Surface hardening of metallic alloys by electrospark deposition followed by plasma nitriding

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Abstract

This paper presents the results of a study concerned with the surface hardening of nonferrous and ferrous alloys, by integrating the electrospark deposition and plasma nitriding processes. Specimens of an aluminium bronze and of a grey cast iron were firstly electrospark coated with AISI-304 stainless steel and, then, ion nitrided in a $25\%N_2 + 75\%H_2$ dc plasma. It is shown that by using these two treatments, the surface hardness of this two materials can be substantially increased.

Keywords: Electrospark; Plasma nitriding; Surface hardening; Cast iron; Copper alloys

1. Introduction

Material deposition is one of the most important means for improving the mechanical performance of some metallic components. For example, the wear resistance of some soft metals can be notoriously increased by some treatments that raise their surface hardness to levels comparable to those of refractory compounds [1].

For material depositing, several processes exist [1], among which the following ones are commonly used in industrial applications: welding [2], thermal spraying [3] and electroplating [4]. Welding and thermal spraying are normally used for coating metals with ceramic materials as chromium carbides. Electroplating is typically used for hard chromium depositing; but, although chromium electroplating is an economical process, its use is being limited due to the associated pollution problems [5].

Another method for metals hardening is electrospark deposition (ESD), which is essentially a pulsed microwelding technique [6]. This is a relatively cheap thermal process which has been used during several decades for covering locally the surface of metallic substrates with the material of an electrode [7]. This process normally produces coatings very well joined to the substrate, due to the metallurgical bonding obtained. At the present time, electrospark deposition is used even in demanding applications as aerospace and nuclear components [6].

The purpose of this work was to study the possibility of hardening the surface of specimens of some nonferrous and ferrous alloys that do not harden significantly by means of the nitriding process only. To achieve this goal, firstly specimens of an aluminium bronze and of a cast iron were coated with a chromium rich steel by using ESD, and afterwards the specimens were processed by plasma nitriding [8].

2. Experimental

A scheme of the electrospark deposition process is shown in Fig. 1. The anode was a tube, 5 mm external diameter and 2 mm internal diameter, made of AISI-304 stainless steel (18.7%Cr, 7.7%Ni, 70.6%Fe, 2.5%Mn, 0.4%Si, 0.07%C). The cathode (workpiece) was a plane bar of either an as-received aluminium bronze (5 mm × 5 mm × 30 mm) or an annealed grey cast iron (10 mm × 5 mm × 50 mm), the nominal composition of which are given in Table 1.

ESD was performed by using a relaxation circuit constituted by a capacitor (C) and an electrical resistance (R), the values of which are given in Table 2. For avoiding workpieces oxidation, an inert gas (He or N_2) was forced through the centre of the anode. The anode was moved vertically by an electromagnet, which was energized by a 50 Hz alternative electrical current and, consequently, contacted intermittently the cathode at a frequency of 100 Hz. The cathode was moved transversally at a constant velocity V_c (see Table 2).

After electrospark deposition, the specimens were ion nitrided in a dc plasma during $t = 3.6$–21.6 ks, at the operational conditions given also in Table 2.

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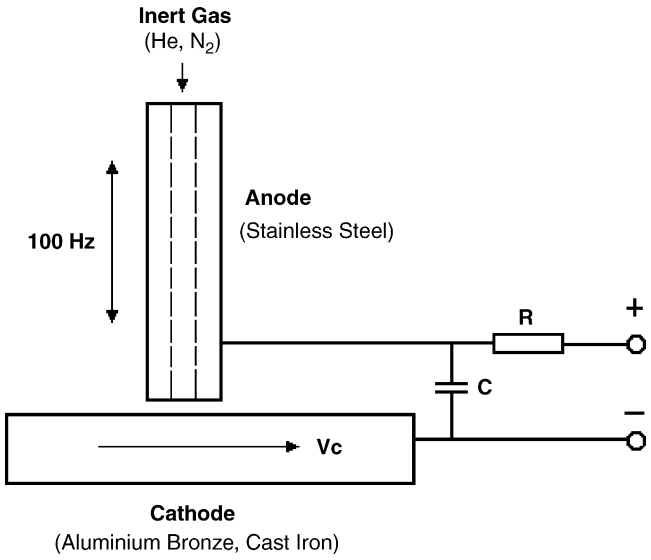

Fig. 1. Electrospark deposition process.

