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Influence of molybdenum on corrosion and mechanical properties of carbon steel joint welds

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The results of experimental studies of the molybdenum impurity influence on corrosion and mechanical properties of carbon steel (Grade 20) joint welds are presented in the article. In particular, it has been found that the highest and stable values of the impact strength and resistance properties of cracks (K_{1s} and δ_s), as well as the resistance to sulfide corrosion cracking of the metal of tubular steel joints, are achieved at a concentration of molybdenum in it from 0,2 to 0,4%, which is realized by putting a molybdenum powder in the electrode coating in the amount of 0,5-1,0%. On the basis of the obtained results an optimal chemical composition of the weld metal was determined which is characterized by a fine-grained structure with a small amount of non-metallic impurities of globular shape. Optimal content of the doping micro-additive - molybdenum should be selected, based on both the influence of molybdenum on the size of structural components, but, most importantly, on its effect on the corrosion and mechanical properties of metal joint weld.

Keywords: welding, corrosion, crack resistance, strength, sulfide, hydrogen.

Вплив молібдену на корозійно-механічні властивості зварювальних з'єднань вуглецевої сталі

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Наведено результати експериментальних досліджень впливу молібденової домішки на корозійно-механічні властивості наплавленого металу зварювальних з'єднань вуглецевої сталі марки 20. Встановлено, що найбільш високі й стабільні значення ударної в'язкості й характеристик спротиву розвитку тріщин (K_{1c} і δ_c), а також стійкості проти сульфідного корозійного розтріскування метала шва трубних сталей досягаються при концентрації молібдену в ньому від 0,2 до 0,4%, яка реалізується вводом в електродне покриття молібденового порошку в кількості 0.5-1.0%. На базі отриманих результатів визначено оптимальний хімічний склад наплавленого метала, який характеризується дрібнозернистою структурою з незначною кількістю неметалевих вкраплень глобулярної форми. Такий хімічний і структурний склад зварювального шва реалізується оптимальним вмістом і співвідношенням феросплавів (FeMn, FeSi і FeTi) в електродному покритті. Оптимальний вміст легуючої мікродобавки – молібдену слід вибирати, виходячи одночасно не лише з впливу молібдену на розмір структурних складових, але, головне, з її впливу на корозійно-механічні властивості метала зварювального шва. Покращення механічних властивостей, зокрема, ударної в'язкості і параметрів в'язкості руйнування метала шва, легованого молібденом, можна пояснити його сприятливим впливом на структурну та хімічну неоднорідність наплавленого метала. Для оцінювання ступеню цього впливу стосовно електродів з основним покриттям, проведено дослідження сучасними методами металографічного аналізу. Порівняння даних структурного та мікрорентгеноспектрального аналізу дозволяє передбачати, що покращення пластичних властивостей метала шва при легуванні молібденом зв'язано з тим, що молібден зміщає область $\gamma - \alpha$ - перетворення вбік більш низьких температур, сприяючи тим самим утворенню достатньо дисперсної та однорідної структури нижнього бейніту з мінімальною шириною доевтектойдної феритної оторочки.

Ключові слова: зварювання, корозія, тріщиностійкість, міцність, сульфіди, водень.

Introduction

The highest and most stable values of impact strength and crack resistance, as well as resistance to sulfide corrosion cracking of weld metal joint of pipe steels are achieved by adding molybdenum powder to the electrode coating. On the basis of this approach, an optimal chemical composition of the weld metal, which is characterized by a fine-grained structure with a small number of non-metallic globular form impurities, was determined.

Review of research sources and publications

The analysis of literature data [1, 2, 5, 7, 9, 10] showed that high and stable values of the impact strength of metal joint s on carbon and low-alloy steels are to a large extent provided by deoxidation and doping of the metal joint with manganese, silicon and molybdenum. As follows from works [1, 2, 9, 10], thus the content of silicon and manganese in the weld metal should be in the following limits: from 0,10 to 0,60% Si and from 0,60 to 1,50% Mn.

