

Industrialization of Ni- μ SiC electrodeposition on copper moulds for steel continuous casting

M. Lekka, P.L. Bonora, A. Lanzutti, S. Benoni, P. Caoduro, L. Fedrizzi

Copper moulds usually used for steel continuous casting suffer from severe wear at relatively high temperatures and low friction loads. The more severe solid friction occurs at about 10-40cm distance from the meniscus, depending on the process parameters, where the temperature is about 300-350°C. The copper moulds have been traditionally coated with hard chromium and actually also with thick nickel deposits even if they present lower wear resistance. The aim of this work was the development of a composite Ni- SiC electrodeposit with higher hardness and wear resistance than the pure nickel using the existing plating bath and commercially available SiC micro-powders. Different types of SiC micro-particles have been purchased and Ni- SiC deposits have been produced and analyzed, initially, in laboratory scale to evaluate the ability of the powders to be codeposited into the nickel matrix. After the choice of the SiC powder and the determination of the plating parameters a pilot 6000 lt plating tank has been equipped with a system of Venturi pumps in order to maintain the particles in suspension. Preliminary tests have been performed in industrial scale to evaluate the process parameters such as anode-cathode distance, applied voltage, plating time and pumps positioning effect onto the SiC content and its distribution in the nickel matrix. The produced specimens have been observed by Metallographic microscope and Scanning Electron Microscope in cross section to evaluate the SiC content and the microstructure of the nickel matrix. Vickers microhardness measurements have been also performed in cross section and revealed that the co-deposition of the SiC micro-particles leads to a microhardness increase of about 180%. Wear tests at both room temperature and at 350°C have been performed on pure nickel deposits and composite nickel deposits and the wear tracks have been analyzed using both a profilometer and SEM to determine the wear both coefficient and mechanism of each coating. The testing results revealed that the developed Ni- SiC deposit exhibits a much higher wear resistance in comparison to pure nickel deposits at high temperature and the production process can be easily transferred in industrial scale with slight modifications of the existing deposition plants. Real scale copper moulds have been finally coated with Ni- SiC composite deposits and are presently under testing in actual working conditions at a steel producing plant.

Keywords:

composite materials, nickel and alloys, continuous casting, coatings, tribology

INTRODUCTION

Steel continuous casting is mainly a heat-extraction process. The requirement for high thermal conductivity leads thus to the choice of copper and its alloys as the base materials for the moulds. Copper moulds used for continuous casting suffer from severe wear at relatively high temperatures as the solidifying strand moves through the vibrating at low frequencies mould. Wear resistance of the moulds inner part is at least as impor-

tant as heat conductivity. The more severe solid friction occurs at about 10-40cm distance from the liquid metal meniscus, depending on the process parameters, where the temperature is about 300-350°C [1-2].

For this reason the mould inner part has been traditionally coated by electrolytic hard chromium, nickel and their combination. During the last years the hexavalent chromium compounds are increasingly subjected to restrictions in Maximum Exposure Limits (MEL) monitoring rules, leading to increasing costs. For this reason many attempts have been made to replace hard chromium coatings mainly with either thermal spray or HVOF coatings [3-4]. In particular it was shown that a composite coating system consisting of a hard metal layer from the tungsten carbide family obtained by HVOF and subsequently treated with a slurry coating forming a pore free refractory oxide layer lead to a four-fold increase in the casting mould life [3]. On the other hand, the use of HVOF coating to replace hard chromium requires a complete change of the existing production plants and increased production costs in comparison to the traditional galvanic deposition.

A cheaper technology made available with slight modifications

M. Lekka, P.L. Bonora, A. Lanzutti, L. Fedrizzi

Department of Chemistry, Physics and Environment,
University of Udine, Via Cotonificio 108, 33100 Udine (UD), Italy;
mail:maria.lekka@uniud.it

S. Benoni

Benoni s.n.c.,

Via Gessi 24, 25135 S. Eufemia (BS), Italy;

E-mail:benoni@benoni.it

P. Caoduro

Caoduro Impianti S.r.l.,

Via Saviabona 102/G, 36010 Monticello Conte Otto (VI), Italy;

E-mail:info@caoduroimpianti.it

of the existing plants might be the co-deposition of hard particles in metal matrix coatings. The wear properties of the Ni/ SiC composite have been studied by many different research groups which demonstrated that these coatings could be a good candidate to substitute hard chromium coatings [5-12]. The addition of the SiC micro- or submicro-particles in the nickel matrix and their intrinsic hardness lead to a significant increase to both hardness and wear resistance of the composite coating. The aim of this work was the development of a composite Ni- μ SiC electrodeposit with higher both hardness and wear resistance than the pure nickel coating, using an existing plating bath and commercially available SiC micro-powder, leading to the industrialization of the process.

EXPERIMENTAL

Laboratory scale

Eight types of SiC powder with mean diameter ranging from 0.5 μ m to 2 μ m have been purchased from different suppliers in order to choose the most suitable one for the specific application. The different SiC powders have been observed by Scanning Electron Microscope (EVO 40 Zeiss). Composite Ni- SiC deposits have been produced in laboratory scale applying the same parameters used in industrial scale for the production of the pure nickel deposits. All the produced specimens have been embedded in resin in cross section, grinded, polished and observed by Scanning Electron Microscope in order to check the amount of codeposited SiC.