Table 1
Nominal composition (wt.%) and workpiece metallurgical condition before ESD

Aluminium bronze		Cast iron	
Cu	82.2	C	3.3–3.5
Al	6.9	Si	1.9–2.2
Mn	6.3	Mn	0.6–0.8
Ni	2.5	P	0.25 max
Fe	2.1	S	0.12 max
		Fe	Balance
Condition: as-received		Condition: annealed (1163 K, 1.8 ks)	

Table 2
Operational parameters for ESD and plasma nitriding

	Aluminium bronze	Cast Iron
Electrospark deposition		
Capacitor, C (μF)	300	100–200
Resistance, R (Ω)	8.3	12.5–25
RC constant (ms)	2.5	2.5
Sparking voltage, V_s (V)	40–80	25–70
Shielding gas	He	N_2
Cathode velocity, V_c (mm/s)	0.033	0.06
Plasma nitriding		
Plasma	25%N_2 + 75%H_2	25%N_2 + 75%H_2
Temperature (K)	803	803
Pressure (kPa)	0.2	0.4

3. Results and discussion

3.1. Original hardness of the workpieces

3.1.1. Aluminium bronze

Due to the machining operations, the microhardness values of the as-received aluminium–bronze specimens, measured along depth, were not uniform. At the surface, the microhardness was of about 300 $HV_{0.2}$, while for a depth greater than 200 μm was of about 230 $HV_{0.2}$. By heating during 7.2 ks some of these specimens, at the same temperature used for the nitriding treatment (803 K), the microhardness decreased to a relatively uniform value of about 200 $HV_{0.2}$, as shown in Fig. 2.

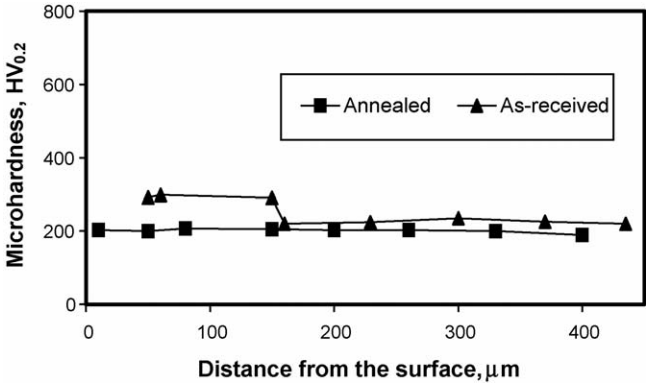

Fig. 2. Microhardness: aluminium bronze.

3.1.2. Cast iron

The microhardness of the cast iron workpieces, annealed at 1163 K during 1.8 ks, was of 220 $HV_{0.2}$.

3.2. Electrospark deposition

3.2.1. Aluminium bronze

Optical micrograph of two aluminium bronze workpieces coated with stainless steel are shown in Fig. 3. The coating thickness average values, as a function of the sparking voltage (V_s), for $C = 300$ μF and $V_c = 0.033$ mm/s, are shown in Fig. 4. Since each coating is generated by overlapping randomly discrete quantities of metal, the obtained thickness was not uniform. The average value of the thickness depended on the sparks energy. At relatively low values of V_s, the thickness increased with the spark

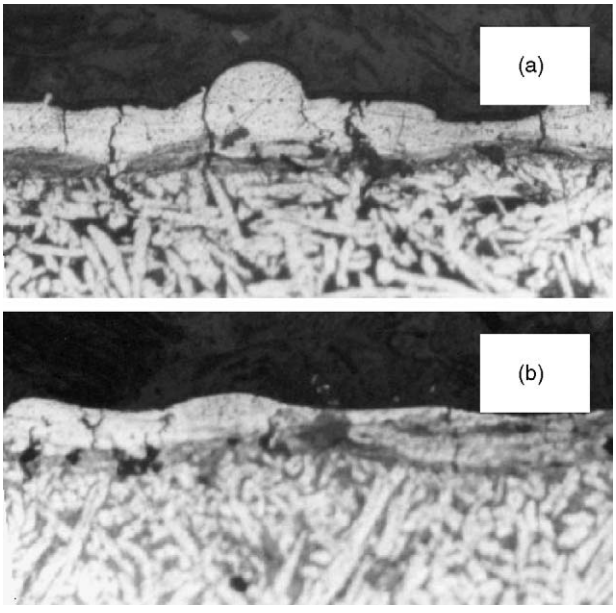

Fig. 3. Optical micrographs showing the deposits on aluminium bronze: (a) $V_s = 60$ V, (b) $V_s = 80$ V.

