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NITROGEN ALLOYING OF WELD METAL IN ARC WELDING OF CORROSION-RESISTANT STEELS (Review)

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The paper shows the favourable effect of nitrogen alloying of high-alloyed corrosion-resistant steels and weld metal on stabilization of the structure, prevention of grain boundary segregation in the HAZ and weld metal, and ensuring high corrosion resistance and technological strength of welded joints. 15 Ref., 2 Tables, 10 Figures.

Keywords: *arc welding, corrosion-resistant steels, nitrogen alloying, structure, corrosion resistance, technological strength, coated electrodes*

Today corrosion-resistant austenite and two-phase (duplex) nitrogen alloyed steels make a considerable portion among structural steels used in operation in contact with high and even highly corrosive media [1–3]. They are used in production of technological equipment for manufacture of sulfate and phosphorous fertilizers, carbamide, in pulp-and-paper industry, oil-and-gas and pharmaceutical industry. Such steels demonstrate high resistance to effect of sulfuric, ortophosphoric, acetic, formic acids and sea water.

Alloying of noted steels with nitrogen allows [4, 5]:

● reduce without damage to life time, reliability and life duration of the material, content in it of nickel at conservation of set austenite or austenite-ferrite structure;

● increase without variation of phase composition the content in steels of elements-ferritizers (Mo, V, W) having positive effect on life duration, mechanical and corrosion characteristics of products;

● strengthen α- and γ-solid solutions at virtually invariable levels of their ductility and toughness and, thus, rising allowable stresses in the structures;

● provide increased resistance of equipment to intercrystalline corrosion (Figure 1) and stress corrosion, and at simultaneous nitrogen and molybdenum alloying — increased resistance to general, pitting and crevice corrosion;

● eliminate alloying of steels with titanium or niobium and, thus, preventing the possibility of appearance of «knife-like» corrosion in welded joints (Figure 2);

● improve the characteristics of technological ductility as a result of expansion of interval of existence of austenite in high-temperature field;

● provide an economical effect due to implementation of new, more sparsely-alloyed steels, having increased mechanical characteristics, reliability and life duration of operation of equipment made of them.

The publications do not describe in a lot of details the effect of nitrogen in high-alloy steels on their weldability. Nevertheless, work [7] outlines the relevance of elimination of titanium or niobium from

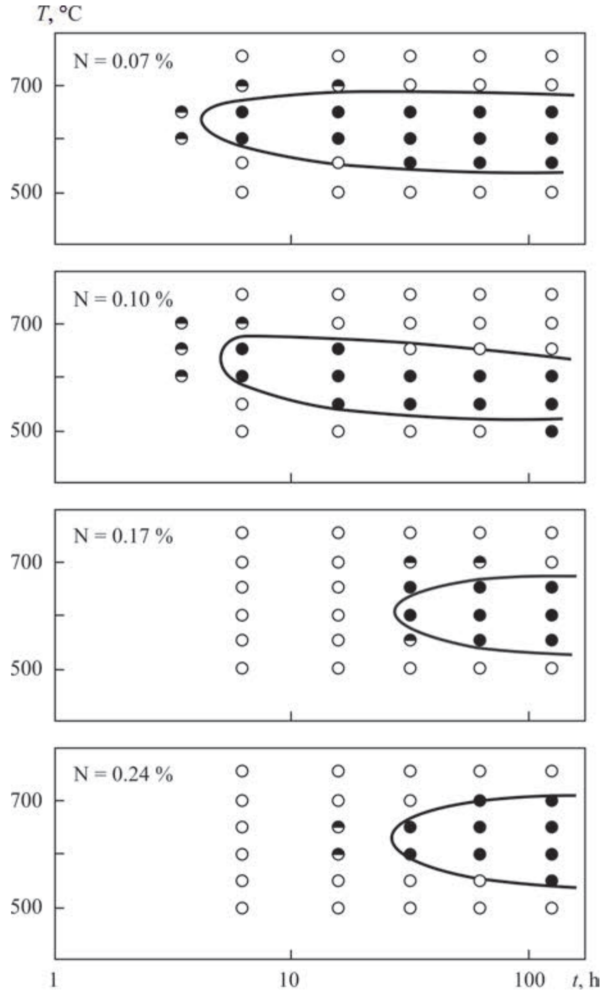

Figure 1. Temperature fields of susceptibility of 03Kh19N10AG3 steel to ICC (method DU GOST 6032–84 [6]

