Interfacial distribution of titanium, aluminium and nitrogen in steels with nitride hardening

Lyudmila Isaeva

Candidate of chemical sciences
National Metallurgical Academy of Ukraine,
Dnipropetrovsk

Yuriy Proydak

D.Sc. in engineering
National Metallurgical Academy of Ukraine,
Dnipropetrovsk

Isaak Lev

D.Sc. in engineering
National Metallurgical Academy of Ukraine,
Dnipropetrovsk

Gennadiy Tregubenko

D.Sc. in engineering
National Metallurgical Academy of Ukraine,
Dnipropetrovsk

Georgiy Polyakov

Head of laboratory problems
National Metallurgical Academy of Ukraine,
Dnipropetrovsk

Abstract
Distribution of nitrogen aluminum and titanium between the nitrides and solid solution in the steel when hot rolling is established. Optimal amount of titanium and aluminum to obtain dispersed nitride is determined. Optimum temperature and time regimes for heat treatment

are recommended.

Key words: CARBON, LOW ALLOY STEEL, NITROGEN, TITANIUM, ALUMINUM, INTERFACIAL DISTRIBUTION

Introduction

The titanium nitrides and carbides (TiN and TIS), which are the germs of primary grains, are usually formed in the molten metal during carbon and low alloy steels production of mass assignment. Their cubic crystalline structures are so similar, and lattice distances dimensions are relatively equal; thus, complete mutual solubility with titanium carbonitrides Ti(N,C) formation and lattice distances from 0.42440 nm to 0.43280 nm is their most characteristic feature in an equilibrium state.

There can be compounds of the titanium in the form of two phases (Ti (N, C) and Ti (C, N)) with the relatively equal lattice distances in the alloy steels, where nitrogen is applied as the alloying element; but these titanium compounds do not form uniform solid solution. It is caused by their temperature history, which does not provide the equilibrium state as a result of diffusive processes [1].

Fe-C-N system and systems related to it are well studied [2]. The simple nitrides and carbides may be formed in the alloys if there is no titanium there; their quantity depends on steel chemical composition and heat treatment. Limited solid solutions areas lead to structural modifications, which are actually carbonitrides. The nitrogen solubility in the cement carbide is not high, and face-centered cubic structure Fe_4N (γ') and close-packed hexagonal structure ($\sim Fe_3N$) are easily stabilized by nitrogen. Thus, nitrogen is a powerful tool of carbonitrides of $Fe_2(C,N)$ type stabilization; at that, phases succession, which is finished with formation of Fe_2N, is implemented with increase of nitrogen content [2].

It is necessary to emphasize that all these carbides, nitrides and carbonitrides of iron are actually metastable structures, and true equilibrium is reached between α-Fe, γ-Fe and graphite or gaseous nitrogen. Their reactions play a major role in the steels, for example, when carbonization and nitriding. The iron carbonitrides are also closely connected with nitrous and carbon martensite. The last form continuous series of solid solutions, but when low-temperature tempering, the carbonitride precipitations in the form of fine phases can be formed. These processes substantially depend on the temperature, time, preliminary heat treatment and, of course, on the ratio [N]/[C] and diffusion development degree. They can be controlled and directed to the necessary side by means of alloying additives introduction to the steel. These complex carbonitrides are capable to arise in the matrix on boundaries of grains and subgrains, and at early stages, they can be concentrated in the form of atoms (C+N) around the dislocations (Cottrell clouds) having considerable impact on the steel durability.

Objectives and tasks. During the analysis of improvement ways of carbon low alloyed steel quality, it was established [3,4] that it is important to know not only the general content of nitrides forming elements, but also their distribution between phases for considerable grain refining and mechanical and operational properties improvement.

Depending on conditions of steel structure formation, the titanium and aluminum nitrides can be precipitated in the form of rather small and large particles or both at the same time. The more nitrides forming elements are there (present) in steel, the larger precipitated nitrides will be. In paper [5], it is shown that the titanium concentration increase from 3·10-3% to 20·10-3% provides sharp increase in amount of titanium nitrides at rather constant nitrogen content (12-14) ·10-3% in steel 20GATYuL. At that, rather small precipitations of TiN of 15-200 nm in size are mainly formed. At increase of titanium concentration from 20·10-3% to 40·10-3%, the durability growth of titanium nitrides distribution is reduced due to redistribution of number of large and small inclusions towards the former. Further increase of the titanium concentration from 40·10-3% to 120·10-3% does not practically affect the nitrides distribution density, but considerably increases their size (1-35 microns) and changes their phase composition.