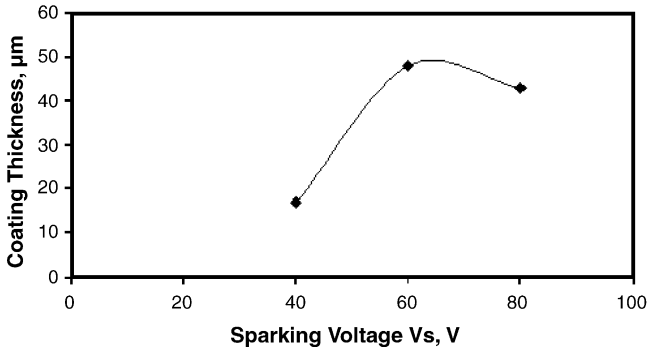

Fig. 4. Average values of the coating thickness. Substrate: aluminium bronze.

energy (E), attaining a maximum value of 50 µm for $E = 0.54$ J ($V_s = 60$ V). For greater E-values the coating thickness diminished: thus, for $V_s = 80$ V its value was of 40 µm only. This trend is typical in ESD [7]. On the other hand, as a consequence of the high cooling rate because of the high thermal conductivity of the substrate, the coatings showed some cracks (as happen in EDM), the density of which decreased as spark energy increased.

The Fe, Cr and Cu content, for a workpiece electrosparked at $V_s = 80$ V was measured at a depth of 25 µm (middle thickness of the coating), and the obtained values are presented in Table 3. The Fe and Cr resultant content was notoriously lower than its value in the 304 stainless steel. The Cu resultant content, which is an element that does not contain the 304 steel, was very significant. These results show that the coating material obtained by electrospark was not the same as that of the anode, and consequently a surface alloying of the stainless steel with some molten metal of the substrate took place. The resultant surface microhardness of this workpiece was of about 350 $HV_{0.2}$.

3.2.2. Cast iron

Fig. 5 shows the optical micrograph of a deposit obtained with $C = 150$ µF and $V_s = 50$ V ($E = 0.19$ J). The micrograph shows a coating zone of 20–25 µm thickness, but due to the non-uniformity, the coating average thickness was of about 10 µm.

Fig. 6 shows the values of the weight gain of cast iron workpieces treated by using different sparking voltages and different capacities ($V_c = 0.06$ mm/s). It is seen that the maximum weight gain increased with increasing the capacity. But, by increasing the capacity, the deposition process becomes very dependant of the sparking voltage. Thus, the combination $C = 150$ µF and $V_s = 50$ V ($E = 0.19$ J) resulted an adequate one for performing the deposition.

By using the 150 µF–50 V combination, the surface microhardness of the deposit was of about 600 $HV_{0.2}$, and the Cr content, at the middle of the deposit, was similar to the Cr content of the AISI-304 stainless steel. Thus, the alloying produced by electrospark deposition of stainless steel on cast iron was minimum.

Table 3
Chemical composition at 25 µm depth of an ESDed aluminium bronze (wt.%)

Fe	54.38
Cr	14.08
Cu	20.01
Others	11.53

$V_s = 80$ V.

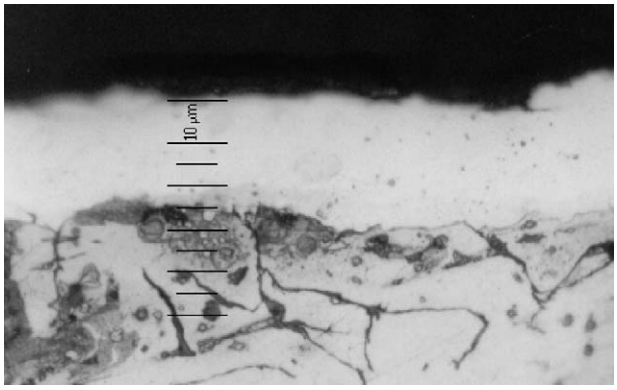

Fig. 5. Optical micrograph showing the deposit on grey cast iron ($C = 150$ µF, $V_s = 50$ V).

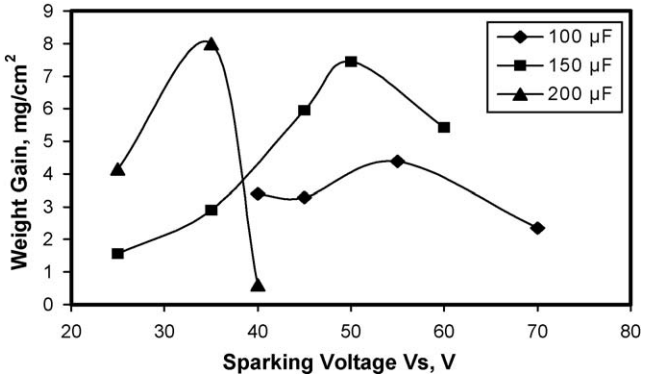

Fig. 6. Weight gain for different sparking voltages and different capacities. Substrate: grey cast iron.

