U.P.B. Sci. Bull., Series B, Vol. 71, Iss. 3, 2009 ISSN 1454-2331

CONTRIBUTIONS TO THE NITRIDING CHEMICAL TREATMENT OF A NITRALLOY STEEL

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Sunt prezentate rezultate experimentale privind efectele variației parametrilor termici şi temporali ai procesului de nitrurare gazoasă asupra cineticii formării stratului şi a proprietăților acestuia reflectate prin macroduritatea suprafeței(HV_{5kgf}).

Materialul utilizat în cadrul experimentărilor a fost oțelul de tip nitralloy cu următoarea compoziție chimică: 0.38% C; 0.45%Mn; 0.25% Si; 1.4%Cr; 0.20 Mo; 1.1% Al.

Stabilirea dependenței dintre grosimea stratului nitrurat şi a macrodurității funcție de temperatură şi durata de menținere s-a realizat utilizând metoda de planificare a experimentului. S-a utilizat un program rotabil compozițional central de ordinul II.

Pe baza rezultatelor experimentale şi calculelor de regresie au fost stabilite următoarele ecuații de interdependență:

- pentru dependența dimensiunii stratului de parametri tehnologici ai procesului

$$Y=0.445+0.144X_1+0.107X_2$$

- pentru dependența macrodurității stratului de parametri tehnologici ai procesului

$$Y=1008.3-93.1X_1-82.5X_1X_2$$

unde X_1 , X_2 reprezintă valorile codificate ale parametrilor independenți, temperatură respectiv timp de menținere izotermă la nitrurare.

The experimental results regarding the effects of the variation of the thermal and time parameters of the gaseous nitriding process upon the kinetics of layer formation and of the properties reflected by the macrohardness (HV_{5kgf}) are presented.

The material used for these experiments was the nitralloy steel with the following chemical composition: 0.38% C; 0.45%Mn; 0.25% Si; 1.4% Cr; 0.20 Mo; 1.1% Al.

The determination of the dependence between the thickness of the nitride layer and the macrohardness versus the holding temperature and time was achieved using the method of planned experiment. A second degree rotary central compositional programme was used.

Based on the experimental results and on the regression calculus the following interdependence equations were determined:

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- for the dependence of the layer thickness upon the technological parameters of the process

$$Y=0.445+0.144X_1+0.107X_2$$

- for the dependence of layer macrohardness upon the technological parameters of the process

$$Y=1008.3-93.1X_1-82.5X_1X_2$$

where X_1 , X_2 represents the code values of the independent parameters, nitriding holding temperature and time, respectively.

Keywords: nitriding chemical treatment of a nitralloy steel

1. Introduction

Nitriding represents a thermochemical process with multiple destinations, intended to harden of a wide range of metals and alloys such as: structural steels, tool steels, refractory and stainless steels, cast irons, etc. Hardening is achieved due to the formation of a nitrided layer consisting of a surface nitride area and sublayer diffusion area.

Performances such as high hardness, refractoriness, and fatigue resistance depend on the structure of the internal nitriding area (the structure of the diffusion area). The structure of the diffusion area depends on the chemical composition and the distribution of the hardening nitrides within the metallic matrix. At its turn this distribution is affected by several factors such as the temperature and the time period of the nitriding process, the concentration of the element in active state, the value of the diffusion coefficient, the thermodynamic activity of the alloying elements, etc. The separation of the excess phases in the diffusion area - internal nitriding area occurs through germination and growth mechanisms of the nuclei similar to those that are formed during the precipitation- hardening of the disperse-hardened alloys. It was established [1, 2] that during the nitriding of iron alloys and other alloys that contain transition elements the nitrides of these elements are formed in the internal nitriding areas. At lower nitriding temperatures, 500-520°C, the occurrence of Guinier-Preston areas coherent with the metallic matrix can be noticed [3, 4].

