

Carbon influence in the nitrocarburized layers

A. Bavaro, G. Pizzi, A. Visconti

MEMORIE

In this paper the influence of carbon in the nitrocarburized layers is evaluated. The nitrocarburized layer can be obtained by various processes (salt and gaseous methods), that produce layers with different carbon content percentages. By the simple test method that consists in calculating the numbers and lengths of cracks generated by Vickers indentations, it has been possible to classify the various processes of nitrocarburizing. The tests have demonstrated the importance of carbon percentages on the fracture toughness of nitrocarburized layers.

INTRODUCTION

In Our days ferritic nitrocarburizing is performed according to different processes that anyway cause on the treated materials the presence of

a) A layer of compounds (or of combinations) constituted by carbonitrides ϵ and/or γ' of a variable thickness of 3 to 20 micron to which are usually attributed especially all the capacities of resistance to anti - friction and nitrocarburized, corrosion -of the pieces that have been nitrocarburised.

b) A diffusion layer with various quantities of precipitate nitrides of variable thickness of 100 to 500 microns to which are mainly attributed all the capacities of fatigue resistance and to the specific pressures of the treated pieces,

In some special applications (e.g. pieces of piston rods of the crank shafts) the layer of the compounds must also have an exceptional ductility to resist the strong and variable specific pressures that arise in the contact zones of the bearings. What is required from the compounds are:

- a) A determinate thickness
- b) To be "compact"
- c) To be "adhesive"

The "thickness" can be easily regulated by the action especially on the time of "soaking time" and on the composition of the atmosphere (relation between ammonia and hydrogen).

The "compactness" was really a capacity at a risk" especially with the old processes performed in salt baths while nowadays it can be easily obtained as a standard feature of the modern processes.

The "adhesion" that used to be normally evaluated by a metallurgical test (sic!) while locating eventual "break" lines between the layer and the "basic material".

In fact this latter feature should be interpreted as a "ductility" or "fragility" of the nitrocarburized layers that has been influenced, in the same type of treated materials, by the process parameters that, keeping the same temperature, depend from the composition of the diffusive means (atmosphere or salt) that has been used.

The aim of this research job has been to verify the influence that the composition of the medium has on the (tenacity) toughness of the compound layer.

TYPES OF FERRITIC NITROCARBURIZING PROCESSES

The various types of processes as they have been proposed or used are summarized as (1) (2) (3) (4) (5) on table I (gaseous) and table II (salts),

| Type of gas | Gas ratio | Diffused elements | Commercial name |
|---|-------------|-------------------|-----------------|
| $\text{NH}_3 + \text{Endo}$ | 1\1 | N + C | NITEMPER |
| $\text{NH}_3 + \text{N}_2 + \text{CO}$ | 1\1.33\0,18 | N + C | NIT + CARB |
| $\text{NH}_3 + \text{N}_2 + \text{CO}_2$ | 1\1.38\0.23 | N + C + O | NITROC |
| $\text{NH}_3 + \text{Eso}$ | 1\1 | N + C + O | NITROC |
| $\text{NH}_3 + \text{N}_2 + \text{N}_2\text{O}$ | | N + O | ALNAT NO |
| $\text{NH}_3 + \text{N}_2 + \text{CH}_4$ | 1\1.43\0.08 | N + C | - |
| $\text{NH}_3 + \text{N}_2 + \text{C}_3\text{H}_8$ | | N + C | - |
| $\text{NH}_3 + \text{N}_2 + \text{Aria}$ | 1\1.25\0.25 | N + O | |
| $\text{NH}_3 + \text{Endo} + \text{Eso} + \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$ | | N + C + O | NITROTEC |
| $\text{N}_2 + \text{H}_2 + \text{CH}_4$ | | N + C | NITROC IONICA |
| $\text{NH}_3 + \text{N}_2 + \text{CH}_3\text{OH}_{\text{diss}}$ | 1\0.3\0.3 | N + C | BASONIT |

Table I - Ferritic nitrocarburizing processes.

