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Improved surface properties of D2 steel by laser surface alloying

ENORI GEMELLI
Department of Mechanical Engineering, Center of Technological Sciences, UDESC—Santa Catarina State University, Bom Retiro, P.O. Box 631, 89223-100, Joinville/SC, Brazil
E-mail: gemelli@joinville.udesc.br

ALAIN GALLERIE
Ecole National Supérieure d'Electrochemie et d'Electrométallurgie de Grenoble, Institut National Polytechnique de Grenoble, BP 75 Domaine Universitaire, 38402 Saint Martin d'Hères, France

FERNANDO C. T. KOPP, NELSON H. A. CAMARGO
Department of Mechanical Engineering, Center of Technological Sciences, UDESC—Santa Catarina State University, Bom Retiro, P.O. Box 631, 89223-100, Joinville/SC, Brazil

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The wear and the high-temperature oxidation resistance of the D2 steel (Fe-1.5 C-12 Cr-0.95 Mo-0.9 V-0.3 Mn) were increased by laser surface alloying after coating the surface with SiC or Cr_3C_2 powder. The surface alloys exhibit two microstructures: hypoeutectic and hypereutectic, respectively, all containing iron solid solutions and iron-chromium carbides, $(Fe,Cr)_7C_3$. The oxidation resistance of these alloys was measured in isothermal and cyclic conditions, and was shown to increase with silicon or chromium additions, particularly due to the formation of a chromia scale with excellent behaviour during thermal shoks. The surface alloy obtained with Cr_3C_2 also has shown a better resistance to wear due to its hypereutectic microstructure.

1. Introduction

The use of laser surface alloying can afford interesting properties to materials exposed to aggressive environments [1, 2]. Such a surface treatment was used here on a tool steel in order to improve its wear and high-temperature oxidation resistance. Foreign chemical species were applied to the steel surface through a pre-deposit of silicon carbide (SiC) or chromium carbide (Cr_3C_2) followed by a simultaneous fusion, through laser beam, of the pre-deposit and the substrate superficial part. This same technique was used before on two low ferritic steels [3, 4] on which SiC or Cr_3C_2, pure or associated with SiC, have been applied to the substrate surface. These works have evidenced the potential this technique has for the development of surface alloys incorporating these elements.

In recent paper [5] we have shown that the combination, in the same coating, of chromium and silicon can provide increased resistance to oxidation at high temperature, a combination which until then had been used only in massive alloys [6–9]. The present investigation deals with a steel initially having 12% chromium. The addition of silicon to the steel surface should improve the resistance to oxidation to the minimum levels required by the steel high operating temperatures. On the other hand, it has also been shown [3, 4] that the chromium and carbon addition leads to the formation of hard phases [$(Fe,Cr)_7C_3$] necessary for a good anti-wear behaviour. The increase of the chromium concentration in solid solution and the presence of carbide in the coating, obtained by the addition of Cr_3C_2, should then increase not only the resistance to oxidation, but also the resistance to wear. In the present paper, an attempt in obtaining the same effects by the addition of silicon carbide or chromium carbide to the D2 steel surface has also been investigated.

2. Experimental procedure

Samples of D2 steel (Fe-1.5 wt% C-12 wt% Cr-0.95 wt% Mo-0.9 wt% V-0.3 wt% Mn), with dimensions $12 \times 12 \times 2.5\ mm^3$ were polished to a 1200 grade paper finish and cleaned with alcohol. SiC and Cr_3C_2 powder, with grain size in the 5 to 10 μm range, were deposited on the substrate by pneumatic pulverization (35% powder volume in acetone suspension). After drying, the covered samples were irradiated under an argon atmosphere by means of a Nd-YAG laser in order to have the pre-deposit incorporated by the substrate. The Nd-YAG laser used has a continuous wavelength

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TABLE I Conditions of preparation of the surface alloys

Pre-deposit	Pre-deposited Mass ($kg \cdot m^{-2}$)	Power (W)	Power density $MW \cdot m^{-2}$
Cr_3C_2	0.20	250	352.70
SiC	0.05	227	320.25

of 1.06 μm and a maximum power of 300 W. The light was transported to the sample by an optical fibre, providing a circular spot with a size of 950 μm in diameter. The samples were scanned under the beam at a constant rate of 5.0×10^{-3} $m \cdot s^{-1}$ to give parallel tracks. Each laser track overlapped 68% of the preceding to ensure regularity in the thickness of the alloys. Elaboration conditions of the surface alloys are mentioned in Table I.