The hardening provided by the formation of the nitride layer, like in the case of the hardening provided by the precipitation of the excess phases during the aging of the alloys solution hardening, is the result of the slowing of the motions of the dislocations towards the precipitating phases. The results of the determinations performed for particles in the precipitated phase with the diameters within the l20-40Å and distances between the centres varying within the limits 40-10000 Å [5] led to the conclusion that a substantial growth of the hardening level for the Mo-Al-Cr alloys is obtained by volume alloying with nitrogen (for example 39MoAlCr15): at a distance between the centres of the hardening phases of 400 Å, the increase of the critical shear stress is up to 75MPa.

With the exception of transition metals nitrides a special importance is held by aluminium, silicon and magnesium nitrides in the nitrided cast irons and steels. Aluminium nitride AlN was noticed in steels deoxidized with aluminium. At high nitrogen concentrations it is probable that parts of the aluminium to be dissolved into γ' and ε phases. The occurrence of the aluminium nitride is inevitable in the nitrided layers of the alloys that contain these elements in high concentrations in the range 8-10%. In the alloys that contain aluminium within the limits 0.5-2% (the case of nitralloy) after nitriding at low temperatures (~500°C) only the presence of the Fe_4N type nitrides and $Fe_{16}N_2$, respectively was noticed [6]. The aluminium nitride is stable up to high temperatures (>1800°C) and exhibit a low sublimation and dissociation tension, an aspect which differentiates it from the transition metal nitrides.

By the nitriding of the iron alloys in the ε and γ' phases part of the iron atoms are replaced with alloying elements and complex nitrides $(Fe, Me)_4$ N, $(Fe, Me)_3$ N, $(Fe, Me)_2N$ type occur. The alloying of ε phase determines an increase of hardness and wear resistance.

2. Experimental materials and methods

The experimental research aimed at the qualitative and quantitative determination of the effects of the variation of thermal and time parameters of the gaseous nitriding process upon the growth kinetics of the nitride layer and of its macrohardness. In order to obtain this the method of planned experiments was used, in particular a second degree rotary central compositional programme [7]. Subsequently the kinetic parameters of the nitriding process were determined as well as the manner in which they depend on the applied nitriding regime.

The material used in the research was the nitralloy-type steel standardised in Romania, 39MoAlCr15,(0.38%C; 0.45%Mn; 0.25%Si; 1.14%Cr; 0.20%Mo; 1.1%Al), in improved state (hardening at 930°C/oil, followed by recovery at 630°C/oil). Samples of sizes Ø10x15 mm were made which were next subject to nitriding in a vertical muffle furnace with the size of the useful space of about Ø360x600mm, electrically heated (P=24KW). The selection of this nitralloy was due to the fact that the hardness and the strength characteristics obtained after nitriding are maximum for this alloy, and differentiates it greatly from the other improved alloyed steels from the perspective of the exploitation performances in nitrided state. Obviously the difficulties generated during processing, the decrease of plasticity and of the hardenability caused by the presence of the aluminium in the steel cannot be overlooked. The additions of elements which can reduce the effect of the aluminium presence upon the plasticity and hardenability did not find any economic justification. The obtained results were analysed by methods specific to optical metallography: optical microscopy using a Reichert type microscope and Vickers macrohardness (load of 5 kgf).

3. Results and discussion

The research conditions imposed by the type of used programming and the results of the experiments are presented in Table 1

Table 1

Independent parameters, variation range and the matrix of second degree central compositional programming II*

