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On the coefficient of compositional stability of nitrogen for high-nitrogen alloys of the Fe-Cr-Mn-Mo-N system, obtained by the SHS method under nitrogen pressure

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The value of the nitrogen compositional stability coefficient has been determined for the alloys of the Fe-Cr-Mn-Mo-N system obtained by self-propagating synthesis, namely, aluminothermy under nitrogen pressure. It is shown that the heat treatment of the alloy containing 14.3 wt.% of chromium, 12.2 wt.% of manganese, 4.0 wt.% of molybdenum and 0.92 wt.% of nitrogen at 1250°C for 2 h leads to the dissolution of a pseudo-perlitic structure (ferrite-nitride mixture) and complete austenization of samples. In this case, the alloy hardness decreases from 255 to 208 HB. The obtained results permit to predict the maximum possible content of nitrogen in continuous ingots (without bubbles and gas porosity in the volume) and, consequently, the structural-phase composition of alloy and optimal regimes of alloying. A method based on iterative calculation is proposed.

Keywords: high-nitrogen alloy, nitrogen compositional stability coefficient, self-propagating high-temperature synthesis.

1. Introduction

The development and investigation of high-nitrogen steels (HNSs) is one of the most promising trends in the creation of sparingly-alloyed corrosion-resistant steels with better mechanical properties than those of their nitrogen-free analogs [1–5]. In HNSs, nitrogen provides noticeable solid-solution strengthening of austenite, and the nitrogen austenite-forming ability allows decreasing the content of nickel or replacing nickel with nitrogen in the composition of nitrogen steel [6, 7]. However, the introduction of nitrogen into steel in overequilibrium concentrations by ordinary metallurgical remelting technologies is a rather laborious and costly process. Self-propagating high-temperature synthesis (SHS) is more economically feasible for obtaining steels with overequilibrium content of nitrogen [8–11]. The use of the SHS method permits to easily create high nitrogen pressure in the reactor, which in its turn provides the possibility of obtaining steels with the overequilibrium content of nitrogen during lean alloying (obtaining nickel-free austenitic steels). When an optimal technique for alloying is selected, it is reasonable to take into account that, according to the literature data [12], chromium, manganese and molybdenum enhance the nitrogen solubility in iron-based solid solutions (the effectiveness of the elements is in the indicated order). In addition, chromium, molybdenum and nitrogen provide high pitting-corrosion resistance of steels [13]. Thus, the task to develop optimal technological regimes for obtaining corrosion-resistant steels of the Fe-Cr-Mn-Mo-N system with the highest possible content of nitrogen is very important.

For determining the maximum nitrogen content, at which a solid ingot without bubbles and gas porosity in the volume can be obtained, the coefficient of compositional stability of nitrogen K is normally used in the practice of metallurgical production; the coefficient characterizes the ratio of the nitrogen solubility limit [N] in a melt and compositionally stable content of nitrogen $[N]_K$ (the maximum content of nitrogen in a solid ingot without bubbles and gas porosity in the volume) [12]:

$$K = \frac{[N]_K}{[N]}. \quad (1)$$

In [12] it is stated that the coefficient of the compositional stability of nitrogen can be determined empirically and depends on the partial pressure of the nitrogen above a melt and the metal chemical and phase composition in the temperature range of solidus-liquidus. According to the data [12], the coefficient K for austenitic chromium-nickel-manganese steels is 0.78, for duplex steels it can be in the range of 0.45 – 0.50 and for iron it is 0.28. However, there are no literature data about the applicability of the above values of the coefficient K for nickel-free high-nitrogen steels of the Fe-Cr-Mn-Mo-N system obtained by SHS under nitrogen pressure.

In this connection, the purpose of the present paper is to determine the coefficient of the compositional stability of nitrogen for high-nitrogen alloys (HNSs) of the Fe-Cr-Mn-Mo-N system obtained by self-propagating synthesis under nitrogen pressure.

