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Improvement of the properties of low-alloy constructional steels microalloyed with the nitrogen-titan-aluminum complex

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Abstract
The relevance of research aimed at developing cast cost-effective low-alloy steels with carbonitride hardening due to complex microalloying with inexpensive and accessible elements such as titanium, aluminum and nitrogen is shown.
It has been established that for the most effective use of the nitrogen-titanium-aluminum complex when the microalloying of structural steels, it is necessary to create conditions for obtaining maximum amount of fine titanium carbonitrides and to ensure the formation of sufficient number of aluminum nitrides. It is determined that the best quality of the metal is provided at optimal joint micro additives of titanium (0.01-0.03%), aluminum (0.02-0.06%) and nitrogen (0.014-0.020%). At the same time, heat treatment of ferritic-pearlitic steels of (15-20) G (S) ATYUL grade must be carried out in two modes: normalization or quenching at 900-920 °C (during 1.5-2.5 hours) followed by tempering at 650- 690 °C.
The use of complex microalloying with nitrogen, titanium and aluminum of steels of (15-20) G (S) L grade allowed achieving the metal grain refining no less than 2 times; increasing in the yield point in the normalized state by 30-80 MPa, and after quenching and high tempering by 60-130 MPa; increasing in cyclic durability of steel by 1.7 times; increasing in yield strength at 250-450 °C by 2.0-2.5 times under industrial conditions.
Key words: STEEL, MICROALLOYING, NITROGEN, TITAN, ALUMINIUM, CARBONITRIDE HARDENING, STRUCTURE, PROPERTIES

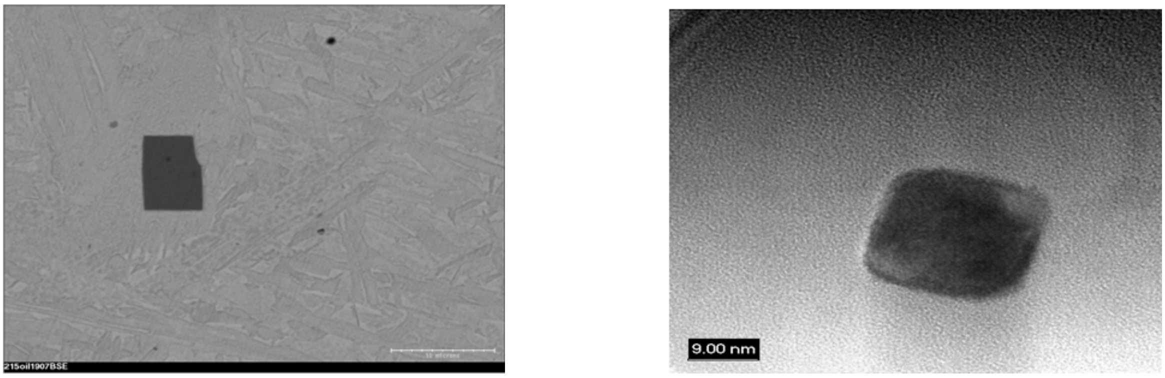
Cast low-alloy steels are usually smelted in electric arc furnaces and, therefore, they contain an increased amount of nitrogen (0.008-0.012%), which negatively affects their quality. However, the binding of free nitrogen to special carbonitrides or nitrides improves the structure and properties of the steel. In the opinion of the authors of [1], the complex carbonitride hardening is the most effective, which leads to the formation in a relatively wide temperature range of nitrides of various elements possessing a sufficiently high but significantly different affinity to nitrogen. As such elements, in addition to the basic vanadium, niobium is usually chosen; aluminum, titanium, zirconium are less often selected.

However, the main disadvantage of using vanadium and niobium is the very high cost of alloying materials. Therefore, studies aimed at developing cast low-alloy steels with carbonitride hardening due to complex microalloying with relatively inexpensive and sufficiently accessible in Ukraine elements (titanium and aluminum) are relevant.

A number of studies have noted the beneficial effect of complex micro-alloying with nitrogen, titanium and aluminum on the quality of cast steels. It has been established [2] that joint additions of nitrogen (0.024-0.045%), titanium (0.16-0.18%) and aluminum (0.06-0.12%) influence better the structure and properties of 40G2L steel than the use of microalloying complex NV-Al. However, the overwhelming majority of researchers ([3]) believe that microalloying with nitrogen and titanium cannot favorably affect the properties of cast low-alloy steels. This is due to the formation of large titanium carbonitrides (up to 35 microns) located in the volume of the grain and not soluble during heat treatment.

