DEVELOPMENT OF POST-OXIDATION TREATMENTS TO IMPROVE WEAR AND CORROSION RESISTANCE

R. Sola, R. Giovanardi, P. Veronesi, G. Poli, S. Masini, A. Zanotti

Gas nitrocarburizing and post-oxidation treatments were performed on 42CrMo4 steel and GS600 cast iron, to improve wear and corrosion resistance. In both materials the compounds layer after nitrocarburizing, mainly composed by ε-Fe$_{2-3}$(N,C) and γ'- Fe$_4$N phase. First the oxidizing step, a subsequent impregnation with two different lubricating oils was performed in order to further enhance corrosion resistance. Wear resistance was measured using a ball-on-disk tribometer with Al$_2$O$_3$ and 100Cr6 counterpart and the corrosion resistance of the samples was studied using salt spray test in accordance with ASTM B117 and electrochemical cell. Experimental results show that the nitrocarburizing treatment improves significantly the wear resistance of the steel but not the wear resistance of the studied cast irons. The application of nitrocarburizing alone does not significantly improve corrosion resistance and it may even promote localized corrosion. The subsequent post-oxidation step leads to a slight decrease of the corrosion rate, because it partially seals the porous nitrocarburized layer. The final oil impregnation step resulted much more effective in further decreasing the corrosion rate by one order of magnitude.

KEYWORDS: nitrocarburizing, post-oxidation, oil-impregnation, wear, corrosion

INTRODUCTION

Nitrocarburizing treatment has been used for many years in order to improve the wear and fatigue resistance of steel. It is a thermo-chemical treatment involving nitrogen and carbon diffusion, which leads to surface hardening of the parts treated, due to the presence of compressive internal stresses within the nitrogen/carbon enriched layer. In the nitrocarburized layer it is possible to identify two different zones. Superficially the nitrocarburizing treatment forms the white compound layer; it is usually very thin (5-30 μm) and it is mainly constituted by the nitrides and carbides of alloying elements. Under the compound layer there is the diffusion zone, in which nitrogen and carbon are dispersed as compounds but especially in a solid solution with the crystal lattice.

The compound layer is usually porous and this tends to decrease the corrosion resistance [1]. A possible solution to improve corrosion resistance consists in the post-oxidation treatment. This second treatment causes the subsequent partial decomposition of the Fe-carbonitrides in oxides (mainly Fe$_3$O$_4$) and the next constipation of the superficial micro-porosity of the compound layer [2]. The post-oxidation leaves a little superficial porosity able to

hold a lubricant oil, which can be used to increase the corrosion and wear resistance.

Aim of this work is the characterization and optimisation of three post-nitrocarbuzing treatments on ferrous alloys, in order to improve corrosion resistance and to reduce wear and friction. In particular, post-oxidation and post-oxidation followed by oil impregnation (2 different oils) have been applied to 42CrMo4 steel and to a spheroidal cast iron (GS600), after ferritic nitrocarburizing.

MATERIALS AND EXPERIMENTAL PROCEDURE

As substrate materials, 42CrMo4 steel and GS600 spheroidal cast iron were used in the experimental studies. To verify the chemical composition of the steel a simultaneous quantometer ARL 3580 and a glow discharge optical emission spectroscopy (LECO GDS-750) were used and the resulting average chemical compositions are given in the Tab. 1.

The samples for gaseous nitrocarburizing were disks 8 mm thick cut from a bright rod (40 mm in diameter) steel stock. A central hole was drilled in the disk to facilitate suspension in the nitrocarburizing furnace. The surface of the disks was polished on silicon carbide paper, with a final grid on 2000 grade paper. The disks were cleaned and degreased prior to nitrocarburizing.

The treatments considered in this research are:
1) Gaseous nitrocarburizing (samples indicated by "NC")
2) Gaseous nitrocarburizing + post-oxidation (samples indicated by "NC+O")
3) Gaseous nitrocarburizing + post-oxidation + impregnation in

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|	C	Si	S	P	Mn	Ni	Cr	Mo	V	Al	Fe	Mg	Cu
42CrMo4	0.432	0.19	0.029	0.029	0.75	0.09	0.97	0.18	0.09	0.020	rest	-	-
GS600	3.50	1.56	0.009	0.009	0.15	0.027	0.025	0.002	0.014	-	rest	0.029	0.126

▲
Tab. 1

Chemical composition of 42CrMo4 and GS600.
Composizione chimica del 42CrMo4 e della GS600.