In order to determine the optimal content of the molybdenum powder in the coating, ensuring the required concentration of molybdenum in the metal joint and high impact strength of the joint s at temperatures up to -30 °C, additional research was required on the steel pipe of the steel grade 20, which is most widely used in industrial production in conditions of sign-changing temperatures, pressures and loads.

Definition of unsolved aspects of the problem.

It is known [1 – 4, 8, 12 – 14] that the choice of pipe and welding materials for pipelines of TES industrial plants is carried out in accordance with the Rules and Standards of Ukraine's boiler control. Reliability of pipelines largely depends on the corrosion and mechanical properties of steel pipe and welding materials, but existing scientific and technical and technological developments concerning the increase of operational reliability and durability of pipelines (P) reveal contradictions and uncertainty both as among researchers so among operators, lack of a clear idea of the factors that cause the failure and destruction of the P, as well as scientifically substantiated practical recommendations regarding the optimal choice of welding materials, the technology of welded tubular steels, which are exploited under conditions of chemical aggressive media under variable temperature-baric regimes of industrial production [3 – 5, 10].

Problem statement

In connection with this, there was a need to find ways to increase the operational reliability of pipelines by ensuring high corrosion and mechanical properties of joint welds, which will serve as the basis for the development of technological and operational measures to improve the safe resource of pipelines, in particular oil and gas.

Basic material and results

As experimental, the electrodes with the main type of coverage of the brand ANO-26, were used. In the process of manufacturing the electrodes in the charge, a microfertilizer of molybdenum was put in the form of powder in quantity (in %): 1,0 (P1); 2,5 (P2); 3,0 (P3); 4,0 (P4). Welding was carried out by electrodes of 4 mm diameter from the rectifier VDU-504 in the modes: U_d = 23 – 24V; I_{sv} =180 A (DC, reverse polarity). Before welding, the electrodes were calcined in a thermo-oven at a temperature of 4000C for 1 hour. In the weld metal, the molybdenum content varied from 0 to 0,60%. The chemical composition of the weld metal was (in %): 0,071 – 0,075 C; 1,08 – 1,20 Mn; 0,32 – 0,40 Si; 0,016 – 0,023 S; 0,020 – 0,024 P.

Initially, using a standard method [2, 5], the critical tensile stresses of the samples cut from the welds in the longitudinal direction were determined. Test results are presented in Fig. 1.

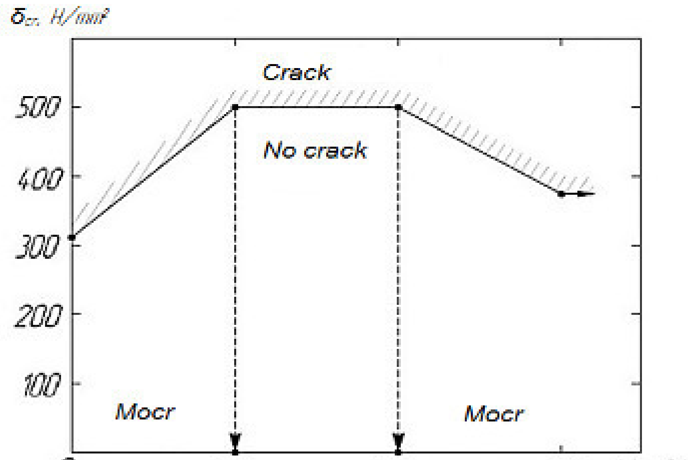

Figure 1 – Dependence of the critical tensile stress on molybdenum concentration in the weld joint. joint 20

It is seen that the limiting values of molybdenum content in the deposited metal are in the range of 0,20 – 0,40% for steel 20. The value of σ_{cr} corresponds to the critical value of the tensile stresses, where the origin and growth of the crack occurs up to destruction. As the research has shown, doping of a metal with molybdenum allows to improve also other widely used in fracture mechanics the viscosity characteristics of weld metal, in particular, parameters of the critical stress intensity (K_{1s}, $MPa \cdot m^{1/2}$) and the critical crack opening (δ_s, mm), which characterize the resistance of the metal joint s to the opening of the crack [6].

