

UTILIZATION OF WELDED COATING ALLOY TO IMPROVE THE SURFACE PROPERTIES OF VCO AND VH13 STEELS

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Abstract. *Coatings were processed by electric arc surface alloying of Fe-30Cr-4C electrode on the low-alloyed VCO and VH13 ferritic steels. The obtained surface alloy (coating) shows a hypereutectic structure formed by primary $(Fe,Cr)_7C_3$ platelets surrounded by the eutectic, austenitic solid solution and $(Fe,Cr)_7C_3$ carbides. This surface alloy presents a high hardness (850 Hv), compared to the VCO (400 Hv) or VH13 (450 Hv) steel, and a decrease in the wear ratio by a factor close to two. Contrary to the substrates, the surface alloy exhibits an excellent high temperature oxidation resistance due to a microcrystallized chromium oxide layer formed after 100 h of oxidation at 950 °C. Oxidation kinetics and formed oxides of the surface alloy and substrates are discussed in the light of thermodynamics and diffusion processes.*

Key-words: *Electric arc, Coatings, Ferritic steels, Oxidation, Hardness.*

1. INTRODUCTION

Welding processes using concentrated energy sources have undergone significant improvement in recent years. Because of its great versatility, these processes have been in use in many industrial applications, one of the most recent being the surface treatment of different materials (Svensson, 1986, Powell, 1994). This technique makes it possible to improve surface properties such as resistance to wear and corrosion, which in turn allows for a decrease in manufacturing costs (because the treatment is applied to the surface only) as well as repair and maintenance of cutting tools, dies, etc. Among existing techniques, electric arc alloying appears to suit well the surface treatment requirements because of its flexibility, effectiveness, simplicity, and low cost.

The solidification process of the fusion spot generated by the electric arc is a function of the thermal conditions, the liquid bath geometry, and the speed of the solid-liquid interface (Granjon and Dadian, 1972, Davies and Garland, 1975, Savage and al., 1976). This rapid fusion and solidification process associated with a liquid spot is also encountered in the laser fusion surface treatment technique (Rapazz and al., 1987, Fouquet, 1991). The coatings (surface alloys) obtained by the electric arc technique have then the same characteristics as those obtained by the laser fusion surface technique with matter incorporation.

Surface alloys of hyper-eutectic composition obtained by the laser technique with addition of chromium and carbon on a low ferritic alloy (Gemelli and al., 1997) exhibit a

chromium increase in solid solution and the formation of iron and chromium carbides. The chemical and morphologic characteristics of this surface alloys lead to an increase in hardness, a decrease in the wear ratio (Puig, 1989), and to an excellent resistance to oxidation at high temperatures. Data available in the literature (Svensson, 1986, Powell, 1994) have shown that this type of structure can be obtained by the electric arc technique with special iron-chromium-carbon electrodes. The authors claim that these surface alloys display good anti-wear and anti-oxidation properties due to presence of carbides and a chromium concentration in solid solution high enough to form a protective chromium oxide layer in high temperature oxidizing atmospheres.

In the present investigation, VCO and VH13 steels samples treated by the electric arc technique surface were used to assess the increase in surface hardness and resistance to oxidation of dies and cutting tools made of these materials. In preparing these samples, special Fe-Cr-C electrodes were used because of their ability to form a barrier against high temperatures oxidation processes. In addition, these electrodes promote the formation of enhanced hardness compounds such as iron-chromium carbides. This factor contribute to an overall increase in the wear resistance of the pieces so manufactured.

2. EXPERIMENTAL PROCEDURE

2.1 Manufacturing procedure

Disk plates, 50 mm in diameter and 10 mm thick, were obtained from VCO and VH13 rods. These disks were then polished on silicon carbide papers to 100 grit, rinsed with water, further cleaned with alcohol, and dried using a hand-held hair drier. Next, the samples were treated by the electric arc technique using coated Fe-Cr-C electrodes. The manufacturing conditions were as follows: vertically oriented electrode, 250 A alternate current (direct polarity), electrode sweeping speed of 8 mm/s, electrode overall diameter (including the coating) of 8 mm and wire (electrode's core) diameter of 3 mm.

The overlap of adjacent weeps required for adequate coating of the whole surface was 20% approximately. Each sweep was 8 mm wide.