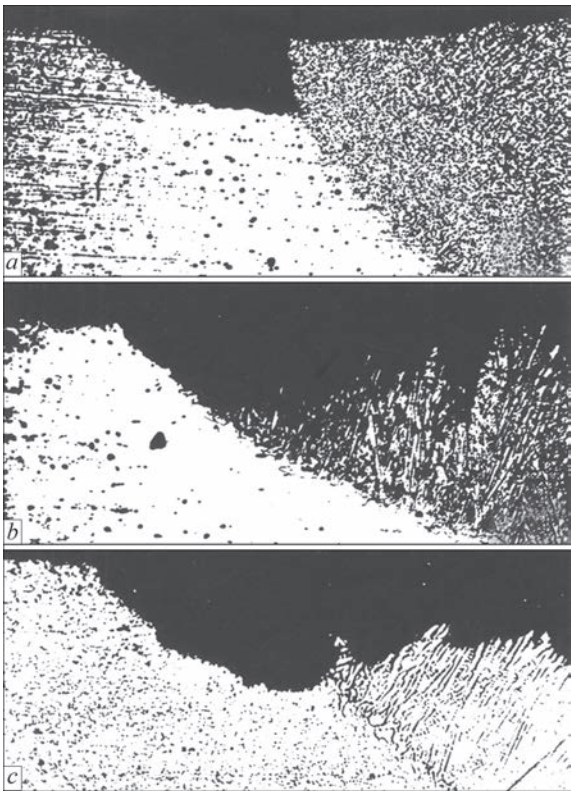

Figure 2. Knife corrosion of welded joints in production of nitrophoska: *a* — welded joint of steel 10Kh17N13M3T (EA-400/(10u electrodes) (×100); *b* — welded joint of 06KhN28MDT alloy (KhL-1 electrodes) (×200); *c* — welded joint of 03Kh21N21M4GB steel (OZL-17U electrodes) (×100)

composition of steel 03Kh12N21M4GB and alloys 03KhN28MDT and 06KhN28MDT titanium or niobium, limitation in their content of sulfur and phosphor and their additional alloying with nitrogen in the limits of equilibrium solubility (0.15–0.25 %). It is shown that in this case the materials are not susceptible to knife-like corrosion (Figure 3), demonstrate increased ICC corrosion resistance (Figure 4) as well as have resistance to near-weld crack formation (Figures 5, 6). This effect is achieved due to effect of nitrogen on suppression of segregation processes in high-temperature segment of near-weld metal zone [8].

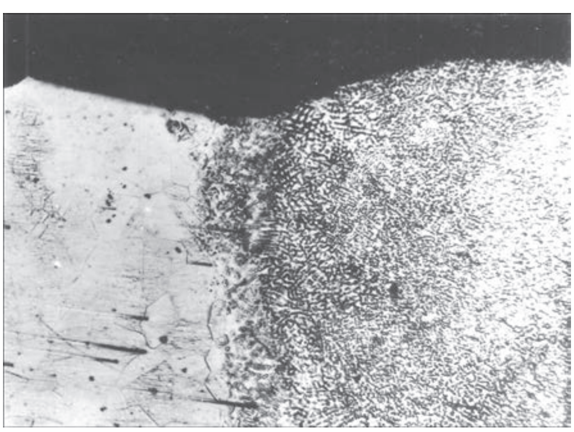

Figure 3. Microstructure (×200) of fusion zone of welded joint of steel 02Kh22N20M4AG after corrosion tests on susceptibility to knife corrosion