For the manufacture of samples, the steel joint s were heated by 20 electrodes of diameter 4 mm (variants P1 – P4) at constant current (I_{sv} = 180 A, U_d = 23-24 V) from the power source – VDU-504. A notch on the welded specimens was applied along the joint. Electrodes ANO-26 were used as experimental electrodes, in the coating of which instead of iron powder, molybdenum was used in the amount of 0; 1,0; 2,0 and 4.0%. The fatigue cracks in the specimens were grown by means of a hydropulsator CDM-10 (Germany) at a load frequency of 10 – 15 Hz and a coefficient of asymmetry of the cycle R = 0,1 – 0,2. Tests to determine the parameters of the viscosity of destruction were carried out at the installation of UME-10 according to the standard method [2, 6, 9].

Results of measurements are given in fig. 2.

It can be seen that the metal of welded joints, which is doped with molybdenum (0.2-0.4%), has higher coefficients of K_{1s} and δ_s over the whole range of temperatures than the main metal (steel 20), that is, it is characterized by a higher fracture failure. The highest values of the critical magnitude of the stress intensity factor K_{1s} and the coefficient of crack opening δ_s are obtained for welds with a molybdenum concentration of 0,2 – 0,3%.

The improvement of mechanical properties, in particular, the impact strength and viscosity parameters of the metal joint doped with molybdenum, can be explained by its beneficial effect on the structural and chemical heterogeneity of the deposited metal. In order to assess the degree of this effect with respect to the electrode with the main coating, additional research was carried out using modern methods of the metallographic analysis.

a) b)

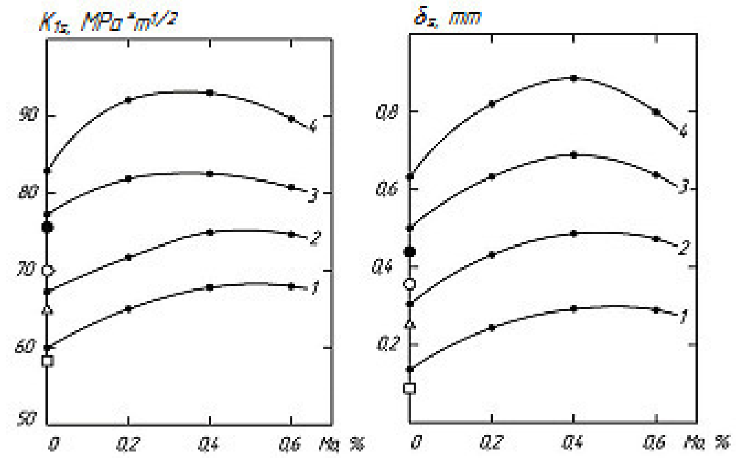

Figure 2 – Dependence of crack resistance coefficients K_{1s}(a) and δ_s(b) on the concentration of molybdenum in the welding joint.

Temperature (in °C): 1 – (-30); 2 – (-20); 3 – (-10); 4 – (+20). Steel 20

The metal single-layer welds made by test electrodes with varying molybdenum content in the coating (electrodes with indexes P1, P2, P3 and P4) were studied. The chemical composition of the welded metal is given in the text above. Welded on a direct current at the return polarity from the straightener model VDU-504 in the mode: I = 180 A, U_d = 23-24 V.

The structure of the metal joint was studied on a scattering electron microscope of the model "JSM-35CF" (firm "Jelol", Japan). The results of studies have shown that the structure of the metal joint of new electrodes is characterized by the following features. Non-equilibrium grains of upper bainite (diameters of 200 – 600 μm and length 0,5 – 1,6 mm) are surrounded by polycrystalline hypoeutectoid ferrite plain in the width of 15 – 25 μm, which does not retain the secretion phase of the introduction, but with non-metallic inclusions and perlite colonies along its borders. In the body of grains there are plates of carbides (mainly iron carbides) in the thickness of 10-15 microns, small perlite colonies and non-metallic inclusions, usually spherical shapes with a diameter of 0,5-2,5 microns.