Table 1 presents the chemical composition of the substrates.

Table 1. Chemical composition of the VCO and VH13 steels (wt%).

Material	C	Mn	Cr	Ni	Mo	V	Si	Fe
VCO	0,50	0,50	1,00	3,25	0,30	-	-	Bal.
VH13	0,40	0,35	5,00	-	1,50	1,00	1,00	Bal.

2.2 Electrode selection

Initially, Fe-Cr-C electrodes of different compositions were chosen so as to check their ability to form carbides during the solidification following the electric arc treatment. Next, samples were coated using the chosen electrodes and the resulting coatings composition was checked under the microscope. For each sample, tests were then made of its hardness and resistance to oxidation in order to determine the chemical composition of the electrode alloying for the most advantageous trade-off between the two parameters. These tests showed that the hypereutectic surface alloys exhibited a greater hardness and resistance to oxidation than the eutectic or the hypoeutectic ones. The chemical composition of the electrode selected for the tests to follow was Fe-30Cr-4C. In these tests, an investigation was made of the

microstructure, hardness, and resistance to wear of the surface alloys obtained by the electric arc technique.

The oxidation tests were carried out in a furnace at 850 or 950 °C, with no control of the air composition (the tests were made using the ambient air inside the furnace). Before and after oxidation, the samples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and microprobe analysis by wave dispersion spectroscopy (WDS). It was then possible to visualize and analyze the surface alloys structure and the oxidation products formed. The surface alloys and the substrates hardness was measured by Vickers indentation under a 5 N load.

The pin-on-disk wear tests were carried out in a dry environment at ambient temperature (without chip evacuation) after the surface alloys and the substrates were polished using 600 grade paper finish. The test conditions were used: (a) alumina sphere diameter of 6 mm; (b) load of 10 N; (c) sphere track radius of 6 mm; (d) sphere dislocation speed on the disk of 0,1 m/s; (e) test duration of 10^4 laps.

3. EXPERIMENTAL RESULTS

3.1 Microstructure of the surface alloys

The micrographics observations made from cross-sectional cuts of the treated samples revealed that the morphology and the structure of the surface alloys obtained with Fe-30Cr-4C electrodes are not affected by the substrate used. Therefore, the coatings on VCO and VH13 steels are identical with an approximate thickness of 1 mm where the electrode structure is maintained after the coating solidification. In the interface with the substrate, it can be seen an intergranular penetration of coating material in the substrate to about 250 μm in depth (figure 1).

The results from X-ray diffraction analysis of the coating alloys have shown a prevailing presence of γFe solid solution and $(\text{Fe,Cr})_7\text{C}_3$ carbides. Traces of αFe (probably martensite) were also observed.

The SEM metallographics have shown that the surface alloy is formed by two distinct metallurgical structures:

- ◆ a intergranular eutectic structure in the substrate interface (figure 1) consisting of iron solid solution and $(\text{Fe,Cr})_7\text{C}_3$ carbides. The small difference in the chemical composition of VCO and VH13 steel does not affect this region structure,
- ◆ a hypereutectic structure (figure 2) in the upper region consisting of $(\text{Fe,Cr})_7\text{C}_3$ primary precipitates completely surrounded by the eutectic, iron solid solution and $(\text{Fe,Cr})_7\text{C}_3$ carbides.

3.2 Wear and hardness tests

The average wear ratio measured on the surface alloys and substrates shows that the electric arc deposition of Fe-30Cr-4C leads to a significant increase in the hardness and wear resistance in relation to the substrates. The surface average hardness of the steels increases from about 400 (VCO steel) or 450 Hv (VH13 steel), before the treatment, to about 850 Hv (after surface alloying) and the wear ratio decreases to a factor close to two.

3.3 Oxidation tests

Weight gains ($\Delta m/s$) versus time (t) obtained at 950 °C in isothermal oxidation are presented in figure 3. The chromium containing surface alloy exhibit an excellent behavior compared to the untreated steels. It can be observed that the surface alloy oxidize according to a parabolic law and its weight gain after 50 h oxidation is respectively 35 and 50 times lower than that of untreated VH13 and VCO steels.

