Methods of acceleration of saturation processes during carbonitriding treatment

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The presentation is devoted to the analysis of the techniques developed at VAZ car plant for stimulation of saturation processes during high-temperature carbonitriding in atmosphere of 20%H_2, and low-temperature modes of nitride hardening (carbonitriding) in ammonia and exothermic gas.

Keywords: heat treatments

THE INFLUENCE OF PRE-OXIDATION AND COMBINED SATURATION CYCLES ON ACCELERATION OF CARBONITRIDING PROCESS

The introduction of controlled atmospheres using the automatic control of carbon potential has promoted the creation of the new generation of pusher-furnaces. This enabled the reduction of the duration of the carbon saturation process through the introduction of preliminary oxidation, combination cycles and the implementation of the direct hardening with cooling-down.

The pre-oxidation of samples and parts made of 19CN5 and 20NCD2 steel grades, has been run in air and water steam, at various temperatures. Table 1 shows the results of research on how pre-oxidation impacts to the carbonitrided effective depth with 19CN5 and 20NCD2 steels.

Steel grade	Oxidation time, min	Effective depth of hardened layer h_{eff},* mm	Treated depth relative increase k,%
20NCD2	30	0.70/0.90	28
	20	0.42/0.62	48
19CN5	60	0.65/0.83	28

* - First line of values provides those obtained in carbonitriding without additional oxidation;
- Second line – the values obtained in carbonitriding with pre-oxidation.

Table 1 – Pre-oxidation impacts to the carbonitrided effective depth with 19CN5 and 20NCD2 steels.

Tabella 1 – Influenza della pre-ossidazione sullo spessore effettivo carbonitrurato con acciai 19CN5 e 20NCD2.

As is evident from the Table 1, the preliminary oxidation increases by 28% and more the saturation rate during the carbonitriding. It should be noted that the accelerating effect of pre-oxidation is only occurring during formation of low-depth carbonitrided layers (0,3-0,7mm). In prolonged processes of carbonitriding and carburizing - with over 1mm layer-depth, no impact of pre-oxidation was revealed on acceleration of the saturation process.

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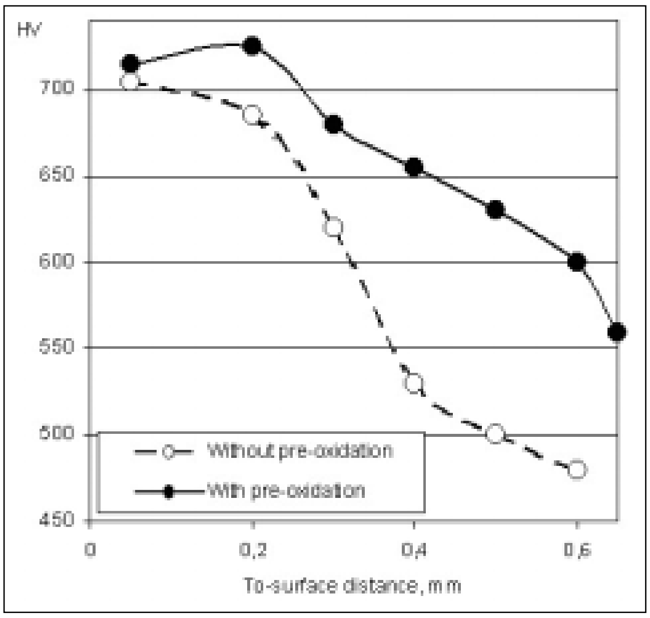


Fig. 1 – The influence of pre-oxidation on the hardness spreading throughout the depth of carbonitrided layer on 20NCD2 steel.

Fig. 1 – Influenza della preossidazione sulla durezza diffusa attraverso lo spessore dello strato carbonitrurato su un acciaio 20NCD2.

Fig. 1 shows how the pre-oxidation impacts to the hardness-value spreading over the carbonitrided depth for 20NCD2 steel. It can be seen, that with oxidation the saturation depth is increased. The carbon content on pre-oxidized steel is growing through the full depth of the diffused layer. But the nitrogen content on oxidized steel surface is less compared to non-oxidized steel, however it penetrates to deeper depth what is shown on Fig. 2.