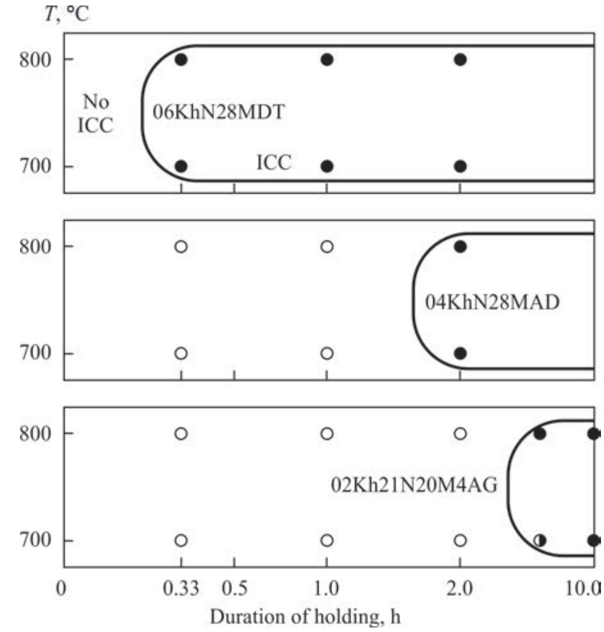

Figure 4. Resistance of materials to ICC

Today, nitrogen alloying is used for steels designed for manufacture of welding equipment and apparatuses, in the amounts, as a rule, corresponding to its normal solubility under atmospheric pressure, and other alloying elements in the amounts, providing after

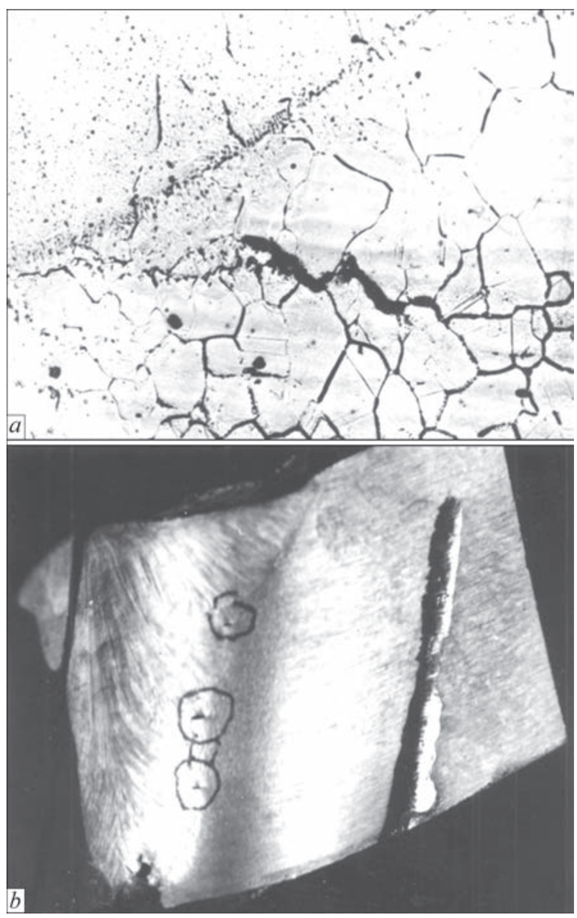

Figure 5. Hot cracks in near-weld zone of welded joints: *a* — steel 03Kh21N21M4GB (ANV-17 grade electrodes) (×250); *b* — alloy 06KhN28MDT (ANV-28 grade electrodes) (×1.5)

quenching conservation of nitrogen in solid solution for obtaining the maximum corrosion resistance.

Below, Table 1 provides the typical compositions of modern high-alloy nitrogen-containing steels, found wide application in different branches of industry, mainly, abroad.

It can be interesting to analyze the efficiency of application of nitrogen as an alloying element in the metal of corrosion-resistant welds. Paper [9] showed that in order to reach corrosion resistance equivalent to base metal of 03Kh17N14AM5 type it is reasonable also to alloy it with nitrogen in 0.14–0.20 % amount. At that, weld metal containing 0.06 % of carbon and alloyed with nitrogen, without Ti and Nb stabilizing, is not susceptible to ICC.

The investigations, carried at the E.O. Paton Electric Welding Institute, revealed that alloying of austenite weld metal with nitrogen promotes increase of its resistance to hot cracking. The effect is strengthened at simultaneous alloying of welds with nitrogen together with manganese. These peculiarities were used in development of welding wire 01Kh19N18G10AM4 and electrodes of ANV-17 grade [10].

It was also determined that nitrogen alloying of weld metal of 03Kh18N18G5AM4 type in welded joint of steel 03Kh16N15M3 even under conditions of testing in 65 % boiling HNO_3 does not reveal tendency to ICC (Figure 7).

