FORMATION OF NITRIDE- AND CARBIDE PHASES UNDER DISPERSION HARDENING OF CR-MN-V-N AUSTENITIC STEELS

L.Ye. Isayeva¹, Candidate of Chemical sciences, Assistant Professor
I.Ye. Lev², Doctor of Technical sciences, Full Professor
S.Y. Shypitsyn³, Doctor of Technical sciences, Head of Department
The National Metallurgical Academy of Ukraine, Ukraine¹,²
Physical and Engineering Institute of Metals and Alloys, Ukraine³

In this paper authors consider the influence of conditions for formation of nitride phases on the cavitation stability of the Cr-Mn-V-N austenitic steels. Influence of isothermal treatment on the mode of austenite hardening had been established by the electrochemical phase, X-ray structure and mechanical methods of analysis. The temperature of annealing at 700°C determined in this work is new to the subject. It creates the opportunity to form the greatest quantity of dispersion hardening nitrdes. Such temperature provides optimum conditions for obtaining cavitation resistance for steel “17Х15Г19АФ”.

Keywords: nitrides, cavitation resistance, chromium-manganese-vanadium-nitrogen steels, dispersion hardening of austenite.

Conference participants, National Research Analytics Championship, Open European-Asian Research Analytics Championship

http://dx.doi.org/10.18007/gisap:tsca.v0i8.1429

One of the main trends in development of the heat power-generating industry is the growth of the specific power of energy blocks while correspondingly increasing their efficiency to 48-50%. This predetermines the transition to higher steam parameters: pressure up to 35 MPa, temperature up to 650°C [1, 2].

The necessary condition for attaining the set aim is introduction of the new promising scientific and engineering innovations, which would allow to handle a number of technical problems comprehensively. These problems arise when developing the blocking and regulating details, which work under conditions of micro-impact action of the medium flow, i.e. cavitation.

Analysis of the state of the problem has shown today austenitic stainless steel 08X18H10T remains the main constructional material for manufacturing the blocking-regulating units of pipeline fittings in the global and home practice [3]. But as for the level of strength characteristics and durability under conditions of cavitation action of the medium flow and scratching the contact surface, this steel does not meet the present-day demands. It restrains the progress in rising the operating parameters, reliability and service life of equipment. Besides, the substantial disadvantage of austenitic chromium-nickel steel is the necessity to alloy it with expensive and not readily available nickel. Introduction of manganese and nitrogen contributes to more economical mode of alloying. The lack of deep scientific and engineering research in this field however constitutes one of the main reasons to explain why the technology of alloying steel with nitrogen, manganese and nitride-forming elements is not demanded for developing the corrosion-proof and cavitation resistant steels. Another reason for that is the problem of structure formation and distribution of nitrogen between solid solution and nitride phases isolated in the process stages (hot and cold steel deformation), and in the process of micro-impact of the surroundings under conditions of cavitation. The problems of influence of the chemical composition, schedules of heat treatment, phase steel composition, parameters of micro- and substructure, low degrees of cold plastic deformation and micro-impact action on the kinetics of γ→ε→α phase transformation and hardening of phases under formation, change of micro- and substructure and the influence of these factors on the destruction resistance of steel during micro-impact action remain to be studied.

To solve the existing problem, the alloying system Cr-Mn-V-N had been chosen as the object of study in the present work. This system creates a possibility to develop high-strength corrosion-resistant grades of steel with nitride hardening.

Smelting of steels was carried out in the induction furnace IST 0.16 with acid lining, using the method of re-melting technically pure materials. The final deoxidizing and modification of steels was implemented with aluminum and silicocalcium.

To attain 3 basic kinds of austenite hardening – solid solution, dispersion and mixed hardening – the quantity and composition of nitride and carbide phases being formed depending on the temperature of isothermal treatment – chemical phase analysis was used.

With the purpose of reaching the steel balance, the time of isothermal soaking had been determined from the work [4] on the basis of the data about influence of the temperature (from 1200 till 700°C) on the mass speed of isolating VN particles in the Cr-N austenite.

The chemical analysis of the steel under study is presented in the Table 1.