From the data in Fig. 3 it follows that in the metal of the joint weld, the micro-additive - molybdenum causes a decrease in the length of columnar dendrites (ℓ), and at the same time their width is reduced (h). It is noteworthy that with an increase in the concentration of molybdenum in the metal up to 0,4%, the length of dendrites decreases by about 1,5 – 2,5 times, and their width to 1,5-2 times. So, when the length and width of the dendrites of the metal joints, which do not contain molybdenum, is 4,7 – 5,6 mm and 3,7 – 3.9 μm respectively, then, when doping with a micro-additive – molybdenum in volume 0,25% of columnar dendrites have the following parameters: ℓ = 3 – 3,7 mm and h = 25 – 3 μm. In addition, it is evident that the change of these quantities is already subtracted when doping a joint weld with molybdenum in the amount of 0,1 – 0,2%. For these values, the microstructural parameters have the following values ℓ = 3,5 – 4,1 mm and h = 28 – 32 μm. It should be noted that at the same time, the micro-hardness of molybdenum positively affects the fragmentation of equilibrium dendrites – the parameter d (see Fig. 3). It is seen that with increasing content of molybdenum in weld metal, such as 0,1 to 0,25% dendrites diameter decreases from 30 – 36 to 18 – 22 μm, that is, the value of dendrites diameter is reduced by an average 1,5 – 2,0 times. It should be noted that the optimal content of the doping micro-additive - molybdenum should be selected, based on both the influence of molybdenum on the size of structural components, but, most importantly, on its effect on the corrosion and mechanical properties of metal joint weld.

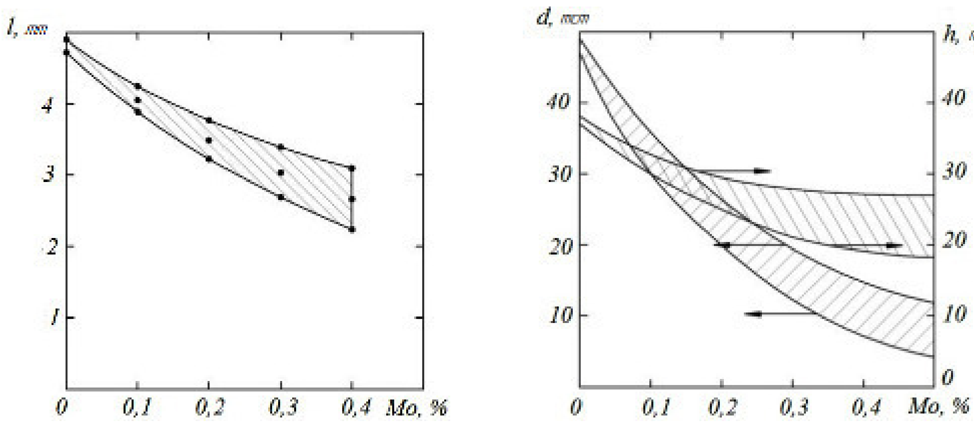

Figure 3 – Influence of microadditives of molybdenum on the length of dendrites (ℓ) and size in a welding joint.
Denomination: h – width of stained dendrites; d – the diameter of equilibrium dendrites

Comparison of the data of structural and micro-ray spectral analysis allows predicting that the improvement of the plastic properties of the metal joint in molybdenum doping is associated with the fact that the molybdenum displaces the region of γ-α-transformation towards lower temperatures, thereby contributing to the formation of a sufficiently dispersed and homogeneous structure lower bainite with a minimum width of a dovetectoid ferrite flange. Such a structure, as it is known [7, 9, 10], contributes to the high mechanical properties of the metal joint , in particular its impact strength.