One more positive feature of nitrogen in weld metal alloying was determined in evaluation of behavior of welded joints of steels 03Kh16N15M3, 03Kh17N14M3, used in carbamide production. Tests of joints with purely austenite weld metal structure (electrodes ANV-17) and austenite-ferrite (electrodes NZh-13, 09Kh19N10G2M2B alloying type), showed that in the second case there is development of structure-selective corrosion on ferrite phase (Figure 8). It was determined that this phenomenon is caused by redistribution of alloying elements between austenite and ferrite phases, resulting in appearance of a galvanic microcouple (ferrite is the anode).

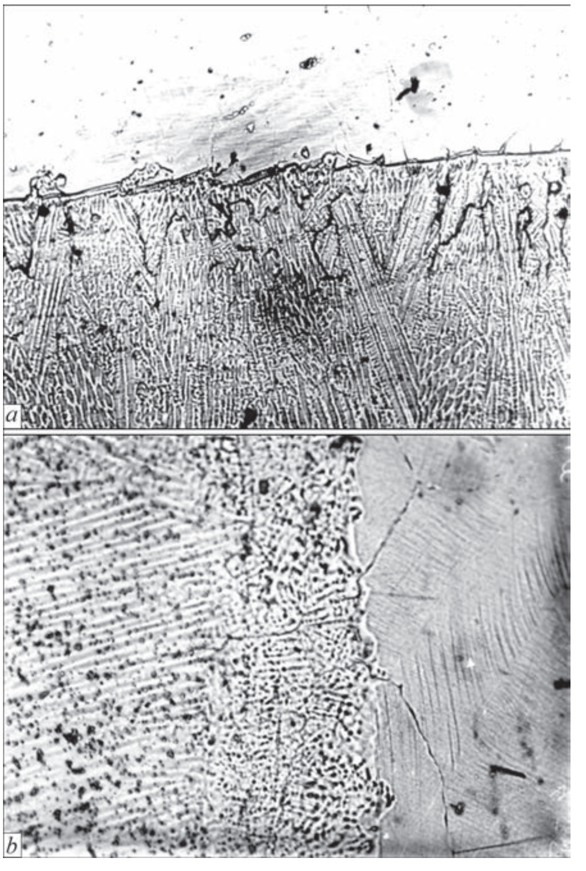

Figure 6. Microstructure of fusion zone: *a* — steel 02Kh22N20M4AG4 (×100); *b* — alloy 04KhN28MAD (×400)

High-alloy weld metal, having molybdenum in its content, can show a tendency to embrittlement due to precipitation in it of σ-phase. This phase precipitates at metal staying in 600–900 °C temperature range. Its appearance was determined, for example, in performance of multipass welding of steel 10Kh1713M3T of 45 mm thickness with NZh-13 grade electrodes (content of ferrite phase in the deposited metal 2–8 %). Purely austenite welds with nitrogen, made of

Table 1. High-alloy corrosion-resistant nitrogen-containing steels

Steel grade on standards		Alloying type	Average content of nitrogen, wt.%	Field of application
EN	ASTM/AISI			
Austenitic				Oxidizing media, production of carbamide, sea tankers, pulp and paper industry, chemical and oil and chemical branches, production of fertilizers
1.4311	303LN	0318AN10	0.13	
1.4439	317LN	03Kh17N13AM5	0.12	
1.4539	N08904	04Kh25N20AM5	0.25	
2293NL	2209	02Kh23N9M3AG	0.16	
25104L	2594	02Kh25N10AM4	0.25	
Duplex				
1.4482	S32001	02Kh20N2G5AD	0.15	
1.4655		02Kh23N5G2AD	0.10	
1.4462	S32205	02Kh22N6M3AG	0.18	
1.4507	S32550	02Kh26N6M3AG	0.17	
1.4501	S32760	02Kh25N7M4GAD	0.27	