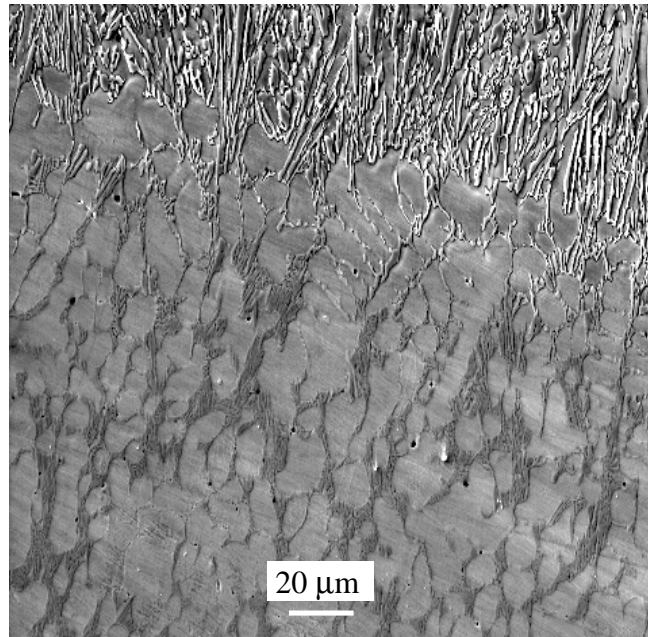


Figure 1. Scanning electron micrograph showing the intergranular electrode materials penetration in the interface surface alloy/substrate obtained by arc electric alloying of Fe-30Cr-4C on the VCO steel.

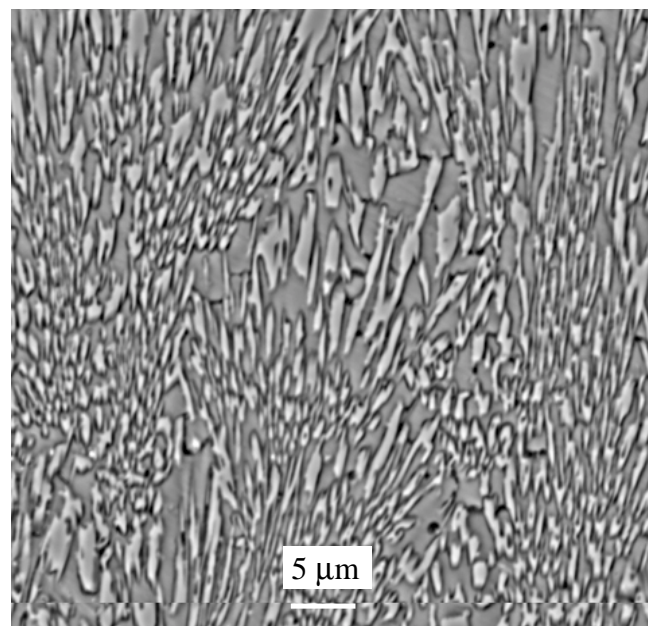


Figure 2. Detailed observation of the primary $(Fe,Cr)_7C_3$ carbide platelets in the eutectic material on top of figure 1.

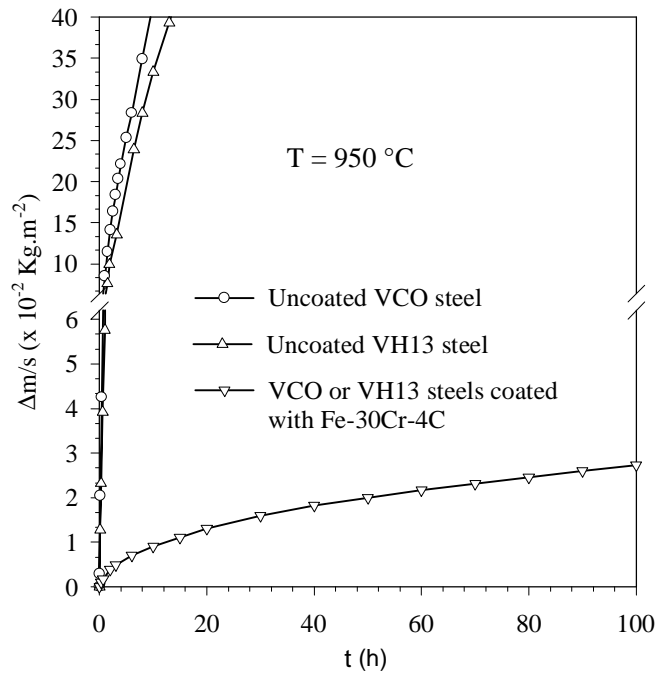


Figure 3. Oxidation kinetics at 950 °C (1 atm air) of the substrates and of the surface alloys obtained by arc electric alloying of Fe-30Cr-4C on the VCO and VH13 steels.