Phases under study had been isolated using the electrochemical method of dissolving the metallic samples base [5]. Electrolytic metal dissolving and compounds isolating were carried out on samples Ø 20 mm and h = 80 mm. Electrolysis was carried out in the field of direct dependence of overvoltage value on the current density logarithm. In

| Chemical analysis of the steel grade “17X15Г19АФ” |
|-----------------------------------------------|
| Chemical analysis, % |
| C    | Si   | Cr   | Mn   | N    | V    | Al   | S    | P    |
| 0.17  | 0.08 | 14.89| 18.97| 0.223| 0.32 | 0.045| 0.011| 0.013|

Tab. 1.
accordance with the Tafel’s equation [6] this field corresponds to electrochemical stage of the process. Extraction of the nitrogen-containing phases had been carried out in the aqueous electrolyte containing 15% NaCl and 2.5% tartrate acid in potentiostatic operating regime created by the potentiostat 10-20PEB. Nitride and carbonitride phases in the shape of anodic precipitate had been isolated from the steel, because their oxidizing potentials in the given electrolyte were bigger than that of the metallic base. Implementation of electrolysis with the potential smaller than that of the phases under isolation favored such result. A small collodium bag had been set in the electrolytic cell between the sample and cathode for the purpose of collecting inclusions. After finishing the electrolysis the precipitate together with electrolyte had been moved from the collodium small bag into wide polyethylene test-tubes and was washed off from the electrolyte using the step-by-step operations of centrifuging at 5000 rpm and decantation. Isolation of inclusions has been carried out in two series of experiments. In the first series inclusions were prepared for X-ray structure analysis. For this purpose inclusions had been dried up to the constant weight in the exicator above the concentrated H₂SO₄. In the second series of experiments isolation of inclusions has been carried out to determine their chemical analysis. Inclusions were dissolved in concentrated H₂SO₄ with additional wet fusion in the melt of Na₂SO₄ with H₂SO₄. Obtained solutions have been transferred to the measuring flasks, and the content of elements combined in nitride and carbide phases (N_comb, Cr_comb, Mn_comb, V_comb, and Al_comb) has been determined in aliquote parts.

Nitrogen was determined using the photocolorimetric method by the intensity of complex compound coloring – oxiamidodimercure, formed by the interaction of NH₄⁺ ions with K₂[HgJ₄] [7]. As a preliminary, nitrogen in the form of NH₃ has been isolated from the alkaline solution using the steam aspiration method. Vanadium and chrome have been determined by the oxidation-reducing method by means of volume analysis. Titration has been carried out step-by-step in one and the same solution, at first VO₃⁻ ion was reduced using the solution of FeSO₄, then, after the oxidation, the sum of VO₃⁻ + Cr₂O₇⁻ was reduced in its turn [8]. The content of manganese has been determined by the volume method, by reducing MnO₄⁻ ions using the solution of sodium arsenite [9]. Aluminum has been determined using the photocolorimetric method by coloring intensivity of the complex compound of aluminum with aluminone [10]. The results of analysis are presented in the Table 2.

As follows from the obtained results,
after solidification and homogenizing annealing at 1200°C (sample K.1) the steel contains minimum quantity of nitrogen in the combined state (Fig. 1,a). Lower temperatures of isothermal soaking within the determined interval lead to increasing N comb, i.e., to increasing the formation of nitrogen containing phases. Other alloying elements, with the exception of chromium (at 700°C) show the same trend (Fig. 1b). Since isolated phases contain more chromium, the general dependence of quantity of the formed phases is specified by the curves shown on the Fig. 1c.

Determination of the qualitative and semi-quantitative composition of different crystal phases in samples has been carried out on the unit ДРОН-3 (DRON-3) in copper radiation. When identifying the structures the authors used the Diffraction Data File of the American Society for Testing Materials (ASTM File [11]) and reference data in the tables of the File [12].

The results of the phase analysis of isolated compounds showed that during high-temperature isothermal treatment the formation of nitrides in the steel under study took place to a very insignificant degree. Alumina (α – Al2O3) is present in inclusions isolated from samples under high-temperature treatment (K.1, K.2 and K.3), as well as very little of AlN and VN. The most intensive maxima of alumina has been also determined: d = 3.47 Å; 2.55 Å; 2.08 Å; 1.74 Å and 1.60Å.

The main quantity of dispersion hardening phases is formed at lower temperatures of isothermal treatment. In the first place, these are hexagonal nitrides VN_{0.35} which gave the most intensive reflections in diffractograms of samples K.5 and K.6 corresponding to d = 2.153Å; 2.08 Å; 1.74 Å and 1.60Å. Chromium in these samples forms a few phases: hexagonal nitrides Cr2N with d = 2.40 Å; 2.22 Å; 2.11 Å; 1.83 Å and 1.66 Å; cubic nitrides CrN with d = 1.463 Å; 1.249 Å; 1.197 Å and 0.846 Å, as well as cubic carbides Cr13C6 with d = 2.37 Å; 2.7 Å; 1.26 Å; 1.23 Å and others. Proceeding from the calculation of the element content in precipitates, the data of X-ray structure analysis of precipitates and the literary data about the possible presence of non-metallic phases in Cr-Mn-V-N austenitic steels [13], the authors have determined the phase steel composition and the changes depending on the temperature of isothermal treatment (Table 3).