FOR THE EXPLANATION OF THE EFFECTS OF PRE-OXIDIZING WE ARE PRESENTING THE MECHANISM BY TIKHONOV - KRISHTAL

The scale layer on iron and steel is known to be loose one. It absorbs the gases: initially in its own volume and then on the surface of existing numerous and ramified cracks. In oxidation the metal surface becomes rough and its absorption ability increases, causing the increase of the diffusion flow during saturation. The steel surface catalyses the decomposition reactions of CO ($2CO \rightarrow C + CO_2$) and of ammonia ($NH_3 \rightarrow N + 3/2H_2$), resulted in their penetration th-

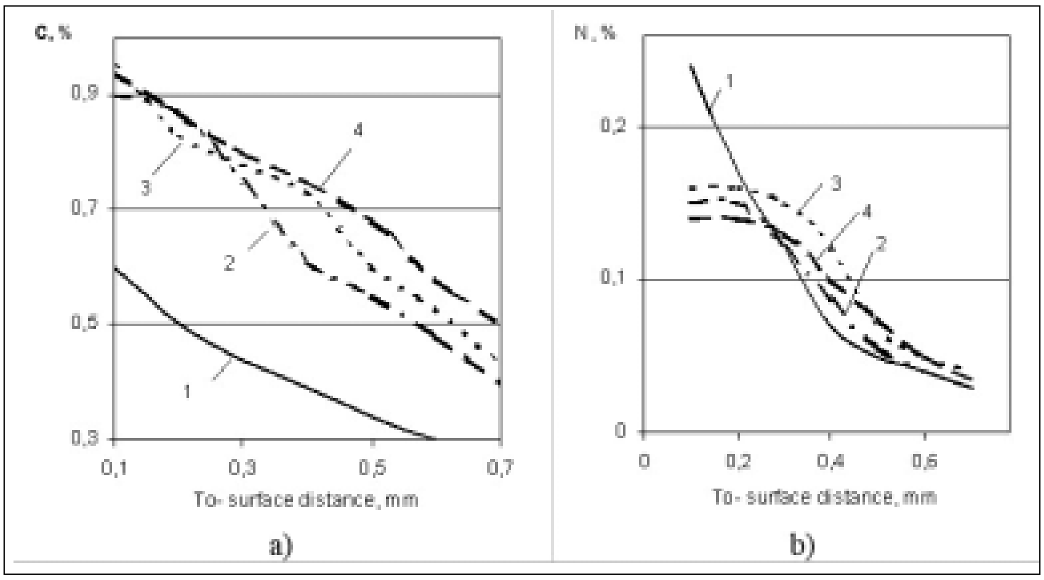


Fig. 2 – The influence of pre-oxidation on carbon and nitrogen distribution throughout the diffusion layer on the 20NCD2 steel samples passed carbonitriding
1 – without pre-oxidizing
2, 3, 4 – pre-oxidizing for 1/2, 1 and 2 hours respectively

Fig. 2 – Influenza della preossidazione sulla distribuzione di carbonio e azoto attraverso lo strato dei campioni di acciaio 20NCD2 sottoposti a carbonitrurazione
1 – senza preossidazione
2, 3, 4 – con preossidazione rispettivamente per 1/2, 1 e 2 ore

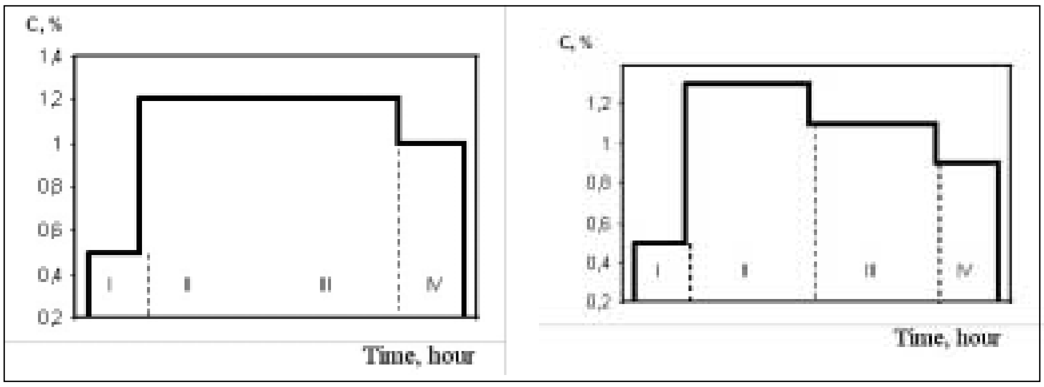


Fig. 3 – Combination carbonizing cycles (Patent No. 1076724).