3.3. Plasma nitrided workpieces

3.3.1. Aluminium bronze

In Fig. 7, the influence of the nitriding duration on the microhardness of an 80 V electrosparked workpiece is shown. It is clear that up to $t = 14.4$ ks, the nitriding process did not increase significantly the surface hardness. Only with a nitriding time

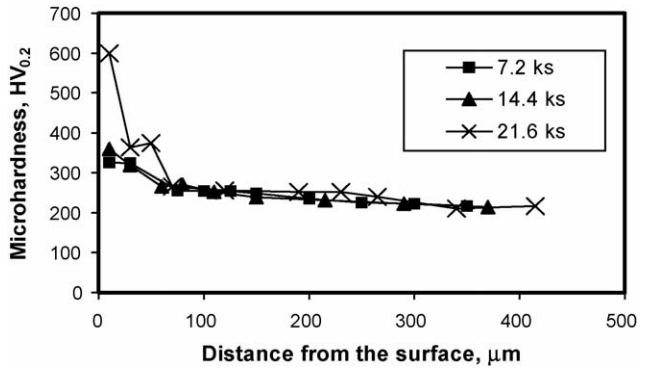

Fig. 7. Microhardness profiles of ion nitrided workpieces. $V_s = 80$ V. Substrate: aluminium bronze.

Table 4
Chemical composition at 25 μm depth of an ESDed and nitrided aluminium bronze (wt.%)

Fe	41.22
Cr	10.46
Cu	35.36
Others	12.96

$V_s = 80$ V, $t = 21.6$ ks.

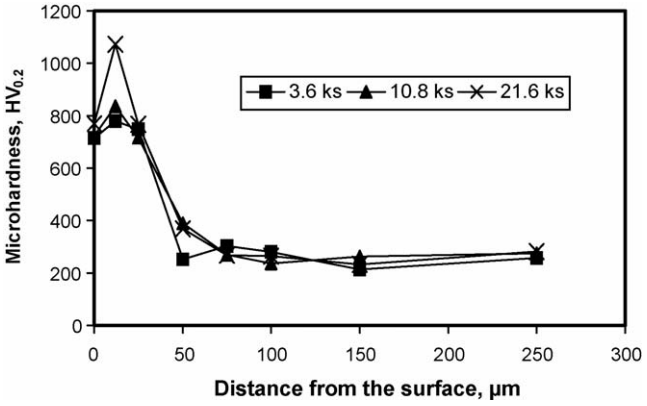

Fig. 8. Microhardness profiles of ion nitrided workpieces. $C = 150$ μF, $V_s = 50$ V. Substrate: grey cast iron.

of 21.6 ks, the hardness increased, attaining a maximum value of about 600 $HV_{0.2}$. Thus, the nitriding kinetics was relatively slow and the maximum hardness was relatively low, in comparison with the values obtained normally in the nitriding of the AISI-304 stainless steel [8,9].

On the other hand, the Fe, Cr and Cu content, at 25 μm from the surface of a workpiece electrospark treated at $V_s = 80$ V and plasma nitrided during $t = 21.6$ ks, is presented in Table 4. Clearly, the diffusion of some elements occurred during nitriding: the Fe and Cr contents decreased, while the Cu content increased. Although the chromium content diminished, the amount of chromium still would be sufficiently high like producing a high hardening of the workpiece surface [10,11]. Then, the surface enrichment in Cu (due to both ESD and nitriding) would be the most important factor that would explain the relatively low value of the surface hardness of the aluminium bronze. On the other hand, the results of [12] also show that the stainless steels containing copper have a slow nitriding kinetics. This would be related to the fact that the nitrogen is insoluble in solid or liquid copper [13]. Due to this reason copper coatings are used when it is desirable to protect some areas of a steel part against nitriding [14].

3.3.2. Cast iron

Fig. 8 shows the influence of the nitriding duration on the microhardness values of the cast iron workpieces electrospark coated by the 150 μF–50 V combination. The microhardness maximum value of this coating was of about 1100 $HV_{0.2}$ being the Cr content at the middle of the coating, after nitriding, again similar to the Cr content in the AISI-304 stainless steel. The obtained microhardness maximum value is notoriously greater than the maximum value obtained by plasma nitriding a cast iron without any coating [15], and similar to the value that is obtained by plasma nitriding an AISI-304 stainless steel workpiece [8].

4. Conclusions

It is shown that nonferrous and ferrous metallic alloys can be surface hardened by using a duplex treatment of electrospark deposition followed by plasma nitriding. When the metallic alloys are coated with AISI-304 stainless steel, it is possible to attain a surface microhardness of 600 $HV_{0.2}$ on a substrate of aluminium bronze, and a surface microhardness of 1100 $HV_{0.2}$ on a substrate of grey cast iron. In this case, the alloying of the stainless steel with Cu would reduce the nitriding kinetics and the maximum surface hardness.

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