Tab. I - Processi di nitrocarburazione ferritica gassosa.

| Commercial name | Diffused elements |
|-----------------|-------------------|
| TENIFER TF1 | N + C (+O) |
| SURSULF | N + C + S (+O) |

Table II - Ferritic salt nitrocarburizing processes.

Tab. II - Processi di nitrocarburazione ferritica salina

FEAURES OF THE NITROCARBURIZING MEDIUMS

Gaseous atmosphere

As the atmosphere has to be nitrocarburizing it shall have to be composed of mixtures that can transfer mainly nitrogen and carbon.

In the "Nitemper" treatment (know due to the studies of prenosil (2)) whose mixture is made up of 50% endo - gas +

A. Bavaro, Laboratorio Prove Bavaro Srl, Caravaggio
G. Pizzi, Soliveri Srl, Caravaggio
A. Visconti, Vacumm Spa, Trezzano S.N.

Paper presented at the 11° Congress of the Int. Fed. For Heat Treatment and Surface Engineering, organised by AIM, Florence, 19-21 October 1998

5/2000

50% of NH₃, in fact there is a % (percentage) of CO equal to 10% over very little % (percentage) of CO₂.

In the "nitroc" type of treatment the atmosphere is composed usually by 50% of NH₃, about 5% of CO₂ and the rest is N₂ (or dissociated ammonia).

The oxidizing action of CO₂ is inhibited by the presence of large quantities of H₂ and therefore there is a carburizing action due to (6) the formation of CO in the atmosphere; in this case there is an increase of the nitriding action of ammonia due to the decrease of hydrogen.

In the processes that use ammonia and nitrogen (or dissociated ammonia) with the addition of methane or propane the carburizing effect is for sure less efficient due to the fact that these hydrocarbons tend to separate at low temperature and to the high presence of large 110 (percentage) of hydrogen.

$$a_c = K' p CH_4 / (pH_2)^2$$

$$a_c - K'' (p CO)^2 / pCO_2$$

At 700°: K' 8 and K'' 0,8, but the % (percentage) of H₂ (partial pressure) is clearly above the partial pressure of CO₂ so that the activity of carbon by the methane is clearly lower than that of CO.

With the Basonit treatment there is a utilization of methanol that has been previously dissociated at 950° C (7) as an element carrying carbon.

In the treatments by ionic discharge the mixture is composed of nitrogen, hydrogen and methane so that it is easy to diversify the relative quantity of nitrogen and carbon.

The treatments called "alnat" cannot be considered nitrocarburizing because of the absence of the very elements give carbon.

Salt processes

The process using melted salts at 570 – 580° produce the diffusion of significant % (percentages) of nitrogen and carbon probably due to the presence of urea that, in case of sur-sulf, due to the presence of very little % (percentage) of sulphur there is an increase of % (percentage) of nitrogen in the layer of the compounds that come out to be composed mainly of nitrates.

THE TESTS

Materials

The tests have been performed on bars made of steel 42CrMo4 (rods diam. 30 mm, H 10 mm) and 41CrAlMo7 (corner cubes 15 mm) composed as shown in table III.

All the samples after rough grinding have been hardened and tempered so that the steel 42CrMo4 showed R - 1000 N/mm² (HV₁ 330) and the steel 41CrAlMo7 R = 1200 N/mm² (HV₁ = 400). Therefore the materials were chosen for their intrinsic ductility and because of their capacity to form nitrides that could be different due especially To very high % (percentage) of aluminium in the samples of 41CrAlMo7.