Fig. 3 – Abbinamento di cicli di carbonizzazione (Brevetto N. 1076724).

rough the loose scale in large amounts. In addition, the hydrogen also causes the increase of the carbon content of the steel surface via reaction with CO: $CO + H_2 \rightarrow C + H_2O$.

The film is recovered in the endothermic atmosphere and it forms the screw dislocation front, which accelerates the diffusion by one order.

To the common knowledge, the nitrogen and the carbon activate-up each other in the iron solid solutions. The data presented on Fig. 2 indicate that in gaseous and absorbed on the steel surface states the nitrogen activates the carbon to a higher degree than the carbon activates the nitrogen. This is resulted from the fact that the carbon concentration on the surface during the saturation of the oxidized steel is much higher compared to non-oxidized steel in the presence of the nitrogen. The high concentration (1% C) and, consequently, the high activity of the carbon promote the large carbon flow into the steel depth. The carbon diffuses in penetration sites, as the nitrogen does, and for this reason the latter is displaced by the carbon, thus the nitrogen concentration on the surface is reduced. Further in depth of the oxidized steel, the nitrogen diffusion flow increases due to the augmentation of its activity in the presence of the carbon but with the carbon concentration being smaller (0.80%).

Of theoretical and practical interest is the fact that the nitrogen promotes significant carbonization when an oxidized surface is prepared, and the carbon, on the contrary, causes the reduction of the nitrogen concentration on the surface of oxidized steel under saturating.

This might be associated with the austenite formation in steel at lower temperature during the diffusion of nitrogen, as well as with the above features of the mutual influence of nitrogen and carbon on the activity levels of each other.

Within AVTOVAZ company, the 4-stage saturation cycle (Fig. 3b) has become most commonly used. The cycle is as follows. The endogas is supplied to the first zone of the furnace, where low carbon potential is maintained for to prevent from the carbon black deposition on the parts surface and the furnace lining. In the third furnace zone the maximum temperature is maintained and the maximum supply of the natural gas as well, with the carbon potential somewhat above the solubility of carbon in austenite (above 1.2%). This is accompanied by the high-rate saturation of the parts surface by carbon, and the minimal soot deposition in the furnace workspace.

In the fourth zone, the diffusion area, the atmosphere's carbon potential is reduced to 0.8-1.2% C, with the saturation layer depth increasing without the formation of carbides. Since the entire carbon is used practically for the saturation of the layer, no deposition of it occurs.

In the last zone, the cooling-down area, the carbon potential is controlled and can be of 0.8 - 0.9% C, depending on the steel grade, the hardening temperature, and the required layer characteristics.

The four-stage cycle carbonitriding ensures the saturation rate increase with minimal soot deposition in the furnace workspace.

The combination cycles can be performed in modern pusher- and batch-type furnaces with the automatic carbon potential control [1].

In a batch-type furnace, the gas regime can be adjusted quite easily by simply variation in time of the supplied atmosphere parameters.

The amount of ammonia should be precisely limited not to exceed the level, calculated per the ‘Novikova-Tikhonov’ formula (1), since the excess of nitrogen in atmosphere will result in formation of mesh or skin of carbonitrides, big amount of retained austenite, troostite network, dark component, thus leading to the loss of strength properties.

$$y = (I-0.55x)/0.7x \qquad (1)$$

where: y - amount of ammonia delivered to furnace, %
x - depth of diffusion layer, mm

Thus the precondition which guarantees the absence of the structure defects of carbonitrided layer is the combination saturation cycle - based on the carbon potential, the limitation of ammonia in line with Novikova-Tikhonov formula, and the delivery of ammonia to the furnace upon the expiration of the 1/3 of the total carbonitriding cycle time - to ensure the formation of carbonitrided layer in the single-phase γ-area.