Modification and optimization of the existing pilot plant

After the choice of the SiC powder and the determination of the plating parameters a pilot 1500 lt plating tank has been equipped with a system of Venturi pumps in order to maintain the particles in suspension (fig. 1).

Some preliminary tests have been performed using water and colored glass spheres to determine the right position of the Venturi pumps, to adjust the flow and to get a uniform suspension of the glass spheres in the whole volume of the plating tank. As soon as the correct pumps position was established, the tank has been filled with nickel plating bath containing the SiC powder. The bath has been stirred for 48h and then two 100x36cm low carbon steel plates have been coated with composite deposit at high voltage for 24h (plate A) and at low voltage for 48h (plate B). The dimension of the steel plates has been chosen in order to cover the whole usable space of the plating tank. 18 specimens have been cut from each plate according the scheme of fig.2.

From each of these specimens 3 samples have been taken, embedded in resin, polished and observed in cross section by Light Optical Microscope. The SiC percentage in the metal matrix has been calculated using image elaboration.

Characterization of pure and composite nickel deposits

After the preliminary tests on steel plates aimed to verify the homogeneity of the SiC codeposition, both pure nickel and composite nickel have been deposited on copper both plates and disks using a low voltage for 72h (standard parameters for the deposition of thick nickel coatings on copper moulds plates). The microstructure of the obtained specimens has been observed by SEM in cross section after metallographic etching (50% nitric acid- 50% acetic acid). Vickers 0.3 microhardness measurements have been also performed in cross section using a Struers Duramin Vickers microhardness tester.

Wear measurements have been performed using a CETR UMT tribometer in a ball on disc configuration at both room temperature and at 350oC. The testing parameters are summarized in table 1.

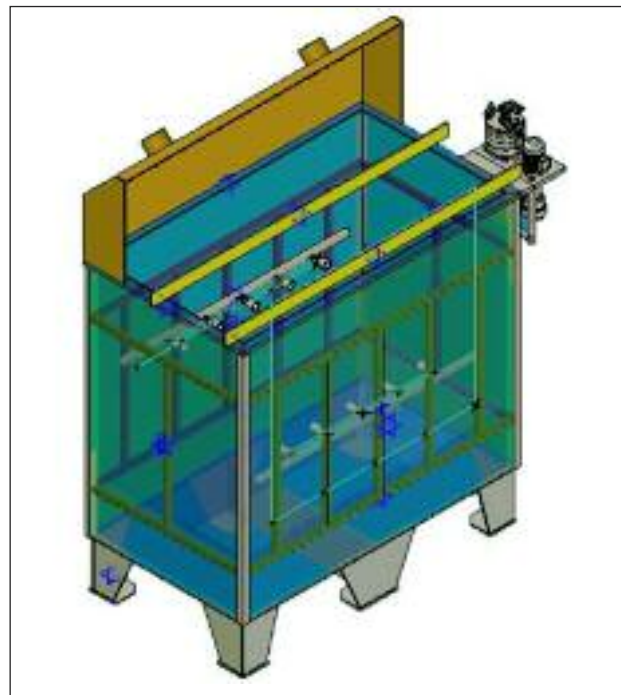


FIG. 1 Pilot plating plant.
Impianto pilota di deposizione.

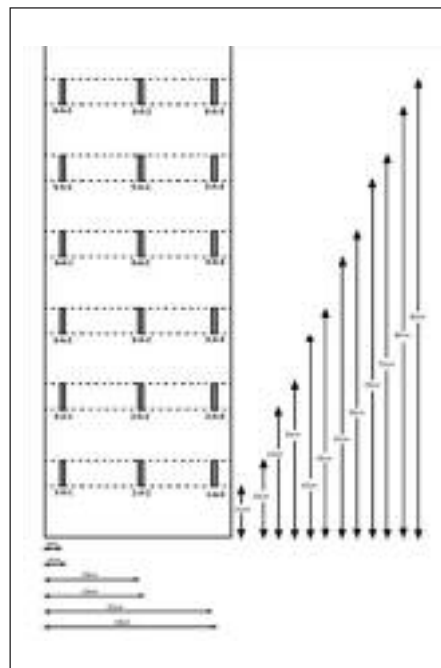


FIG. 2 Positioning and labelling of the specimens taken from the coated steel plates.
Localizzazione e denominazione dei campioni estratti dalle piastre in acciaio rivestite.

Counter material	WC sphere (d=9.5mm)
Applied load	70N
Test radius	18mm
Rotation speed	300rpm
Sliding speed	0.565m/s
Test duration	60min

TAB. 1 Wear tests parameters.
Parametri delle prove di usura.

The wear tracks have been observed by SEM in order to define the wear mechanism and the volume loss has been evaluated using a stylus profilometer (DEKTAK 150Veeco). The wear coefficient K [$10^{-6} \text{mm}^3/\text{Nm}$] has been calculated using the following equation:

$$K = \frac{V}{S \cdot F_z} \quad (1)$$

where V : volume loss calculated by the profilometer, S : the total wear distance and F_z the applied load.