Surface treatments

N. 3 samples rectified and polished for any type of application have been exposed To the following surface heat treatments:

| Campione | C | Mn | Si | P | S | Cr | Ni | Mo | Al |
|-----------|------|------|------|-------|-------|------|------|------|-------|
| 42CrMo4 | 0.41 | 0.89 | 0.38 | 0.011 | 0.024 | 1.15 | 0.09 | 0.21 | 0.041 |
| 41CrAlMo7 | 0.40 | 0.57 | 0.38 | 0.015 | 0.021 | 1.55 | 0.2 | 0.35 | 1.12 |

Tab. III - Chemical composition of the tested.

Tab. III - Composizione chimica dei campioni provati.

- Gas nitriding at 560° C for 4 hours in atmosphere composed of ammonia and nitrogen (treatment n° 1)
- Ferritic nitrocarburizing at 560° C for 4 hours in atmosphere composed of ammonia, nitrogen and carbon dioxide ("nitroc" type) (treatment n° 2)
- Ferritic nitrocarburizing at 560°C for 4 hours in atmosphere composed of ammonia dissociated methyl alcohol and nitrogen ("Basonit" type) (treatment n° 3)
- Ionic ferritic nitrocarburizing at 560° per 4 hours in a mixture of gas N₂ + CH₄ + H₂ (treatment n° 4)
- Ferritic salt nitrocarburizing at 580° C for 4 hours in Tenifer TFI salts (treatment n° 5)
- Ferritic gas nitrocarburizing al 560° C for 4 hours in atmosphere composed of dissociated ammonia and also not - dissociated plus propane (treatment n° 6).

The nitriding treatment (n° 1) has been performed in order to obtain samples with combined layers without diffused carbon.

Surveys after surface treatments

Surface hardness

See table IV.

| Treatment | Steel | Hardness | | |
|-----------|-----------|----------|------|------|
| | | HV 0,5 | HV1 | HV5 |
| 1 | 42CrMo4 | 730 | 730 | 680 |
| | 41CrAlMo7 | 1100 | 1100 | 1050 |
| 2 | 42CrMo4 | 700 | 700 | 670 |
| | 41CrAlMo7 | 1150 | 1280 | 1225 |
| 3 | 42CrMo4 | 690 | 680 | 620 |
| | 41CrAlMo7 | 1200 | 1250 | 1150 |
| 4 | 42CrMo4 | 800 | 740 | 630 |
| | 41CrAlMo7 | 1030 | 1030 | 930 |
| 5 | 42CrMo4 | 680 | 680 | 570 |
| | 41CrAlMo7 | 900 | 900 | 900 |
| 6 | 42CrMo4 | 650 | 650 | 620 |
| | 41CrAlMo7 | 1170 | 1150 | 1030 |

Tab. IV - Surface hardness.

Tab. IV - Durezza superficiali.

Surface carbon content

The first survey has been performed by spectrographic analysis on the flat surfaces treated after light polishing with abrasive paper "grit 1000".

The average results that were obtained are show in table V. Due to the low % (percentage) of C on the sample of the ionic treatment, the metallographic survey has confirmed the absence of a compound layer probably due to the positioning.

The nitriding treatment causes an impoverishment of the surface due to the "decarburizing" action of the hydrogen.

The salt processes and those with dissociated (methanol) methyl alcohol show the largest contribution of carbon.

Compound layer thickness

This has been microscopically measured and the results are shown in table VI.

| Treatment | Steel | C% |
|-----------|-----------|------|
| 1 | 42CrMo4 | 0.15 |
| | 41CrAlMo7 | 0.12 |
| 2 | 42CrMo4 | 0.51 |
| | 41CrAlMo7 | 0.50 |
| 3 | 42CrMo4 | 1.4 |
| | 41CrAlMo7 | 1.21 |
| 4 | 42CrMo4 | 0.70 |
| | 41CrAlMo7 | 0.36 |
| 5 | 42CrMo4 | 1.30 |
| | 41CrAlMo7 | 1.50 |
| 6 | 42CrMo4 | 0.70 |
| | 41CrAlMo7 | 0.74 |

Tab. V - Surface carbon value.

