Original Article

Laser composite surfaced of A681 steel with WC + Cr + Co for improved wear resistance

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\textbf{A B S T R A C T} \\
Laser surface alloying (LSA) is a surface treatment technique. It involves the near surface melting by a powerful laser beam with pre-deposited or concomitantly added alloying element along with a part of the underlying substrate to form a surface alloyed zone. In this paper, it is reported the treatment by laser surface alloying of a cold work steel ASTM A681 substrate simultaneously fed with a powder mixture of 86 wt.% WC + 8 wt.% Cr + 6 wt.% Co. It was carried out using a continuous wave $\lambda = 1064$ nm fiber-coupled diode laser with five different laser intensities – resulting in five specimens – and then studied and analyzed their microstructure, phases, composition and microhardness. One of these configurations was applied to enhance a deep drawing tool for automotive steel sheet stamping. The process modified the specimens near surface layer, from a ferritic structure into an austenitic matrix with a refined dendritic microstructure, with an enhanced surface hardness from 250 HV to $\sim 560$ HV. The treated deep drawing tool showed remarkable wear improvement compared to a non-treated one after one thousand stamps. This result allows the process for industrial applications.

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1. Introduction

Laser surface alloying (LSA) involves the near surface melting by a powerful laser beam with pre-deposited or concomitantly added alloying element along with a part of the underlying substrate to form a surface alloyed zone. The irradiation results in the deposit’s transient melting with a part of the underlying substrate, rapid intermixing by diffusion and convection in the melt pool and ultrafast solidification to form the alloyed zone [1–3]. This zone shows different composition and microstructure which may significantly improve
its metallurgical and chemical properties [4–6]. During laser materials processing, the laser-matter interaction within the near surface region achieves extreme heating and cooling rates ($10^7$–$10^{10}$ K/s), while the total deposited energy (typically $10^9$–$10^{10}$ J/cm²) is insufficient to affect the temperature of the bulk material [2,7]. The fast quenching of the alloyed liquid layer can create a wide variety of metastable crystalline or amorphous (metallic glasses) [8] solid solutions; these properties strongly depend on the laser power and scan speed. Here we used a process, sometimes referred as “laser composite surfacing” or “laser particle injection”, wherein ceramic particles are simultaneously injected into the melting pool during laser irradiation [5,9]. As we focused on wear improvements, the chosen powder consists of a mixture of chromium and cobalt as binding elements with a prevailing tungsten carbide (WC) ceramic phase. Since WC particles possess high hardness, low coefficient of thermal expansion and wettability by molten Cr and Co metals, it is expected that the chosen powder would be appropriate for wear resistance applications. Additional advantages include uniform dispersion of ceramic particles, microstructure refinement and good coupling between the heat affected zone and substrate. In this paper, it is reported the treatment of an A681 steel substrate by five different laser intensities simultaneously fed with a WC-Cr-Co powder mixture. The microstructure, hardness, phase, chemical composition and continuity of the composite layer were characterized and the best condition was then applied to treat a deep drawing tool, which was used to draw low carbon steel sheets for automotive applications with its wear monitored during one thousand stampings in order to evaluate its lifetime.

2. Methods

2.1. Materials

A high chromium ASTM A681 steel with composition (in wt.%) 82.34 Fe, 1.5 C, 12.0 Cr, 1.0 Co, 0.6 Mn, 0.8 Mo, 0.030 P, 0.60 Si, 0.030 S, 1.1 V with dimensions of 80 mm × 60 mm × 20 mm was used as substrate for the LSA process. A powder mix with (in wt.%) 86 WC + 8 Cr + 6 Co and particle size between 20 μm and 53 μm was used as filler material. S460MC steel metal sheets with 3 mm thickness were used in the stamping processes.

2.2. Preparation

A continuous wave $\lambda = 1064$ nm fiber-coupled diode laser 6 kW from Laserline was used. A681 steel samples were prepared with different laser powers in order to evaluate its influence on the near surface region. The powder feed rate, composition and scan speed of the laser beam were kept constant. Fig. 1 shows the powder, feeding gas and laser beam schematics used to treat the samples.