3.4 Corrosion Products

The untreated VCO steel oxidizes at 850 °C forming three external subscales: Fe₂O₃ (~ 75 μm), Fe₃O₄ (~ 150 μm), FeO (~ 150 μm) and an internal subscale (~ 300 μm) after 50 h oxidation. The internal part of the oxidized scale, evidently grown by inward diffusion, is constituted by manganese and chromium containing magnetite (~ 1 at% Mn and 2 at% Cr in Fe₃O₄) whereas no chromium or manganese were identified in the external part of the scale. Metallic nickel-rich nodules are also present in this part.

The untreated VH13 steel oxidizes forming three different oxide layers at 850 °C after 50 h oxidation: an external Fe₂O₃ layer (~ 60 μm), an intermediate Fe₃O₄ layer (120 μm) and an internal chromium (5 at%), silicon (2 at%) and manganese (< 1 at%) containing magnetite layer (~ 200 μm). It is well known that manganese and chromium easily dissolves in magnetite (Landkof, 1985, Stott and Wei, 1989) but it is difficult to determine if silicon is also dissolved or finely precipitated as amorphous silica.

On the surface alloy the corrosion scale formed at 950 °C after 100 h oxidation is very thin (2 to 5 μm) and constituted of quasi-pure Cr₂O₃ (1 to 2 at% iron) micrometric crystals (figure 4).

4. DISCUSSION

4.1 Wear and hardness

The increase in the wear resistance seems to be associated with the hardness increase. The Archard law (1953), which correlates the wear volume to hardness, is verified in this 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 $(\text{Fe,Cr})_7\text{C}_3$ carbides precipitation.

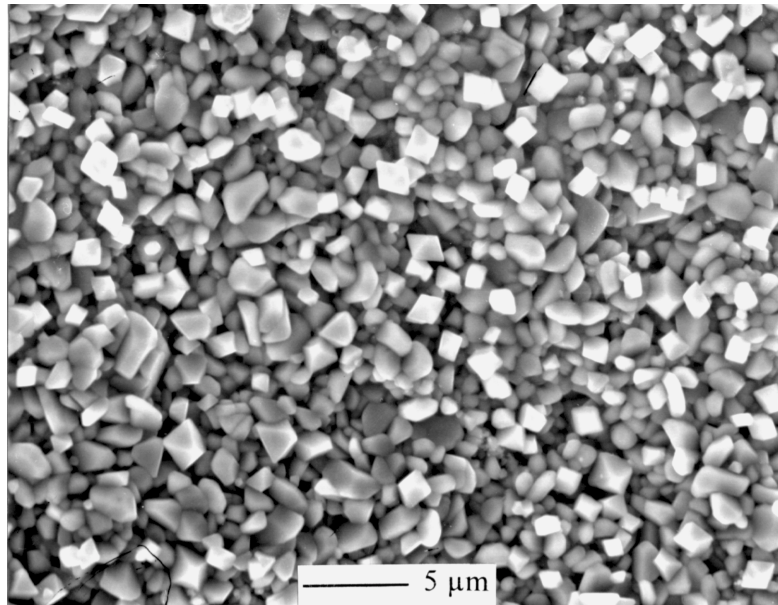


Figure 4. Cr_2O_3 micrometric crystals formed on the VCO steel after electric arc Alloying of Fe-30Cr-4C and oxidized for 100 h at 950 °C (1 atm air).