RUST VETO TB oil (samples indicated by "oil TB")
4) Gaseous nitrocarburizing + post-oxidation + impregnation in RUST VETO 377 oil (samples indicated by "oil 377")
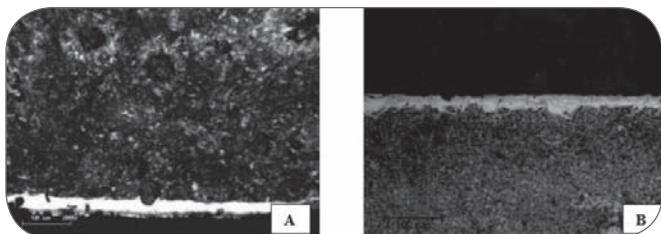All samples were treated in a furnace at 560°C for 8 h, and subsequently some of them were post-oxidised at 530°C for 3 h. Some of post-oxidised samples were impregnated in the lubricant oil by immersion.
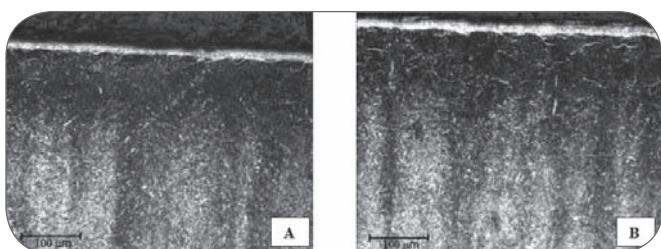
▲
Fig. 1

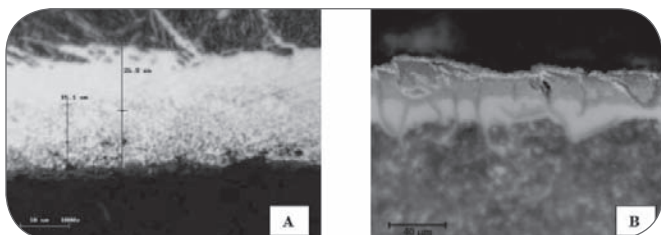**A. 42CrMo4 nitrocarburized. B. 42CrMo4 nitrocarburized and post-oxidised.**
A. 42CrMo4 nitrocarburato. B. 42CrMo4 nitrocarburato e post-ossidato.

▲
Fig. 2

A. GS600 nitrocarburized. B. GS600 nitrocarburized and post-oxidation.
A. GS600 nitrocarburata. B. GS600 nitrocarburata e post-ossidata.

▲
Fig. 3

The superficial oxide layer in the 42CrMo4 (A) and GS600 (B) nitrocarburized and post-oxidised.
lo strato di ossido superficiale in 42CrMo4 (A) e GS600 (B) nitrocarburati e post-ossidati.

To characterize the nitrocarburized and post-oxidised layers, all the sample were initially analyzed with optical and scanning electron microscopy, and their microhardness profile (Vickers, 0.5 kg) and X ray-diffraction (CoKα radiation).
The corrosion behaviour was determined using salt-spray (fog) test according to ASTM B117 and ISO9227 standards for metals and alloys, and monitoring the open circuit potential in an HCl solution (0.1M).
The wear testing was done on a ball-on-disk CSM High Temperature Tribometer without lubrication under 5 N load and at sliding velocity of 0.2 m/s for a distance of 1000 m (ending condition). During test, the samples rotate against stationary Al_2O_3 and 100Cr6 ball of 6 mm in diameter. The wear properties were evaluated by measuring wear track profile using a CSM Conscan optical profilometer and the wear track morphology is also observed with stereo-microscope and scanning-electron microscope.