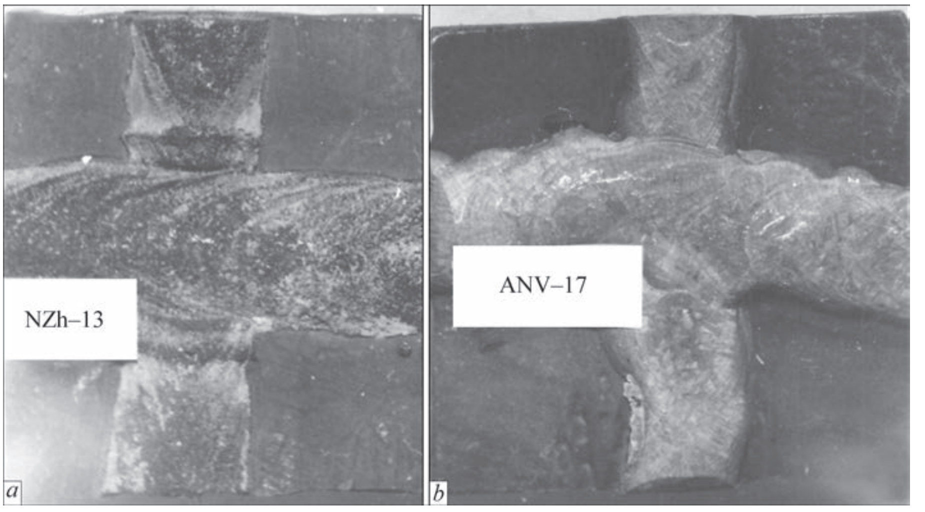

Figure 7. Samples with cross welds on steel 06Kh17N16M3T: *a* — NZh-13 electrodes (5.7 % of ferrite); *b* — ANV-17 electrodes (purely austenitic) after boiling in 65 % HNO_3 200 h

this steel with ANV-17 electrodes, do not demonstrate such susceptibility [11].

In general, with increase of content of element-ferritizers (chromium, molybdenum) in a composition of high-alloy austenite steels and homogeneous to them weld metal for the purpose of improvement of corrosion resistance in highly corrosive medium there is a rise of susceptibility to appearance of intermetallic phases. It can result in loss of their corrosion resistance (Figure 9). And in this case the weld metal alloying with nitrogen promotes prevention of appearance of excessive phases and conservation of high corrosion resistance.

Application of nitrogen as an alloying element in welding consumables has found application in modern developments of such well-known companies as ESAB, Kobelco, Sandvik, voistalpine Bohler Welding and others.

Let's consider such alloying realized by the example of a range of coated electrodes of ESAB Concern [12].

OK 64.30 grade electrodes (04Kh19N13M4AG alloying type, nitrogen content in the deposited metal 0.08 wt.%). The electrodes are used for welding of standard austenite steels of 17-13-3 type, but due to increased content of chromium and molybdenum in the deposited metal it is possible to achieve increase of total corrosion resistance and resistance to pitting corrosion in joint weld metal. Nitrogen can help to provide improvement of ICC resistance as well as

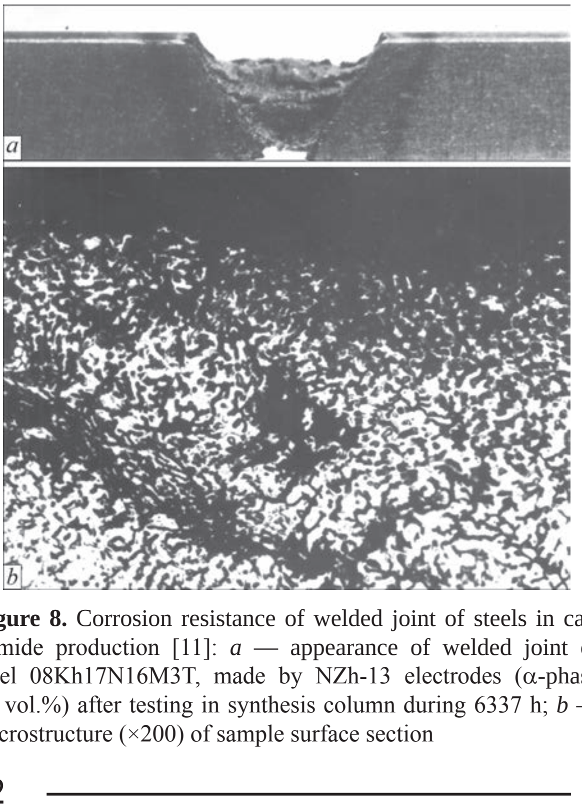

Figure 8. Corrosion resistance of welded joint of steels in carbamide production [11]: *a* — appearance of welded joint of steel 08Kh17N16M3T, made by NZh-13 electrodes (α-phase 75 vol.%) after testing in synthesis column during 6337 h; *b* — microstructure (×200) of sample surface section

