in the melt depth, with the consequence that the alloy becomes more diluted. In the same way, at constant power a direct proportionality between the hardness and the scanning rate is observed, and can be understood by noting that the higher the scanning rate, the lower the interaction time; and the shallower the melt region with a subsequent high enrichment by TiC. It is worth noting that this effect is predominant, compared to a slight evolution in the scale of the microstructure. With a power of 175 W and a scanning speed of 3 mm s^{-1} , the maximum hardness measured on the treated flat surface was 650 $\text{HV}_{0.1}$.

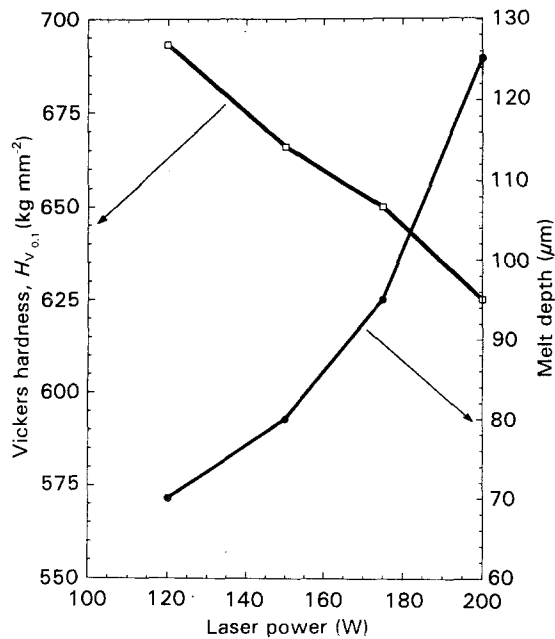


Figure 2 Vickers microhardness (measured at the surface and at the centre of the laser pass) and melt depth as a function of the applied power. Surface coverage = 2 mg cm^{-2} ; scan rate = 3 mm s^{-1} .

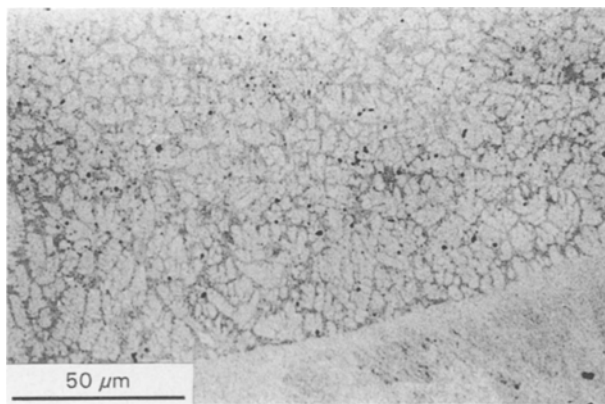


Figure 3 SEM photomicrograph of a Fe-TiC sample showing the distribution of TiC along the grain boundaries. Surface coverage = 2 mg cm^{-2} ; laser power = 175 W ; scan rate = 3 mm s^{-1} .

The observations performed by SEM show the layer to be crack-free, with a regular dendritic microstructure and titanium carbide found mainly between the grains of α -Fe (Fig. 3). This is confirmed by the X-ray map of titanium. Moreover, a chemical etching reveals the interdendritic precipitation of a eutectic (α -Fe)-TiC (Fig. 4). The formation of this eutectic is the result of the dissolution of the initial particles of TiC in the melt and their further reprecipitation during the solidification process. The melting of the TiC particles is made easy because of their very small size: approximately 50 nm (Fig. 5). This dissolution was also observed by Ayers *et al.* [8] who studied the hardening of 304 stainless steel by TiC but as a minor effect, because of the large main size (100 – $200 \mu\text{m}$) of the TiC particles used for their experiments.