2. Preparation of specimens and methods of investigation

At the selection of the limits for the chemical composition of the alloys of the Fe-Cr-Mn-Mo-N system, the concepts

of optimal chemical compositions of nickel-free austenitic HNSs and peculiarities of their obtaining considered in [8,10,12] were taken into account:

- chromium, manganese and molybdenum enhance the nitrogen solubility in iron-based solid solutions (chromium produces the highest effect) [12];

- the structural-phase composition of a solid ingot, containing the mass fraction of chromium 23%, manganese 8.6% and nitrogen 1.15% and obtained by SHS, is a mixture of austenite, ferrite and chromium nitrides in the as-cast state; after heat treatment the complete austenization of the ingot steel takes place [8];

- it is possible to obtain solid ingots by the aluminothermic process using up to 3% of the chromium nitride powder in the initial mixture [10];

- the coefficient of the compositional stability of nitrogen is taken equal to 0.28 for iron [12].

The selected chemical composition limits for alloys of the system Fe-Cr-Mn-Mo-N are given in Table 1.

The experimental determination of the coefficient *K* value was performed by the iteration method. First, a composition was selected for the first ingot, for which the coefficient *K* value was 4 – 6% higher than that for iron; after that, steel of the specified composition was synthesized. For the obtaining of a solid ingot the following iterative selection of the ingot composition was carried out. At each iteration, the ingot composition was selected so that the coefficient *K* value was 4 – 6% higher than the value of the corresponding coefficient at the previous iteration. The sought value of the coefficient *K* was considered to be the value, the use of which would lead to the obtaining of an ingot with gas porosity at the next iteration.

Taking into account the chemical composition limits (Table 1), the chemical composition of ingot No. 1 was selected as follows:

- a chemical composition was selected at the lower permissible limit of the alloying element content;

- according to the recommendations given in [14,15], for the selected composition the temperature of liquidus T_L was calculated using the following relation:

$$T_L = 1539 - [Cr] - 3[Mn] - 2[Mo] - 60[N], \qquad (2)$$

where the mass fractions of corresponding chemical elements were indicated in the brackets;

- using the calculated value of T_L and the expected value of the nitrogen working pressure of 95 – 115 atm in the reactor, the nitrogen limit in the melt was calculated by the following relation [12]:

$$\lg N_{(T)} = -\frac{560}{T} - 1.06 - \left(\frac{2600}{T} - 0.39\right)\{-0.048([Cr] + 0.5[Mn] - 2.45[C] - 0.9[Si] - 0.23[Ni] + 0.27[Mo] + 2.04[V] - 0.12[Cu] - 0.15[S] - [P]) + 0.00035([Cr] + 0.5[Mn] - 2.45[C] - 0.9[Si] - 0.23[Ni] + 0.27[Mo] + 2.04[V] - 0.12[Cu] - 0.15[S] - [P])^2 + 0.13[N]\} + \qquad (3)$$

where the mass fractions of corresponding chemical elements were indicated in the square brackets;

- the coefficient *K* was calculated using relation (1).

Table 1. Selected chemical composition limits for alloys of the Fe-Cr-Mn-Mo-N system.

Mass fraction of chemical elements, %				
Fe	Cr	Mn	Mo	N
Base	13.50 – 14.50	10.00 – 12.50	3.20 – 4.00	0.90 – 0.95

The search for possible chemical compositions for ingots was continued until the calculated coefficient of compositional stability *K* took a value higher by 4 – 6% than the value of the corresponding coefficient for iron.

For the experimental meltings by aluminothermy under the nitrogen pressure, the mixtures were prepared using the following materials as reagents: the powders of p. a. (Pro Analysi) grade iron oxide Fe_2O_3 TU 6-09-5346-87; OHM-0 grade chromium oxide Cr_2O_3 GOST 2912-79; pur. (Purum) grade manganese oxide MnO_2 GOST 4470-79; Ch [high-purity] grade molybdenum oxide TU 6-09-4471-77; PAM-4 grade aluminum-manganese powder GOST 5593-78 or ASD-1 grade aluminum powder TU 1791-99-019-98, and chromium nitride obtained by the nitriding of PH-1M grade chromium powder TU 14-1-1474-75 by SHS. To remove moist and to increase the specific surface, the oxide components of the mixture were preliminary dried in an electric furnace at 250°C for 1 – 2 h and ground in a ball mill. The weighed components of the mixture were processed in a mixer. The aluminothermic synthesis of the HNSs was performed in a SHS-reactor RVS-10 under nitrogen pressure up to 15 MPa. The calculation of the mixture components and the selection of the HNS synthesis parameters were conducted with regard for the process peculiarities described in [8 – 10].

