NEW EXPERIENCE WITH NITRAL TECHNOLOGY

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Abstract

Nitriding technology under reduced pressure allows to realize other types of diffusion processes, such as carbonitriding, oxynitriding or sulfonitriding. Some results of experiments and verification of possibilities are the subject of this lecture.

1.0 Introduction

Nitriding under reduced pressure is a relatively new technology. Its priority is especially the non-standard use of the vacuum tempering furnace and favorable results of nitriding layers for various applications. It can be used very well as an additional technology in commercial heat treatment plants in combination with, for example, the offer of plasma nitriding. However, based on practical experience, it must be stated that it cannot 100% cover the requirements for all possible types of applications, as well as other plasma or gas technologies.

One of its advantages is the simple variation of the composition of gases in the atmosphere, and thus also technologies such as nitrocarburizing, oxinitriding or sulfonitriding. The aim of the research was to verify these possibilities and their feasibility in practice.

2.0 Nitriding

The nitriding process under reduced pressure takes place in an atmosphere of ammonia, nitrogen and nitrogen protoxide under the expected reactions:

$2\ NH_3 \rightarrow N_2 + 3\ H_2$
$2\ N_2O + Fe \rightarrow 2\ N_2 + FeO$
$2\ NH_3 + 3\ FeO \rightarrow 2\ N + 3\ H_2O + 3\ Fe$

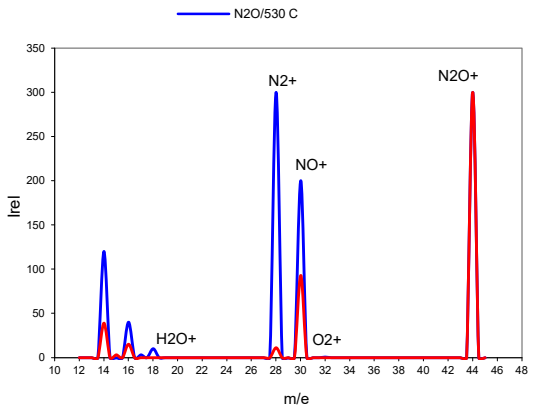


Fig. 1

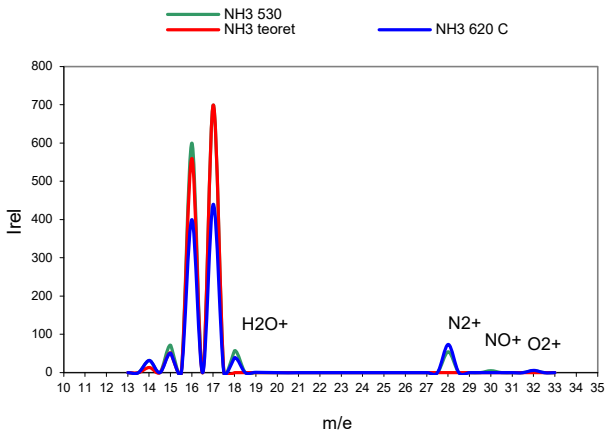


Fig. 2

It follows from the above equations that the precondition for a successful nitrogen transfer from the atmosphere is the formation of an activation layer Fe_xO_y on the steel surface. Therefore, the period of oxidation of the steel surface in N_2O is included in the first phase of the process. In Fig. 1 shows the mass spectra of N_2O for the theoretical gas, and the spectra of N_2O at 300 mbar and a temperature of 530 C.

The spectral curves of N_2O show that the thermal decomposition of this gas at 530 C strongly increases the proportion of NO^+, molecular and atomic nitrogen $N2^+$ and N^+, and atomic oxygen O^+. At m/e = 32 for O_2, the oxygen spectral lines are completely missing, and it follows that all the released O^+ oxygen is consumed in reaction with the surface without recombination to O_2.

In the next phase, the nitriding takes place, when the source of nitrogen atoms becomes thermally cracked ammonia (Fig. 2). Its dissociation curve corresponds theoretically to the dissociation temperature, resp. according to the nitriding temperature. It seems probable that, in addition to atomic nitrogen, the NH_3^+, NH_2^+ and NH^+ radicals also contribute to the diffusion, as is the case in some theoretical works for plasma nitriding [1] according to the scheme

$Fe\ NH_2 + H \rightarrow Fe\ NH + H_2$
$Fe\ NH + Fe \rightarrow Fe_2\ NH$
$Fe_{1-3}\ NH_2 + Fe \rightarrow Fe_{2-4}\ N + H_2$

The activator of these reactions is hydrogen, which is released by thermal dissociation of ammonia, and from unstable intermediates.