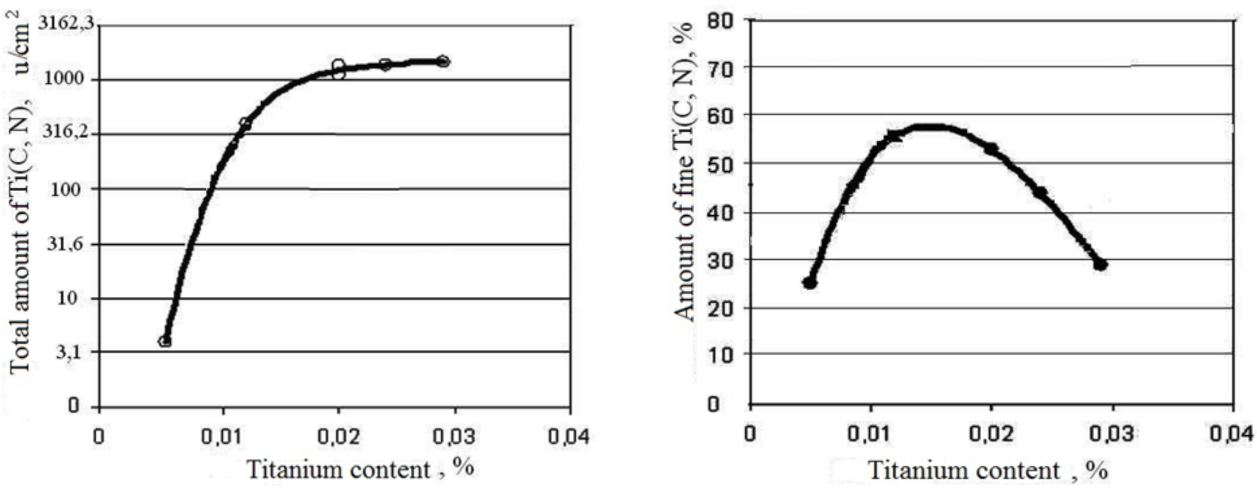
It is known [1] that the intragranular arrangement of titanium carbonitrides positively influences the formation of the primary structure and the grain size and the properties of the cast metal, respectively. In the development of ATYU grade steels, the authors of [4] have proceeded from the premise that titanium carbonitrides predominantly regulate the cast structure and aluminum nitrides - grain formation during heat treatment.

The work [4] shows that the formation of two types of titanium carbonitrides is possible in the production of St20ATYU hot-rolled steel. The first type of Ti (C, N) (Fig. 1, a) has rather large dimensions (1-12 microns) and is formed in liquid steel. The second type of titanium carbonitrides (Fig. 1, b) has nano sizes (10-200 nm) and is most likely released upon solidification and cooling of the steel in the solid state. As follows from the data of [4], for the most effective use of complex microalloying of cast low-alloy steels with nitrogen, titanium and aluminum, it is necessary to create conditions for obtaining as many fine titanium carbonitrides as possible and to provide thermodynamic and kinetic possibilities for the formation of aluminum nitrides in sufficient volume.



a) × 2500 b) × 800000

Figure 1. Titanium carbonitrides in steel of St20ATYU grade [4]



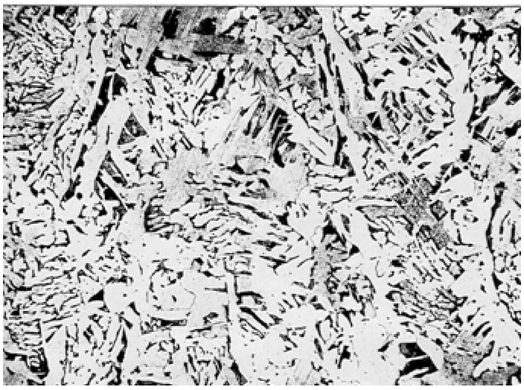
a) b)

Figure 2. Influence of the titanium content on the total amount (a) and the fraction of fine (b) carbonitrides in 20GATYUL steel