RESULTS AND DISCUSSION

Microstructure, microhardness and diffraction

Microscopy analysis shows that after nitrocarburizing treatment the samples maintain the same bulk microstructure, as expected according to the low temperature treatment. In the 42CrMo4 it is evident that the nitrocarburizing process produce a superficially two-phase compound layer (18-20μm thickness) which XRD indicated composed of the ε-Fe2-3(C,N) and γ'-Fe4N (vedi Fig. 1). Below the compound layer a diffusion layer can be seen (160-170 μm) . In the 42CrMo4 the post-oxidation treatment allowed the formation of an oxidized layer about 2 μm thick, over the compound zone, and causes a dimensional increase the compound layer and diffusion layer, because during this treatment C and N atoms can further diffuse inside the material.
In the GS600 the compound layer resulted more irregular than in the 42CrMo4, and the diffusion layer is thicker than 42CrMo4, probably because the presence of graphite inhibits the C and N diffusion inside the material. Also in this case the post-oxidation treatment increase the compound layer and diffusion layer thickness (vedi Fig. 2 e Fig. 3).
These results are confirmed by microhardness test. The hardening depth is higher in the steel than in cast iron, probably because the graphite doesn't allow to C and N atoms to diffuse deeply , in addiction the steels reach higher hardness. In table Tab. 2 the HV0.5 values measured on the surface of the sample, the total hardening depth (distance from external surface of hardened layer to the point in which the hardness value is equal to the hardness value of material before the treatments) and effective hardening depth (distance from external surface of the hardened layer to the point in which the hardness is equal the conventional value of 100 HV more than material hardness before the treatment) are reported.
The nitrocarburized samples present a porous compound layer, but after post-oxidation treatment the porosity is partially constipated by oxides. This is clearly shown in the SEM microphotographs reported below (Fig.4).
From X-ray diffractograms of nitrocarburized samples it is evident that the superficial layer of both materials is mainly composed of $Fe_{2,3}N$ and γ'-Fe_4(N,C) carbonitrides. The superficial layer of nitrocarburized + post-oxidised samples is mainly composed of magnetite (Fe_3O_4), promoted by the NOx of the oxidiz-

material	treatment	$HV_{0.5}$	effective hardening depth [mm]	total hardening depth [mm]
42CrMo4	untreated	298		
	nitrocarbuurized	705	0.2	0.32
	nitrocarburized + post-oxidised	710	0.25	0.40
GS600	untreated	210		
	nitrocarburized	520	0.16	0.20
	nitrocarburized + post-oxidised	515	0.19	0.25

▲
Tab. 2

$HV_{0.5}$ surface microhardness measured on the surface of the samples, and relative effective and total hardening depth.
Microdurezza $HV_{0.5}$ misurata sulla superficie dei campioni e relative profondità di indurimento totale ed efficace.
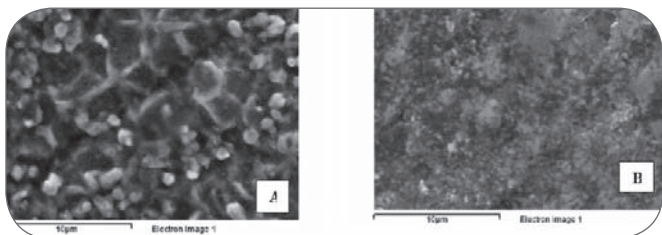

▲
Fig. 4

SEM photomicrographs. A. nitrocarburized. B. post-oxidised.
Micrografie SEM. A. Campione nitrocarburato. B. campione nitrocarburato e post-ossidato.

ing atmosphere and ematite (Fe_2O_3) (vedi Fig. 5).
The results obtained could be explained considering the mechanism of carbonitrides formation and the phenomena that happened during the subsequent post-oxidation process. The first compounds formed during the nitrocarburizing treatments are γ' carbonitrides, then increasing the nitrogen concentration, ε carbonitrides appear. When nitrogen exceeds the saturation threshold of ε carbonitrides, nitrogen recombination in molecular form (N_2) happens and this causes the micro-hole formation in the compound layer. Therefore, γ' carbonitrides, due to their lower nitrogen content respect to ε carbonitrides, are usually formed near the interface with the untreated material. The oxi-

dation of nitrocarburized layer is characterized by the ε carbonitrides decomposition and the successive formation of Fe oxide (Fe_3O_4) that constipates the superficial micro-porosity [3,4] . In the oxidizing atmosphere the first oxide formed is Fe_3O_4, but, with oxygen concentration increasing, Fe_2O_3 is formed as well.

