Surface hardening of Al 7075 alloy by diffusion treatments of electrolytic Ni coatings

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A surface hardening process based on Ni coating and subsequent diffusion heat treatments was studied for Al7075 alloy. Nickel coatings with different thickness on 7075 Al alloy were obtained by electrolytic and electroless processes . Heat treatments in inert atmosphere at 500 °C and 530 °C for different times were performed in order to obtain surface hardening of the aluminum alloy by diffusion of Ni into the substrate. The effect of temperature and time on the depth of hardening was studied by SEM, EDS, Glow discharge optical spectrometry, microhardness tests and tribological tests.

Surface hardness higher than 1000 HV and depth of hardening higher than 100 mm were achieved by diffusion of Ni layers and formation of Al_3Ni_2 and Al_3Ni intermetallic phases .

The tribological test on Al7075 alloy against a hard Cr coated steel cylinder in air showed an average coefficient of friction μ of about 0.5 with a wide variation range, while all the coated and treated samples exhibited a coefficient friction of about 0.7. However, the wear scar depth of the hardened alloy is about 30 times lower than that of the Al 7075 alloy.

Key words: Aluminum alloys, Hardening, Ni coating, Heat treatments, Electron Microscopy, Wear

INTRODUCTION

Aluminum and its alloys are attractive for many application in chemical, automobile and aerospace industries because of their excellent properties as height strength-to- weight ratio, high electrical and thermal conductivities and good formability. However their hardness, wear resistance and mechanical properties are poor in comparison to steel resistance and continuous efforts are made in the research into new possibilities for making use of the advantage of the aluminum in application that were reserved up to now for harder and more wear-resistant materials. The solution mainly adopted is to produce a thick hardened layer on the substrate by laser surface alloying process [1-2], plasma vapor deposited PVD [3], chemical vapor deposited CVD [4] and diamond-like hydrocarbons coatings [5].

Recently, a method based on Ni-B electroless plating followed by diffusion heat treatment was proposed for improve the wear resistance of titanium alloys [6]. The diffusion of nickel and boron present in the coating allowed a remarkable hardening of the titanium alloy. It has been chosen to use the same method for the aluminum alloys. In this work, the effect of the diffusion of nickel and boron coating, obtained by electroless deposition, and Ni coating, obtaining by electrolytic process, on the hardening of the Al 7075 was examined.

EXPERIMENTAL

Specimens of 7075 Al alloy with a surface area of 12 cm^2 were obtained from a untreated rod and mechanically polished using standard metallographic procedures. The surface

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Component	Electroless bath	Electrolytic bath
Nickel chloride	24 g l^{-1}	-
Sodium acetate	36 g l^{-1}	-
DMAB	10 g l^{-1}	-
Sodium lauryl sulphate	0.1 g l^{-1}	-
Nickel sulphate hexahydrate	-	225- 410 g l^{-1}
Nickel(II)-chlorid-hexahydrat	-	30-60 g l^{-1}
Boric acid	-	30-40 g l^{-1}
pH	7	2-3
Temperature	65-70 °C	55 °C
Voltage	-	1 V
Current Density	-	0.1-0.2 A/cm^2

Table 1 – Composition of the deposition baths.

Tabella 1 – Composizione dei bagni di deposizione.

of the specimens was degreased with alcohol and air dried, then activated by chemical etching in a 6 % HF aqueous solution for 5 seconds. After chemical etching, the specimens were rinsed with a deionized water and immersed either in the solution for the electroless Ni-B deposition or in the solution for the electrolytic Ni deposition. The chemical compositions of the solutions are reported in Table 1. The procedures for preparing the solutions were suggested in the literature [7-10], even if the composition for electroless Ni-B deposition was optimized after several experiments, because the deposition was made without a preliminary Zn conversion coating on the samples, which is frequently used to improve electroless deposit adhesion.

