Classification of laser beam induced surface engineering technologies and \textit{in situ} synthesis of steel matrix surface nanocomposites

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A new classification of different laser beam induced surface engineering technologies is offered in this paper. An \textit{in situ} laser melt injection technology is applied in this paper to modify the surface of an inexpensive carbon steel substrate. Relatively large WC–Ti particles were blown into a laser melt steel pool, and the desired (Ti,W)C carbide particles were precipitated upon cooling and solidification. Although these primary (Ti,W)C carbide particles were micrometre sized, additional nanosized (Fe,W)$_6$C particles were found to precipitate during the subsequent heat treatment from an oversaturated steel matrix. Thus, a steel matrix surface nanocomposite was produced by the combination of \textit{in situ} laser melt injection technology and subsequent heat treatment.

**Keywords:** Steels, Nanocomposites, Carbide precipitates, Laser melt injection, Heat treatment

**Introduction**

The laser beam is an important tool for surface engineering. The classification of different surface engineering technologies using a laser beam is introduced in this paper. Particularly, the combination of the \textit{in situ} laser melt injection technology and a subsequent heat treatment is applied to produce a steel matrix surface nanocomposite material. The structural characterisation of this surface nanocomposite material will be discussed herein.

**Classification of laser beam induced surface engineering technologies**

There are hundreds of papers describing the effect of a laser beam of different characteristics on the surface of engineering materials, with or without precoated layers or added powders (see reviews).\textsuperscript{1,2} In order to sort all these surface laser technologies, a classification system given in Fig. 1 is offered herein, summarising the various technological routes.

Technologies without precoatings or added powders are shown along route (A$1\rightarrow$B$1\rightarrow$C$1$). These technologies are called ‘laser cleaning’,\textsuperscript{3} ‘laser surface hardening’,\textsuperscript{4,5} ‘laser melting’,\textsuperscript{6–10} ‘laser remelting’,\textsuperscript{11–16} ‘laser melting with subsequent heat treatment’\textsuperscript{17} or ‘laser melt quenching’,\textsuperscript{18} depending on the energy of the laser beam and the various physical changes in the target surface of the engineering material.

When the substrate is coated with a preplaced coating and a laser beam is applied along route A$2\rightarrow$B$1\rightarrow$C$2$, this technology is called ‘laser cladding’. In this case, the surface of the initial substrate is melted slightly to ensure a strong cohesive bond between the coating and the substrate with a minimal dilution of the coating by the substrate material.\textsuperscript{19–24} When the surface of the substrate is melted in a similarly way or deeper than the thickness of the original coating on the substrate (route A$2\rightarrow$B$1\rightarrow$C$3$ or A$2\rightarrow$B$1\rightarrow$C$5$), the process is called ‘laser surface alloying’.\textsuperscript{25–30} Laser cladding can become laser surface alloying by gradually increasing the depth of the melted zone.\textsuperscript{31} When the preplaced coating is not fully soluble in the substrate and the substrate is deeply melted, the \textit{in situ} formation of metal–matrix composites can take place along route A$2\rightarrow$B$1\rightarrow$C$5$.\textsuperscript{32–36}

Laser cladding can be also performed without any pre-placed coating; the process involves blowing and depositing a powder at the surface of a substrate during the laser treatment along route A$1\rightarrow$B$2\rightarrow$C$2$.\textsuperscript{24,30,31,37,39} When several cladded layers are built upon each other (route A$1\rightarrow$B$2\rightarrow$C$2^+$), the process is called ‘laser metal forming’.\textsuperscript{50} ‘direct laser fabrication’,\textsuperscript{51,52} ‘direct metal deposition’,\textsuperscript{53–56} ‘direct laser deposition’,\textsuperscript{57,58} ‘laser metal deposition’,\textsuperscript{59,60} ‘laser rapid forming’,\textsuperscript{61} or ‘selective laser sintering’.\textsuperscript{62} Using this technique, functionally graded materials can be produced.\textsuperscript{57}