4.2 Formed oxides and morphology

During the oxidation of the untreated VCO steel, manganese, chromium and nickel are quasi-immobile, allowing the external growth of iron-rich oxide layers. These elements remain in the inward-growing part of the scale, in solid solution within magnetite or in the form of elementary nickel, unoxidized in this low-oxygen potential environment. The presence of this magnetite layer under wüstite may possibly be due to the presence of dissolved manganese and chromium ions lowering the free enthalpy of formation of Fe_3O_4 . Assuming a linear variation of this free enthalpy with the manganese and chromium concentration, the stability of the manganese and chromium containing magnetite exceeds that of wüstite as soon as the average concentration between manganese and chromium is equal to 3.2 at%. This roughly calculated value is of the same order as that of 3 at%, measured in the internal part of the corrosion scale by microprobe analysis. Moreover, taking into account the lowering of the iron activity in the surface alloy at its interface with the oxidized scale due to iron outward diffusion, the calculated value falls and is, for example, 1.2 at% for an iron activity of 0.5.

The microprobe analysis on a cross-section showed an important depletion in a 10-20 μm zone of the surface alloy 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.

4.3 Oxidation kinetics

The parabolic kinetic law observed on the surface alloy show that the oxidation kinetic is limited by ionic transport in the chromium oxide. It is known that in this oxide the relative importance of the anionic and cationic diffusions may be strongly influenced by the impurities (Beauvais-Reveillon,1994). Scales grown on similar surface alloy (Gemelli, 1997) showed evidence that the predominant matter transport in the scale is oxygen diffusion (Pieraggi and

Rapp, 1993).

5. CONCLUSION

This study has shown that it is possible to elaborate interesting surface alloys by electric arc with special electrode on ferritic steels. The surface deposition of a Fe-30Cr-4C alloy on the VCO and VH13 steels is efficient in increasing the surface hardness and wear resistance of these steels due to high $(\text{Fe,Cr})_7\text{C}_3$ carbides precipitation. The surface alloy also leads to an excellent resistance to oxidation at high temperature in isothermal conditions. The protection against the oxidation is assured, essentially, by a microcrystallized chromium oxide layer which is formed due to the high chromium content in the surface alloy. Consequently, the surface alloy presents a stainless steel behaviour with a reduction in the oxidation rate by a factor of 35 and 50 respectively on the VH13 and VCO steels after 50 h of oxidation (1 atm air) at 950 °C.

REFERENCES

- Archard, J.F., 1953, *J. Appl. Phys.*, Vol. 24, pp. 981-988.
- Beauvais-Reveillon, S., 1994, Ph.D. Thesis, University of Paris-Sud, Centre d'Orsay, France.
- Davies, C.J., and Garland, J.G., 1975, *Int. Met. Rev.*, Vol. 20, n. 6, pp. 83-106.
- Fouquet, F. and al., 1991, *Alliages de Surface avec Prédépôts, Revêtements et Alliages avec Projection*, in *Laser de Puissance et Traitements des Matériaux*, edited by A. B. Vannes, Presses Polytechniques et Universitaires, Lausanne, Switzerland, pp. 217-249.
- Gemelli, E., Galerie, A., and Caillet, M., 1997, *Solid State Ionics*, Vol. 95, pp. 81-86.
- Granjon, H., and Dadian, H., 1972, *Soud. Tec. Con.*, Vol. 26, n. 5/6, pp. 181-195.
- Landkof, M., and al., 1985, *Corr.*, Vol. 41, pp. 344-357.
- Pieraggi, O.B., and Rapp, R.A., 1993, *J. Electrochem. Soc.*, Vol. 140, pp. 2844-.
- Powell, G.L.F., Carlson, R.A., and Randle, V., 1994, *J. Mater. Sci.*, Vol. 29, pp. 4889-4895.
- Puig, T., 1989, Ph.D. Thesis, University of Paris-Sud, Centre d'Orsay, France.
- Rappaz, M. and al., 1987, *Solidification Front and Growth Rate During Laser Remelting*, in *Laser Treatment of Materials*, edited by B. L. Mordike, DGM Verlag, Oberursel, pp. 43-54.
- Savage and al., 1976, *Weld. J.*, Vol 55, n. 8, pp. 213s-221s.
- Stott, F.H., and Wei, F.I., 1989, *Mat. Sci. Technol.*, Vol. 5, pp. 1141-1147.
- Svensson, L.E., and al., 1986, *J. Mater. Sci.*, Vol. 21, pp. 1015-1020.