Diffusion heat treatment of the plated specimens were carried out in a tubular furnace at 500° C and 530°C for different times in inert atmosphere. The coating morphology and alloy microstructure were characterized by optical microscope and by a Cambridge Stereoscan 440 SEM equipped with Philips PV9800 EDS. The specimen concentration profiles were obtained by a LECO GDS 750 A glow dischar-

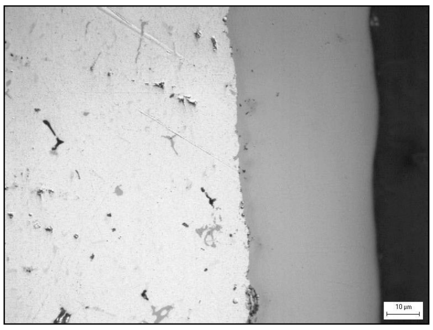

Fig. 1 – Ni electrolytic coating on Al substrate.

Fig. 1 – Rivestimento di Ni elettrolitico sul substrato di Al.

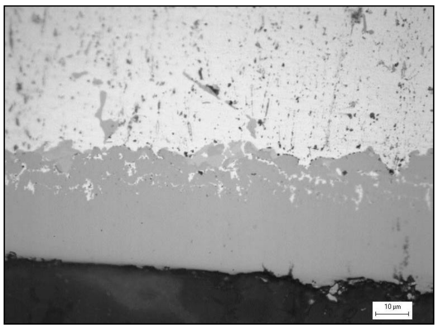

Fig. 2 – Ni electrolytic coating after heat treatment at 530°C for 12 h.

Fig. 2 – Rivestimento di Ni elettrolitico dopo trattamento termico a 530° C per 12h

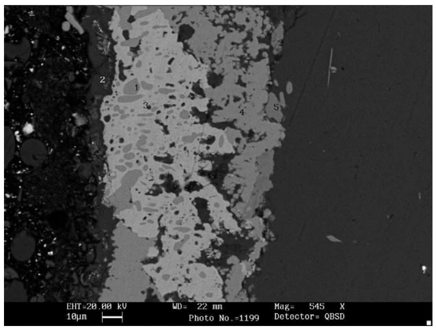

Fig. 3 – Ni electrolytic coating after heat treatment at 530°C for 24 h.

Fig. 3 – Rivestimento di Ni elettrolitico dopo trattamento termico a 530° C per 24h.

ge optical spectrometer (GDOS) with an anode surface of 4 mm^2 at 700 V with a current of 20 mA. The microhardness profile were obtained by a Leitz-Werlag microhardness tester with 100 g weight. The tribological behavior was investigated by dry sliding tests with a slider-on-cylinder tribometer. The stationary sliders consisted of the plated samples under investigation, whereas the rotating countermaterial was a hard chromium plated steel cylinder (thickness of the Cr coating: 300 µm; micro-hardness: 900 $HV_{0.3}$; roughness R_a: 0.1 µm).
The tests were carried out at 5 N applied load with a sliding speed of 0,6 m/s and sliding distance of 5000 m at room temperature. Both friction resistance and system wear (i.e. wear of the slider plus wear of cylinder) were continuously measured, using a bending load cell and a LVDT respectively, and recorded as a function of sliding distance. Values of the wear scar depths and widths on the slider and the cylinder were also evaluated at the end of each test by stylus profilometer. Wear tracks were examined by SEM and OM.

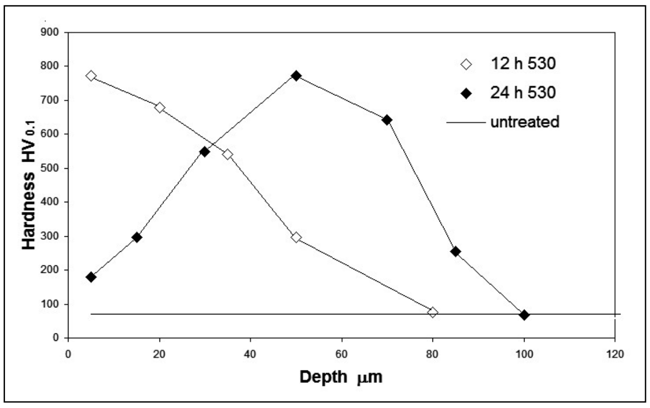

Fig. 4 – Hardness profiles of samples heat treated at 530°C for different times.