Technologies involving melting the surface of the substrate and injecting solid particles into the melt pool are shown along routes A$1\rightarrow$B$2\rightarrow$C$3$ (or A$1\rightarrow$B$2\rightarrow$C$4$ or A$1\rightarrow$B$2\rightarrow$C$5$). The conditions to inject solid particles into laser melt metallic pools are summarised in Refs. 63–70. Particularly, routes A$1\rightarrow$B$2\rightarrow$C$3$ and A$1\rightarrow$B$2\rightarrow$C$5$ are called
‘surface alloying’,\textsuperscript{27} route A1–B2–C4 is called laser melt (particle) injection (LMI),\textsuperscript{67,71–94} while route A1–B2–C5 is specifically called ‘\textit{in situ} LMI’ in this paper.\textsuperscript{95–99} Functionally graded materials can be also produced by this method.\textsuperscript{87,100} During the LMI process (route A1–B2–C4), the particles before and after their injection are essentially the same both chemically and morphologically. However, during the specially designed ‘\textit{in situ} LMI’ process (route A1–B2–C5), the injected particles dissolve in the melted matrix and new particles, being chemically and/or morphologically different, are precipitated from the matrix upon cooling. At least a partial dissolution and a partial precipitation of original and new particles have been reported in a number of papers.\textsuperscript{76–78,80–83,85–87,91,93,94}

A new wire-dosing technique (route A1–B3) has been developed by Buza and colleagues.\textsuperscript{101,102} Using this technique, different routes can be realised: A1–B3–C4\textsuperscript{101} or A1–B3–C5.\textsuperscript{102}

This paper will describe the possibilities of the \textit{in situ} LMI technology to improve a surface of a cheap carbon tool steel substrate. The technology includes the addition of large WC+Ti particles into a melt steel pool, and the desired solid carbides (Ti,W)C are precipitated upon cooling and solidification. Some additional carbides (Fe,W)\textsubscript{6}C will precipitate during the subsequent heat treatment.

**Experimental procedure**

A cheap carbon tool steel was selected as a substrate material (called U8A according to GOST 5950-73, Russian specification), with the following compositions of the main components: Fe–0.83C–0.25Mn–0.26Si–0.021S–0.01P–0.12Cr–0.13Ni–0.022Al (wt-%). The size of the substrate specimens was $17 \times 17 \times 4$ mm. The upper $17 \times 17$ mm plane of the substrate was coated by a thin layer of graphite to increase the absorption ratio of the laser beam. Pure Ti and WC powders with the size range of 45–70 $\mu$m were blown into a laser melt pool of the U8A substrate.

The LMI setup is shown in Fig. 2. A 5 kW CO\textsubscript{2} continuous wave laser (Trumpf TLC 105) was used to melt the surface of the substrate with a laser power of 3–0 kW. A laser beam with a diameter of 2 mm moved along the substrate with a velocity of 400 mm min$^{-1}$. Each laser track was 10 mm long. Ten laser tracks were drawn parallel to each other, with a 50% overlap. The laser system was equipped with a concurrent powder feed system. A 1:1 molar mixture of tungsten carbide and titanium powders was blown into the melt pool at a 45° angle using argon as the carrier gas. The flowrate of the gas stream was about 5 L min$^{-1}$, blown through a powder nozzle with a 3 mm diameter. This corresponds to a gas stream velocity of $u=12$ m s$^{-1}$. The distance between the powder nozzle and the melt pool was about 15 mm. The feeding rate of the powder mixture was 4.7 g min$^{-1}$ (about 0.01 vol.-% in the gas stream). The experiments were performed under the argon shielding gas, with a flowrate of 15 L min$^{-1}$. The steel substrates were brazed to a large copper heat sink, cooled by cold water. Owing to this intensive heat extraction, each
volume element of the melted substrate was in a liquid state for a short period of time.

As will be shown below, the LMI process itself did not lead to the formation of nanosized precipitates. Therefore, some of the LMI treated specimens were heat treated with the following three-step process: first at temperature $T = 1000–1050$ °C during 10–15 s, followed by quenching and a subsequent heat treatment at $T = 350$ °C for 1 h and finally at $T = 560$ °C for 1 h.

After the LMI and the combined (LMI+heat treatment) processes, the specimens were ground, polished, etched and analysed. A high resolution scanning electron microscopy (SEM, type Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscopy (EDAX) system and an X-ray diffraction (XRD, type D8 Advance Bruker AXS) equipment were used to characterise the samples.