The samples devoted to the oxidation kinetic studies were laser treated on all sides. The tests were carried out in a flowing atmosphere of pure oxygen (3 l/h), in isothermal and cycling conditions. The latter was subjected to a heating/cooling cycle. The thermal cycle was made of the following stages: (1) isothermal (850 or 950°C) for $11^1/_2$ h; (2) rapid cooldown to 150°C in approximately 2 min; (3) isothermal (150°C) for 30 min; (4) heating to the previous high temperatures in about 1 min. The cycle was then repeated.

Wear tests by disc-sphere friction were performed in order to measure the surface alloys resistance. The used discs which correspond to samples to be tested, have diameters of 25 mm and a thickness of 10 mm. The laser treatment was carried out on one sample surface after polishing (800 grade paper finish) and pre-deposition of the ceramic powders.

The wear tests were carried out in a dry environment temperature (without chip evacuation). The following conditions were used: (a) alumina sphere diameter of 5 mm; (b) load of 0.5 N; (c) sphere track radius of 9 mm; (d) sphere dislocation speed on the disc of 10 cm/s; (e) test duration of 10^4 laps.

The hardness was measured on the surface alloys by Vickers indentation (Hv) under a 5 N load.

The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), microprobe analysis by wavelength dispersive spectroscopy (WDS) and Auger electron spectroscopy (AES). Auger profiles of chemical elements were performed through the oxide layers in order to study the nature of the oxides formed in the early ages of oxidation. The Auger profiles were obtained with a JEOL JAMP-10S Auger microprobe and the energy scale of each spectrum was calibrated by the chromium peak, with an accuracy of 1 eV. The in-depth profiles were obtained under a ionic beam of 1 mm^2 at a constant rate of 10 Å/min.

3. Experimental results

3.1. Nature and microstructure of the surface alloys

The average thickness of the surface alloy obtained by the adding of SiC was approximately 140 μm. The average chemical composition from the microprobe analysis was Fe-3 wt% C-10 wt% Cr-4 wt% Si. It

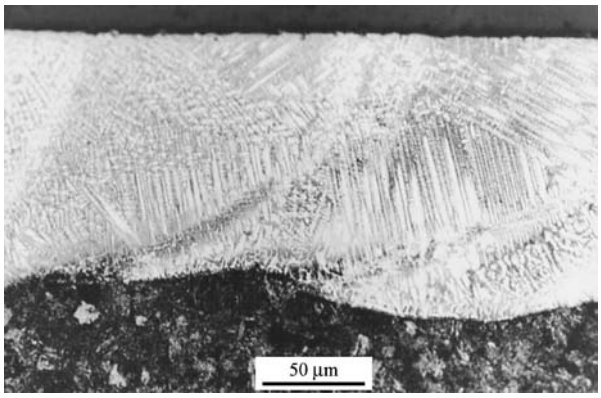

Figure 1 General cross-section view of the dendritic microstructure showing the influence of laser track overlapping on the surface alloy obtained with SiC.

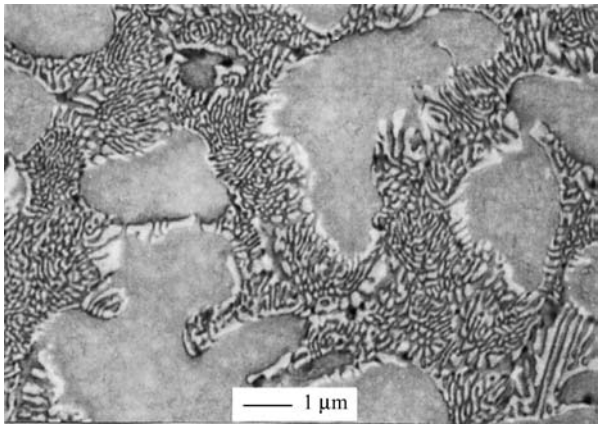

Figure 2 Detailed observation of the different phases formed on the surface alloy obtained with SiC.

can thus be concluded that the laser treatment leads to a slight decrease in the chromium content and to a substantial increase in the silicon content. The surface alloy exhibits the classical hypoeutectic microstructure with a very thin flat interface solidification zone and a large dendritic area (Fig. 1). It is observed that the centre of the laser tracks presents fine dendrites whereas the overlapping zones are more coarsely crystallized, with a little less alloying elements. The dendrites are constituted by austenitic and martensitic Fe-Cr-Si-C solid solutions and the eutectic interdendritic material (Fig. 2) by alternated $(Fe,Cr)_7C_3$ and solid solutions strips.