In the presence of chromium nitrides in the initial mixture, the aluminothermy of the nitrogen iron-based alloys can be described by the following chemical reactions proceeding according to the scheme:

- reduction of the oxides of a base metal and alloying metals:

$$\frac{2}{m}Me_nO_m + \frac{4}{3}Al \rightarrow \frac{2}{3}Al_2O_3 + \frac{2n}{m}Me + Q,$$

where Me_nO_m is the reacting metal oxide, *n* and *m* are integers, Me is the metal obtained as a result of the reduction by aluminum, *Q* is the heat effect of the reaction.

- dissociation of chromium nitrides present in the initial mixture:

$$CrN \rightarrow Cr + \frac{1}{2}N_2,$$

$$Cr_2N \rightarrow 2Cr + \frac{1}{2}N_2,$$

- nitriding:

$$nMe + \frac{k}{2}N_2 \rightarrow [Me_n \cdot N_k]_{alloy},$$

where *k* is an integer.

Specimens for the investigation were obtained by the spark cutting of the ingots. The metal was studied both in the as-cast state and after heat treatment (holding at 1250°C for 2 h followed by water quenching).

The nitrogen content was determined by gas analysis on an analyzer Metavak-AK by reduction melting in a helium atmosphere using a katharometer as a detector.

The metal content was determined by chemical analysis on an atomic emission spectrometer Spectroflame Modula S.

The metallographic investigations of the specimens were conducted on a microscope NEOPHOT-21 after the sections of the metal in the as-cast state were etched in Marble's reagent consisting of 4 g of $CuSO_4$ in 20 ml of HCl and 20 ml of H_2O and the sections of the heat-treated metal were etched in the solution of concentrated nitric and hydrochloric acids (10 ml of HNO_3 and 30 ml of HCl). X-ray phase analysis was performed on a diffractometer DRON-6 (CoK_α-radiation, graphite used as a monochromator).

Hardness was determined by Brinell method performed on a tester ITBRV-187.5-AM according to GOST 9012-59.

3. Results and discussion

The first synthesis is conducted at the working nitrogen pressure of 95 atm; its product is ingot No. 1 with an easily separated layer of slag in the upper part. Ingot No. 1 weighs 160 g; its chemical composition is presented in Table 2.

The visual analysis and metallographic studies of ingot No. 1 show that the ingot is continuous, without bubbles and gas porosity. The ingot microstructure in the as-cast state (Fig. 1) is the mixture of austenite (light areas) and pseudo-pearlite (dark areas). A similar pseudo-pearlitic structure is described in [8], which is a finely dispersed ferrite-nitride mixture.

The liquidus temperature of ingot No. 1 calculated using relation (2) is 1424.9°C. The nitrogen solubility limit [N] in the melt calculated by relation (3) is 3.142 wt.% for ingot No. 1 at the calculated liquidus temperature and actual working pressure of nitrogen of 95 atm.

Taking into account that the obtained mass fraction of nitrogen in ingot No.1 is 0.92% ($[N]_K$=0.92 wt.%), the coefficient K for the metal of ingot No. 1 calculated using relation (1) is 0.293 (higher by 5% than the coefficient of the nitrogen compositional stability for iron).

The X-ray phase analysis of a specimen cut from ingot No. 1 (the diffraction pattern in Fig. 2) shows the presence of 70% of ferrite and 30% of austenite. The austenite presence can be explained by that after solidification the ingot was cooled down in the reactor. Thus, the time, during which the ingot remained in the reactor at the elevated temperature, could be sufficient for the diffusion processes to take place and to cause the dissolution of part of nitrides in the formed austenite; as a result, the nitrogen from the nitrides stabilized the austenite [10] (the X-ray phase analysis may not reveal nitrides due to their high dispersion ability and small amount).

During the subsequent homogenizing heat treatment of the as-cast specimens at 1250°C for 2 h, they are completely austenized. Most likely, it is due to that the nitrogen of dissolved nitrides (mainly chromium nitrides) stabilizes austenite (the melt mixing was conducted in accordance with the parameters ultimately minimizing the amount of formed aluminum nitrides [8,10]). As a result, only peaks related to austenite are observed on the XRD pattern (Fig. 3).

The metallographic studies of the specimen after heat treatment at 1250°C for 2 h show the typical microstructure of austenite (Fig. 4).