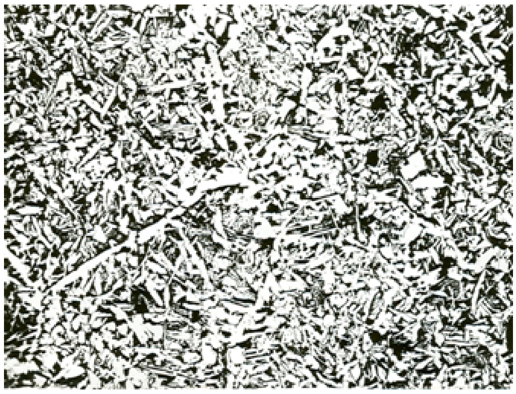
By a metallographic analysis of 20GL steel samples containing 0.014-0.015% nitrogen, the influence of the titanium concentration (0.003-0.11%) on the size and quantity of carbonitrides was determined. It has been found that when the content of titanium in steel rises from 0.003 to 0.020%, a sharp increase in the amount of carbonitrides (Fig. 2a) occurs, the size of which is within the range of 10-200 nm. It is determined that the greatest amount of fine particles of Ti (C, N) occurs at a titanium concentration of 0.012-0.018%. When the titanium content rises from 0.020 to 0.030%, the increase in the amount of carbonitrides decreases, and their size increases to 1-10 microns. However, the number of fine titanium carbonitrides (30-50% of the total amount (Fig. 2, b)) is sufficient for significant reduction of the size of the primary grain, dispersion and grain boundary hardening. Further increase in the concentration of titanium from 0.031% to 0.110% almost does not affect the amount of its carbonitrides, but significantly increases their sizes (up to 15-35 microns) and changes the stoichiometric composition (towards the greater carbon content).

Thus, it is necessary to regulate the titanium content in the range from 0.010 to 0.030% in order to obtain a great number of fine titanium carbonitrides, which favorably influence their structure (Fig.3) and properties (Table 1) in the cast steel of ATYU grade.

The mechanical properties of steels containing the ATYU complex (Table 1) correlate well with the results of metallographic analysis. Microalloying with titanium in optimal limits significantly increases the strength and impact toughness of 20GATYUL steel. In this case, the maximum increase in strength (50-80 MPa) is observed with a titanium content of 0.020-0.025%, i.e. with the greatest total amount of titanium carbonitrides, as well as with a high proportion of fine particles (≥ 45 %). At the same time, the increase in the impact strength (by 1.5-2.0 times) affects only the rise in the number of fine particles of Ti (C, N) ([Ti] = 0.012-0.018%). It should be noted that with titanium content ≥ 0.031 %, the plasticity of the metal falls sharply.



0.003% Ti



0.016% Ti

Figure 3. Effect of titanium on the cast structure of 20G (C) ATYUL (x100) steel

Table 1. Influence of titanium content on the properties of 20GATYL steel in the normalized state

No	[Ti], %	Mechanical properties			
		σ, MPa	σ, MPa	δ , %	KCU^{-60}, J/cm^2
1.	0.003	390	580	25	35.5
2.	0.008	405	590	26	39.0
3.	0.010	420	600	28	42.5
4.	0.012	445	640	23	54.5
5.	0.013	430	630	25	57.0
6.	0.016	420	600	26	61.5
7.	0.018	430	610	28	70.5
8.	0.020	460	660	26	52.5
9.	0.022	450	640	28	48.0
10.	0.023	450	630	26	52.0
11.	0.025	470	660	23	39.0
12.	0.028	420	610	25	50.0
13.	0.031	415	640	17	49.0
14.	0.046	410	610	16	46.0
15.	0.060	410	610	16	42.0
16.	0.110	440	640	14	24.5

To obtain a large amount of titanium carbonitrides and especially aluminum nitrides, the concentration of nitrogen in the steel should be as high as possible, but it also should not lead to the formation of gas bubbles, which are responsible for the casting defects. On the basis of thermodynamic calculations and the data of [5, 6], the content of nitrogen in cast ferritic-pearlitic steels of (15-20) G (S) ATYUL grade should be from 0.014 to 0.020%.

Microalloying with aluminum should ensure the most complete purification of the solid solution from nitrogen, maximize grain refinement and not deteriorate the flowability of steel. An expression for calculating the optimal aluminum content in a metal was obtained by the thermodynamic analysis of the formation of aluminum nitrides in cast steels of (15-20) G (C) ATYUL grade and the data of [6]:

$$\lg\left([Al]-[Al]_{ox.}-[Al]_{sol.solut.}\right)=-\frac{6770}{\grave{O}}+1.33-0.183[C]+ \\ +0,045[Mn]-0,044[Si]-\lg\left([N]-[N]_{Ti(N,C)}-[N]_{sol.solut}\right), \quad (1)$$

where [Al], [C], [Mn], [Si], [N] – content of aluminum, carbon, manganese, silicon and nitrogen respectively,%;

$[Al]_{ox.}$ - content of aluminum bound to oxides;

$[Al]_{sol.solut}$ and $[N]_{sol.solut}$ - content of aluminum and nitrogen in the solid solution respectively, %;

$[N]_{Ti\{N,C\}}$ - content of nitrogen bound to titanium carbonitrides,%.