RESULTS AND DISCUSSION

Laboratory Scale

The SEM micrographs of the 8 different SiC powders are reported in fig. 3 and the dimensions of the microparticles in table 2. As can be observed powders 1-3 have an acicular shape and a mean diameter of about $0.5 \mu\text{m}$. Powder 4 has acicular shape and a mean diameter of about $1 \mu\text{m}$, powders 5 and 8 an acicular shape and a mean diameter of about $2 \mu\text{m}$, while powders 6 and 7 a round shape and a mean diameter of about $2 \mu\text{m}$. The SiC amount in the nickel matrix composite deposits obtained in laboratory scale using the eight different types of powder is reported in fig. 4. The SiC volume percentage has been evaluated as the area percentage covered by SiC particles, using image analysis on the cross-section SEM micrographs of the composites.

As can be observed from fig. 3 the co-deposited SiC amount is much higher for the powder 5. This powder has been chosen to produce the specimens in industrial scale.

Optimization of the pilot plant

The SiC $v/v\%$ calculated by image analysis on the micrographs of the specimens taken from the steel plates according the scheme of fig. 2 is reported in fig. 5. The vertical position of the samples is reported in the horizontal axis and the horizontal position is reported with different grey tones.

As can be observed from fig 4 the coating deposited at low voltage presents a higher amount of SiC and a more uniform distribution along the whole plate, hence it was decided to proceed using the low voltage for the deposition.

As mentioned before, Vickers microhardness 0.3 measurements have been performed on the same specimens in cross section. The results are reported in fig. 6. From fig. 6 is evident that the composite deposits present higher microhardness values due to the presence of the SiC particles. The higher percentage of SiC in plate B leads to a microhardness increase of about 50HV.

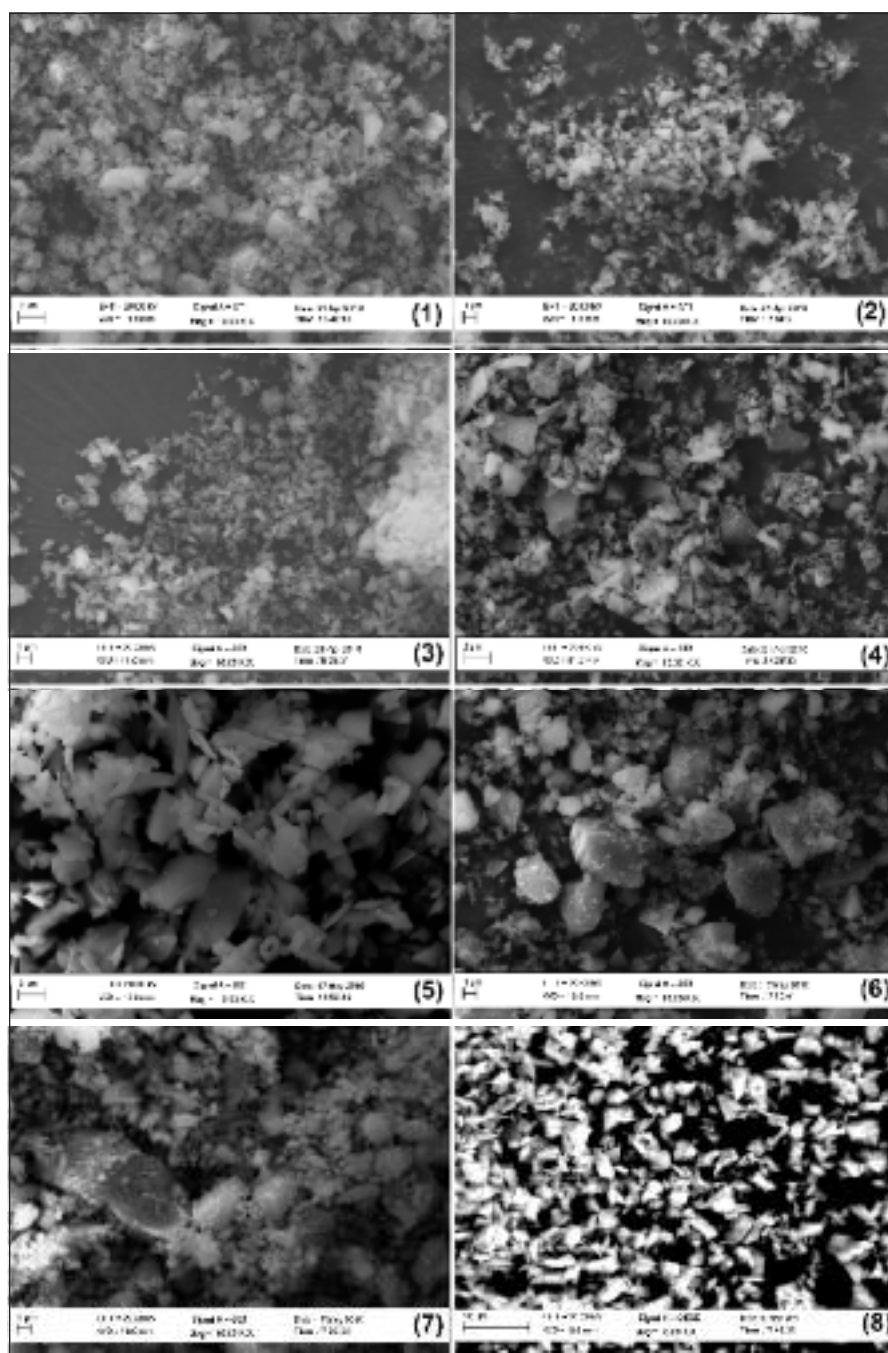


FIG. 3
SEM micrographs of the 8 types of SiC powders.