The measured hardness of the specimen after heat treatment at 1250°C for 2 h is 208 HB. The comparison of the hardness of the as-cast specimen with that of the specimen

Table 2. Chemical composition of ingot No. 1.

Mass fraction of chemical elements, %				
Fe	Cr	Mn	Mo	N
Base	14.3	12.2	4.0	0.92

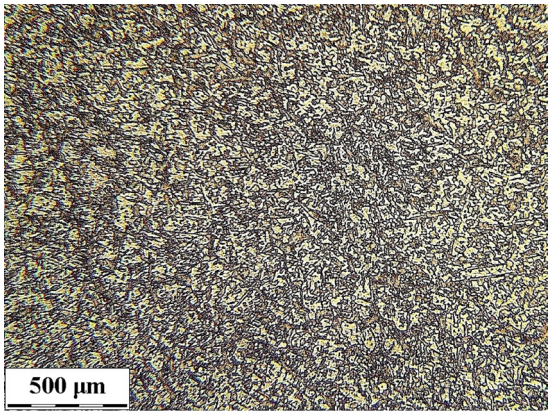

Fig. 1. (Color online) Microstructure of ingot No. 1 in the as-cast state.

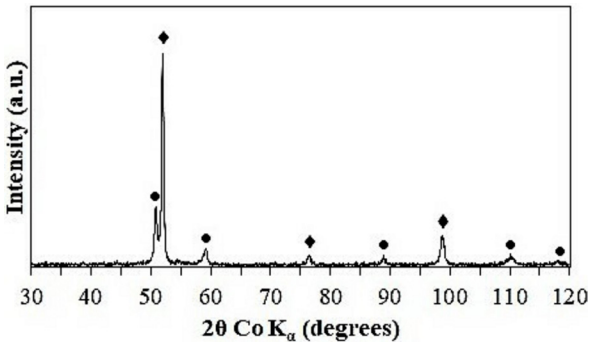

Fig. 2. XRD pattern of a specimen cut from ingot No. 1 in the as-cast state: the ferrite peaks are indicated by rhombi, and the austenite peaks are indicated by circles.

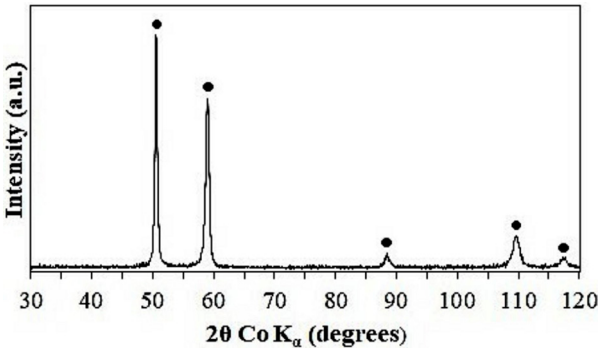

Fig. 3. XRD pattern of a specimen cut from ingot No. 1 in the quenched state: the austenite peaks are indicated by circles.

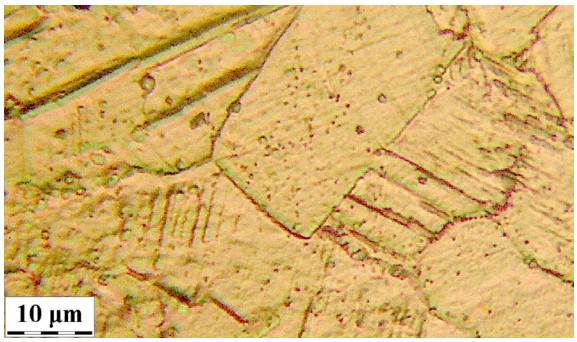

Fig. 4. (Color online) Microstructure of a specimen cut from ingot No. 1 after heat treatment at 1250°C for 2 h.

after heat treatment at 1250°C for 2 h indicates that during the heat-treatment the dissolution of the pseudo-perlitic structure (ferrite-nitride mixture) occurs. This is confirmed by the results of the metallographic study (Fig. 4).