A mixture of $NH_3 + N_2 + N_2O$ gases is used in the nitriding process itself. The addition of nitrogen reduces the nitriding number of the atmosphere, the addition of N_2O then maintains the reaction activity on the steel surface. During the tests, it was found that the reaction did not actually take place without the use of oxidizing gas.

2.1 Results of nitriding

The following figures show a typical nitriding layer from the NITRAL process for material 14220 (16MnCr5) (Fig. 3) and 12050 (C45) (Fig. 4). The process parameters were T = 540 C, pT = 300 mbar and t = 7.5 hours. The surface layer is homogeneous, continuous by th. 8-10 µm, resp. 10-15 µm. The etching layer appears darker on the surface and lighter at the bottom. No visible differences can be observed in the subjective evaluation of the surface, except that the surface layer is very brittle. However, when observed under an electron microscope at 1000x magnification, no significant differences in its homogeneity or porosity are seen (Figures 5 and 6).

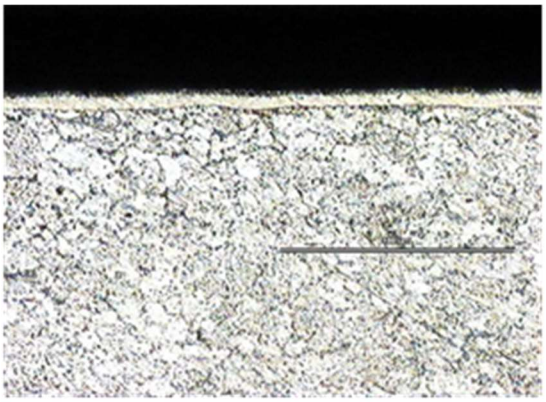


Fig. 3

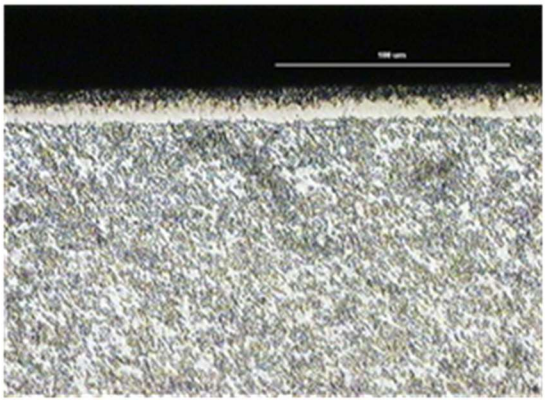


Fig. 4

2.2 Surface oxidation

Surface oxidation is another possible technology that can be solved under reduced pressure. Its aim is to create a surface layer of iron oxides, which ensures both better corrosion resistance and stability of the surface, as well as a layer of black color replacing chemical blackening technology. In conventional technologies, water vapor is used to oxidize the surface, either during cooling of the charge or at a temperature of about 450 C, which ensures the formation of such a layer. However, in a reduced pressure process, this principle cannot be used due to possible contamination of the vacuum pump oil. Therefore, the process is again based on the reaction of the surface with nitrogen protoxide N_2O to form a thin layer of Fe_3O_4 with a thickness of 1-3 µm.