Micrografie SEM delle 8 tipologie di polveri di SiC.

Powder 1	0.2 – 2 μm
Powder 2	0.2 – 1.5 μm
Powder 3	0.2 – 1 μm
Powder 4	0.4 – 2.5 μm
Powder 5	0.5 – 5 μm
Powder 6	0.4 – 6 μm
Powder 7	0.4 – 5.3 μm
Powder 8	0.4 – 4 μm

TAB. 2 *SiC powders dimensions.*
Dimensioni delle polveri di SiC.

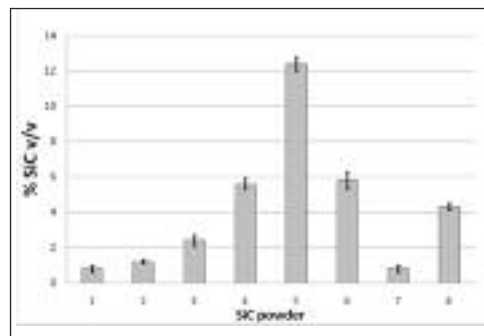
Characterization of pure and composite nickel deposits

The microstructure of both pure nickel deposits and composite nickel deposits in cross section after metallographic etching, obtained on copper substrate, at low voltage for 72h deposition (standard deposition parameters for the copper moulds) is reported in fig. 7.

As can be observed by the SEM micrographs the pure nickel deposit consists of large columnar grains, typical microstructure of this type of electrodeposits. The micro-composite coating presents a large amount of embedded particles randomly distributed. The codeposition of the micro-particles interrupts the columnar grain growth. The grain refinement of the metal matrix structure is typical for the nano-composite coatings and not for the micro-composite ones [8]. In this case the pure nickel coating presented very large columnar grains due to both the high thickness and the typical features of the plating bath used: thus even the codeposition of “large” particles lead to a grain refinement.

Also in this case Vickers 0.3 microhardness measurements have been performed in cross section and compared to the microhardness of hard chromium coatings. The results are reported in table 3.

Fig. 4
% SiC v/v in the nickel matrix for the 8 types of SiC powder in laboratory scale.



% SiC v/v nella matrice in nichel per le 8 tipologie di polveri di SiC utilizzate in scala di laboratorio.

The codeposition of the SiC microparticles lead to a microhardness increase of about 180%.

The friction coefficient of both types of coatings monitored during the wear tests at both room temperature and at 350oC is reported in fig. 8.

Regarding the pure nickel deposit tested at room temperature, the friction coefficient presents an almost stable value (about 0.65) for the first 3000s. Afterwards some oscillations are noticed which might be attributed to the detachment of a nickel oxide formed on the wear track during the test. The friction coefficient monitored during the wear test at 350oC presents an initial decrease and then remains almost stable at values of about 0.5. Also in this case there is the formation of a thicker nickel oxide which lowers the friction coefficient. The small oscillations might be attributed to the continuous detachment and re-formation of this oxide.

The composite coating tested at room temperature presents a friction coefficient of about 0.68 which remains almost stable during the whole test. The slight oscillations at the end of the test could be attributed to the detachment of oxides formed during the wear but these are less marked in comparison to the

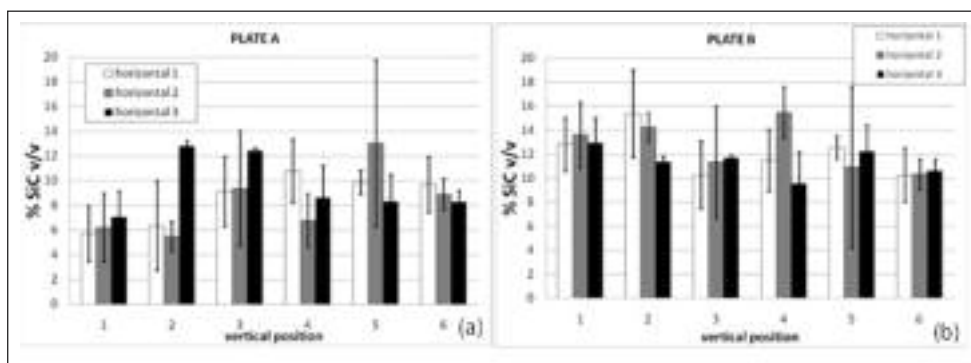


FIG. 5
%SiC v/v in the nickel matrix of the specimens taken from: a) plate A: high voltage – 24h of deposition, b) plate B: low voltage – 48h of deposition.

%SiC v/v nella matrice in nichel dei campioni prelevati da: a) lastra A: alta tensione – 24h di deposizione, b) lastra B: bassa tensione – 48h di deposizione.