The chromium and nickel equivalents for the metal of ingot No. 1 calculated using (4) and (5) and equal to 20.3 and 16.3, respectively, [16] show that in accordance with Scheffler's diagram modified by Speidel (Fig. 5) the obtained steel refers to the austenitic steel class.

$$Cr_{eq} = [Cr] + 1.5[Mo] \quad (4)$$

$$Ni_{eq} = 0.1[Mn] - 0.01[Mn]^2 + 18[N] \quad (5)$$

Then, ingot No. 2 is synthesized, the chemical composition of which should provide the value of the coefficient of the compositional stability of nitrogen K by 4 – 6% higher than the value of the coefficient K for ingot No. 1.

The product of the second synthesis, carried out at the working pressure of nitrogen of 112 atm, is ingot No. 2 with an easily separated layer of slag in the upper part.

Ingot No. 2 weight is 225 g. The ingot chemical composition is shown in Table 3.

The visual analysis and metallographic studies show the presence of pores in ingot No. 2. The microstructure of the ingot with pores is presented in Fig. 6.

The X-ray phase analysis of ingot No. 2 in the as-cast state (Fig. 7) shows only the presence of ferrite. Most likely, nitrides containing the main part of nitrogen found in the metal are not detected by the conducted chemical analysis and are not observed on the XRD pattern due to the high dispersion ability.

Apparently, during the process of crystallization in the temperature range of liquidus - solidus, nitrogen forms bubbles. This occurs due to the excess concentration of nitrogen for the given partial pressure. Part of the bubbles manages to move to the interface between the metal and slag, and the other part remains in the metal. This explains why during the mixture calculation for melting for obtaining

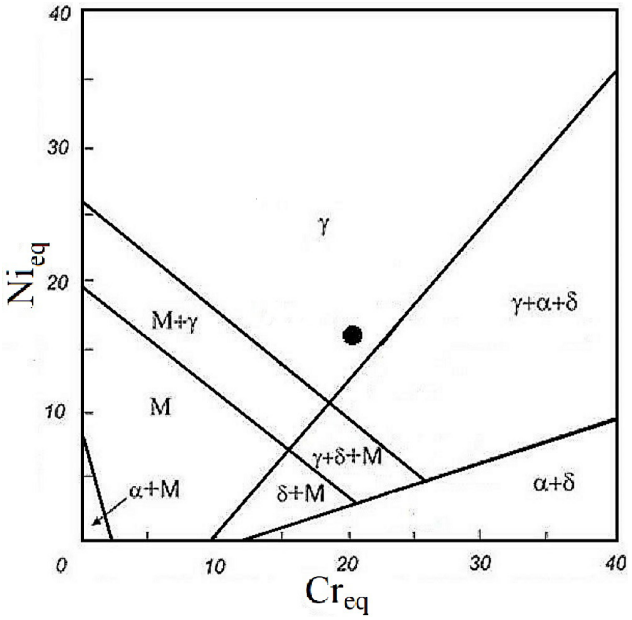

Fig. 5. The position of the metal of ingot No. 1 on modified Scheffler's diagram (black circle).

Table 3. Chemical composition of ingot No. 2.

Mass fraction of chemical elements, %				
Fe	Cr	Mn	Mo	N
Base	13.8	10.49	3.4	0.53

0.92 wt.% of nitrogen in the metal, the actual mass fraction of nitrogen of 0.53 wt.% is obtained.

The metal liquidus temperature for ingot No. 2 calculated by relation (2) is equal to 1431.7°C. The limit of the nitrogen solubility [N] in the melt is 2.954 wt.% for the metal of ingot No. 2 calculated using relation (3) at the calculated temperature of liquidus and actual working pressure 112 atm.

Taking into account that the mixture weights have been calculated for obtaining 0.92 wt.% of nitrogen in the metal (consequently, $[N]_K$ should be 0.92 wt.%), the coefficient K calculated by relation (1) for the metal of ingot No. 2 should be 0.311 (higher by 6% than the corresponding coefficient for the metal of ingot No. 1 at the previous iteration).

Consequently, the obtained value of the coefficient of the compositional stability of nitrogen 0.293 permits to predict the maximum nitrogen content in solid ingots (without bubbles and gas porosity in the volume) of high-nitrogen alloys of the system Fe-Cr-Mn-Mo-N prepared by aluminothermy under nitrogen pressure. Additionally, it is possible to predict the structural-phase composition of steel and optimal regimes of alloying.