Argon gas was used as shrouding environment in order to get oxide-free alloyed layers. Therefore, the samples were named P1–P5 in ascending order of increasing laser power. Each one was cleaned for 5 min with acetone in an ultra sound bath prior to the LSA process. The laser procedure created a treated area of five sequential tracks with overlap rate of 50% and an area of 55 × 10 mm (that was called sample). The samples were produced sequentially from the lowest to the highest laser power (P1 – 750 W; P2 – 1000 W; P3 – 1250 W; P4 – 1500 W; P5 – 2000 W) and beginning with the workpiece at room temperature. After the surface alloying, the entire workpiece surface was milled in 0.1 mm in order to flatten the roughness due to surface evaporation effect. Each sample was separated from the workpiece with the help of a cut-off and a cross section was obtained in their middle regions, forming five smaller pieces, which were embedded in Bakelite for metallurgical analysis.

A model KB-630 Schuler press with a maximum force of 6300 kN and S460MC steel metal sheets of 3 mm thickness were used in the stamping processes.

2.3. Characterization

The cross sections microhardness of the samples were measured with a microhardness tester, model M-400-H, from Akashi Corporation. The X-ray diffraction (XRD) patterns were obtained using a PANalytical X’PERT MPD-PRO diffractometer with Cu K$_{α1}$ radiation ($\lambda = 1.5418$ Å) using the $\theta$–$\theta$ configuration. Scanning Electron Microscopy (SEM) images were obtained with a JEOL JSM 6390LV Scanning Electron Microscope. The image analyses were carried out using Pocket ImAT 1.0 software. Elemental mapping was generated by Energy-Dispersive X-ray Spectroscopy (EDS) using an EDAX Sapphire Si(Li) DU and an accelerating voltage of 15 kV. The deep drawing tool roughness was measured close to the input radius using a T8000T profilometer from HOMMEL-ETAMIC after each hundred drawing steps.

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the XRD profiles of the powder filler material, the substrate and the five samples. The powder filler XRD profile shows peaks which confirm the presence of the crystalline phases of WC, Co and Cr (JCPDS 00-051-0939; 00-015-0806; 00-006-0694, respectively).
The substrate XRD profile shows three well-defined peaks at 44.8°, 65.1° and 82.3°, corresponding to the crystallographic planes (110), (200) and (211) respectively, characteristic of the ferritic steel identified by JCPDS card 00-006-0696. At 39.6° there is a very small peak of the $\text{Cr}_7\text{C}_3$ phase, which is a minor constituent of the ASTM A681 steel [10].

The cross section XRD profiles of all five samples show very small ferritic peaks in addition to three greater and well defined peaks at 43.2°, 50.4° and 74.0°, identified as austenite by the JCPDS card 00-033-0397. Its presence indicates an austenitization of the alloyed zone after the laser treatment favored by the cobalt concentration increase provided by the powder filler. The very fast cooling rate of LSA processes can promote the alloyed zone amorphization, as observed by [8]. A partial amorphization in this zone could explain the decrease of the diffraction peaks intensities with increased laser power. Due to XRD peak broadening in the samples profiles, martensite and austenite peaks might be overlapped, making difficult their identification. However, the presence of both phases with fine microstructure after LSA processes is reported in literature and could induce a solid solution strengthening improving the alloyed layer hardness [11].

It was noticed that, in the XRD profile of sample P1, the austenite peak at 43.2° is more intense than the others, although from samples P3–P5 the peak at 50.4° becomes the most intense. This is possible by preferential growth of the crystalline dendritic planes in the composite layer induced by the laser treatment, since the whole thermal process occurs outside thermodynamic equilibrium.