Tribological analysis
The sliding tests allow to acquire quantitative information regarding sample and static partner wear resistance, by measurement of sample and static partner volume removed. The sample and static partner volume removed are reported in the Tab. 3 and 4.
In the steel all the treatments induce an exceptional reduction of the sample volume removed and thus a great increase of wear resistance. Among the treated samples, there aren't significant differences: all them show a great improve of the wear resistance. The TB oil impregnation leads to the lowest volume removed, and hence the best wear resistance. This behaviour is almost unchanges in case of Al_2O_3 pin, but, as expected, the volume removed increases wiht respect to 100Cr6 pin.
Instead, the GS600 wear behaviour is different significantly from 42CrMo4. In fact, the untreated sample exhibits the best wear resistance and the treatments increase the volume removed. It's important underlying that, in any case, the volume removed values are very low. In particular it's very evident the difference between the sample removed volume of untreated materials in favour of cast iron which is more than two order of magnitude lower, probably due to the presence of graphite that acts as solid lubricant [5]. However in the cast iron the treatments inhibit the

static partner (pin) 100Cr6				
	42CrMo4		GS600	
treatment	sample volume removed [mm³]	static partner volume removed [mm³]	sample volume removed [mm³]	static partner volume removed [mm³]
untreated	$7.34 \cdot 10^1$	$1.35 \cdot 10^2$	$3.19 \cdot 10^2$	$5.65 \cdot 10^2$
NC	$1.64 \cdot 10^1$	$6.16 \cdot 10^2$	$7.64 \cdot 10^2$	$2.00 \cdot 10^1$
NC+0	$1.81 \cdot 10^1$	$1.51 \cdot 10^1$	$1.03 \cdot 10^1$	$2.01 \cdot 10^1$
oilTB	$6.74 \cdot 10^2$	$2.50 \cdot 10^3$	$6.39 \cdot 10^2$	$4.17 \cdot 10^3$
oil377	$6.73 \cdot 10^2$	$1.22 \cdot 10^1$	$9.27 \cdot 10^2$	$1.09 \cdot 10^1$

▲
Tab. 3

42CrMo4 and GS600 sample and static partner volume removed, load 5N, pin 100Cr6.
Volume asportato per il 42CrMo4 e per la GS600, carico 5N, pin 100Cr6.

static partner (pin) Al_2O_3				
	42CrMo4		**GS600**	
treatment	sample volume removed [mm³]	static partner volume removed [mm³]	sample volume removed [mm³]	static partner volume removed [mm³]
untreated	*1.10·10⁰*	*2.36·10⁻³*	*5.28·10⁻²*	*2.51·10⁻³*
NC	*2.13·10¹*	*1.06·10⁻³*	*2.46·10¹*	*1.34·10⁻³*
NC+0	*9.25·10⁻²*	*2.15·10⁻³*	*1.55·10¹*	*3.89·10⁻³*
oilTB	*8.34·10⁻²*	*1.00·10⁻³*	*2.34·10¹*	*3.14·10⁻³*
oil377	*2.67·10¹*	*2.35·10⁻³*	*2.54·10¹*	*3.88·10⁻³*

▲
Tab. 4

42CrMo4 and GS600 sample and static partner volume removed, load 5N, pin Al_2O_3.
volume asportato per il 42CrMo4 e per la GS600, carico 5N, pin Al_2O_3.

effect of the grafite on the surface, hence they decrease the material wear resistance and this phenomenon it's emphasized in case of Al_2O_3.

In general, the 42CrMo4 and GS600 samples subjected to the superficial treatment present almost the same sample removed volume, in spite of the sample removed volume of untreated material is very different. This is due to the treatments that form superficially the same compounds (also confirmed by X-ray diffraction), and the wear resistance is determined especially by the superficial properties and marginally by the substrate.

▲
Fig. 5

X-ray diffractograms for the nitrocarburizing and nitrocarburizing+post-oxidized samples.
Diffrattogrammi relativi a campioni nitrocarburati e nitrocarburati e post-ossidati.

Regarding the volume removed for test performed with 100Cr6 pin, the untreated sample induces a neglectible wear to the pin, especially the untreated GS600 (probably due to the presence of graphite). The treatments increase the static partner volume removed, in fact they form superficially very hard compounds (carbonitrides and oxides) that contribute to the pin wear. The lubricant effect of TB oil impregnation is decisive, in fact in this case the pin wear is very low. Very different is the 377 oil behaviour, because it doesn't change significantly the pin volume removed with respect to nitrocarburized and nitrocarburized + post-oxidised samples, due to the physical and chemical difference between 377 and TB oils.