Data of fractographic analysis of samples tested on impact bend (in the range of temperatures + 20 ... – 30 °C), showed that metal breakage of the joint doped with molybdenum, are viscous parts of the dimple type. In this case, the fraction of the viscous component in breaking these samples is not less than 90%, while in samples without molybdenum, does not exceed 40 – 50%.

At the same time, welds, which are doped with 0,2% molybdenum, collapse along the plane of the chip of the lower bainite packets. The above changes in the nature of the destruction of the joint as the molybdenum concentration increases from 0,2 to 0,4%, apparently, are the cause of the observed growth in its impact strength.

The increase of impact strength due to the doping of the joint with molybdenum is due not only to the fragmentation of the structure of the metal joint , but also to the effect of molybdenum on the dislocation structure of the ferrite matrix and bainite packets [5]. Molybdenum, which is part of the bainite packets, reduces their hardness, thereby contributing to plastic deformation [7].

Considering the fact that metal pipes, for example, chemical and agrarian production, in particular evaporators, steam boilers, steam lines, etc., for a long time have been in contact with a chemically aggressive medium containing sulfur, which causes sulfide corrosion, including its specific type - sulfide cracking of welded joints, then samples were tested for sulfide cracking according to the standard NACE TM-01-77 [11]. As a model medium served a saturated hydrogen sulfide solution containing 5% NaCl and 0,5% acetic acid. In this case, the content of H2S was 50 g/ liter. The initial pH value was 3,8, the final value was 4.1. The ambient temperature is 220C, the basic test time is 680 hours.

The results of corrosion-sulfide cracking tests are given in Fig. 4, from which it is evident that the content of molybdenum in the volume of 0,2 – 0,4% has a beneficial effect on the resistance of the metal against sulfide cracking, and this trend is manifested in the same way as in investigations on the fracture resistance of the metal joint (parameters К1s і δs).

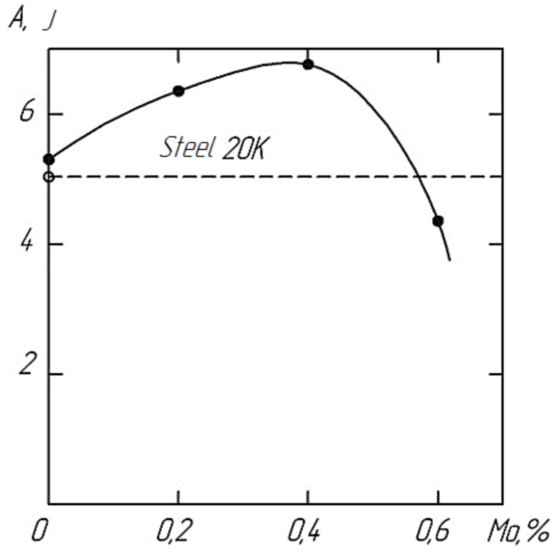

Figure 4 – The work of breaking welds depending on the concentration of molybdenum. NACE environment

Conclusion

It was established that the highest and stable values of the impact strength (65 – 77 J/cm^2 at t =-30°C) and the resistance properties of cracks (K_{1s}= 65 – 75 MPa·m$^{1/2}$ and δ_s= 0,23 – 0,47 mm at t =-30 °C), as well as resistance to sulfide corrosion cracking of tubular steels metal joint are achieved at a concentration of molybdenum in it from 0,2 to 0,4%, which is realized by introducing into the electrode coating molybdenum powder in the amount of 0,5 – 1,0%.

The optimum chemical composition of the welded metal is determined, which ensures the obtaining of fine-grained structure, containing a small amount of globular form non-metallic inclusions (in %): C < 0,18 – 0,22; 0,25 – 0,35 Si; 0,8 – 1,0 Mn; 0,2 – 0,4 Ni; S, P < 0,025, realized by the optimal content and ratio of ferroalloys in the electrode coating: 4 – 6% FeMn, 6 – 8% FeSi, 8 – 10% FeTi; FeTi : FeSi : FeMn = 2 : 1,5 : 1.

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