No	Experiment factors and conditions	Temperature		Time		X1 X2	X²1	X² 2	Y	
		Z1,̊C	X1	Z2 , hours	X2				δ.mm	HV 5kg
1	Base level, Xio	550	0	20	0	-	-	-	-	-
2	Variation level .ΔXi	50	-	10	-	-	-	-	-	-
3	Superior level Xio + ΔXi	600	+1	30	+1	-	-	-	-	-
4	Inferior level Xio - ΔXi	500	-1	10	-1	-	-	-	-	-
5	Experience 1	500	-1	10	-1	+1	+1	+1	0.2	840
6	Experience 2	500	-1	30	+1	-1	+1	+1	0.39	1160
7	Experience 3	600	+1	10	-1	-1	+1	+1	0.41	880
8	Experience 4	600	+1	30	+1	+1	+1	+1	0.7	870
9	Experience 5	620.7	+1.414	20	0	0	+2	0	0.68	850
10	Experience 6	479.3	-1.414	20	0	0	+2	0	0.23	1200
11	Experience 7	500	0	34.1	+1.414	0	0	+2	0.57	940
12	Experience 8	500	0	5.86	-1.414	0	0	+2	0.3	1140
13	Experience 9	500	0	20	0	0	0	0	0.44	1000
14	Experience 10	500	0	20	0	0	0	0	0.48	1050
15	Experience11	500	0	20	0	0	0	0	0.40	1070
16	Experience12	500	0	20	0	0	0	0	0.52	950
17	Experience 13	500	0	20	0	0	0	0	0.39	970

***Note*:** The activity of the atmosphere expressed by the dissociation degree of the ammonia was maintained constant and equal to α=40%

Z1, Z2, X1 and X2 represent the natural values, codified values respectively, of the independent parameters, nitriding thermal holding temperature and nitriding thermal holding time; Y represents the value of the analysed dependent parameters – the total size of the nitrided layer and the macrohardness of the layer HV_{5kgf}

After the determination and statistical verification of the regression coefficients, respectively of the concordance of the adopted mathematical models, the following particular forms of the calculated models were obtained:

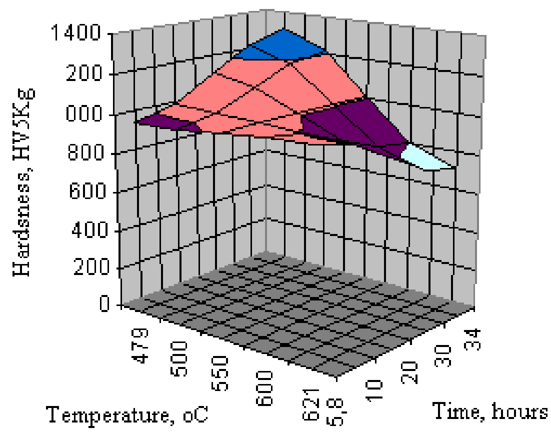
- for the dependence of the thickness of the nitrided layer on the technological parameters of the process:

$$Y=0.445+0.144X_1+0.107X_2$$

- for the dependence of the macrohardness of the nitrided layer on the technological parameters of the process (see Fig. 1):