The matrix appears, after stronger etching, to be mainly composed of needle-shaped martensite. Dur-

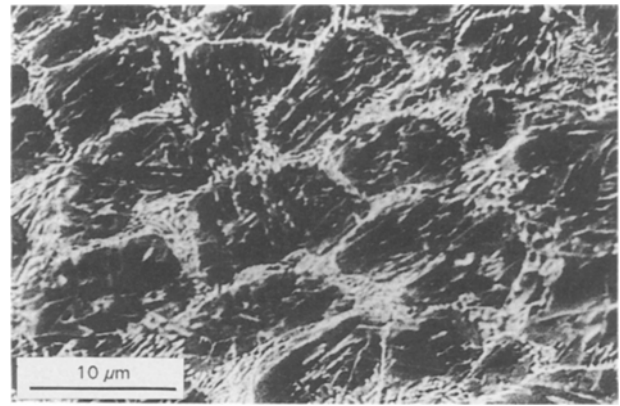


Figure 4 SEM photomicrograph of a Fe-TiC sample, after chemical etching, showing a eutectic structure between the grains of α -Fe (martensite).

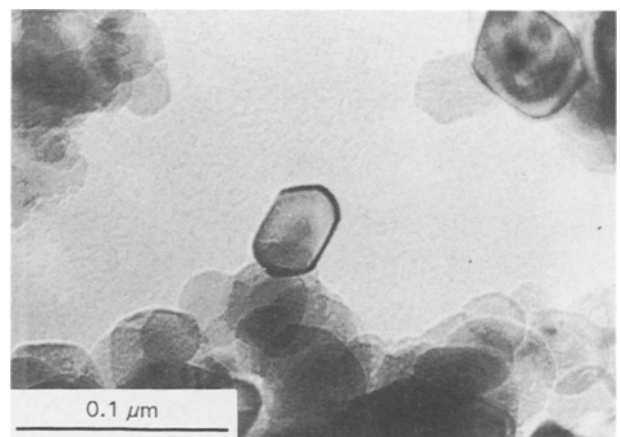


Figure 5 TEM photomicrograph of the TiC particles supplied by CEREX.

ing cooling, the ferrite (primary and eutectic) is replaced by austenite, which is later transformed into martensite due to the rapid cooling rate. The carbon contained in the austenite results from the dissolution of titanium carbide and probably also of carbon due to an incomplete vaporization of the polymer during the treatment.

With the techniques (EDX EPMA) used to analyse the surface layers, it was very difficult to determine precisely the concentration of TiC at the different places of the composite layer. With the average and most studied laser conditions of 175 W and 3 mm s^{-1} , the mean concentration of TiC in the layer was estimated to be about $2.5 \text{ wt } \%$.

3.3.2. Surface coverage of 9.2 mg cm^{-2}

At such a high value of surface coverage, the use of the previous laser operating conditions (175 W , 3 mm s^{-1}) led to a heterogeneous structure, with large TiC islands in addition to the regular structure described previously (Fig. 6). These particles are thought to result from an agglomeration of powders to a size (a few μm to $50 \mu\text{m}$) which does not allow them to melt during the treatment. A similar phenomenon was also observed in the Fe-TiN system [11]. To prevent this

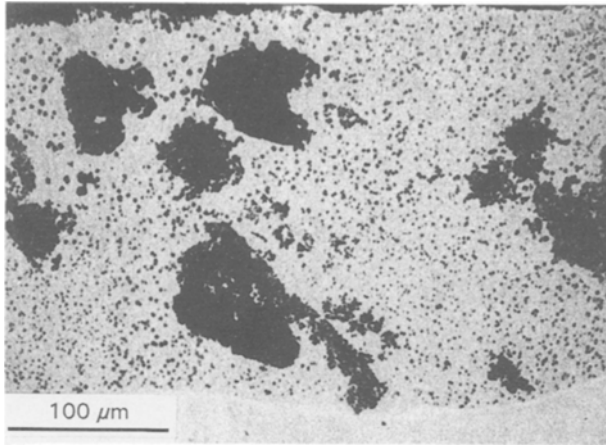


Figure 6 SEM BEI (backscattered electron image) indicating the presence of coalescing TiC due to an increase of the surface coverage (9.2 mg cm^{-2}), Laser power = 175 W ; scan rate = 3 mm s^{-1} .