The surface alloy obtained by the incorporation of Cr_3C_2 shows three zones, from the substrate to the external surface (Fig. 3):

– a dendritic/cellular hypoeutectic zone (5–20 μm),
– a purely eutectic zone (thickness 25 μm),
– a thick hypereutectic zone (thickness 70 μm),

with primary $(Fe,Cr)_7C_3$ platelets surrounded by the eutectic material, austenitic solid solution and $(Fe,Cr)_7C_3$ carbides (Fig. 4). Average concentrations were Fe-5 wt% C-30 wt% Cr. Due to their size, the $(Fe,Cr)_7C_3$ platelets could be significantly analyzed and were shown to lie near the composition $Fe_{2.5}Cr_{4.5}C_3$. It can be noticed that the initial material Cr_3C_2 was never detected in the surface alloy, confirming complete

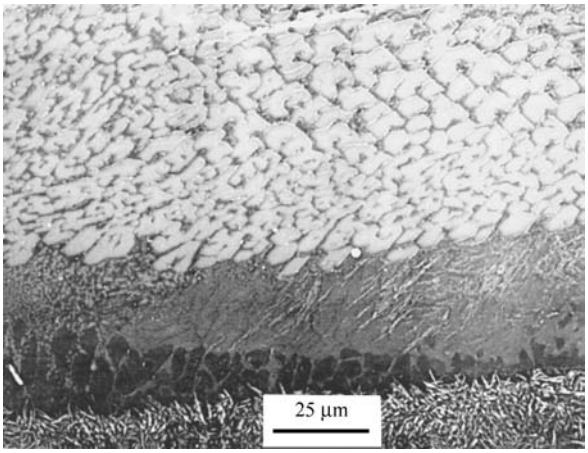

Figure 3 General cross-section view of the hypereutectic microstructure on top of eutectic and dendritic regions on the surface alloy obtained with Cr_3C_2.

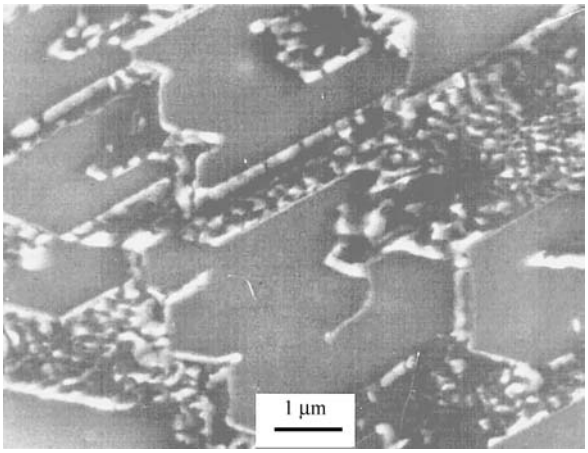

Figure 4 Detailed observation of the primary $(Fe, Cr)_7C_3$ carbide platelets in the eutectic region formed on the surface alloy obtained with Cr_3C_2.

dissolution and mixing in the liquid state before solidification. It was also observed that the microstructure of the alloy is in good agreement with the published Fe-Cr-C ternary diagrams [10].

3.2. Wear and hardness tests

The average hardness and wear ratio measured on the samples and substrate are given in the Figs 5 and 6 respectively. These results show that only the laser treatment with Cr_3C_2 incorporation leads to a significant increase in the hardness and wear resistance in relation to the substrate. The hardness of this surface alloy increases from 550 Hv (before the treatment) to about 850 Hv (after surface alloying) and the wear ratio decreases to a factor close to two. The hardness of the hypoeutectic surface alloy obtained with SiC is about 650 Hv and its wear ratio is slightly lower than that of the untreated D2 steel.