For carbonitriding, the endothermic atmosphere is globally used with 40 and 20% of hydrogen content. The data appeared in 1900 on negative effect of the hydrogen content in furnace-atmosphere to mechanical properties of the thermo hardened steel. Houdremon [2] also paid attention to that, and Scheindlin [3] indicated the same in his works.

In our comparative studies performed on the samples, carbonitrided in furnace atmosphere with 20% and 40% of hydrogen content, it was revealed that the saturation rate appeared to be the same. However the strength properties of the samples treated in atmosphere of 20%H_2 are better than that with 40%H_2, the impact viscosity is 40% higher, the angle of torsion in twisting is 50% up, so are other characteristics shown in tables 3 and 4 [4].

THE METHODS OF ACCELERATION OF THE SATURATION PROCESSES DURING NITRIDING (LOW TEMPERATURE CARBONITRIDING)

Among the key methods of achieving the high hardness, wear-resistance and corrosion-resistance of parts - is that of obtaining of nitrated case on their surface composed of the nitride phases.

For this purpose, the two methods of surface nitride layer creation are used at AVTOVAZ - the short-term gas nitriding, and the ion nitriding.

The short-term gas nitriding represents the saturation at 610°C lasting for 2-4 hours, in the mixture of ammonia and exogas - with their ratio of 1:1 or 1:2.

The process atmosphere is to be controlled for the hydrogen content.

Hydrogen content in endothermic atmosphere	**Carbonizing depth, mm**	**Carbonitriding depth, mm**	
		in 6-zone aggregate	**in 5-zone aggregate**
20%	1,3	0,81	0,77
40%	1,4	0,81	0,74

Table 2 – The effective depth of layer during the parts treatment in endothermic atmosphere of 20% and 40% hydrogen content.

Tabella 2 – Profondità effettiva dello strato durante il trattamento delle parti in atmosfera endotermica con contenuto di idrogeno del 20% e 40%.

Hydrogen content in endothermic atmosphere	**Angle of torsion in twisting, angle degree**	**Mechanical properties Impact viscosity, Joule/cm²**	**Bending strength, N/mm²**
20%	153	17	1880
40%	108	12	1730
Test sample shape:	Diameter of 10 mm, Length of 50 mm	10 x 10 x 55 mm	6 x 10 x 60 mm

Table 3 – Comparative testing results: the mechanical properties of test samples treated in endothermic atmosphere of 20% and 40% hydrogen content.

Tabella 3 – Confronto dei risultati di prova: proprietà meccaniche dei campioni trattati in in atmosfera endotermica con contenuto di idrogeno del 20% e 40%.

Hydrogen content in endothermic atmosphere	**Max breaking force, N**			
	Notched samples		**Samples without notch**	
	6 hours after tempering	**1,5 hours after tempering**	**6 hours after tempering**	**1,5 hours after tempering**
20%	3990	3740	9320	8970
40%	2390	2360	9110	8130

NOTES: The test samples used: 6 x 10 x 60 mm without notch, and 6 x 10 x 60 mm notched - with the notch profile of 2±0,1mm depth, 1±0,1mm width and 0,5±0,05mm fillet radius.
To be noticed also, the generating of 20%H_2-atmosphere by endothermic generator of Lo-Dew type is cheaper by 20% compared to 40%H_2-atmosphere.

Table 4 – Comparative testing results: the static bending of test samples treated in endothermic atmosphere of 20% and 40% hydrogen content and post-tempered per different modes.

Tabella 4 – Confronto dei risultati di prova: flessione statica dei campioni trattati in in atmosfera endotermica con contenuto di idrogeno del 20% e 40% e post-induriti mediante metodi diversi.

After nitriding, a dense, homogenous, 8 to 15mm-depth layer of compounds is formed on the parts' surface. This layer represents the carbonitride, $Fe_3(NC)$, or the oxicarbonitride of iron, Fe(NCO).