In case of Al_2O_3 pin there is a lower sample removed volume with 42CrMo4 and GS600 nitrocarburized and with 42CrMo4 impregnated into oil TB. In this case the lubricant effect of TB oil is greater than 377 oil, especially whem 42CrMo4 is used as substrate. In fact, the GS600 wears the Al_2O_3 pin more than 42CrMo4. Moreover to that it's important underlying that with Al_2O_3 pin there aren't relevant differences between static partner volume removed with untreated material and static partner volume removed with treated sample, because the Al_2O_3 pin is hard and it is scarcely worn by the treated and untreated samples indistinctly.

CORROSION TESTS

The salt-spray (fog) test, according to ASTM B117 and ISO 9227, shows that all the materials, with the same treatment, exhibit almost the same behaviour. After 24 h the TQ samples are already covered by corrosion products, while some pits are present on NC and NC+O surface; on the impregnated samples there are any trace of corrosion pits or products. Therefore, a little increment in the corrosion resistance is given by nitrocarburizing and the post-oxidation slightly improve the corrosion resistance with respect to NC. These treatments improves the corrosion resistance because they promote the superficial formation of nitrocarbides and oxides that, in general, are less reactive that the untreated material.

A decisive corrosion resistance improvement is given by lubricant oil impregnation and comparing 377 and TB oil, also in this case, the best behaviour is observed in TB oil, in fact after 72 h only the 377 samples present some corrosion pit and after 120 h the 377 samples show macroscopic areas with corrosion products, while the TB samples present only some corrosion pits. This
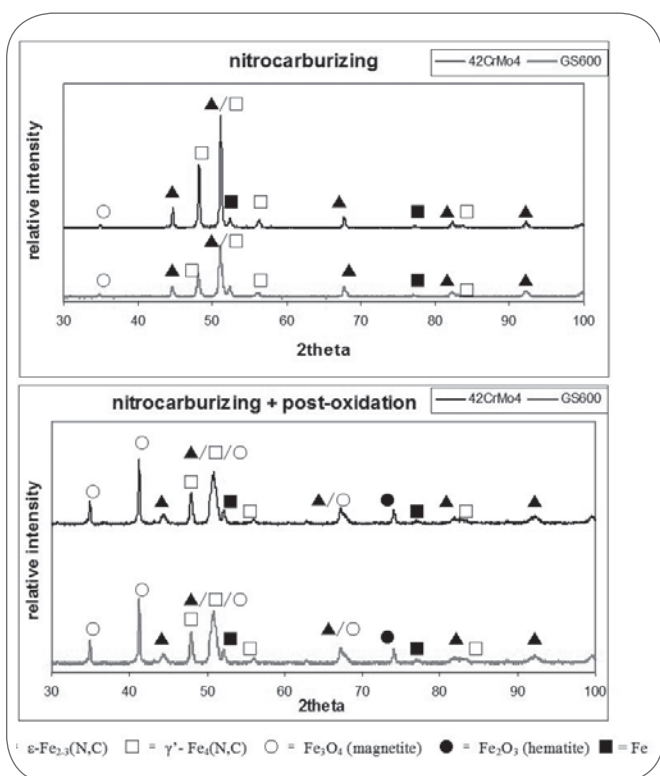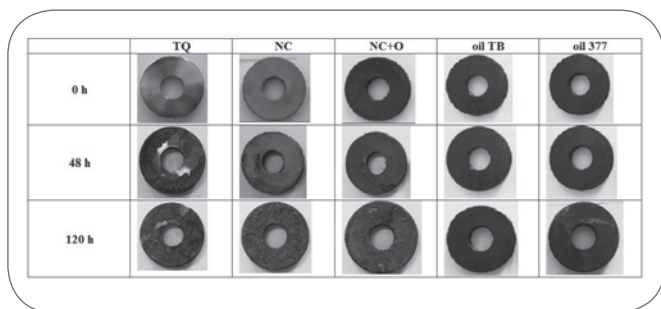
▲
Fig. 6

Corroded 42CrMo4 samples after salt spray test (fog).
Campioni di 42CrMo4 dopo il test di corrosione in nebbia salina.

fact probably occurs because the 377 oil diffuses sooner into solution, so it gives a minor protection to the samples. In the Fig. 6 are showed the images acquired on 42CrMo4 samples at the beginning of the test, after 48 h and after 120 h.