3.3. Oxidation kinetics

Weight gain ($\Delta m/s$) versus time (t) obtained at 850 and 950°C in isothermal and cycling oxidation are presented in Figs 7 and 8. The chromium or chromium

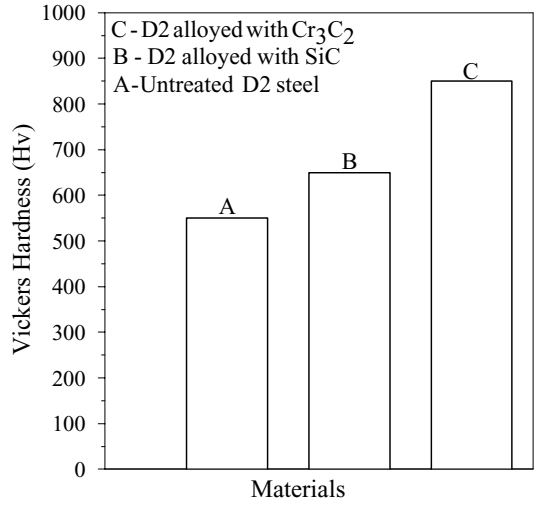

Figure 5 Vickers hardness of the substrate and of the surface alloys obtained by laser alloying of SiC or Cr_3C_2 on the D2 steel.

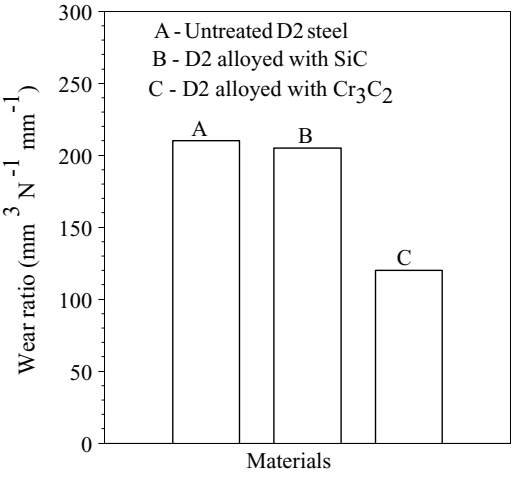

Figure 6 Wear-resistance test of the substrate and of the surface alloys obtained by laser alloying of SiC or Cr_3C_2 on the D2 steel.

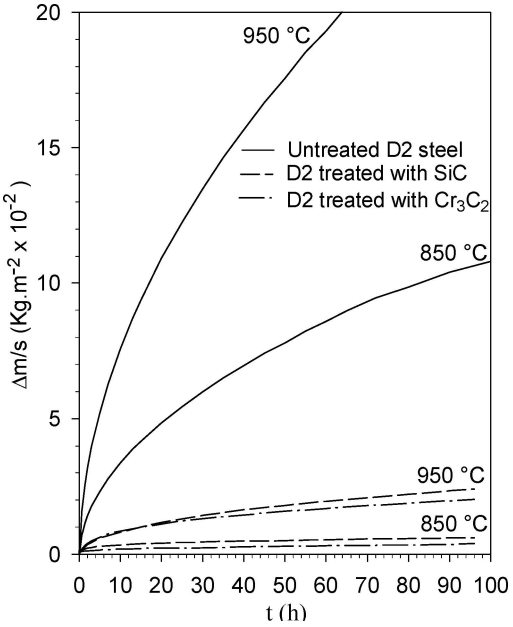

Figure 7 Oxidation kinetics at 850 and 950°C (1 atm O_2) of the substrate and of the surface alloys obtained by laser alloying of SiC or Cr_3C_2 on the D2 steel.