Fig. 4 – Profilo di durezza dei campioni trattati a 530° C per diversi tempi.

RESULT AND DISCUSSION

Ni electrolytic deposition

Optical microscopy analysis of the electrolytic coating showed that the layer, constituted by metallic nickel, was uniform, adherent and thick about 20-40 µm (fig.1).
The diffusion heat treatments, performed at 530° C for 4, 12, 24 h, induced the migration of Ni into the substrate and the diffusion of the alloying elements towards the surface with the formation of a diffusion layer about 40-60 µm depth, as it is shown in the fig. 2.
Increasing the time of heat treatment the thickness of diffusion zone increased and became less uniform (fig.3). EDS analysis showed that after 12 h heat treatment, the zone of diffusion was constituted mainly by Al (82% at.) and Ni (18% at.). After 24 h heat treatment the composition was not homogenous and it was possible to distinguish three different zones (fig.3). The dark thin surface one of about 5 µm was constituted mainly by Al (81 % at.) and Mg (17.39 % at.) and only by 0.77 % at. of Ni. In the intermediate layer, thick about 50 µm, it was detected a constant amount of 20% at. of Ni with a variable composition of Al and Cu. The concentration of Al and Cu was 64% and 2% in the light grey phases, while 77% and 14% in the dark grey phases. The atomic ratio Al/Ni was near to 3, suggesting that Al_3Ni was formed. At the interface with substrate there were some little areas rich in Fe (4% at). The hardness profiles of the heat treated at 530°C for 12-24 hours were reported in Fig. 4. The sample 12 h treated showed a surface hardness of 770 HV_{100} which rapidly decrease to about 300 HV_{100} in 50 µm which correspond to the depth of diffusion layer, suggesting that the presence of Ni is the responsible of increase of hardness. For the samples 24 h heat treated a surface hardness of 180 HV_{100} was recorded, which increases to about 800 HV_{100} at 50 µm depth. This because, as showed form SEM analysis, the outer layer is rich in Al and Mg migrated from the bulk to the surface, while the intermediate zone is constituted mainly in Al_3Ni, as revealed by EDS analysis, suggested that this intermetallic is the main responsible of the hardening of this layer. Moreover the high spread of the hardness values was ascribable to the different amount of Cu founded by EDS analysis and in particular the highest values have been measured at about 40 µm from the surface where the concentration of copper is lower. Obviously the longer diffusion time produces a thicker diffusion layer.
Because both the front of diffusion and profile of hardness were not uniform it has been chosen to diminish the temperature of heat treatment from 530°C to 500°C, to limit the phenomena of element migration from substrate to surface, maintaining the diffusion time of 24 h.
Fig. 5 showed the sample treated at 500°C for 24 h, where is present an unique uniform and compact zone of diffusion of

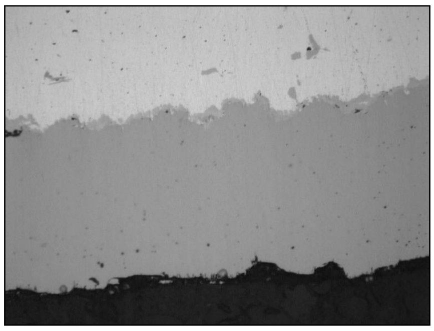

Fig. 5 – Ni electrolytic coating after heat treatment at 500°C for 24 h.

Fig. 5 - Rivestimento di Ni elettrolitico dopo trattamento termico a 500° C per 24h.

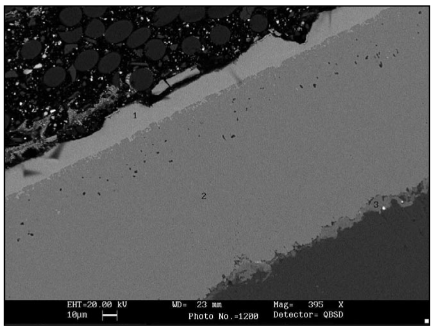

Fig. 6 – Ni electrolytic coating of about 80 μm after heat treatment at 500°C for 24 h.