Similarly, if the aluminum content in steel is increased to its stoichiometric content in nitride, the nitrogen content in solid solution decreases, and the quantity of fine AlN [5] increases. However, further increase of aluminum concentration reduces the content of its fine

nitrides.

The size of fine particles also depends on their formation temperature. At low temperatures, a large number of fine-grained TiN and AlN is formed, and large nitrides are formed at more high temperatures, but their number is less. For example, when forming of aluminum nitrides at 1000^0C, their size is about 10 nm, and if AlN is precipitated at 600^0C, they are of ~1 nm in size [6]. In paper [7], it is shown that using isotherms, it is possible to predict AlN particles distribution according to their sizes in hot-rolled (~ 1200ºC) and normalized (~ 900ºC) steels. The size of aluminum nitrides can be predicted using the equation:

$$\lg r = - (5267 / T) + 2.593 + \lg (\tau / 3), \qquad (2)$$

where r - particles radius, nm; T – temperature, K; τ – time, hrs.

It is known [8] that aluminum nitrides are not formed when constructional steels smelting in liquid metal. The amount of AlN formation free energy is reduced while cooling of the hardened metal, but the kinetics of their implementation is difficult. Dependence of aluminum nitrides precipitation in austenite from the temperature in the equilibrium conditions and under long isothermal time is determined in paper [9]:

$$\lg K_{AlN} = \lg[Al] \cdot [N] = \frac{7400}{T} + 1.95 \qquad (3)$$

If the aluminum and nitrogen concentration production value exceeds equilibrium value of $\lg K_{AlN}$ at a certain temperature, there is a thermodynamic opportunity for AlN particles precipitation.

Calculations of the equations (2) and (3)

show that in the steels, where aluminum containing is more than $30 \cdot 10^{-3}$% and nitrogen containing is $15 \cdot 10^{-3}$%, the formation of rather large AlN (3-4) $\cdot 10^{-3}$% at a temperature of hot rolling is possible. At a temperature of such steels heat treatment (~900ºC), the formation of more and finer AlN particles at the smaller content of nitrogen ($\geq 10 \cdot 10^{-3}$%) is possible.

Positive effect of titanium and aluminum nitrides on grain refining and the properties complex of steels of ATYu type are shown only at high degree of their dispersion and their rather large number. However, it is necessary to know the interfacial distribution of the titanium, aluminum and nitrogen for more effective use of nitride hardening opportunities of steels of this type.

Researches results. In this paper, the samples of hot-rolled steel from the two experimental-industrial melts in the conditions of

OJSC ESPTs-1 "Electrometallurgy plant "Dneprospetsstal" were analyzed as program research for necessary data obtaining for mass industrial introduction of the offered way of constructional steels hardening and steels for railway transport, pipelines, etc. Commercial mild steels St20 according to DSTU 2651 (GOST 1050), microalloyed additionally by nitrogen, titanium and aluminum, were melted in 25 t furnace. Nitrogen was added one time by the nitrided manganese 3 minutes before tapping. The second melting was different in that there was 3 times less of titanium than in the first one. The actual chemical composition of melting is given in Table 1.

Table 1. Melting chemical composition

Melting number	Sample number	Elements content, %							
		C	Mn	Si	P	S	N	Ti	Al
1	1-1(12)*	0.19	0.71	0.30	0.024	0.010	0.018	0.016	0.028
2	2-1(22)*	0.19	0.63	0.28	0.015	0.014	0.020	0.005	0.029

* Note: a sample from the lower part of an ingot

In the paper advanced electrochemical technique of outlining and analysis of nitrogen-containing inclusions in iron alloys was applied [10, 11].

By means of these techniques and the invention of " Way of aluminum nitride determination in the nonmetallic inclusions precipitated from steels and alloys" [12], nitride and carbonitride phases were outlined and

analyzed in the studied samples. Electrolytic dissolution of metal and outlining of connections were carried out in samples of 18 mm in diameter and 80 m in high in the water electrolyte containing 15% of NaCl and 2.5% of tartaric acid in the potentiostatic mode, which was created by potentiostat 10-20 PEB. Electrolysis was carried out in the areas of direct dependence of overhead tension on the current density logarithm. The inclusions outlining was carried out for their