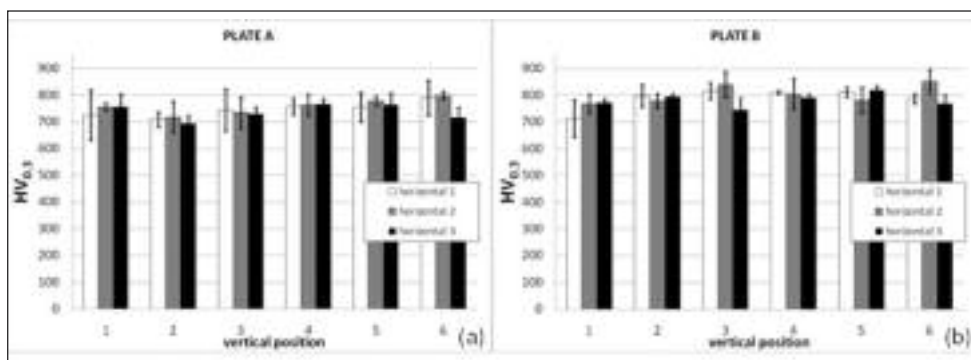


FIG. 6
HV_{0.3} of specimens taken from: a) plate A: high voltage – 24h of deposition, b) plate B: low voltage – 48h of deposition.

HV_{0.3} di campioni prelevati da a) lastra A: alta tensione – 24h di deposizione, b) lastra B: bassa tensione – 48h di deposizione.

Pure nickel	267 ± 9
Ni+ μ SiC	756 ± 20

TAB. 3 *Vickers 0.3 microhardness.*

Microdurezza Vickers 0.3.

pure nickel coating. The friction coefficient monitored during the wear test at 350°C presents a mean value of about 0.35, lower than that of the pure nickel. This could be attributed to the formation of a more stable oxide. Also in this case, the observed oscillations might be due to the continuous detachment and re-formation of the oxide layer.

The SEM micrographs of the wear tracks at the end of the tests are reported in fig. 9.

The wear track morphology and the EDXS analyses performed on different areas revealed that the wear mechanism of the pure nickel coating tested at room temperature is oxidative for the nickel and adhesive for the nickel oxide formed during the wear. Indeed on the light grey zones of fig. 9a a high amount of oxygen has been revealed as well as traces of Co and W coming from the counter material. It might thus be stated that initially there is a formation of a nickel oxide layer on the whole surface of the wear track. After the first 3000s there is the detachment of oxide flakes due to the adhesive wear between the counter material and the nickel oxide. The detached oxide flakes contribute to the wear mechanism acting as third abrasive body causing the scratches visible in fig. 8a.

During wear at 350°C on the pure nickel deposit there is the formation of a compact thick nickel oxide layer. Some small areas where the oxide flakes have been detached (light grey zones) are observable in fig. 9b. The detached material did not cause third body wearing in this case.

Considering the morphology of the Ni+ SiC wear track and the results of the EDXS analyses performed on different zones of the track it is possible to deduce that there is an oxidative wear fol-

lowed by adhesive wear. The light grey zones of fig. 9c are composed by nickel oxide with high amounts of W and Co (counter material). Compared to the pure Ni wear track there is a thicker and more stable Ni oxide layer and there are no scratches caused by the detachment of SiC particles. It could thus be deduced that the SiC particles firmly embedded in the nickel matrix cause a higher wear to the counter material and increase the contact area decreasing the contact pressure. Moreover the particles support the major part of the wear action and thus allow the formation of a thicker and stable nickel oxide. As a consequence the friction coefficient is more stable in comparison to that of the pure nickel coating tested under the same conditions. During the wear test at 350°C there is the formation of a compact nickel oxide layer (fig. 9d). Also in this case there are no scratches caused by the detachment of the SiC particles. Some small areas where the nickel oxide has been detached are observed in the wear track. The detachment of small oxide flakes might cause the observed oscillations of the friction coefficient. The wear tracks maps obtained using the stylus profilometer for the two types of coatings tested at both room temperature and at 350°C are reported in fig. 10. As can be observed the composite nickel coatings presented shallower and more uniform wear tracks at both room temperature and 350°C.

The volume loss during wear has been calculated from the profilometer wear track maps. The wear coefficient, calculated using eq. 1, for all types of coatings is reported in fig. 11.

Regarding the wear tests performed at room temperature, the composite nickel coating presents the lowest wear coefficient. The differences become more evident for the tests performed at high temperature. The codeposition of the SiC particles lead to a drastic increase of the wear resistance as the wear coefficient has been halved in comparison to pure nickel coatings.

Based on the laboratory and scaling-up positive results two tubular copper moulds and four copper mould plates have been coated with the micro-composite nickel coating and are now tested under real working conditions in a steel producing plant.

FIG. 7
Cross section SEM micrographs of: a) pure nickel, b) Ni+ SiC deposits after metallographic etching.

Micrografie SEM in sezione di depositi in a) nichel puro, b) Ni+ SiC dopo attacco metallografico.