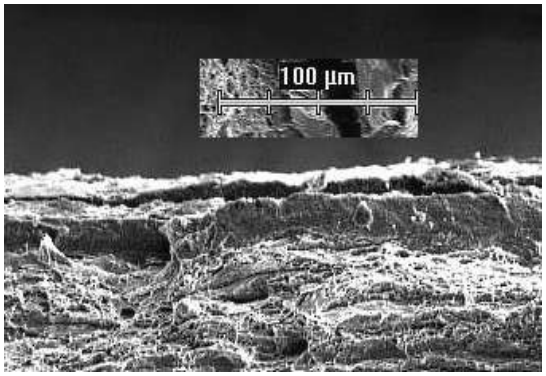


Fig. 5

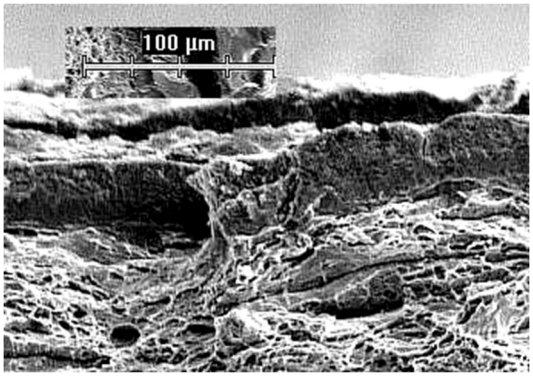


Fig. 6

3.0 Nitrocarburizing

The nitrocarburizing process is mostly applied to pure carbon steels or low-alloy steels, in which the aim is to create a thick surface layer of nitrides, resp. iron carbonitrides. In the classic technology, this process is mostly carried out in a mixture of gases $NH_3 + CO_2$, or $NH_3 + CO$, resp. in ENDO gas. Similar conditions can be induced by nitrocarburizing under reduced pressure in a similar gas mixture. Fig. 7 is an example of a layer from a nitrocarburizing process under reduced pressure in a mixture of $NH_3 + CO + N_2$ gases on material 11373 (DIN 1.0038), in Fig. 8 on material 12050 (C45).

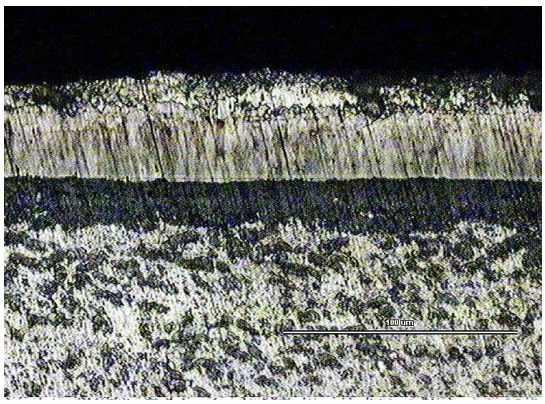


Fig. 7

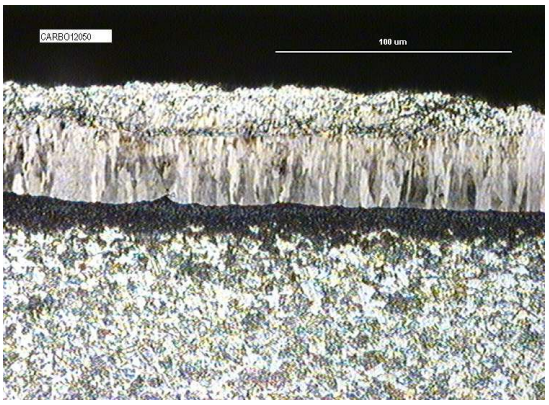


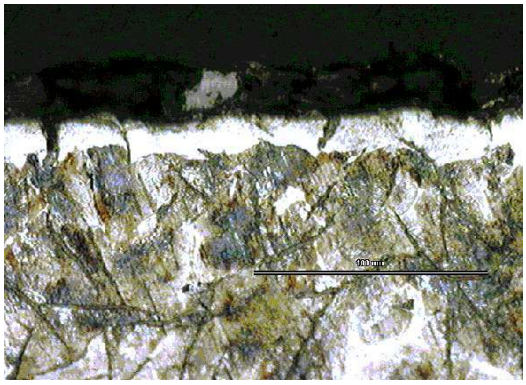
Fig. 8

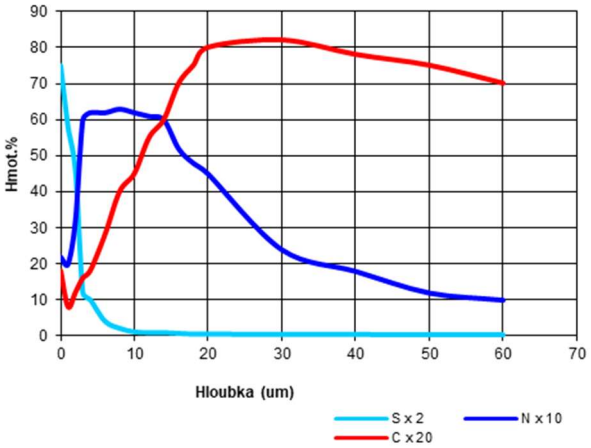
In both cases, the layer consists of 3 characteristic parts. It is a dark layer under its own surface layer. This is probably related to surface pre-oxidation in N_2O. There is also a layer of Fe carbonitrides with columnar formations up to about 30 µm thick, and a final surface layer 20-24 µm thick, appearing to be porous.