The carbonitride of iron $Fe_3(NC)$, versus the iron nitride Fe_3N, obtainable by conventional nitriding in partially dissociated ammonia, is featured by higher ductility and wear-resistance, and hence, by lower brittleness and susceptibility to flaking and grumbling.

The unique feature of the nitriding process used at AVTOVAZ is the application of the pre-oxidation operation, which represents the general method of the surface preparation for the saturation process and the way to accelerate the saturation. The comparative study of the saturation processes in nitriding with and without the pre-oxidizing has shown the growth of carbonitrided depth from 10 to 16 µm, i.e. by 60%.

The process temperature rise up to values above the temperature of the eutectoid conversion (diagram Fe+N+C) is the second option for the saturation process acceleration during low-temperature carbonitriding. After such treatment, the surface of parts develops a heterogeneous low-porosity layer composed of the ductile layers of $Fe_3(NC)$ of epsilon-phase and the nitrous austenite.

The mechanism of the positive effect of the saturation temperature elevation to the process of the carbonitride layer formation and its properties appears to be as follows: the saturation temperature increase leads in the first place to the growth of the ammonia dissociation degree, thus to reduction of the NH_3 content and the reduced nitrogen potential. On the other hand, the elevated temperature speeds up the diffusion processes and, hence, increases the depth of the carbonitrided and diffusion layers.

The interaction of the above tendencies ensures more uniform nitrogen distribution over the carbonitrided layer depth, as compared to the nitrogen profile obtained at nitriding temperature of 570°C, which reduces the over-saturation by nitrogen of the close-to-surface carbonitrided layer, improves its ductility and makes it less susceptible to flaking and grumbling.

Such process of treatment allows to reduce the saturation rime 1.3- to 1.6-fold, to achieve 1.3- to 1.6-fold saving of ammonia, to improve the production ecology and buildup the equipment efficiency.

To ensure the level of wear- resistance and corrosion-resistance of front brakes pistons of wheel cylinders, the hard chroming technology is used.

We have developed the process of gas nitriding in the mixture of exogas and ammonia with post-oxidation, which results in 7-fold corrosion resistance level.

Fig.4 shows the corrosion spreading on the surfaces of chrome-plated and nitrided parts in the salt-spray-chamber.

Cyanidation at temperature of 535°C for cutting tools, and sulfo-cyanidation at 570°C for stamping tools - in the prussiates' melts – the process we used earlier – was the high-toxic one.

The short-term gas nitriding developed at AVTOVAZ, in ammonia with carbon-bearing gases (exogas, endogas, CO_2) and nitrogen, has some advantages of the steel liquid process of saturation with nitrogen and carbon:

- the process is non toxic;
- α-phase favorable for cutting is created (Fig. 5) on the cutting tools; and carbonitride $\varepsilon+\gamma$-phase (Fig. 6) – on the stamping tools surface, thus reducing the friction coefficient and the friction couples' seizing tendency;
- twice increased tool and stamps life on steels of P5M6 type (EN/DIN 1.3343), treated at 530-550∞C;
- lower process cost (50% of the liquid nitriding on average);
- use of multipurpose furnaces including vacuum furnaces.

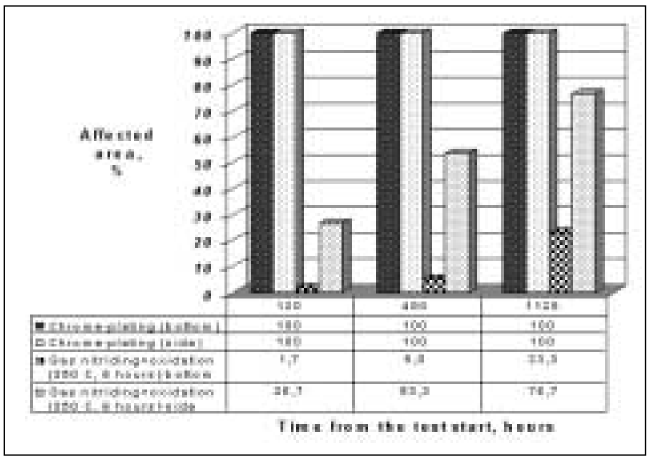


Fig. 4 – Dynamic of the corrosion spreading on the surfaces of researching parts in the salt-spray-chamber.