The salt-spray test results are partially confirmed by the value of open circuit potential measured in an electrochemical cell (FLAT CELL K0235, PAR), using as working electrode the samples tested, the counterelectrode is a platinum grid, and a silver / silver chloride or Ag/AgCl (satured) as the reference electrode. The electrolytic solution is HCl 0.1M. The potential (E) reported in the Tab. 5 are the potential value measured at the beginning of the test, as soon as the sample is in contact with the acid solution, and the potential value after 50 minutes of degassing with a nitrogen flux at high partial pressure.

Using the instrument convention, the nitrocarburizing, in both materials, doesn't improve the corrosion resistance with respect to untreated samples, unlike what emerged from the salt spray test. This is probably due to the different media used to carry out the two experiment. Instead the post-oxidation and the lubricant oil impregnation determine a decisive corrosion resistance improvement. During the 50 minutes of degassing, the corrosion protection given by lubricant oil remains, on the contrary the protection given by post-oxidation treatment vanishes during the degassing stage. In general, the 42CrMo4 presents a better corrosion resistance.

In fact, nitrocarburizing, usually, doesn't improve much the corrosion resistance because the inner part of white compound layer is porous, and localized corrosion phenomena are favourite [6]. Post-oxidation treatment, in fact, is performed to improve corrosion resistance, because this treatment promotes the formation of a very thin magnetite (Fe_3O_4) layer (1-2 μm) above the nitrocarburized layer, and causes a partial constipation of pores, present in the nitrocarburized layer, because this oxide grows inside the

pores [7,8]. The decisive improvement measured in case of oil impregnation is ascribed in case of oil coating acting as an electrical barrier, blocking or slowing electronic transfer at the treated material / solution interface [9].

CONCLUSIONS

New post nitrocarburizing treatments, in particular post-oxidation and impregnation in two different lubricant oil were performed on 42CrMo4 and GS600, in order to improve wear and corrosion resistance.
It can be concluded:
1. The gas nitrocarburizing forms a superficially compounds zone (15-20 μm thickness) laying on a diffusion zone that is about 100-120 μm thick in the cast iron and 150-220 μm thick in the steel. In the steel the nitrocarburized layers are homogenous and have constant thickness in whole the sample, but this doesn't occurs in the cast iron. The post-oxidation increases the diffusion layer thickness and the Fe_3O_4 oxide formed fills partially the porosity of the nitrocarburized surface.
2. In the steel, all the treatments improve decisively the wear resistance, specially the lubricant oil impregnation; instead between the nitrocarburized and the nitrocarburized and post-oxidised samples there aren't relevant differences in terms of sample volume removed. Between lubricant oils, the best wear resistance is achieved using TB oil.
3. The application of nitrocarburizing alone does not significantly improve corrosion resistance and it may even promote localized corrosion. The subsequent post-oxidation step leads to a slight decrease of the corrosion rate, because it partially seals the porous nitrocarburized layer. The final oil impregnation step resulted much more effective in further decreasing the corrosion rate by and this final treatment in some cases improves also the wear resistance.
4. In general the GS600 untreated and treated present a better wear resistance and a worse corrosion resistance than 42CrMo4. Regarding wear resistance all the treatments worsen the sample volume removed, instead, the treatments greatly improve the corrosion resistance, specially the final lubricant oil impregnation.

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material	treatment	E (t = 0) [V]	E (t = 50 min) [V]	material	treatment	E (t = 0) [V]	E (t = 50 min) [V]
42CrMo4	TQ	-0.477	-0.524	**GS600**	TQ	-0.519	-0.619
	NC	-0.543	-0.502		NC	-0.522	-0.623
	NC+O	+0.335	-0.508		NC+O	+0.100	-0.647
	oil TB	+0.477	+0.415		oil TB	+0.386	-0.609
	oil 377	+0.405	+0.386		oil 377	+0.258	-0.617

▲
Tab. 5

Open circuit potential. With the notation instrument, the more the potential is positive the more the material in noble.
Potenziali a circuito aperto. Con la convenzione dello strumento, più il potenziale è positivo e più il materiale è nobile.