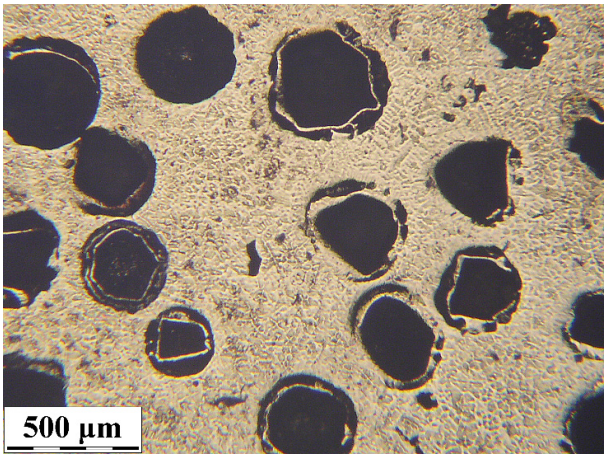

Fig. 6. (Color online) Microstructure of ingot No. 2.

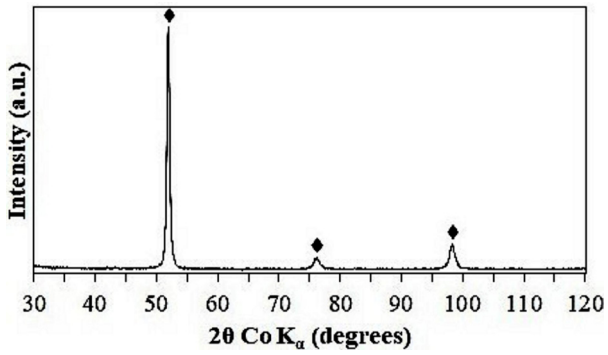

Fig. 7. XRD pattern of the specimen of ingot No. 2 in as-cast state: the ferrite peaks are indicated by rhombi.

Thus, based on the investigation results, for obtaining solid ingots of alloy with the maximum nitrogen content and specified structural-phase composition after homogenizing heat treatment, a calculation procedure in the form of an iterative calculation is proposed. The method includes the following stages at each iteration:

- the selection of the base chemical composition with a desired nitrogen content $[N]_K$ and a minimal content of other alloying elements according to the chosen chemical composition limits for this iteration;

- the determination of the structural-phase composition for the selected composition using modified Scheffler's diagram and the calculations by relations (4) and (5): when the structural-phase composition corresponds to the required composition, the subsequent stage is performed; when there is no correspondence, it is necessary to go back to the first stage and correct the content of alloying elements except nitrogen;

- the calculation of the liquidus temperature by relation (2) for the selected composition;

- the calculation of the maximum nitrogen content [N] in the melt by relation (3) taking into account the calculated value for the liquidus temperature and the nitrogen pressure in the reactor selected according to the technological process;

- the calculation of $[N]_K$ (maximum nitrogen content in a solid ingot without bubbles and gas porosity in the volume) by relation (1) taking into account that the coefficient K is 0.293;

- the comparison of the obtained value of $[N]_K$ with the mass fraction of nitrogen chosen at the first stage of this iteration: if $[N]_{K0} > [N]_K$, at the first stage of the subsequent iteration the nitrogen content is chosen smaller than that at the previous iteration, and if $[N]_{K0} < 0.95[N]_K$, at the first stage of the subsequent iteration the nitrogen content is chosen larger than that at the previous iteration; if $0.95[N]_K < [N]_{K0} < [N]_K$, the calculation is completed.

4. Conclusions

1. The coefficient of the nitrogen compositional stability has been determined for high-nitrogen alloys of the Fe-Cr-Mn-Mo-N system obtained by aluminothermy under nitrogen pressure ($K = 0.293$).

2. A procedure of iterative calculation is proposed for obtaining continuous ingots of high-nitrogen alloys of the Fe-Cr-Mn-Mo-N system by the SHS method under gas pressure. This allows the production of ingots with the maximum possible content of nitrogen and specified structural-phase composition after homogenizing heat treatment.

3. It is established that in the alloys of the Fe-Cr-Mn-Mo-N system, heat treatment at 1250°C for 2 h leads to the dissolution of the pseudo-perlitic structure and as a result the alloy becomes austenitic and stabilized by nitrogen. In this case, the alloy hardness decreases from 255 to 208 HB.

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