### 3.2. Metallographic analysis

The micrographs of sample P1, Fig. 3(a), shows a 330 μm thick alloyed layer and a heat-affected zone (HAZ) with a thickness around 280 μm. The alloyed layer shows quite well dispersed WC particles with size ranging from 22 to 50 μm, which are similar to the original added powder sizes. These particles are surrounded by a halo, indicating that the thermal solidification was different around the unfused WC particles. The alloyed layer austenitic matrix presents big columnar dendrites around 100 μm long intermediated by finer dendritic structures (Fig. 3(b)) growing at the HAZ layer border, preferentially perpendicular to the surface. Similar results were presented in LSA of a tool steel with WC particles by Dobrantski [12]. Fig. 3(b) also shows a refined microstructure within the HAZ with globular structures from 2 to 7 μm in size. Fig. 3(c) shows the micrograph of the sample P2 obtained with 33% more laser power; the alloyed layer presents the same dendritic structures, but in this case the ceramic WC particles are

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**Fig. 2** – XRD profile of the five samples, substrate and powder (•: WC; ▲: Cr; ▼: Co; ■: ferrite; ●: austenite; □: $\text{Cr}_7\text{C}_3$).

**Fig. 3** – Optical micrographs of the samples (a) P1, (c) P2, (e) P3, (g) P4 and (i) P5 with lower magnification (it is shown in each figure – from the top to the bottom – the substrate, the HAZ and the alloyed layer); (b) P1, (d) P2, (f) P3, (h) P4, (j) P5 with higher magnification.
sedimented (Fig. 3(d)), forming a 70 μm thick ‘sub-layer’ (see Table 1) on the bottom of the layer adjacent to the HAZ. The thicknesses of both the alloyed layer and the HAZ layer of P2 are bigger when compared to P1. Samples P3, P4 and P5, which were obtained by the laser power progressive increase, showed a similar behavior. Their micrographs, shown in Fig. 3(e)–(f), present an increasing value in the thickness of both the alloyed layer and the HAZ layer. They show a similar sedimentation, where the WC particles are becoming smaller and segregating in the layer bottom.

Increasing the laser power increases the melted pool depth and also its local temperature, decreasing the melt viscosity. Alongside with it, there is an increase in the convection movement that produces WC particles sedimentation. As the laser power grows, more carbon content from the WC may diffuse into the steel matrix, generating a decrease in the sedimented particles size, which can be seen at the images with higher magnification in Fig. 3. The micrographs also show a perfect connection between the treated layer and the HAZ, which in turn binds quite well to the substrate; no cracks or porosities were observed. The thickness of HAZ is relatively larger when compared with literature values [13,14], because a higher overlap rate of 50% between tracks was used.

### 3.3. Microhardness

The cross section microhardness of samples P1–P5 are plotted against depth in Fig. 4, beginning in the surface down to the substrate. There are three distinct regions (alloyed layer, HAZ and substrate), for which the behavior is similar in all five samples. In the alloyed layer the hardness is almost uniform and is significantly improved to 560 HV in all five samples as compared to 250 HV of the substrate. A similar behavior was reported for a 304 stainless steel with WC particles incorporated by LSA presenting an improvement in hardness from 220 HV until 700–1350 HV by Anandan et al. [15]. Anandan et al. has reported the presence of a small amount of W2C due to partial dissolution of the WC (WC → W2C + C) in the composite layers’ austenitic matrix during the process. This free carbon may diffuse and combine with chromium forming fine carbide precipitates, increasing the matrix hardness [15]. Although it was not possible to clearly identify the W2C or chromium carbides by XRD due to their small concentration, the shrinking of the WC particles (Fig. 3) may be an evidence of their presence.

The length of the uniform region of 560 HV correlates quite well with the alloyed layer thickness in Table 1. The hardness of the first point of each graph in Fig. 4 is due to surface crumbling and is not meaningful. Going in depth, it is observed another microhardness increase up to 600 HV in regions that correspond to the HAZ due to its refined microstructure. Then the microhardness sharply decreases to a constant value of 250 HV throughout the substrate. The measured microhardness is the weighted average between the matrix microhardness and the dispersed phase.

### 3.4. EDS chemical analysis

Punctual EDS chemical analysis on the treated layer cross section were performed in order to check its homogeneity for the relevant metallic elements; for each sample, three sequential points were measured and their average values (in wt.%) are shown in Table 2.