The obtained results show that nitrogen combines practically only with vanadium. Mass share of vanadium nitrides at the ageing temperature 700°C attains 0.18%, which makes 44% of the theoretically possible quantity of vanadium nitrides in the case of complete combination of the vanadium in steel and nitrogen into nitrides. Experimental conditions of dispersion nitride vanadium hardening of austenitic matrix are attained most completely under ageing at 700°C.

Homogenizing under conditions 1200°C – 2 hours – water ensures practically homogenous state of the matrix, i.e., only its solid phase hardening with C, N, V, Cr. Under ageing in the interval 900°C - 1000°C the mass share of nitrides VN particles makes only about 50% of their quantity at the ageing temperature 700°C, i.e., it is possible to assume that matrix is in mixed solid solution and dispersion hardening.

An important result of the phase analysis consists in the fact that chromium

| Samples Marking | Conditions of isothermal treatment | Mass share of non-metallic phases, % |
|-----------------|-----------------------------------|-------------------------------------|
|                 | Temperature °C, Duration, hours   | VN | Cr2N | Cr13C6 | Mn | AlN |
| K.1             | 1200 2                             | 0.008 | -  | -   | - | 0.017 |
| K.2             | 1100 4                             | 0.013 | -  | -   | 0.084 | - | 0.019 |
| K.3             | 1000 6                             | 0.083 | 0.008 | 0.104 | - | 0.034 |
| K.4             | 900 10                             | 0.092  | 0.049 | 0.209 | - | 0.037 |
| K.5             | 800 20                             | 0.179  | 0.055 | 0.213 | 0.044 | 0.043 |
| K.6             | 700 30                             | 0.180  | 0.050 | 0.248 | 0.043 | 0.037 |

Note: after isothermal treatments the samples were cooled in water.
depletion of the solid austenite solution due to forming chromium nitrides and carbides with mass share not exceeding 40% can’t decrease corrosion resistance of steel.

It must be also noted that only 25% of nitrogen in steel is used for nitrides formation, what means that austenitizing effect of nitrogen is kept.

When using articles of cavitation resistant steels at elevated temperatures, for example, in power industry, an important factor of their operating longevity is the heat stability of metal strain hardening.

On the basis of results of testing steels for cavitation resistance, as to mass loss, \( \Delta P \times 10^5 \), kg/m² (Fig. 2, a) and as to hardness increase, \( \Delta H_B \) (Fig. 2, b), it was determined in the work that substitution of solid solution hardening of austenite for dispersion hardening raises the degree of strain hardening.

The results of electrochemical phase analysis and X-ray structure analysis correlate with these data. The temperature of annealing 700°C determined in this work is new to the subject. It creates the opportunity of forming the greatest quantity of dispersion hardening nitrides. Such temperature ensures optimum conditions for obtaining cavitation resistance for steel “17X15F19AФ”.

References:

1. Skorobogatyy V.N., Shenkova I.A., Kozlov P.A. Novye materialy dlja perspektivnych jenergeticheskix ustanovok [New materials for perspective power stations]. Armaturestroenie [Armature engineering]. – Moskva, Mashinostroenie [Engineering]., 2010, No. 3., pp. 56-59.

2. Kliveland P. Armatura dlja tzhelyx usloviy [Reinforcement for severe conditions]. Dostojnyj otpor davleniju novyh realij [Worthy repulse to pressure of new realities]., Armaturostroenie, 2010. No. 3., pp. 60-64.

3. Harina I.L., Safonov I.A. Novye metody ispytanija metallov [New methods of testing metals]. CNIIChM collection of works. – Moskva., Metallurgizdat., 1969. – 191 p.

4. Babaskin Ju.Z., Shipicy S.Ja., Kirch R.F. Konstrukcione i special'nye stalej s nitridnoj fazoj [Constructional and special steels with the nitride phase]. – Kiev., Naukova dumka [Scientific thought]. - 2005. – 371 p.

5. Isaeva L.E., Lev I.E. Issledovanie usloviy obrazovania i vydeleniya iz stalej nitridov molibdlena, soderzhashhix zhelezo [Research on conditions of formation and allocation of molybdenum nitrides from the steels containing iron].

6. Isaeva L.E., Greshnik A.M., Lev I.E. Issledovanie processa izolirovanija nitridov molibdena iz stalej [Research on the process of isolation of molybdenum nitrides from steel].