Tab. V - Contenuti di carbonio superficiale.

| Treatment | Steel | Effective thickness (µm) |
|-----------|-----------|--------------------------|
| 1 | 42CrMo4 | 15 |
| | 41CrAlMo7 | 14 |
| 2 | 42CrMo4 | 11 |
| | 41CrAlMo7 | 12 |
| 3 | 42CrMo4 | 12 |
| | 41CrAlMo7 | 15 |
| 4 | 42CrMo4 | 12 |
| | 41CrAlMo7 | absent |
| 5 | 42CrMo4 | 20 |
| | 41CrAlMo7 | 13 |
| 6 | 42CrMo4 | 18 |
| | 41CrAlMo7 | 12 |

Tab. VI - Compounds layers' thickness.

Tab. VI Spessori degli strati dei composti.

| Treatment | Steel | Thickness (mm) |
|-----------|-----------|----------------|
| 1 | 42CrMo4 | 0.19 |
| | 41CrAlMo7 | 0.18 |
| 2 | 42CrMo4 | 0.17 |
| | 41CrAlMo7 | 0.18 |
| 3 | 42CrMo4 | 0.22 |
| | 41CrAlMo7 | 0.24 |
| 4 | 42CrMo4 | 0.23 |
| | 41CrAlMo7 | 0.15 |
| 5 | 42CrMo4 | 0.15 |
| | 41CrAlMo7 | 0.15 |
| 6 | 42CrMo4 | 0.25 |
| | 41CrAlMo7 | 0.18 |

Tab. VII - Effective case hard.

Tab. VII - Spessori efficaci di indurimento.

Effective thickness of hardening

This has been surveyed by tests of microhardening choosing as conventional hardness those at core ($HV_1 = 300$ for 42CrMo4 and $HV_1 = 360$ for 41CrAlMo7) + 100 HV.

The results are shown in table VII.

The morphology of the nitrocarburized layers

From the microscopic point of view the layers that have been obtained are not very different in a meaningful proportion.

The layers of the compounds in the salt process come out to be more porous and thicker than those of the gas processes. From the morphological point of view the diffusion layers of the steel 41 CrAlMo7 turn out with the distinctive feature of a more significant presence of nitrides that have precipitated on the edges of the grains comparing to those of samples in 42CrMo4.

Examine figures 1 and 2 that refer to the "Tenifer" process and Fig. 3 and 4 that refer to Basonit process (Dissociated methyl alcohol).

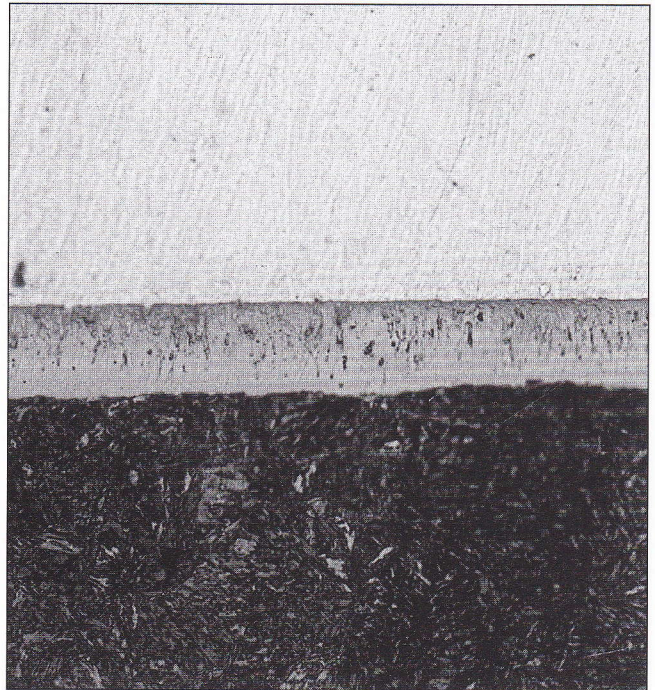


Fig. 1 - 42CrMo4 steel after Tenifer TF1 process (500 X).