Fig. 6 – Rivestimento di Ni elettrolitico di 80 μm dopo trattamento termico a 500° C per 24h.

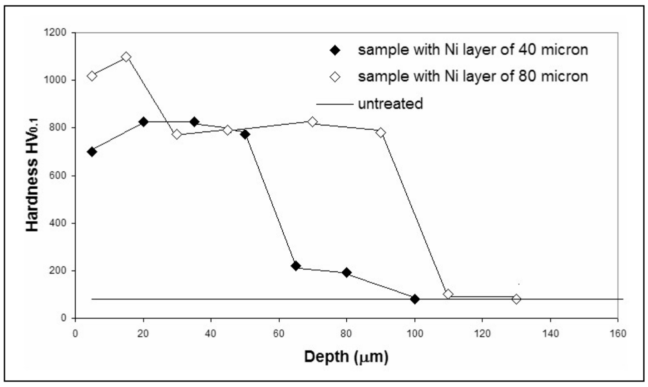

Fig. 7 – Hardness profiles of samples heat treated at 500°C for 24 h.

Fig. 7 – Profilo di durezza dei campioni trattati a 500° C per 24h.

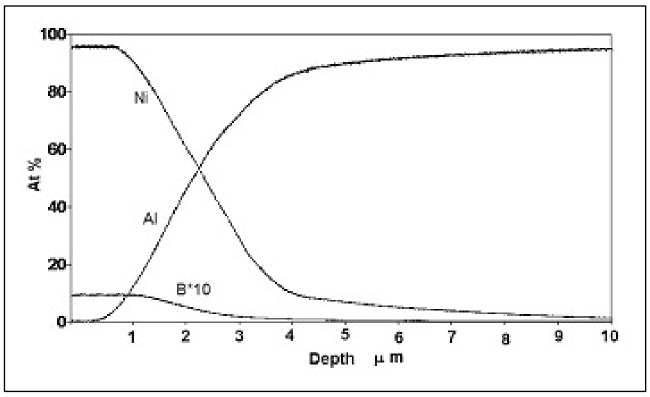

Fig. 8 – GDOS depth profiles of NiB coating on Al substrate.

Fig. 8 – Profilo GDOS del rivestimento NiB sul substrato di Al.

about 60 μm which from EDS analysis resulted to be constituted mainly by Al_3Ni. The hardness profile of the samples are reported in fig.7. The values of hardness are almost constant at 800 HV for about 50 μm due to the presence of Al_3Ni.
Samples with a coating of about 80 μm, twice of the others samples studied, showed, after 24 h heat treatment at 500° C, two different compact layers of diffusion: one outer zone with a thickness of about 10 μm and one inner zone with thickness of about 80 μm (Fig. 6).
From EDS analysis the outer zone resulted constituted mainly of Al_3Ni_2, while the main constituent of the inner zone was Al_3Ni. The hardness profiles showed that in proximity of the surface the hardness values of 1000 HV were reached, which correspond to the hardness of Al_3Ni_2 [11]. The value of 800 HV of the inner zone is ascribable to the presence of Al_3Ni as main constituent.

Ni-B electroless deposition

Analysis of the electroless coating revealed that the plating bath allowed the deposition of an amorphous, uniform and dense Ni-B layer on the 7075 Al alloy.

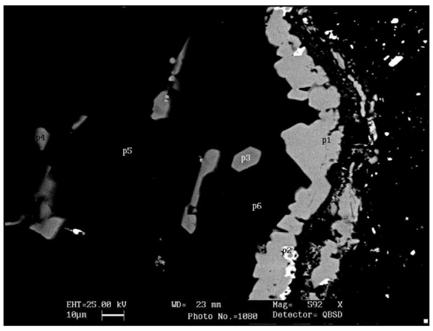

Fig. 9 – NiB coating after heat treatment at 530°C for 24 h.

Fig. 9 – Rivestimento di NiB dopo trattamento termico a 530° C per 24h.