7. Lev I.E., Pokidyshnev V.V., Lazarev B.G., Miccovich N.S. Analiz azotsoderzhashhix soedinenij v splavah zheleza [The analysis of nitrogen-containing compounds in iron alloys]. – Moskva, Metallurgija. 1987. – 120 p.

8. Generozov B.F. Tehnicheskij analiz v metallurgicheskix i koksohimicheskix proizvodstvax [Technical analysis in metallurgical and coke-chemical production]. – Moskva, Metallurgizdat. 1959. – 251 p.

9. Stepin V.V., Silaeva E.V., Pliss A.M., Kurbatova V.I. and others. Analiz chemixh metallov, splavov i marginalnyx rud [Analysis of ferrous metals, alloys and manganese ores]. – Moskva., Metallurgizdat. 1964. – 501 p.

10. Kljachko Ju.A., Shapiro M.M., Jakovleva E.F. Novye metody ispytanija metallov [New methods of testing metals]. CNIIChM collection of works. – Moskva., Metallurgizdat., 1962., pp.75-81.

11. American Society for Testing Materials Diffraction Data File, USA. – Philadelphia., 1969.

12. Narita K. Kristallicheskaja struktura nemetallicheskih vkljuchenij v stali [Crystalline structure of non-metallic inclusions in the steel]. – Moskva., Metallurgija, 1969. – 191 p.

13. Gasik M.I. Margancevyh rud [Manganese]. – Moskva., Metallurgija. 1992. – p. 607.

Literatura:

1. Скоробогатых В.Н., Щенкова И.А., Козлов П.А. Новые материалы для перспективных энергетических установок // Арматуростроение. М. Машиностроение. 2010. №3. С.56-59.

2. Кливеланд П. Арматура для тяжелых условий. Достойный отпор давлению новых реалий // Арматуростроение. М. Машиностроение. 2010. №5. С.36-39.

3. Харина И.Л., Сафонов И.А. Коррозия в пароводяной среде высоких параметров // Арматуростроение. М. Машиностроение. 2010. №3. С.60-64.

4. Бабаскин Ю.З., Шипицын С.Я., Кирку И.Ф. Конструкционные и специальные стали с нитридной фазой. Киев. Наукова думка. 2005. 371 с.

5. Исаева Л.Е., Лев И.Е. Исследование условий образования и выделения из сталей нитридов молибдена, содержащих железо // Вопросы химии и химической технологии. Общегосударственный научно-технический журнал. Днепропетровск. 2010. №2. С.98-101.

6. Исаева Л.Е., Греших А.М., Лев И.Е. Исследование процесса изолирования нитридов молибдена из сталей // Вопросы химии и химической технологии. Общегосударственный научно-технический журнал. Днепропетровск. 2005. №1. С.163-167.

7. Лев И.Е., Покидышев В.В., Лазарев Б.Г., Мичевич Н.С. Анализ азотсодержащих соединений в сплавах железа [The analysis of nitrogen-containing compounds in iron alloys]. – Moskva, Metallurgija. 1987. – 120 p.

8. Генерозов Б.Ф. Технический анализ в металлургическом и коксихимическом производстве [Technical analysis in metallurgical and coke-chemical production]. – Moskva, Metallurgizdat. 1959. – 251 p.

9. Степин В.В., Силаева Е.В., Плисе А.М., Курбатова В.И. и др.
Анализ черных металлов, сплавов и марганцевых руд. М. Металлургиздат. 1964. 501 с.

10. Клячко Ю.А., Шапиро М.М., Яковлева Е.Ф. Новые методы испытания металлов. Сборник трудов ЦНИИЧМ. М. Металлургиздат. 1962. С.75-81.

11. American Society for Testing Materials Diffraction Data File, USA, Philadelphia, 1969.

12. Нарита К. Кристаллическая структура неметаллических включений в стали. М. Металлургия, 1969. 191 с.

13. Гасик М.И. Марганец М. Металлургия. 1992. C.607.

Information about authors:

1. Lyudmila Isayeva – Candidate of Chemical sciences, Assistant Professor, The National Metallurgical Academy of Ukraine; address: Ukraine, Dnepropetrovsk city; e-mail: luda.73@bk.ru

2. Isaac Lev - Doctor of Technical sciences, Full Professor, The National Metallurgical Academy of Ukraine; address: Ukraine, Dnepropetrovsk city; e-mail: luda.73@bk.ru

3. Sergey Shypitsyn – Doctor of Technical sciences, Head of Department, Physical and Engineering Institute of Metals and Alloys; address: Ukraine, Dnepropetrovsk city; e-mail: odus@ptimakiev.ua

http://academy.iuci.eu