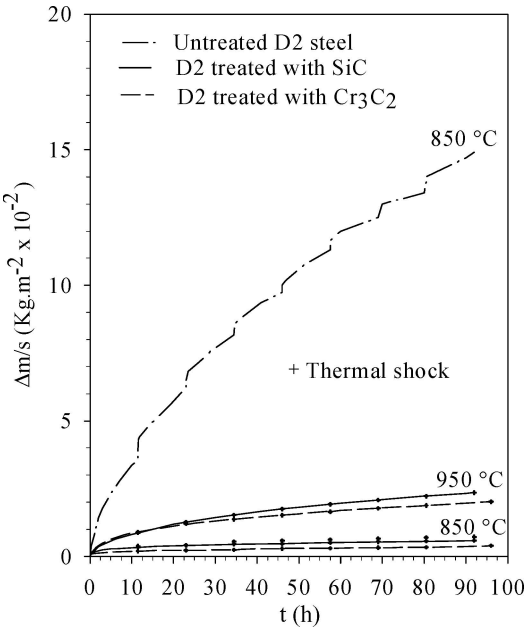

Figure 8 Oxidation in cyclic conditions at 850 and 950°C (1 atm O_2) of the substrate and of the surface alloys obtained by laser alloying of SiC or Cr_3C_2 on the D2 steel.

and silicon containing surface alloys obtained by incorporation of Cr_3C_2 or SiC respectively exhibit an excellent behaviour compared to the untreated steel. It can be observed that the oxidation resistance is about the same in isothermal or cycling conditions, contrary to the untreated steel. These surface alloys oxidize according to a parabolic law.

3.4. Formed products

Evidences from SEM and WDS on cross-section views showed that the untreated D2 steel oxidizes forming three different oxide layers at 850°C: an external Fe_2O_3 layer, an intermediate Fe_3O_4 layer and a chromium containing magnetite layer ($(Fe,Cr)_3O_4$) in contact with the steel.

On the surface alloys the corrosion scale formed at 850 and 950°C is very thin and constituted of a unique and quasi-pure Cr_2O_3 (1 to 2 at% iron) micrometric layer (Fig. 9). It is well known that iron easily dissolves in Cr_2O_3 but it is difficult to determine if silicon is also dissolved or finely precipitated as amorphous silica in the corrosion layer of the steel treated with SiC.

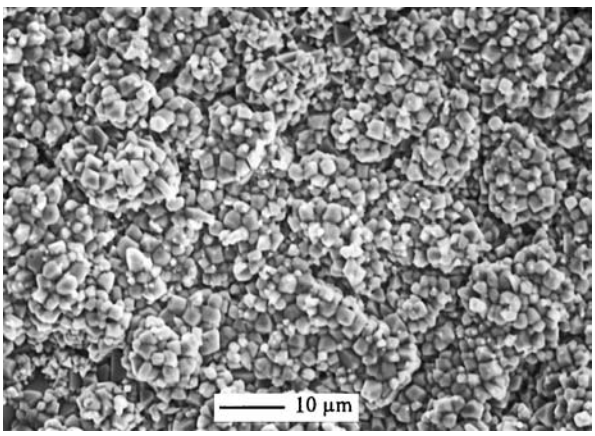

Figure 9 Cr_2O_3 micrometric crystals formed in isothermal conditions on the D2 steel after laser alloying of Cr_3C_2 and oxidized for 100 h at 950°C (1 atm O_2).

4. Discussion

4.1. Wear and hardness

The increase of the wear resistance seems to be correlated with the hardness increase. The Archard law [11] which correlates the wear volume to hardness is then probably the case. Therefore, the results of the wear and microhardness measurements are directly correlated with the microstructure. On the other hand, the increase in the hardness and wear resistance is essentially due to $(Fe,Cr)_7C_3$ carbide precipitations.