chemical composition determination. For this purpose they were dissolved in the concentrated H_2SO_4 with additional wet alloying in the liquid melt Na_2SO_4 with H_2SO_4. The obtained solutions were transferred into measuring flasks, and the nitrogen, titanium and aluminum content connected in nitride and carbonitride phases ($[N]_{con.}$, $[Ti]_{con.}$ and $[Al]_{con.}$) was determined in the aliquot parts. Nitrogen was determined by photocalorimetric method by coloring intensity of complex connection oxyamidodimercury, which is formed at interaction of ions NH_4^+ with $K_2[HgJ_4]$ [13]. Previously, nitrogen in the form of NH_3 was precipitated from alkaline solution by the method of steam aspiration. Aluminum was determined by the photocalorimetric method according to [13, 14]. The method is based on formation of complex compound of aluminum with aluminon ($\lambda_{max} = 530$ nm when pH 4.7-5.1). The titanium impact was eliminated by its separating together with iron, manganese, copper and chrome sodium hydroxide with present of boric acid. The titanium was determined by the photocalorimetric method with application of diantipyrylmethane according to [15]. The titanium quantity was found by measurement of coloring intensity of a titanium yellow complex with the 4.4- diantipyrylmethane ($\lambda_{max} = 385$ nm). The researches results are given in Table 2.

Table 2. Results of the electrochemical phase analysis (Distribution between the phases Ti and N)

Sample number	Ti $1\cdot10^{-3}$ content, mass %			TiN $1\cdot10^{-3}$ content, mass %	N $1\cdot10^{-3}$ content, mass %		
	$[Ti]_{gen.}$	$[Ti]_{con.}$	$[Ti]_{sol.}$		$[N]_{gen.}$	$[N]_{TiN}$	$\Delta[N]_{sol.}$ After precipitation of TiN
1-1	16.0	14.6	1.40	18.9	18.0	4.27	13.7
1-2	16.0	14.0	2.00	18.1	18.0	4.09	13.9
2-1	5.0	4.50	0.50	5.80	20.0	1.31	18.7
2-2	5.0	4.20	0.80	5.46	20.0	1.24	18.8

As it appears from Table 2, TiN formation is limited by the general titanium content. At that, almost all the titanium containing in steel ($\geq 90\%$) was connected in its nitrides. Rather high content of titanium nitride in metal of the first melting $(18.1-18.9)\cdot10^{-3}\%$ provides rather high density rate of its particles in steel (up to 320 u/cm^2). However, in solid solution, there are ~ 37% of aluminum of whole its quantity and total number of nitrides and carbonitrides is 187 units for one ferritic grain. The smaller titanium content in samples 2-1 and 2-2 (see Tab. 2) caused the formation of (5.46-

$5.80)\cdot10^{-3}\%$ of TiN, that is about 3.3 times lower than in the first melting metal. Despite this, the total number of AlN and TiN particles increased to 519 units for one ferritic grain, i.e. almost three times. This may be due to the fact that at rather constant concentration of nitrogen $(18-20)\cdot10^{-3}\%$ and aluminum $(28-29)\cdot10^{-3}\%$, the titanium concentration reduction from $16\cdot10^{-3}\%$ to $5\cdot10^{-3}\%$ makes it possible to increase considerably the content and amount of aluminum nitrides (Table 3) at parallel reduction of the dissolved aluminum quantity (~ 25% from general amount).

Table 3. Results of the electrochemical phase analysis (Distribution between the phases Al and N)

Sample number	Al $1\cdot10^{-3}$ content, mass %			AlN $1\cdot10^{-3}$ content, mass %	N $1\cdot10^{-3}$, content, mass %		
	$[Al]^*_{gen.}$	$[Al]_{con.}$	$[Al]_{sol.}$		$[N]_{gen.}$	$[N]_{AlN}$	$\Delta[N]_{sol.}$ Afet precipitation of TiN and AlN
1-1	28.0	12.2	10.8	18.5	18.0	6.33	7.4
1-2	28.0	13.1	9.9	18.0	18.0	6.80	7.1
2-1	29.0	14.2	9.8	21.6	20.0	7.37	11.3
2-2	29.0	19.4	4.6	29.2	20.0	9.97	8.7

*Note: the content of aluminum in its oxide is $5\cdot10^{-3}\%$ in all the samples

As it follows from the data of Table 3, there is rather high amount of free nitrogen (7.1-

$11.3)\cdot10^{-3}\%$ and aluminum $(4.6-10.8)\cdot10^{-3}\%$ in solid solution of samples from hot-rolled electrical

steels 20ATYu.