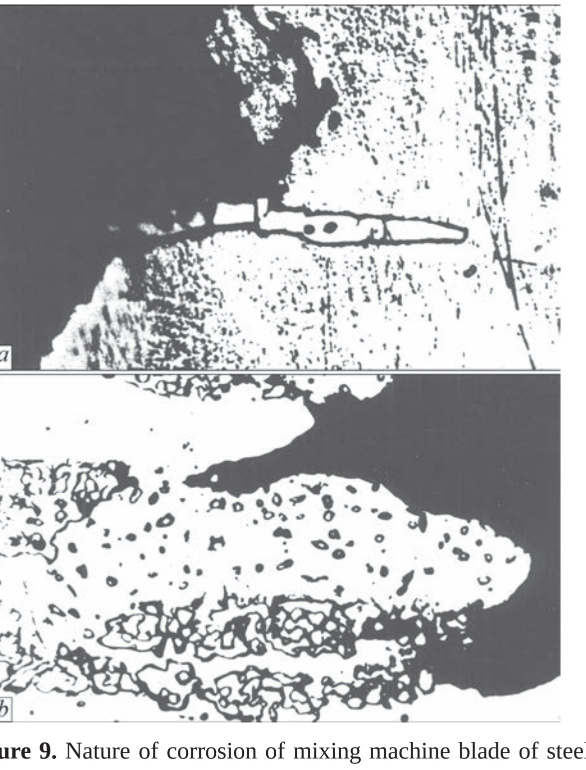

Figure 9. Nature of corrosion of mixing machine blade of steel 05Kh25N25M2T: *a* — after testing at Shchekinsky PJSC «Azot» (×200); *b* — after testing in 40 % HNO_3 + 2 % HF (×1000)

limitation of amount (3–6 %) of ferrite phase in the deposited metal.

OK 310Mo-L grade electrodes (alloying type 04Kh24N22M3AG4, nitrogen content 0.14 wt.%). They are used for welding of steels of carbamide class: 03Kh17N14M3T, 06Kh16N15M3T, 02Kh-25N22AM2 and similar to them. The deposited metal is completely austenite and has exclusively high corrosion resistance in highly corrosive media, for example, in contact with carbamide.

OK 69.33 grade electrodes (03Kh20N25M5AD2 alloying type, nitrogen content 0.08 wt.%). Deposited purely austenite metal is resistant to effect of sulfuric, orthophosphoric, acetic, formic acids and sea water. It is resistant to ICC, pitting and crevice corrosion cracking.

Three grades of coated electrodes are recommended for welding of austenite-ferrite (duplex) steels:

- OK 57.56 electrodes (04Kh23N7AG alloying type, nitrogen content 0.15 wt.%) are used for welding of «budget-friendly» (lower alloying) steels of 08Kh22N6T type and similar to them;
- OK 67.50 electrodes (04Kh22N9M2AG alloying type, nitrogen content 0.16 wt.%) are used for welding of standard duplex steels of 21 % Cr–5 % Ni–3 % Mo–N type or similar to them;
- OK 68.54 electrodes (04Kh25N9M4AG alloying type, nitrogen content 0.16 wt.%) are used for welding of super duplex steels of 25 % Cr–7 % Ni–4 % Mo–N type and similar to them.

Nitrogen alloying provides limitation of content of ferrite phase in weld metal in 25–35 % amount.

Similar materials for welding of nitrogen-containing steels are proposed on the market by voistalpine Bohler Welding Company: FOX CH22/9 (03Kh23N9AM2 alloying type, nitrogen content 0.17 wt.%), FOX ASNS (04Kh19N17M4AG3 type, nitrogen content 0.15 wt.%), FOX CN20/25M-A (04Kh20N25M6G4AD2 alloying type, nitrogen content 0.14 wt.%).

Sumy-Electrode LLC, a leading in Ukraine manufacturer of special electrodes for welding of high-alloy, high-strength steels and dissimilar joints also produces a series of coated electrodes providing nitrogen-containing deposited metal. Among them are the electrodes EA-395/9, NIAT-5, TsT-10 (11Kh15N25M6AG2 alloying type, nitrogen content 0.10–0.12 wt.%), EA-112/15, EA-951/15 (09Kh15N-25M6AG2F alloying type, nitrogen content 0.08–0.10 wt.%), ANV-17 (02Kh19N18G5AGM3 alloying type, nitrogen content 0.2 wt.%).