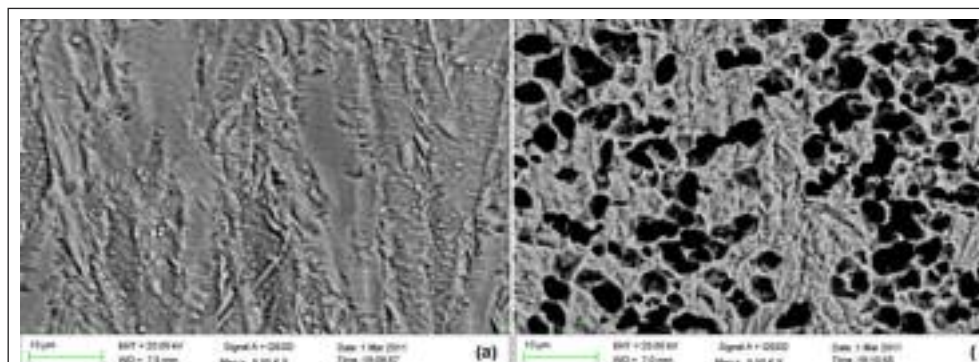
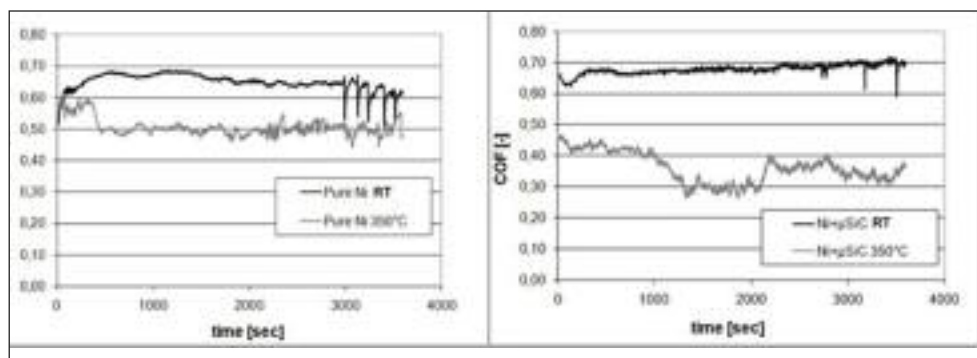


FIG. 8
Friction coefficient of pure nickel and composite nickel coatings during wear at both room temperature and 350°C. Coefficiente di attrito dei rivestimenti in nichel puro e nichel composito durante la prova di usura a temperatura ambiente e a 350°C.



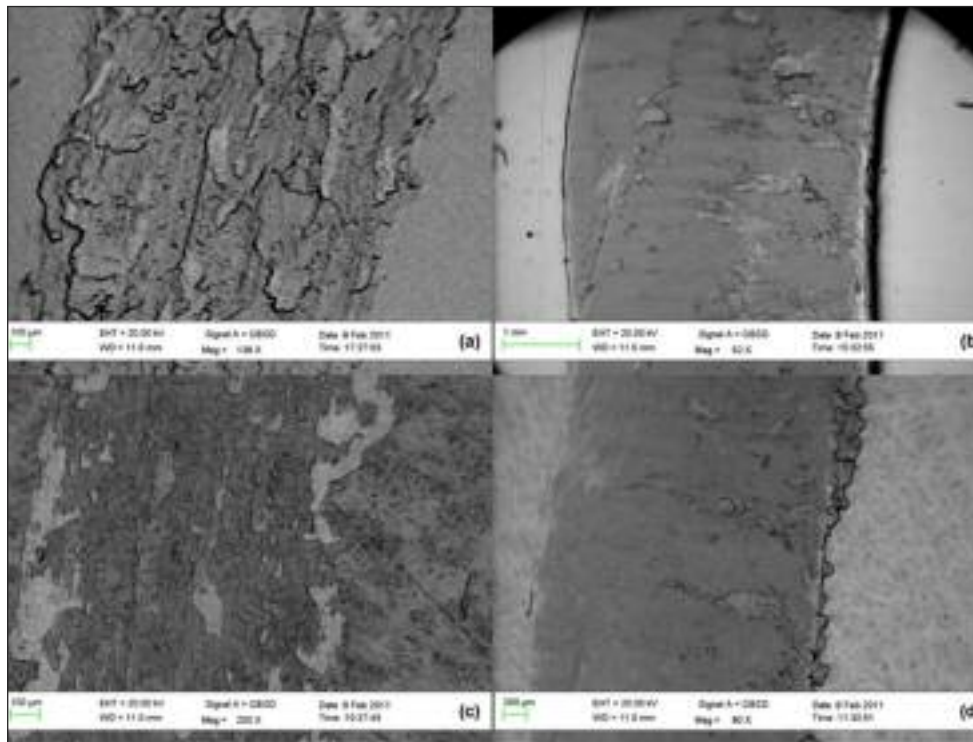


FIG. 9
SEM micrographs of the wear tracks on: a) pure Ni tested at room temperature, b) pure Ni tested at 350°C, c) Ni+ μ SiC tested at room temperature and d) Ni+ μ SiC tested at 350°C.