$$Y=1008.3-93.1X1-82.5X1X2$$

Both technological parameters, the isothermal holding temperature and the isothermal holding time influenced dramatically the thickness of the nitrided layer and the macrohardness of the surface (Fig. 1). For macrohardness the time parameter exerts its action indirectly by the first degree temperature - time interaction. In a first analysis of the calculated and statistically checked models it was noticed that an increase of the nitriding temperature causes an increase of the total thickness of the nitrided layer and a decrease of macrohardness. An increase of the isothermal holding time caused as well an increase of the nitrided layer thickness, the effect upon the macrohardness being determined by the ratio in which it can be found with temperature. In order for the effect of the isothermal holding time to be beneficial for macrohardness it is necessary for this parameter to go in an opposite direction with temperature, an increasing temperature a decreasing isothermal holding period or inversely, causes an increase of hardness. The highest macrohardness was recorded at relatively low nitriding temperatures $500\div520^0$C and reached values of approximately 1200HV. When the nitriding temperatures increased towards 600^0C the values were close to $700\div800$ HV. High values of macrohardness in these temperature conditions were recorded for short intervals of isothermal holding within the limits of $15 \div 30$ minutes.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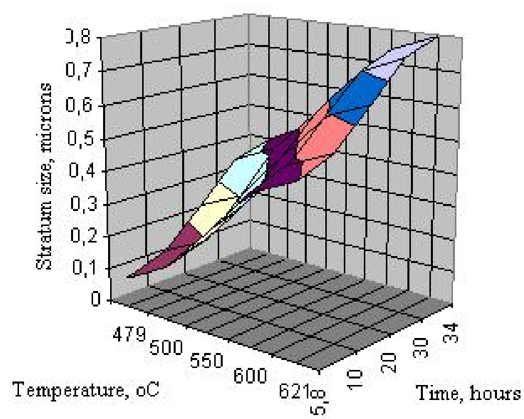
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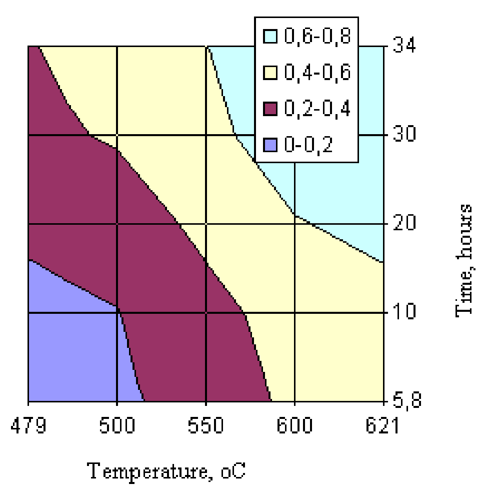
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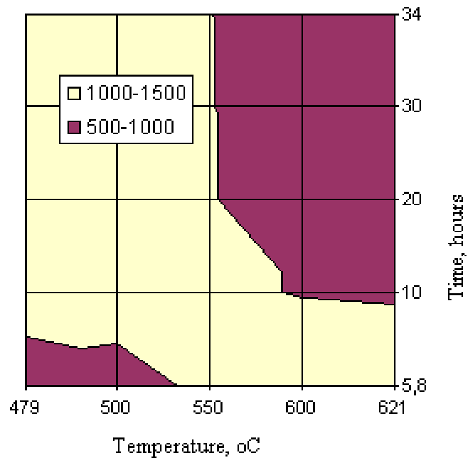


Fig.1. The variation of the total thickness of the nitrided layer (left) and of the hardness of the surface (right) of the steel 39MoAlCr15, thermochemically processed into the atmosphere of partially dissociated ammonium (α=40%). Up-surfaces of answer of the calculated models; down: fields of isoproper

For under-eutectoid temperature nitriding, ε phase can be found at the surface of the diffusion layer, which during cooling decomposes with the separation of $\gamma^{'}$ alloyed phase $(Fe, Me)_4N$. In the same way the relatively compact layer of nitrides which appear at the microscope in white colour (non-etched) a $\varepsilon+\gamma^{'} + \alpha$ triphase area is bonded.

The simultaneous presence of ε and α phases can be explained by the motion of ε phase on the grain boundaries. The main part of the layer, emphasized due to the more intense etching, consists of nitroferrite, deprived of the alloying elements carbides of Me_3C type (that can be put in evidence by X-ray diffraction) and excess $\gamma^{'}$ phase $[(Fe, Me)]_4N$.

It was noticed that isothermal holding at temperatures higher than the eutectoid temperatures (600-650^{0}C) leads to the occurrence of a layer formed of γ-nitroaustenite phase which during the subsequent slow cooling leads to the formation of braunite (the existence of this area could not have been shown by optical metallography due to its morphology very close with that of the neighbouring areas – Fig. 2).