The GDOS analysis showed that the layer was about of 10 μm with an average boron content of 1 wt %, (Fig.8).
The heat treatment were carried out at 530°C for different times. Until 24 h the diffusion was limited. After 24 h heat treatment an irregular diffusion zone between the coating and the substrate, thick only about 10 μm, was observed (fig.9). From EDS analysis, the diffusion zone was constituted mainly by Al with a ratio Al/Ni near to 3. In the white spots of fig.9, the presence of a relevant amount of Cu (6% at.) has been recorded, which was migrated towards the surface during heat treatment. It was observed that the Ni diffused along boundary grain. In fact, isles with a different concentration of Ni (12 % and 6% at., at a depth of 30 μm and 100 μm, respectively) were found until a depth of 100 μm from the surface, while only trace of Ni was detected around the isles of diffusion, even if near to the surface layer of diffusion. An increase in hardness has been recorded in correspondence of the thin layer of diffusion and of the Ni-rich isles, where values of about 550 HV_{100} and 250 HV_{100} have been measured, respectively. The boron diffusion seems to not influence the hardness of the substrate, unlike in titanium alloys [6].

Tribological tests

The first set of tests was carried out at 5N load with a sliding speed of 0,6 m/s for a sliding distance of 5000 m. Untreated samples have been compared with Ni coated and heat treated (at 500° for 24 h) samples. The coefficient of friction of untreated samples as a function of sliding distance displayed a wide range of variation with an average value of about 0.5, while the coefficient friction of all the treated samples showed a smoother trend and an average value of about 0.7 (fig.10). The values of the wear scar depths on the untreated samples were about of 300 μm, 30 times greater than those measured on treated samples, because the surface hardness of treated samples is higher than untreated ones (fig. 11). The lower hardness can also account for the lower average value of the coefficient of friction of untreated samples: the ploughing component of sliding friction is lower for soft untreated samples than for hard treated samples. The wide variation range in the coefficient of friction of untreated samples can be due to stick/slip motion and extensive grooving of the soft slider, whereas the smooth trend of the coefficient of friction of treated samples is due to gradual micropolishing of the hard slider.
The presence of adhesive yielding and cracks was not observed in treated samples, because the stronger bond between coating and substrate after heat treatment, due to the formation of intermetallics, ensures higher deposition adherence.

CONCLUSIONS

Heat treatments of Ni electroplated on 7075 Al substrate for different times and temperatures allowed the interdiffusion of Ni and element of the constituted principally of Ni and Al

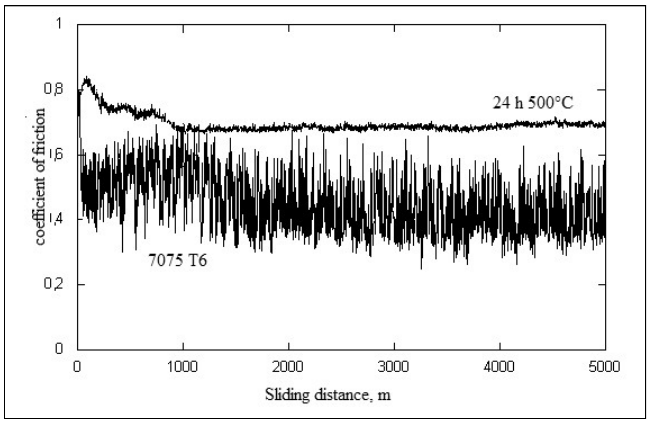

Fig. 10 – Coefficient of friction of Al 7075 T6 and samples Ni coated and treated at 500°C for 24 h.

Fig. 10 – Coefficiente di frizione della lega Al 7075 T6 e del campione nichelato elettrolit. e trattato a 500° C per 24 h.