Micrografie SEM delle tracce di usura su a) Ni puro testato a temperatura ambiente, b) Ni puro testato a 350°C, c) Ni+ μ SiC testato a temperatura ambiente, d) Ni+ μ SiC testato a 350°C.

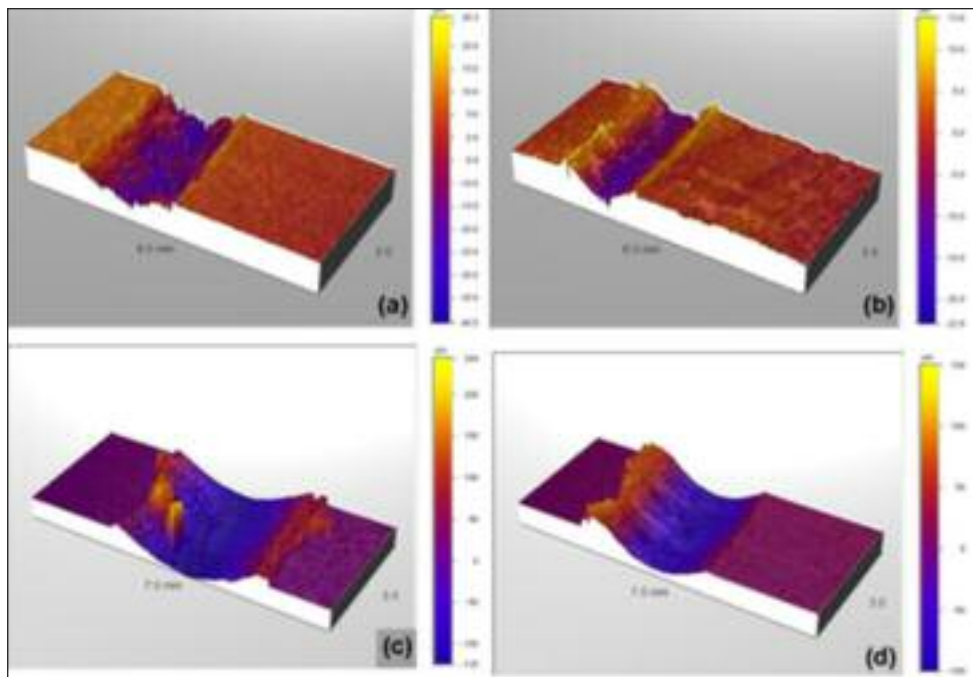


FIG. 10
Wear track maps of: a) pure Ni tested at room temperature, b) Ni+ μ SiC tested at room temperature, c) pure Ni tested at 350°C and d) Ni+ μ SiC tested at 350°C.

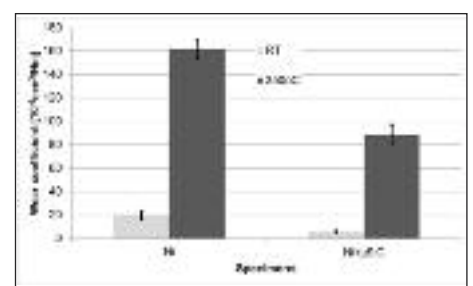
Mappe al profilometro delle tracce di usura di: a) Ni puro testato a temperatura ambiente, b) Ni+ μ SiC testato a temperatura ambiente, c) Ni puro testato a 350°C e d) Ni+ μ SiC testato a 350°C.

CONCLUSIONS

The aim of this work was the development of a composite Ni-SiC electrodeposit with higher both hardness and wear resistance than the pure nickel coating, both at room and at high (350°C) temperature, using existing plating bath and commercially available SiC micro-powder, leading to the industrialization of the process.

In the first part of this work different types of commercially available micrometric SiC powders have been used to choose the most appropriate for the deposition of a micro-composite deposit from a nickel sulphamate plating bath. After the choice of the SiC powder a pilot electrodeposition plant equipped with Venturi

FIG. 11
Wear coefficient of all tested deposits at both room temperature and 350°C.



Tasso di usura di tutti i rivestimenti testati a temperatura ambiente e a 350°C.

pumps aimed to maintain the SiC powder in suspension has been build. Preliminary deposition tests defined the right positioning of the pumps in order to obtain a uniform SiC distribution into the metal matrix.

After the definition of the process parameters the obtained composite deposits have been compared with pure nickel and hard chromium coatings regarding their microstructure, microhardness and wear resistance. It was shown that the pure nickel deposit consists of large columnar grains and that codeposition of the micro-particles interrupts the columnar grain growth. The composite deposits presented a 180% higher microhardness in comparison to the pure nickel coatings. The composite nickel coating presents also the lowest wear coefficient in room temperature.

The differences become more evident for the wear tests performed at high temperature. The codeposition of the SiC particles lead to a drastic increase of the wear resistance as the wear coefficient has been halved in comparison to this of the pure nickel coatings.

In conclusion it was shown that the composite Ni/ SiC coatings presented better performances compared to the pure nickel ones; consequently the production process has been successfully transferred from laboratory to industrial scale. Actual

shape and size copper moulds have been coated with the nickel matrix composite coating and are still tested under real working conditions in a steel producing plant.