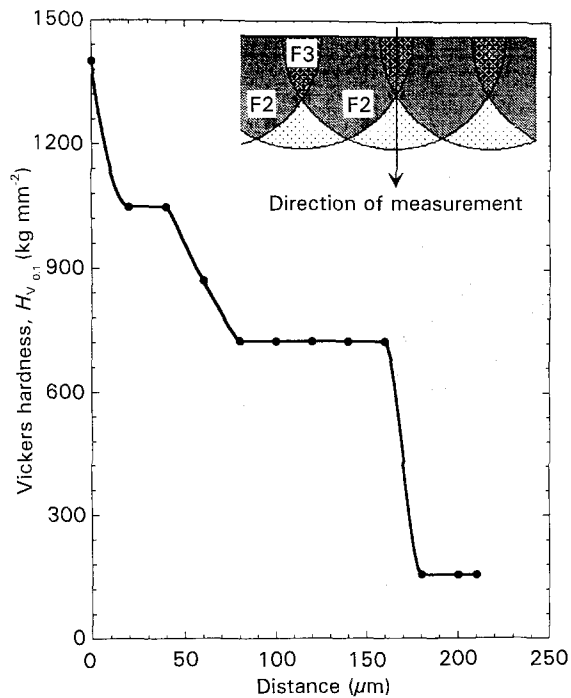


Figure 7 Increase of microhardness (measured along the centre of a laser pass) due to an increase of incorporated TiC (surface coverage = 9.2 mg cm^{-2} ; laser power = 250 W ; scan rate = 10 mm s^{-1}).

phenomenon it was thought that, for further increase in the surface content of TiC and resultant regular microstructure, it would be necessary to increase the power of irradiation. The increase in power up to 200 W and speed up to 10 mm s^{-1} did not produce a significant improvement in homogeneity, but the melt depth and hardness increased to $230 \mu\text{m}$ and $780 \text{ HV}_{0.1}$, respectively. By increasing the power of irradiation further, it was found that $P = 250 \text{ W}$ and $V = 10 \text{ mm s}^{-1}$ led to the best treatment concerning homogeneity and hardness optimization. Microhardness measurements (Fig. 7) exhibit the same trend as before, but with a maximum hardness around $1400 \text{ HV}_{0.1}$ on the surface and a gradual diminution towards the substrate.

SEM observations (Fig. 8) show the benefit of

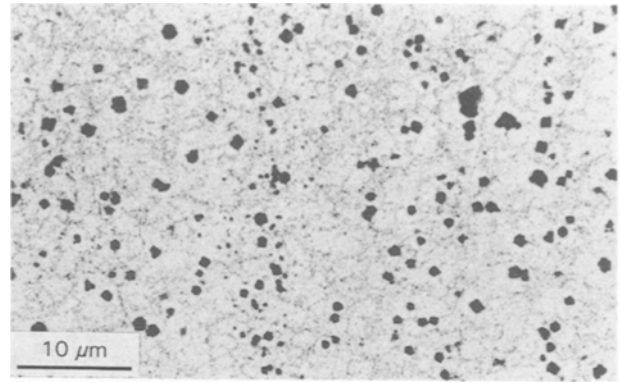


Figure 8 SEM BEI showing the more regular dispersion of un-melted TiC with an increase of power (surface coverage = 9.2 mg cm^{-2} ; laser power = 250 W ; scan rate = 10 mm s^{-1})

higher power on the microstructure. The size of the un-melted TiC particles (a few μm) and their distribution in the composite layer are now much more regular. Moreover, many of these particles are found inside the grains of $\alpha\text{-Fe}$ (martensitic form), suggesting a heterogeneous nucleation of the primary ferrite on the solid carbide particles. This is in good agreement with the smaller size of the grains of $\alpha\text{-Fe}$ (Fig. 8) compared to that observed in the case of the complete melting of TiC (Fig. 4).