Fig. 1 - Acciaio 42CrMo4 dopo processo Tenifer TF1 (500X).

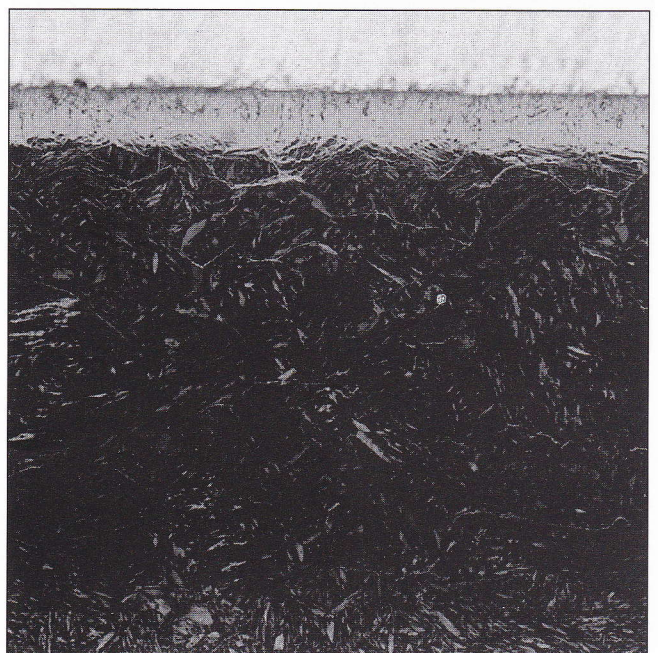


Fig. 2 - 41CrAlMo7 steel after Tenifer TF1 process (500X).

Fig. 2 - Acciaio 41CrAlMo7 dopo processo Tenifer TF1 (500X)

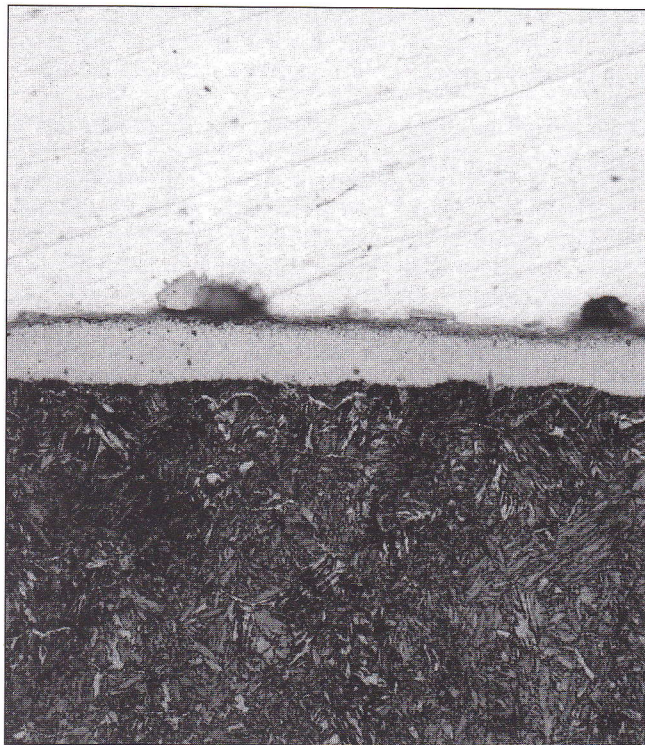


Fig. 3 - 42CrMo4 steel after Basonit Process (500X).
Fig. 3 - Acciaio 42CrMo4 dopo processo Basonit (500X).