REFERENCES

- S. Mazumdar, S. K. Ray, Sadhana, vol 26, Parts 1 & 2, February-April 2001, pp. 179-198
Y. Ma, X.D. Wang, X.Y. Zang, M. Yao, L. Zhang, S.H. Ye, Ironmaking and Steelmaking 37 (2010), 112-118
B.W. Allcock, P.A. Lavin, Surface and Coatings Technology 163-164 (2003), 62-66
A. Sanz, Surface and Coatings Technology 146147 (2001), 55-64
S.K.Kim, H.J.Yoo, Surface and Coatings Technology 108-109 (1998), 546-569
I.Garsia, J. Fransaeer, J.P. Celis, Surface and Coatings Technology 148 (2001), 171-178
K.H. Hou, M.d. Ger, L.M. Wang, S.T. Ke, Wear 253 (2002), 994-1003
M. Lekka, C. Zanella, P.L. Bonora, A. Krolkowska, Electrochimica Acta 55 (2010), 7876-7883
C. Zanella, M. Lekka, P.L. Bonora, Journal of Applied Electrochemistry (2009) 39:31-38
M. Lekka, N. Kouloumbi, M. Gajo, P.L. Bonora, Electrochimica Acta 50 (2005) 4551-4556
I.R. Aslanyan, J.P. Bonino, J.P. Celis, Surface and Coatings Technology 200 (2006), 2909-2916
A.A. Aal, K.M. Ibrahim, A.A. Hamid, Wear 260 (2006), 1070-1075.

Abstract

Industrializzazione dell'elettrodeposizione di rivestimenti in Ni/ μ SiC su lingottiere in rame per la colata continua dell'acciaio

Parole chiave: mat. compositi, nichel e leghe, colata continua, rivestimenti, tribologia

Il processo di colata continua è uno dei punti nevralgici dell'acciaieria moderna. Uno dei componenti più sollecitati dal punto di vista termico e meccanico è la lingottiera della colata continua. Questo vitale componente viene costruito in Cu puro o con leghe di Cu con o senza rivestimento. Le lingottiere, generalmente, sono soggette a un'usura severa causata dall'effetto sinergico di temperatura e carichi usuranti, causati dalla parziale adesione dell'acciaio solidificato e dal movimento alternativo cui il componente è sottoposto. Il danneggiamento della lingottiera avviene a circa 30-40 cm dal menisco (altezza dipendente dai parametri di colata) dove la temperatura della lingottiera è di 300-350 °C. Attualmente le lingottiere vengono rivestite con Cr duro o con rivestimenti spessi di Ni.

Il presente lavoro ha avuto come scopo lo sviluppo di rivestimenti galvanici innovativi compositi Ni- SiC con durezza e resistenza a usura maggiori rispetto al Ni puro. Tali rivestimenti sono stati prodotti con bagni galvanici e polveri di SiC commerciali. Sono stati prodotti, preliminarmente, vari tipi di rivestimenti micro-compositi utilizzando diversi tipi di polveri commerciali. Questi rivestimenti sono stati caratterizzati microstrutturalmente al fine di valutare la quantità di SiC inglobato nella matrice di Ni e la compatibilità del rinforzante ceramico con il processo di co-deposizione. In seguito, si è intervenuti sul processo di deposizione su scala industriale, equipaggiando una vasca galvanica di 6000 lt con agitatori fluidodinamici necessari per mantenere in sospensione le particelle di rinforzante. Gli agitatori scelti in questa ricerca sono di tipo Venturi alimentati da un circuito di pompe. Inoltre, sono stati fatti dei test preliminari su scala industriale per valutare i parametri di deposizione necessari a ottenere un rivestimento di buona qualità. In particolare sono stati valutati i seguenti parametri: distanza anodo catodo, differenza di potenziale applicata, tempo di deposizione e disposizione delle pompe al fine di distribuire omogeneamente le polveri nel bagno galvanico.

I campioni prodotti con impianto pilota sono stati osservati, in sezione trasversale, al microscopio ottico e al microscopio elettronico per valutare il contenuto di particelle rinforzanti e la microstruttura del rivestimento. Sono state eseguite delle misure di micro durezza, sempre in sezione trasversale, al fine di verificare le proprietà meccaniche del rivestimento. I risultati ottenuti hanno dimostrato che l'aggiunta di particelle ceramiche nella matrice di Ni comporta un aumento della durezza di circa il 180%. I test di usura sono stati effettuati in configurazione ball on disk, utilizzando come antagonista una sfera di carburo di tungsteno a secco, a temperatura ambiente e 350°C sia sui rivestimenti in Ni puro sia composito. Le tracce di usura così ottenute sono state analizzate al SEM e al profilometro per determinare il meccanismo di usura e il tasso di usura rispettivamente.

I risultati ottenuti hanno dimostrato che il rivestimento composito sviluppato possiede una maggior resistenza a usura rispetto al rivestimento in Ni tradizionale sia ad alta temperatura sia a temperatura ambiente. La deposizione su scala industriale, alla luce dei risultati ottenuti, è stata effettuata apportando delle leggere modifiche all'impianto galvanico tradizionale preesistente. Infine, sono state prodotte delle lingottiere rivestite con Ni- SiC e sono attualmente poste in esercizio in diversi impianti di colata continua.