**Results and discussion**

From the cross-section of a specimen shown in Fig. 3, one can see that a depth of the laser melt layer is about $0.65 \pm 0.05$ mm. It can also be seen from Fig. 3 that the melt zone is macroscopically homogeneous with no cracks or pores. The same figure is shown with increasing magnifications in Figs. 4–8.

In Figs. 4–7, one can see that both the LMI treated and the (LMI+heat) treated specimens contain some micrometre sized particles. Thus, these particles precipitate during cooling and solidification from the liquid steel. It can be seen that the size of these particles somewhat increases after the heat treatment compared to the simple LMI treatment. In Figs. 4–7, these micrometre sized particles are mostly ‘white’, indicating an element with a higher atomic number than iron (i.e. tungsten). However, the centre of some of those ‘white’ particles is ‘black’ in Figs. 5–7 due to an element with a smaller atomic number than iron (i.e. titanium). It should be noted that these particles are round shaped three-dimensional particles, and during polishing, only a part of them are polished through their centres, and that is why the ‘black spots’ are seen only for some of them. Thus, these micrometre sized particles are most probably (Ti,W)C precipitates with a gradient structure, having Ti rich cores and W rich outside regions. This becomes more obvious from the EDAX line scan shown in Fig. 8b. One can see that the carbon content of the micrometre sized particle is around 50 at.-%, while the Fe content is close to zero. The centre of this micrometre sized particle is enriched in Ti, while there is a slightly higher tungsten content in the outside region of these
particles compared to its centre. Thus, the micrometre sized (Ti,W)C particle has a gradient composition.

In Figs. 6–8, one can see that, after the combined (LMI + heat) treatment, a large amount of new, nanosized particles appear between the micrometre sized (Ti,W)C particles. These nanosized particles are not present after a simple LMI treatment. The size of these particles is between 50 and 90 nm.

In Fig. 9, the XRD spectra of the specimen after LMI (before heat treatment) and after a combined
(LMI + heat) treatment are compared. One can see three main phases denoted as ‘Fe-fcc’, ‘Fe-bcc’ and ‘TiC’ after LMI (before heat treatment) and four main phases denoted as ‘Fe-bcc’, ‘Fe-fcc’, ‘TiC’ and ‘(Fe,W)₆C’ after the combined (LMI + heat) treatment. At this point it should be mentioned that the XRD peaks of TiC and (Ti,W)C phases are very similar. Thus, the micrometre sized phases in Figs. 4–7 are (Ti,W)C carbides, while the 50–90 nm sized phases in Figs. 6–8 are (Fe,W)₆C carbides.

Based on the above observations, the following mechanism is revealed herein.

During the LMI process, the added WC and Ti particles are dissolved and homogeneously distributed within the steel matrix due to high temperatures and strong Marangoni convection.

At a later stage of LMI, during cooling and solidification, TiC-rich carbide particles precipitate from liquid steel, as this carbide has the most negative Gibbs energy of formation and lowest solubility in liquid steel among all possible phases. As the TiC particles grow, their surrounding liquid becomes more and more depleted in dissolved Ti atoms, and thus, more and more W atoms build into the outside regions of the precipitates. This is because WC has a much less negative Gibbs energy of formation and a much higher solubility in liquid steel compared to TiC. In this way, (Ti,W)C mixed carbide particles form with a characteristic gradient structure, having a Ti rich core and a W rich outside region.

During subsequent heat treatment, (Fe,W)₆C particles precipitate from the oversaturated solid steel matrix. The size of these carbide precipitates remain below 100 nm due to limited time and temperature of heat treatment. It is speculated that the size of these (Fe,W)₆C precipitates can be controlled by the parameters of the heat treatment process. Further investigation is planned to reveal more details in the near future.

Conclusions

The classification of various laser technologies for surface engineering has been presented. An in situ laser melt injection technology has been implemented. It includes the addition of large WC+Ti particles into a laser melt steel pool, and the desired solid carbides (Ti,W)C are precipitated upon cooling and solidification. Some additional carbide particles (Fe,W)₆C precipitate during a subsequent heat treatment. These secondary carbide precipitates are sized between 50 and 90 nm.
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References