3.4. Evolution of the hardness with the incorporated TiC fraction

The microhardness of the Fe–TiC composites, produced at different surface coverages and laser operating parameters, increases with the fraction of TiC incorporated in the melted layer (Fig. 9). These variations may be attributed to two phenomena, (a) the presence of an increased amount of the hard carbide phase within the composite, and (b) the formation of martensite within the matrix during cooling. The maximum hardness obtained lies around $1400 \text{ HV}_{0.1}$, needing the use of strong irradiation and cooling rate conditions to achieve a $37 \text{ wt } \%$ Fe–TiC surface composite. For gentler conditions, hardnesses between 550 and $800 \text{ HV}_{0.1}$ are easy to obtain in a large range of TiC weight fractions.

3.5. Influence of pass overlapping

Systematic SEM examinations showed that different microstructures appeared on the same sample depending on the area of location. This originates from the overlapping of multiple laser passes, which is necessary to produce a large treated area. Fig. 10 represents hardness as a function of distance in a direction perpendicular to the laser tracks, measured at about $20 \mu\text{m}$ below the surface. This result clearly depicts that, if only one pass is considered, the hardness is always the highest at the centre of the pass. For multiple passes, irrespective of the TiC surface coverages employed, the more overlapped zones (region F3) always show higher hardness. The microstructure of the more overlapped region confirms the presence of