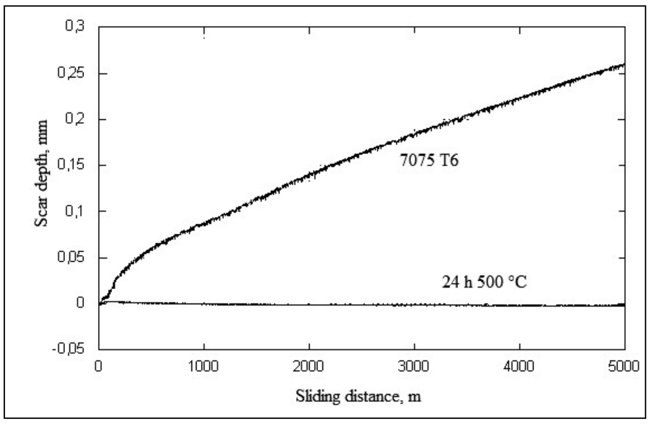

Fig. 11 – Scar depth of Al 7075 T6 and samples Ni coated and treated at 500°C for 24 h.

Fig. 11 – Profondità del solco della lega Al 7075 T6 e del campione nichelato elettrolit. e trattato a 500°C per 24 h.

alloy with the formation of a hard diffusion layer. The better results have been obtained after 24h of heat treatment at 500°C which led to a more uniform zone of diffusion

Surface hardness higher than 1000 HV and depth of hardening of about 100 µm were achieved by diffusion of Ni layers and formation of Al_3Ni_2 and Al_3Ni intermetallic phases.

For Al alloys the presence of boron not increase the hardness of the substrate, and electroless coatings are not so efficient in hardening like electrolytic coatings, because their thickness is lower.

The tribological test on Al7075 alloy against a hard Cr coated steel cylinder in air showed an average coefficient of friction of about 0.5 with a wide variation range, while all the coated and treated samples exhibited a coefficient friction of about 0.7. However, the wear scar depth of the hardened alloy is about 30 times lower than that of the Al7075 alloy.

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ABSTRACT

INDURIMENTO SUPERFICIALE DELLA LEGA AL 7075 MEDIANTE TRATTAMENTI DI DIFFUSIONE DI RICOPRIMENTI DI Ni

Parole chiave: trattamenti termici, alluminio e leghe, microscopia elettronica, tribologia

In questo lavoro è stato studiato un processo di indurimento superficiale per la lega Al 7075 attraverso deposizione di uno strato di Ni e successiva diffusione termica.

I rivestimenti di Ni con spessori variabili tra 10 e 80 _m sono stati ottenuti mediante un processo di deposizione di Ni elettrolitico o di Ni-B chimico (tab.1). I trattamenti termici, il cui scopo è quello di indurre la diffusione del Ni all'interno del substrato, sono stati effettuati in forno in presenza di atmosfera inerte alle temperature di 500° e di 530° C per tempi variabili. L'effetto della temperatura e del tempo di trattamento termico sull'indurimento superficiale della lega è stato investigato mediante SEM, EDS, GDOS, prove di microdurezza e tribologiche.

I trattamenti termici condotti sulla lega di alluminio con lo strato di Ni elettrolitico ha permesso la interdiffusione del Ni e degli elementi del substrato portando alla formazione di uno strato esterno indurito costituito principalmente da Ni e Al. I risultati migliori sono stati ottenuti con il trattamento termico a 500° C per 24 h che ha permesso la formazione di uno stato di diffusione compatto ed uniforme costituito da Al3Ni2 e Al3Ni (fig. 5-6). Con questo trattamento sono stati ottenuti valori di durezza di circa 1000HV100 per uno spessore di 100 _m (fig. 7). Temperature maggiori producono uno strato di diffusione meno uniforme e con valori di durezza inferiori (fig. 3-4).

Per le leghe di alluminio la presenza di boro non contribuisce ad aumentare la durezza del substrato e inoltre la deposizione chimica risulta meno efficace nell'indurimento della lega rispetto a quella elettrolitica in quanto i rivestimenti ottenuti presentano uno spessore inferiore (fig. 9).

Le prove tribologiche condotte con un cilindro di acciaio rivestito al cromo mostrano un valore del coefficiente di frizione di 0,5 per la lega Al7075 e di 0,7 per i campioni nichelati trattati termicamente (fig. 10). Tuttavia la profondità dei solchi dei campioni sottoposti al trattamento di indurimento superficiale risulta inferiore di circa 30 volte rispetto alla lega Al 7075 per le prove condotte con un carico di 5 N (fig. 11).