As reported in the experimental section, the workpiece was milled to remove 0.1 mm of the upper surface in order to reduce the roughness formed after the laser treatment. This is useful for the deep drawing application (Section 3.5), however it may compromise the alloyed layer depending on its thickness. Fig. 5 presents the P3 sample surface chemical

| Table 1 – Thickness of the: alloyed layer, sedimentary sub-layer and HAZ of the samples. |
|-------------------------------|-------|----|----|----|----|
|                              | P1    | P2  | P3  | P4  | P5  |
| Alloyed layer (mm)           | 0.35  | 0.55| 0.67| 0.74| 0.80|
| Sedimentary sub-layer (μm)   | –     | 70  | 90  | 100 | 110 |
| HAZ layer (mm)               | 0.28  | 0.34| 0.40| 0.47| 0.54|

Fig. 4 – Microhardness profiles of the five samples from P1 to P5.
Fig. 5 – (a) SEM image of the chemical mapping measured area; surface chemical mapping in the cross sections for: (b) iron, (c) chromium, (d) cobalt and (e) tungsten.

Fig. 6 – (a) Drawing of the deep drawing tool identifying the measured area; images of the measured area for the (b) untreated and (c) treated tools after one thousand stampings and (d) their respective profilometer analysis.
maps of the cross section for the relevant metallic elements. It can be observed that the elements Fe and Cr are homogeneously distributed over the treated layer, the HAZ and the substrate region. This means that despite the very rapid cooling rate there was an effective chemical diffusion through the sub-millimetric layers. However, the Co element did not diffuse as well, being mainly present in the treated layer. This higher concentration of Co in the treated layer may favor the austenitic phase formation as seen in the Fe-Co-Cr phase diagram at 1450°C obtained by Allibert et al. [16].

Tungsten is detected only in the treated layer revealing that it continues to be present mostly in the WC ceramic particles.

3.5. Application

The input radius surface of a deep drawing tool made of A681 steel was treated with the same parameters used in the P3 sample. A low carbon S460MC steel sheet, usual in automotive industry, was used for deep drawing experiments. The wear resistance of the input region curvature radius of treated and untreated deep drawing tools was evaluated and compared during one thousand deep drawing cycles. Fig. 6 shows images of the surfaces in the marked region (a) of both tools (untreated (b) and treated (c)) after one thousand deep drawing cycles and their respective profilometer analysis showing a remarkable wear resistance improvement in the treated sample, mainly on the lead-in area, where the wear is most severe for the untreated sample. Similar results were obtained on different regions of the matrix.

Fig. 7 shows the roughness evolution in the entrance radius surface during the deep drawing experiments for both deep drawing tools. It is noteworthy that the treated tool, after one thousand stampings, showed a decrease in surface roughness of a ninth in its value when compared to the untreated one.

4. Conclusions

In the present study, it was evaluated the effects of treating specimens of a cold work steel (ASTM A681) by laser surface alloying (LSA) with different power values of a fiber-coupled diode laser. The process modified the specimens in a region near the surface layer, from a ferritic structure into an austenitic matrix with a refined dendritic microstructure. The effects of the laser power including microstructure, formed phases, microhardness properties, chemical analysis and surface roughness were studied in details. The obtained samples allow us to conclude that:

- The cross-sections of the treated specimens had three zones: the alloyed zone, which is the modified near surface region formed by the melted steel and the added powder during the LSA process; the HAZ, which did not melt but was thermally affected by the heating process; and the unaffected bulk material.
- Raising the laser power increases the depth of the melted pool.
- The LSA process increased the alloyed layer microhardness from ~250 to ~560 HV for all samples. This may be due to the presence of a small amount of W2C, which originated from the partial dissolution of WC induced by the LSA process. The binder Cr and Co elements have wetted the WC ceramic particles so effectively that they were mostly incorporated during the laser heating. The WC particles became smaller and sedimented in the liquid pool when using higher laser powers.
- The XRD profiles indicate an austenitization of the alloyed zone after the laser treatment, besides minor peaks of the ferritic phase are still present. A martensite phase may have their diffraction peaks overlapped by the austenite phase, but the XRD profiles are inconclusive.
- Punctual EDS of all samples showed homogeneity for the relevant metallic elements along the cross-section of the alloyed zone.
- The treated deep drawing tool showed significant wear reduction. Its surface roughness was in the order of one ninth when compared to the untreated tool after both went to one thousand deep drawing cycles.

Conflicts of interest

The authors declare no conflicts of interest.
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