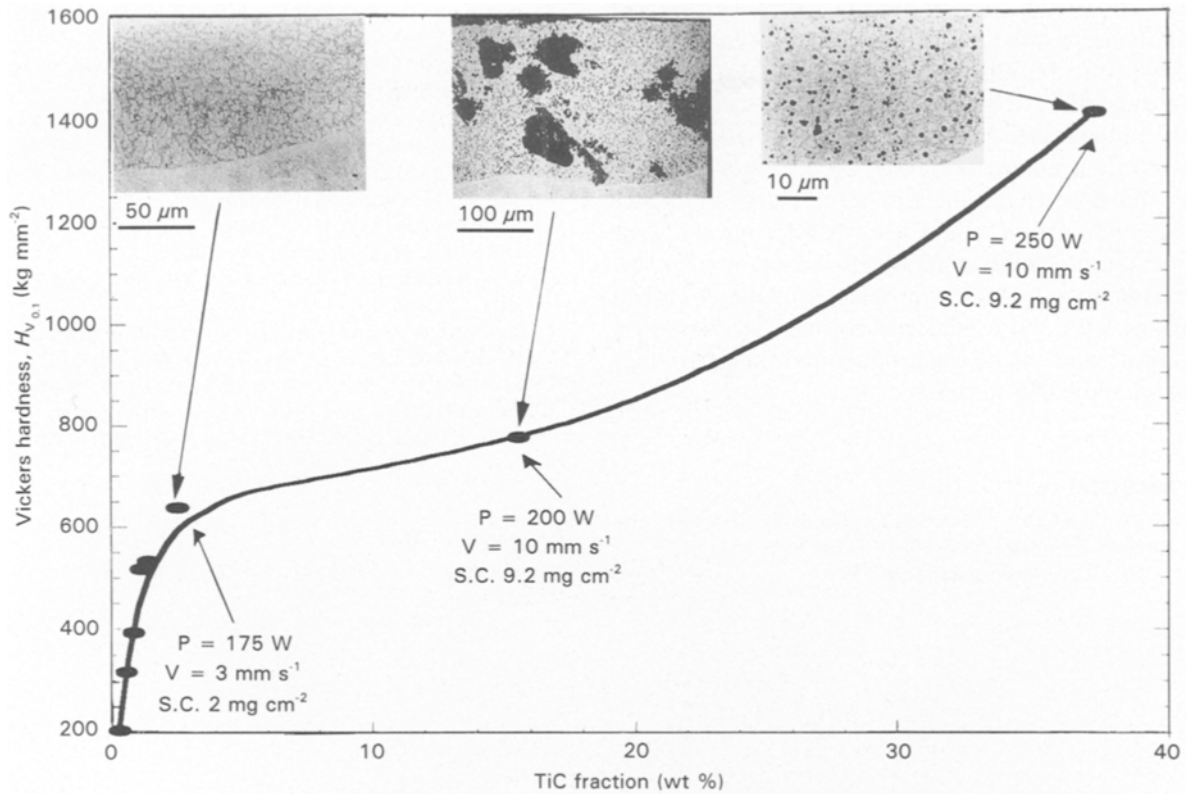


Figure 9 Dependence of the microhardness (measured on the surface) on the content of titanium carbide in the composite layer. P, Laser power; V, scan rate; SC, surface coverage.

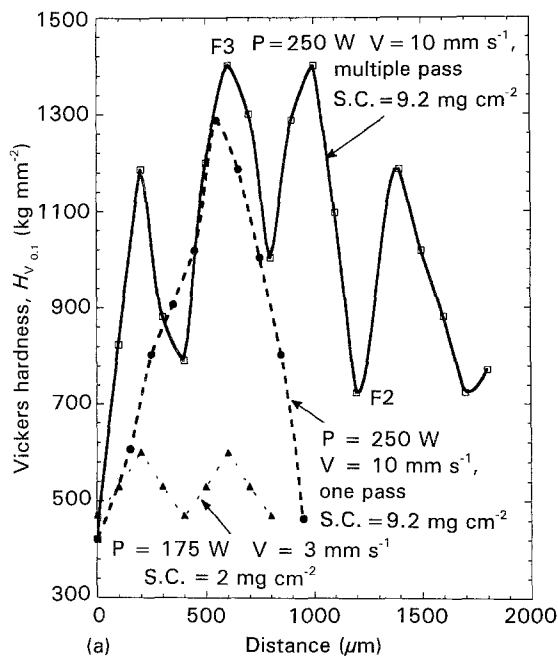


Figure 10 (a) Vickers hardness as a function of transverse distance at 20 μm below the surface, showing the influence of overlapping. (b) Schematic representation of the overlapping passes for an overlapping ratio of 66% (regions F3: two overlappings; region F2: one overlapping). P, Laser power; V, scan rate; SC, surface coverage.

an increased quantity of TiC, explaining the higher hardness value observed.

4. Conclusions

The operating conditions to produce Fe–TiC surface composites on mild steel by laser irradiation of a predeposited PEG slurry containing submicronic TiC particles were determined. The influence of process parameters, power, scanning speed and surface coverage on the microstructure and hardness have been shown. The main advantage of the proposed technique was the use of submicronic particles bonded with a polymer as an initial coating. It is well known that the volume fraction and particle size of the reinforcing phase and the uniformity of the dispersion can affect significantly the mechanical properties of the materials.

Different composites containing fractions of TiC ranging from 0.5 to 37 wt % were prepared by varying the thickness of the PEG–TiC coating. Complete melting of the TiC particles was observed when the surface coverages were lower than 2 mg cm^{-2} . After solidification and quenching, the resulting surface composites are composed of martensite and titanium carbide, the latter being the result of a eutectic crystallization. By increasing the surface coverage up to 9 mg cm^{-2} , only a partial melting of the carbide occurred; the presence of fine carbide islands regularly distributed within the composite layer has led to high hardness values ($1000\text{--}1400 \text{ kg mm}^{-2}$).

The underlying mechanisms (partial vaporization of the polymer, subsequent incorporation of carbon, and relative contribution of the produced phases – martensite and TiC – to the measured hardness) are imperfectly understood. However, it is believed that the composite structure obtained, its homogeneity over large dimensions and the absence of cracks even after rapid solidification, could lead to improve the wear performance of martensitic steels. Future studies will compare the tribological properties of the described coatings with those achieved by the laser injection technique, and extend the production of such coatings towards industrial alloys.

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*Received 18 May
and accepted 13 September 1993*