By thermodynamic calculations using the technic given in [5], it was determined that with optimal microalloying of steels (15-20) G (S) ATYUL grade with nitrogen and titanium, the titanium carbonitrides formed were similar in composition to TiN. Then it can be written:

$$[N]_{Ti(N,C)}=0,29\cdot[Ti], \quad (2)$$

where 0.29 – stoichiometric coefficient for pure titanium nitride;

[Ti] – content of titanium in steel,%.

According to [7], in cast low-alloy steels, the content of aluminum bound to oxides is usually constant and equal to 0.006%. The authors of [8] have established that in ferrite-pearlitic steels of the ATYU grade, the nitrogen content of the solid solution is 0.0071-0.0113%, and that of aluminum is 0.0046-0.0108%. Using the data of [7, 8], calculations based on expressions (1) and (2) for the heat treatment temperature range (Table 2) show that the content of aluminum in steels of (15-20) G (S) ATYUL grade should be 0.020 -0.060%.

Table 2. Influence of the temperature-time mode of heat treatment on the structure of steels of (15-20) G (S) ATYUL grade

Temperature, ° C	Duration of holding, min.	Grade of ferritic grain	General characteristics of the microstructure	Phase characteristics	
				Ferrite	Perlite
850	40	5, 6	Ferrite-pearlite (F-P) with sections of martensite (M) and bainite (B)	Nonequiaxial	Granular
	90	5, 6, 8			
	120	5, 6, 7, 8		Grains of 8 points are equiaxial, and the rest are nonequiaxial.	
	150	6, 5, 8			
870	40	7, 6, 8			
	90	7, 6			
	120	7, 8			
	150	7, 8, (9)			
900	40	8, 7, (9)		Fine grains are equiaxial, large are of irregular form	Lamellar finely-differentiated
	90	8, 9			
	120	8		Equiaxed grains by borders of carbides release	
	150	8	F-P		
920	40	8	F-P with sections of M and B	Equiaxial	
	90	8	F-P		
	120	8		Equiaxial by borders of carbides release	
	150	8			
950	40	8	F-P with sections of M and B	Equiaxial by borders of carbides release	
	90	8			
	120	8			
	150	8			

Based on the analysis of the data given in Table. 2, it is determined that for steels of (15-20) G (S) ATYUL grade, the total completion of recrystallization processes (equiaxed ferrite grain - 8 points, absence of bainite and martensite, thinly differentiated perlite) occurs at a temperature of 920 ° C for 1.5 hours, and at 900 °C for 2.5 hours.

It should be noted that according to GOST 977-88 "Steel castings", the heat treatment temperature for base steels 20GL and 20GSL is 870-890 °C. Thus, microalloying of cast ferritic-pearlitic steels with nitrogen, titanium and aluminum increases the heat treatment temperature by 30 °C.

Taking into account the relatively high content of aluminum and nitrogen in a solid solution of ATYU steels, as well as the fact that during the phase transition

− grefining of the metal grain no less than 2 times;

− increase in the yield point in the normalized state by 30-80 MPa (9-23%), and after quenching and high tempering by 60-130 MPa (13-29%);

− increase in cyclic durability of steel by more than 1.7 times;

− increase in yield strength at 250-450 °C by 170-250 MPa (2.0-2.5 times).

Industrial development of the technology of smelting of 20GATYUL steel was carried out under the conditions of PJSC "Kremenchug Steel Plant" at the production of castings for car building. On the basis of the whole complex of carried out studies, TS U 27.1-33686285-002: 2007 "Castings made of 20GL steel with increased strength for car building" have been developed, which together with "Ukrzaliznytsia" order No. 000180 / TsV allow mass production of 20GL steel micro-alloyed in complex with nitrogen, titanium and aluminum.

Production of steels of (15-20) GSATYUL grade is established under the conditions of PJSC "Armaprom" (Mirgorod). Application of microalloyed steel of 20 GSL grade in accordance with OST 108.961.02 and OST 108.961.03 allows us to increase significantly the operational reliability and durability of cast products for power engineering. The use of 15GSATYUL steel according to TS U 27.1 - 21871578 - 001: 2008 provides a significant reduction in the metal capacity of casting valves, as well as the possibility of its use even under extreme conditions of the Far North ($KCV^{-60} \geq 29.4$ J/cm^2). At the same time, the low carbon equivalent of 15GSATYUL steel allows welding (for example, casting of blocking cast-iron fittings in to the pipeline) under the "field" conditions excluding heating with subsequent heat treatment.

Conclusions

It has been established that the optimal use of complex microalloying of cast low-alloy steels with nitrogen, titanium and aluminum favorably affects their structure and properties. Temperature-time modes of heat treatment of ferrite-pearlitic steels of (15-20) G (S) ATYUL grade, which provide the best quality of metal, are determined.

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