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ABSTRACT

SVILUPPO DI TRATTAMENTI POST-OSSIDATION PER MIGLIORARE LA RESISTENZA A USURA E CORROSIONE

Parole chiave: nitrocarburazione, post-ossidazione, impregnazione in olio, usura, corrosione

La nitrocarburazione ferritica è un noto trattamento termochimico di indurimento superficiale che si esegue su leghe ferrose per incrementarne la resistenza a fatica e la resistenza ad usura. I materiali così trattati mostrano generalmente una resistenza a corrosione non ottimale a causa della porosità dello strato dei composti che si forma durante tale trattamento termochimico, promuovendo quindi fenomeni di corrosione localizzata [1]. Per migliorare la resistenza a corrosione, è oramai pratica comune post-ossidare i componenti nitrocarburati. Il miglioramento della resistenza a corrosione è ottenuto grazie alla formazione di un sottile film di ossido (Fe_3O_4), che riempie parzialmente la porosità dello strato dei composti [2]. Anche a seguito della post-ossidazione permane della porosità superficiale residua che può essere oggetto di un trattamento finale di impregnazione in oli lubrificanti, per apportare un ulteriore contributo alla resistenza a corrosione e usura dei materiali trattati.

Scopo del presente lavoro è lo sviluppo, l'ottimizzazione e la caratterizzazione di tre trattamenti post-nitrocarburazione, nella fattispecie, post-ossidazione, post-ossidazione seguita da impregnazione in olio lubrificante RUST VETO TB e post-ossidazione seguita da impregnazione in olio RUST VETO 377, al fine di incrementare simultaneamente la resistenza a usura e a corrosione dell'acciaio 20MnCr5 e della ghisa sferoidale GS600.

Accanto alle tradizionali indagini metallografiche (microscopia ottica ed elettronica, microdurezza Vickers, diffrazione a RX), la caratterizzazione dei campioni trattati e non trattati ha incluso test di usura con un tribometro in configurazione ball-on-disk, prove di corrosione in nebbia salina (ASTM B117) e la misurazione dei potenziali a circuito aperto in una soluzione acida di HCl 0.1M.

Le prove sperimentali hanno mostrato che:

- La nitrocarburazione forma uno strato di diffusione, dello spessore di 150-220 μm, e superficialmente uno strato dei composti, spesso 15-20 μm. Nell'acciaio lo strato dei composti è omogeneo e presenta una spessore costante in tutto il materiale; al contrario la GS600 esibisce uno strato dei composti non omogeneo e con spessore variabile, probabilmente a causa della presenza della grafite che inibisce la diffusione del carbonio e dell'azoto nel materiale (Fig. 1, Fig. 2, Fig. 3). La post-ossidazione in entrambi i materiali incrementa lo spessore dello strato di diffusione o forma in superficie un film di Fe_3O_4, che riempie parzialmente la porosità dei materiali nitrocarburati (Fig. 4).

- Tutti i trattamenti, nelle condizioni di prova considerate, risultano essere più efficaci nell'acciaio che nella ghisa, sia per quanto riguarda la resistenza a usura che la resistenza a corrosione.

- Nell'acciaio tutti i trattamenti apportano un deciso incremento alla resistenza a usura, specialmente l'impregnazione finale negli oli lubrificanti, che determinano una diminuzione del tasso di usura superiore ad un ordine di grandezza; tra il tasso di usura dei campioni nitrocarburati e post-ossidati non ci sono differenze rilevanti, mentre tra gli impregnati il materiale che manifesta la migliore resistenza ad usura è l'impregnato nel RUST VETO TB.

- In generale la GS600 non trattata esibisce una migliore resistenza a usura ed un peggior comportamento a corrosione rispetto al 42CrMo4. Nelle condizioni di prova considerate, infatti, tutti i trattamenti incrementano il volume asportato dopo il test di usura e migliorano la resistenza a corrosione rispetto alla GS600 non trattata.

- La nitrocarburazione non migliora in modo significativo la resistenza a corrosione sia del 42CrMo4 che della GS600 perché tende a promuovere fenomeni di corrosione localizzata. La post-ossidazione diminuisce sensibilmente la velocità di corrosione dei materiali, poiché riempie parzialmente la porosità della superficie nitrocarburata. Ai fini della resistenza a corrosione decisiva è l'impregnazione finale nell'olio RUST VETO TB, che inoltre garantisce anche un basso tasso di usura.