Fig. 4 - 41CrAlMo7 steel after Basonit process (500X).
Fig. 4 - Acciaio 41CrAlMo7 dopo processo Basonit (500X)

GDS (Glow Discharge Spectrometry) analysis

It has been performed with a GDS 750 a spectrometer (that has been put at our disposal by the kind collaboration of Le-co Italy Srl) using only the samples in steel 41CrAlMo7.

The analysis of the quality type of carbon and nitrogen has shown a presence of carbon relatively high on the surface just polished and a clear net fail beyond the first 2 or 3 microns.

We have to think that the samples used for the analysis had not been prepared correctly before delivery.

Anyway, if we consider the values of the first microns of thickness, we can confirm the classification on the % (percentage) of carbon shown in table IV.

The survey method adopted in this case has already been used by other authors (5) that have expressed some perplexity with reference to values that have been found and that are of difficult interpretation.

Ductility survey

The method used is relatively empirical, by determining the maximum charge applied on a Vickers indenter that causes the formation of cracks both at the top of the marks.

As along the sides (circular cracks) (8).

The survey has been done by microscope at 1 000 X. The average results are exposed in table VIII.

| Process | Steel | Charge HV (kg) |
|---------|-----------|----------------|
| 1 | 42CrMo4 | 3 |
| | 41CrAlMo7 | 0.5 |
| 2 | 42CrMo4 | 5 |
| | 41CrAlMo7 | 2 |
| 3 | 42CrMo4 | 5 |
| | 41CrAlMo7 | 5 |
| 4 | 42CrMo4 | 3 |
| | 41CrAlMo7 | 0.5 |
| 5 | 42CrMo4 | 5 |
| | 41CrAlMo7 | 5 |
| 6 | 42CrMo4 | 5 |
| | 41CrAlMo7 | 2 |

Tab. VIII - Minimum HV charge causing cracks.

Tab. VIII - Carichi minimi HV che hanno determinato la formazione di cricche.

If we relate these values to the % (percentage) of carbon of table V we obtain some comparisons that show a significant proportions with regard to the samples made of the more fragile steel 41CrAlMo7 in the sense that if we increase on a live the percentage of carbon of the layer of the compounds consequently also you have the increase of the charge that causes the cracks in connection with the Vicker's marks.

For the steel 42CrMo4 this interdependence is more scattered even if we have to admit that there is a tendency in this sense (fig. 5).

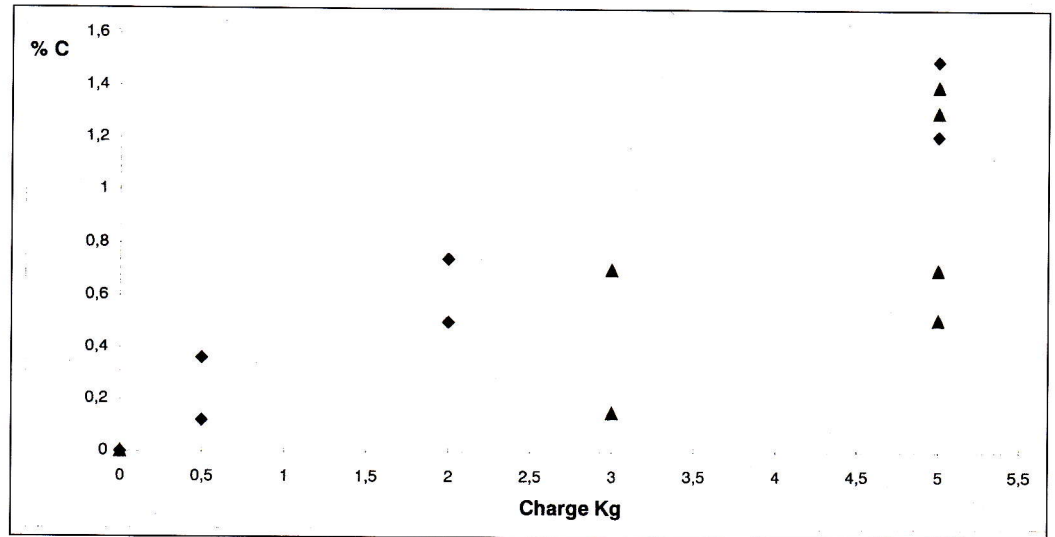
On the other hand, when this latter steel is concerned, we must confirm the higher ductility of the nitrocarburized layers even independently from the carbon % (percentage).