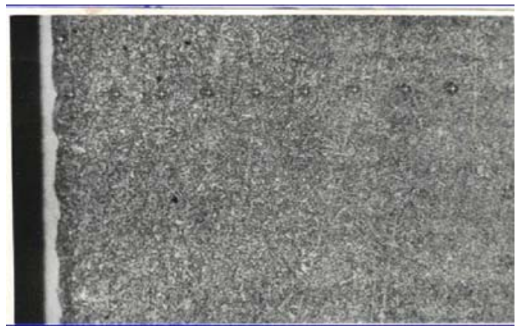
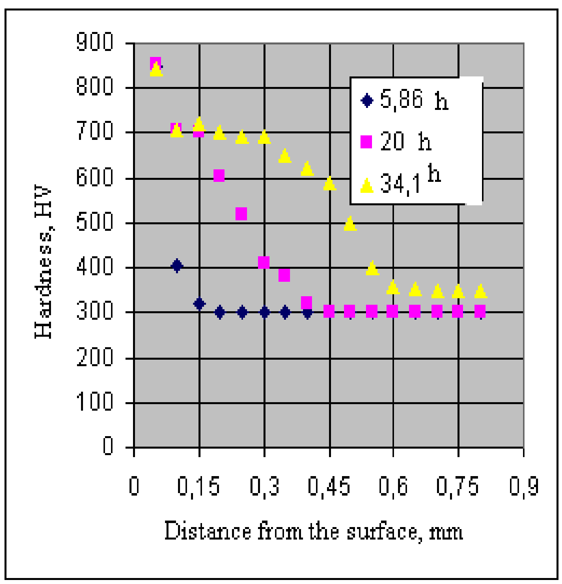
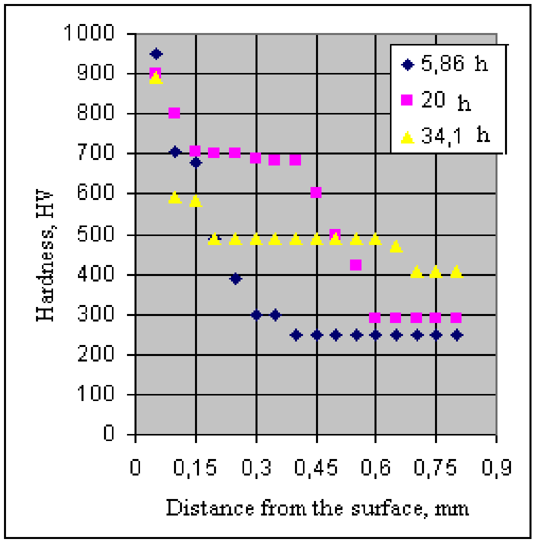


Fig 2- The microstructure of the nitride layer

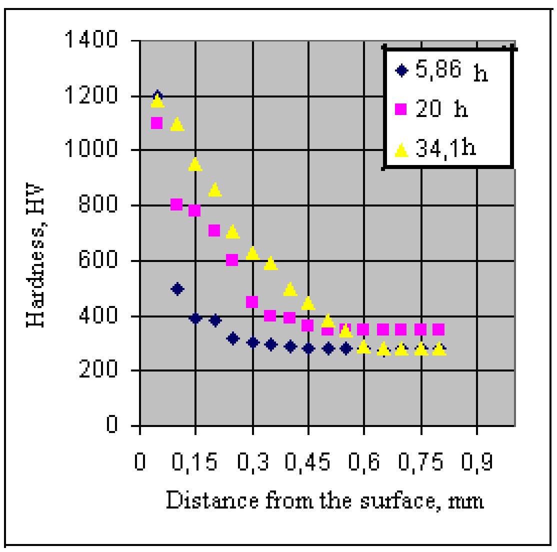
Experimentally it was shown that the higher the nitriding temperatures the slower the hardness variation of the section of the nitrided layer (Fig. 3).



a)



b)



c)

Fig 3 – The variation of the hardness in the nitrided layer depending on the processing conditions. The temperature of nitration: a) 500°C; b)550°C; c)600°C

4. Conclusions

1. The utilisation of the planned experiment in case of gaseous nitriding applied to nitralloy steels enabled the establishment of the regression equations which give the dependence of the nitrided layer thickness and of macrohardness versus the isothermal holding temperature and time. The utility of the regression equations consists of the fact that when one of the independent parameters is imposed (from technological considerations) the value of the other parameter can be determined so that the layer thickness and the macrohardness imposed by the designer can be attained.

2. Experimentally it was shown that the higher the nitriding temperature the slower the variation of harness on the thickness of the nitrided layer, variation which gives the profile of compression stresses in the layer.

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