Therefore, on the basis of the conducted researches, we recommend to subject carbon steels to the corresponding heat treatment at the optimum temperature and time modes; it could increase the amount of fine-grained aluminum nitrides in the metal and, respectively, improve its complex of mechanical and operational characteristics. It is rational to carry out the heat treatment by two modes: normalization or thermohardening at ~900ºC (temperature maximum of precipitation of aluminum nitrides from austenite) and the subsequent tempering at ~650ºC (temperature maximum of precipitation of aluminum nitrides from ferrite). The special attention is required to be paid to the temperature and time parameters of tempering since the aluminum nitrides, which are precipitated from ferrite, with a cubic lattice are finer and provide more strengthening properties of steel than hexagonal AlN, which are formed from austenite.

Conclusions

1. For the first time, the quantitative data on distribution of nitrogen, titanium and aluminum between nitrides and solid solution were obtained for such steels.

2. The optimum quantity of the titanium in carbon steels leading to the best interfacial distribution of nitride forming elements (N, Al, Ti) in the conditions of hot rolling is defined.

3. For the complete nitrogen fixation in AlN nitrides, the aluminum quantity in carbon steel must be $\geq 40 \cdot 10^{-3}$ mass %. The optimum content of aluminum must be $(40 - 60) \cdot 10^{-3}$ mass % for fine nitrides obtaining and rather high flowability of carbon steel maintenance.

4. The rational temperature and time modes of carbon steels heat treatment providing improvement of mechanical and operational properties are recommended.

References

1. Gol'dshteyn M.I. *Uprochnenie konstruktsionnykh staley nitridami.* [Hardening of constructional steels by nitrides]. Moscow, Metallurgiya, 1970. 222 p.
2. Kh. Dzh. Gol'dshmidt *Splavy vnedreniya.* [Interstitial alloy. Translation from English]. Moscow, Mir, 1971, Vol. 2, 424 p.
3. Rabinovich A.V. (2012) Development and production of constructional steels with carbonitride hardening on the basis of complex microalloying of N-Ti-Al. *Metallofizika i noveyshie tekhnologii .* Vol.
4. Rabinovich A. (2007) New steels inoculated by Ti+Al+N. *Advances in metallurgical processes and materials: Proc. International conf.*, Dnepropetrovsk, Higher Metallurgical Education of Ukraine, Vol. 2, p.p. 161– 167.
5. Rabinovich A.V. (2010) The effect of microadditives of the titanium on structure and property of cast electric steels. *Teoriya i praktika metallurgii.* No 5–6, p.p. 60– 63.
6. Povolotskiy D. Ya. *Alyuminiy v konstruktsionnykh stalyakh.*[Aluminum in the constructional steels]. Moscow, Metallurgiya, 1970. 231 p.
7. Borchers H. Z. Arch für Eisenhutterwesen. 1965. Vol. 4, p. 311.
8. Grigor'yev G.A. *Zavodskaya laboratoriya.* [Plant laboratory]. Vol. 29. No 4, 1963, p. 446.
9. Ershov G.S. *Stroenie i svoystva zhidkikh i tverdykh metallov.* [Structure and properties of liquid and solid metals]. Moscow, Metallurgiya, 1978. 248 p.
10. Lev I. E. *Analiz azotsoderzhashchikh soedineniy v splavakh zheleza.* [The analysis of nitrogen-containing compounds in iron alloys]. Moscow, Metallurgiya, 1987. 121p.
11. Isaeva L.E. (2005) Research of the isolation process of molybdenum nitrides from steels. *Voprosy khimii i khimicheskoy tekhnologii.* No1, p.p. 163.
12. Patent 1033439 USSR, C 01 F 7/00, G 01 N 31/00. Way of aluminum nitride determination in the nonmetallic inclusions precipitated from steels and alloys. I.E. Lev, B.G. Lazarev, T.A. Gribanova and others. No 3005589, Appl. 12.02.1980, Publ. 08.04.1983.
13. Babko A. K. *Kalorimetricheskiy analiz.* [Calorimetric analysis]. Moscow, Goskhimizdat, 1951. 408 p.
14. 22536.10-88*: Stal' uglerodistaya i chugun nelegirovannyy. Metody opredeleniya alyuminiya.* [Carbon steel and alloyed cast iron. Methods for determination of aluminum]. Moscow, Gosstandart SSSR, 1990. 13 p.
15. GOST 10280 2010 Steel and iron. Determination of titanium content. Diantipyrylmethane spectrophotometric method. Moscow, Standartinform, 2012. 16 p.