It should be noted that high-alloy nitrogen-containing materials, for example, EA-395/9, NIAT-5 and other, are used in welding of critical structures of alloyed high-strength steels with limited weldability – welding of steels of austenite class of 08Kh18N10T, 10Kh17N-13M2T type and similar to them with steels of pearlite class, performance of transition layer in multipass welds in products of double-layer clad steels. Besides, they are used for preliminary surfacing of edges of products from pearlite class steels in their welding with steels of austenite class. Work [13] demonstrates the cases of appearance of porosity in weld metal in welding with austenite electrodes with core of Sv-10Kh16N25M6AF wire in overhead position. The recommendations were made on limitation of nitrogen content in weld metal by 0.09 % value (instead 0.1–0.2 %).

At once elimination of pores of nitrogen origin can be reached by increase of oxygen concentration in the melt of weld pool [14] by means of addition, for example, oxides of iron or chromium in the electrode coating.

Method of nitrogen addition as alloying element into a weld metal. Alloying via welding wire is mostly used . In a series of cases such alloying is possible using nitrogen-containing metallic powders or ferroalloys in the electrode coatings or flux-cored wire cores. Content of nitrogen in them can reach 25–35 wt.% (Table 2).

Table 2. Composition of nitrated ferroalloys and metallic powders produced by Meldis-Ferro LLC

Material	Main element, wt.%	Content of elements, wt.%				
		Not more				
		N	C	Si	Al	S
Nitrated ferrochrome FeCr55N10	Cr 55–60	8–10	0.06	1.5	5.0	0.02
Nitrated metallic chrome Cr77N20	Cr 75–79	18–22	0.03	0.4	0.7	0.02
Nitrated ferroniobium	Nb 45–50	10–14	0.20	15.0	5.0	0.05
Nitrated ferrovanadium FeV45N10	V 40–50	7–11	0.75	5.0	2.5	0.05
Nitrated ferrovanadium FeV37N10	V 36–45	7–15	0.75	5…15	2.5	0.05
Nitrated metallic manganese Mn85N10	Mn 83–87	8–11	0.20	1.8	–	0.05
Nitrated ferromanganese FeMn8N7	Mn 75–78	7–8	2.0	3.0	–	0.03
Nitrated ferromanganese FeMn8N10	Mn 70–75	9–14	1.5	1.0	–	0.03
Nitrated ferrosilicon FeSi55N25	Si 50–58	20–28	0.15	–	1.5	0.02
Silicon nitride	Si 63–68	25–35	0.1	–	0.4	0.02
Nitrated Ferrosilicomanganese FeSiMnN12	Mn 50–62	10–15	2.5	12–17	–	0.03
Nitrated silicocalcium	Ca 24	15–20	0.5	40.0	2.0	–

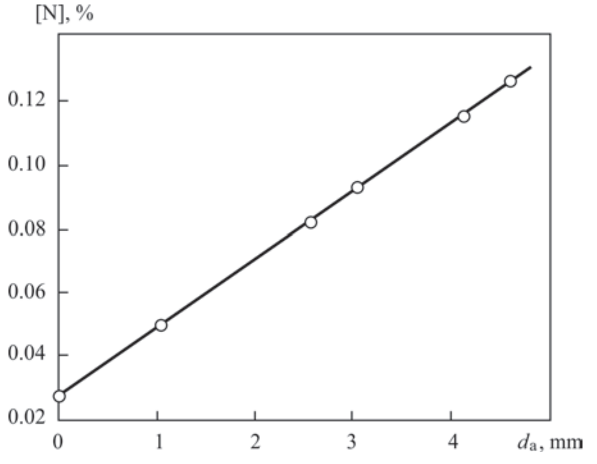

Figure 10. Effect of diameter of torch nozzle on content of nitrogen in austenite deposited metal of 08Kh17N9G3 type

In MIG and MAG processes weld metal alloying with nitrogen can be provided in the same way using a special injector torch (Figure 10).

In the conclusion it should be noted that provided short review indicates favorable effect of nitrogen in content of high-alloy corrosion-resistant weld metals in order to increase their resistance to local types of corrosion, strength characteristics without decrease of ductility and toughness, technological strength, stabilization of structural state.

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