CONCLUSIONS

- a) Many processes of ferritic nitrocarburizing are operational, quite of ten due to commercial interests, if we consider their large and popular diffusion.
- b) From the metallographic point of view all these processes produce nitrocarburized layers that are very similar and show very little variations as the thickness, hardness and the morphological aspect are quite similar to each other.
- c) The compound layer, seen from the chemical point of view shows significant differences according to the type of process performed and due to the process parameters that have been used.
- d) The adherence of the compound layers, that is a determining features of the applications where as high and varia-

Fig. 5 - Relation between the percentages of carbon in the compound layer and the ductility in the steel 42CrMo4 (●) and 41CrAlMo7 (x).

Fig. 5 - Relazione tra percentuale di carbonio nello strato dei composti e duttilità nell'acciaio 42CrMo4 (●) e 41CrAlMo7 (x).



ble mechanical stresses are at work, must in fact be interpreted as ductility and tenacity of the compound layers themselves.

- e) The test that have been performed prove that the ductility of the compound layers especially on the steels that are constitutionally more fragile can be improved if it is composed of carbonitrides that contain % (percentages) of carbon relatively high (> 1 %).
- f) These same test have demonstrated that this characteristic varies significantly according to the process that has been used and according to the parameters that have been chosen for the same processes.

BIBLIOGRAPHY

- 1) Rogers R.D. - Cable J.W.
Nitemper: un nuovo metodo d'indurimento superficiale (Bollettino Ipsen 1970).
- 2) B. Prenosil
Gefuge der badnitrierten und in Ammoniakatmo sphere nit kohlen wassersfotfzusatz hergestellten Schichten

- Harterei - Techn. Mitt. 20 (1965) Heft 1,41.
- 3) A. Bavaro - M. Franzosi - G.M. Mengoni
Carbunitraration gazeuse a basse temperature. Traitement Thermique 1975/92
- 4) C. Leroux
Le nitrocarburation ou nitruration epsilon. Traitement Thermique 196/85
- 5) J.P. Peyere - C. Tournier - P. Baldo
Nitruration par le procede Alnat N caracteristiques dei procede, structure des couches realisees - Traitement Thermique 210/88
- 6) F.M. Montevecchi - I. Montevecchi
Nitrocarburatione con miscele di NH3 e CO2 un approccio fisico - matematico. La Metallurgia Italiana 7 8/1993.
- 7) A. Bavaro - R. Biancardi - A. Visconti
Nitrocarburatione ferritica con atmosfera prodotta da metanolo e ammoniaca. Atti 16° Convegno Nazionale Trattamenti Termici Salsomaggiore 1997.
- 8) R. Roberti - G.M. La Vecchia - G. Colombi
Caratterizzazione degli strati nitrurati - La Metallurgia Italiana 1/1991

**INFLUENZA DEL CONTENUTO DI CARBONIO
NEGLI STRATI NITROCARBURATI**

La nitrocarburação ferritica sia salina che gassosa, denominata comunemente "nitrurazione morbida", è un trattamento superficiale applicabile (e applicato) praticamente a tutte le leghe ferrose e che ha trovato numerosissime applicazioni grazie alle particolari caratteristiche superficiali ottenibili con esso cioè resistenza all'usura, al grippaggio, alla corrosione e alla fatica.