Fig. 4 – Dinamica della diffusione della corrosions sulla superficie delle parti in esame nella camera di salatura.

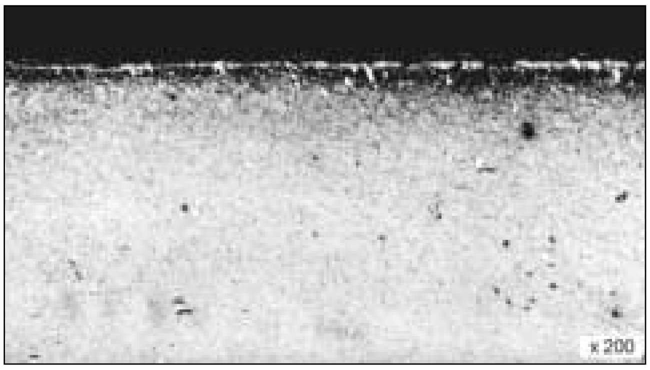


Fig. 5 – Microstructure of diffusion layer of the cutting tool.

Fig. 5 – Microstruttura dello strato di diffusione dell'utensile da taglio cutting tool.

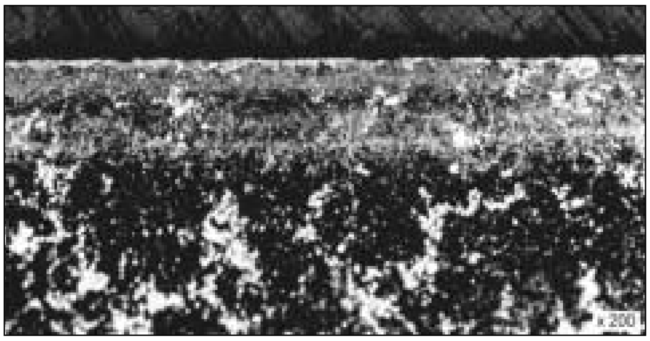


Fig. 6 – Microstructure of diffusion layer of the stamp tooling.

Fig. 6 – Microstruttura dello strato di diffusione dell'utensile da stampaggio.

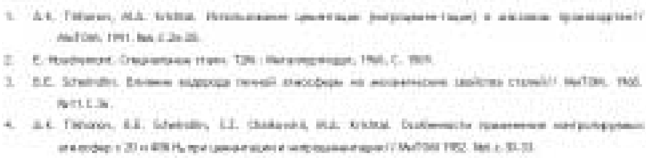
CONCLUSIONS

1. To accelerate the saturation and avoid the structure defects, the carbonitriding process should comprise the pre-oxidation and run per 4-stage cycle, under restricted ammonia supply, per the Novikova-Tikhonov formula. The carbonitriding under above conditions provides 30-35% depth growth of the carbonitrided layer.
2. The endothermic atmosphere implementation, with 20% of hydrogen, improves by more than 30% the strength properties of carbonitrided parts at the same saturation rate, and cheapens the atmosphere generation by 20%.
3. Application of temperature over 610°C for gas nitriding

of the vehicle parts, in NH_3 and exogas blend, reduces the time of treatment by factor of 1,5, and the oxidation stage prior and post nitriding ensures more even distribution of the nitrogen over the carbonitrided zone depth.

4. The use of nitriding process in NH_3+endogas+CO_2 blend doubles the life of the cutting tools and stamp tooling made of P6M6 steel (EN/DIN 1.3343), improves the ecology and is less costly.

REFERENCES



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ABSTRACT

METODI DI ACCELERAZIONE DEI PROCESSI DI SATURAZIONE DURANTE IL TRATTAMENTO DI CARBONITRURAZIONE

Parole chiave:
trattamenti termici

La presente memoria è dedicata all'analisi delle tecniche VAZ di stimolazione dei processi di saturazione durante il trattamento di carbonitrurazione ad alta temperatura in atmosfera di 20%H2, e i metodi di indurimento mediante carbonitrurazione in ammoniaca e gas esotermico, sviluppate presso lo stabilimento automobilistico.