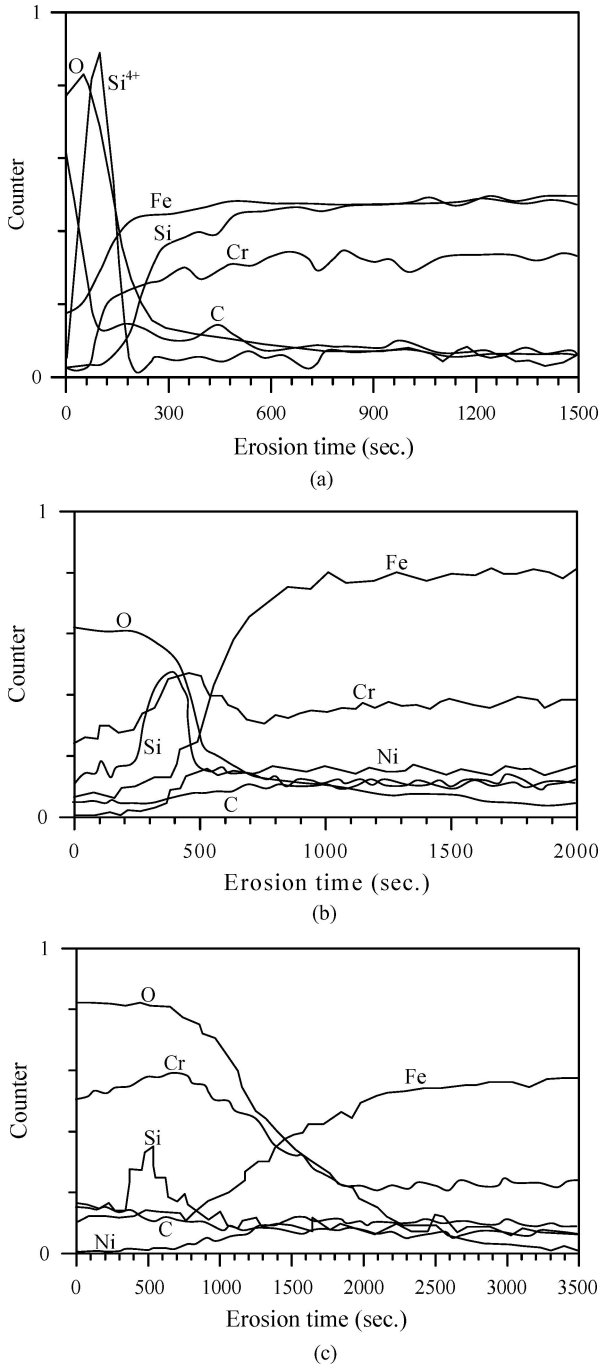

Figure 10 Auger electron spectroscopy diagrams showing the different element profiles in the oxide films formed at 950°C before oxidation (a), and after 30 s (b) and 90 s (c) on the surface alloy obtained with SiC.

4.2. Formed oxides and oxidation kinetics

The growth of Cr_2O_3 on the surface alloy obtained with SiC in which the chromium concentration is slightly lower than that of the untreated steel shows the positive effect of silicon addition in this surface alloy. A concentration of 4 wt%Si is enough to form a Cr_2O_3 compact layer. As a matter of fact, this Cr_2O_3 layer arises after the formation of a thin silica layer, according to the relative stability of these oxides. This phenomenon is perfectly visible on the Auger profiles (AES) performed on the samples submitted to oxidation times between 0 and 5 min at 850°C (Fig. 10). These results present the profiles of O, Fe, Cr and Si elements. Before the oxidation test, the surface alloy presents a silica film of about 1 nm in thickness (Fig. 10a). After 90 seconds of oxidation, the thickness of this film increases to 15 nm (Fig. 10b). At this moment, silica thickness remains constant and Cr_2O_3 starts growing. After 5 min of oxidation the Cr_2O_3 thickness is 100 nm and the silica film dissolves in Cr_2O_3 layer (Fig. 10c).

Careful examinations by microprobe analysis of the alloy-scale interface showed important chromium depletion in a 10–20 μm zone of the surface alloy obtained with Cr_3C_2 beneath the Cr_2O_3 layer. The chromium content in this zone never exceeded 10%, in contrast with the 30% value of the bulk surface alloy. This chromium depletion is the result of Cr_2O_3 layer formation. Chromium diffusion in the surface therefore participates in the kinetic limitation in series with matter transport in the scale. Due to the small size of the Cr_2O_3 grains and the excellent thermal cycling behaviour of the scale, it can be assessed that the predominant matter transport in the scale is oxygen diffusion. The alloy-scale interface is then continuously regenerated, leading to excellent cohesive properties.

5. Conclusion

This study has shown that the laser treatment leads to an excellent resistance to oxidation at high temperature in isothermal and cycling conditions. The protection against the oxidation is assured, essentially, by a microcrystalized chromium oxide layer which is formed due to the high chromium content (surface alloy obtained with Cr_3C_2) or due to the silicon presence (surface alloy obtained with SiC).

The good increase in the hardness or wear resistance of the surface alloy obtained with Cr_3C_2 is due to $(Fe,Cr)_7C_3$ carbide precipitations. Therefore, this treatment permits that the D2 tool steel behaves like a stainless steel presenting the advantage of higher hardness and wear resistance.

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