Quanto sopra, ottenuto utilizzando un processo relativamente semplice e soprattutto di breve durata, è ottenibile solo se lo strato superficiale nitrocarburato presenta buone caratteristiche dello strato dei composti (costituito da carbonitridi ϵ e γ') e cioè: spessore minimo, compatto e duttile. La duttilità, scambiata per "aderenza", è di fondamentale importanza perché in assenza di essa si otterrebbe il facile distacco dello strato e quindi sarebbero compromesse le prestazioni degli organi trattati.

La suddetta caratteristica dipenderà, oltre che dalla composizione chimica e dallo stato del materiale da trattare, dai parametri del processo di cui la composizione chimica del mezzo nitrocarburente svolge un ruolo fondamentale.

Le tabelle I e II riportano le suddette composizioni riferite ai processi comunemente utilizzati nell'industria dei trattamenti termici.

I processi gassosi utilizzano gas di natura diversa che dovrebbero comunque determinare la diffusione di azoto e carbonio in quantità tali da caratterizzare lo strato dei composti soprattutto con riferimento alla quantità di carbonio che, a causa della bassa temperatura di trattamento, diffonde con difficoltà nei materiali ferrosi: ciò è ancora più difficile quando si usano gas diversi da quello classico endotermico ($N_2 + H_2 + CO$).

Nei processi salini questa difficoltà è stata resa maggiore quando i bagni a base di cianuro sono stati sostituiti dai bagni "ecologici" a bassissima percentuale di cianuro.

Allo scopo di verificare l'importanza della quantità di carbonio che deve essere presente nello strato dei composti perché risulti significativamente duttile, sono state eseguite prove su provini realizzati negli acciai di tab. III bonificati e

sottoposti a nitrocarburação ferritica secondo diversi processi (gassosi, ionica e salini). I processi considerati sono stati: la nitrocarburação gassosa tipo Nitroc che utilizza la CO_2 come apportatore di carbonio, la nitrocarburação gassosa tipo Basonit in cui questa azione è attuata dal metano dissociato, la nitrocarburação ionica in cui viene aggiunto metano e la nitrocarburação salina in cui è presente una minima percentuale di cianuro.

Per rendere più significativo il confronto è stato utilizzato anche il processo di sola nitrurazione in cui non vi è alcun apporto di carbonio in quanto l'atmosfera è costituita da solo azoto e ammoniacca.

Successivamente i provini trattati sono stati sottoposti a controlli di durezza superficiale (tab. IV), rilievi della percentuale di carbonio superficiale (tab. V), misurazione degli spessori dello strato dei composti (tab. VI), spessore di indurimento efficace (tab. VII) e morfologia strutturale degli strati nitrocarbureti (fig. 1, 2, 3, 4).

I suddetti rilievi sono stati completati con la determinazione delle caratteristiche di duttilità utilizzando un metodo che determina il carico massimo applicato su un penetratore Vickers che provoca la formazione di cricche sia ai vertici delle stesse impronte che lungo i lati (cricche circolari).

Confrontando i valori dei carichi (tab. VIII) con le percentuali di carbonio della tab. V si ottengono correlazioni significative per i campioni realizzati in acciaio più fragile 41CrAlMo7: aumentando la percentuale di carbonio dello strato dei composti, aumenta il carico che determina la comparsa delle cricche in corrispondenza delle impronte Vickers (fig.5).

Viene così dimostrato che la duttilità degli strati nitrocarbureti aumenta con la percentuale di carbonio presente negli stessi strati dei composti.

A questo proposito è utile ricordare come la "coltre bianca" presente sugli acciai sottoposti a nitrurazione gassosa è considerata dannosa a causa della sua eccessiva fragilità. Tale caratteristica è determinata effettivamente dal fatto che con tale trattamento la percentuale di carbonio superficiale diventa inferiore a quella dello stesso acciaio trattato e ciò a causa dell'effetto decarburante dell'atmosfera utilizzata ricca di idrogeno e priva di elementi carburanti.

MEMORIA

5/2000