4.0 Sulfonitriding

The sulfonitriding process has recently almost disappeared from the range of surface diffusion treatment processes due to the fact that it was based mainly on cyanide salt baths with a reaction such as $SO_3^2 + 3\ CN^- > 3\ CNO + S$. In Fig. 9 is a surface layer of gray cast iron sulfonitriding formed by reduced pressure technology with the addition of H_2S gas. The layer is homogeneous and continuous by th. 14 to 18 µm, only in some parts it is intersected by graphite flakes. The phase composition of the layer in weight percent was found to be approximately as follows: ε-$Fe_{(2-3)}N$ - 65%, Υ-Fe_4N - 5%, FeS - 30%.

During the chemical analysis by optical emission spectroscopy on the LECO SA-2000 instrument, it was found that there is a layer with a high sulfur content (approx. 30%) on the surface, and a layer with a constant high nitrogen content (approx. 6%). Furthermore, the amount of nitrogen monotonically decreases in depth. On the other hand, the carbon concentration on the surface is the lowest around 0.5% and its concentration increases with depth to more than 4%.





Obr.č. 9

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5.0 Conclusion

The technology of diffusion processes under reduced pressure seems to be really promising. It is quite easy to vary its individual parameters, especially the composition of the atmosphere. It is also advantageous because the furnace temperature is completely uniform throughout the working space (vacuum tempering furnacesm Class 2). It is also acceptable because the entire device is computer controlled and therefore a relatively high reproducibility of the technology is guaranteed.

According to current experience, it gives excellent results for medium-alloyed materials such as 14340 (34CrAl6), 15340 (41CrAlMo7-10) or 15330 (31CrMoV9). However, for steels of types 14220 (16MnCr5), 15142 (42CrMo4), etc., the hardness values lag behind the plasma processing. The technology can also be advantageously used for nitriding complex shapes, eg molds for plastics, for die casting Al, Zn from steels 1.2311, 1.2312, 1.2343, 1.2344, etc., where the technology in the plasma is not optimal due to the poor uniformity of the layer, and where even nitriding in the gas usually does not satisfy with respect to the cleanliness of the surface.

On the contrary, its use is practically impossible for steels with a chromium content > 8% due to the formed surface passivation layer of chromium oxides. It is far more stable than the F_xO_y layer and forms a diffusion barrier. This problem prevents the use of this technology for nitriding stainless materials, or 12% ledeburitic tool steels.

In addition to being sensitive to the steels used, the technology also requires high purity of the inlet gases. In particular, the content of water vapor in ammonia can disrupt the whole technology to such an extent that the reaction is completely suspended.

[1] Tibbets G.G. – J.Appl. Phys. 45, (1974), s. 5072 - 5073

Technologie difuzních procesů za sníženého tlaku se zdá být skutečně perspektivní. Lze vcelku jednoduše variovat její jednotlivé parametry, především složení atmosféry. Je výhodná rovněž proto, že v celém objemu pracovního prostoru (vakuové popouštěcí pece) je zcela rovnoměrná teplota pece. Je akceptovatelná i proto, že celé zařízení je počítačově řízeno a je tedy zaručena relativně vysoká reprodukovatelnost technologie.

Podle stávajících zkušeností dává vynikající výsledky u materiálů středně legovaných jako např. 14340, 15340 nebo 15330. U ocelí typu 14220, 15142, 42CrMo4V apod. však hodnoty tvrdosti zaostávají za zpracováním v plazmě. Technologii lze rovněž výhodně využít pro nitridaci složitých tvarů, např. forem na plasty, na tlakové lití Al, Zn z mat. 1.2311, 1.2312, 1.2343, 1.2344 apod., kde technologie v plazmě není optimální z důvodu rovnoměrnosti vrstvy, a kde ani nitridace v plynu většinou nevyhoví s ohledem na čistotu povrchu.

Naopak její využití je prakticky nemožné u ocelí s obsahem chromu >8% z důvodu vytvořené povrchové pasivační vrstvy oxidů chromu. Ta je daleko stabilnější než-li vrstva F_xO_y, a vytváří difuzní bariéru. Tento problém brání využít tuto technologii pro nitridaci nerezových materiálů, nebo 12% ledeburitických nástrojových ocelí.

Kromě toho, že technologie je citlivá na použité oceli, vyžaduje rovněž vysokou čistotu vstupních plynů. Především obsah vodní páry ve čpavku může celou technologii narušit natolik, že dojde k celkovému pozastavení reakce.

[1] Tibbets G.G. – J.Appl. Phys. 45, (1974), s. 5072 - 5073