RESEARCH OF MICROSTRUCTURE OF MOLYBDENUM DOPED WELDINGS OF OIL AND GAS PIPELINES

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Abstract: Still existing scientific, technical and technological developments to improve the quality of welded joints of metal pipe structures contain contradictions and uncertainty about the effects of alloying elements, such as molybdenum, mechanical and visco-plastic properties, as well as metallographic component joints. All this indicates the need for a systematic study of these problems for the development of rational metallurgical and technological measures to significantly improve the technological and corrosion-mechanical properties of weld metal. Metallographic studies, using laboratory equipment with high identifying ability, found that the doping of weld metal with molybdenum in the amount of 0.2-0.4% causes fragmentation of ferrite-pearlite structure, including carbides Mn and Fe, and also reduces the number and size of non-metallic inclusions – sulfides, oxides and silicates. Moreover, non-metallic inclusions have a dispersed appearance, which promotes plasticization of the structure, which directly increases the viscous-plastic characteristics and resistance of the metal joints to crack formation. Based on the results of metallographic research, the optimum content in the weld metal of the alloyed element – molybdenum, which is 0.2-0.4%, is determined.

Key words: structure, fracture, corrosion, crystal lattice, non-metallic inclusions

INTRODUCTION
Responsible metal structures of agricultural processing and food production, in particular factory and city thermal pipeline networks used for water supply and transportation of water-vapour mixtures for technological needs at enterprises, often work in extreme climatic-baric and stress-strain conditions, contacting during the term of operation corrosion-active products and environments. Their destruction is accompanied by major material and environmental consequences, which cause significant damage to businesses. As the basis of pipeline construction is welding and installation work, which largely determines the reliability of the objects under construction, in the real pipeline structures the occurrence of cracks is most often due to the presence of welding connections. Therefore, the quality of welding in the construction of such objects are very strict requirements. Still existing scientific, technical and technological developments to improve the quality of welded joints of metal pipe structures contain contradictions and uncertainty about the effects of alloying elements, such as molybdenum, mechanical and visco-plastic properties, as well as metallographic component joints. All this indicates the need for a systematic study of these problems for the development of rational metallurgical and technological measures to significantly improve the technological and corrosion-mechanical properties of fused metal.
LITERATURE REVIEW

It is already known that doping welding connections, made basic type coated electrodes, allowing sufficient effectively regulate the mechanical properties of metals by changing the morphology [1, 2, 3], distribution and dispersion structural components [4, 5, 6, 7, 8, 9, 10, 11], as well as changes in the composition [12, 13, 14, 15] and condition of the grain boundaries [16, 17]. Most researchers consider the influence of alloying elements on the properties of metals at single doping [5, 6, 7]. Established [2, 9, 12, 15, 17] that the optimal system de-oxidation and weld metal recovery system is a "manganese-silicon" with optimal manganese 0.6-1.5% and 0.3-0.6% silicon. The authors [13, 14, 15, 16, 17] believe that to obtain high mechanical properties of the weld metal ratio should be done: Mn,%/Si,% ≥ 2, with content Mn = 0.6-1.5%.

The positive effect of molybdenum on the impact toughness of low-alloy steels (for example, grades 09G2S, 17G1S), the authors of [3, 6, 15, 16] attribute to its low absorption at the grain boundaries and strong absorption on the surface of the carbides, which is difficult growth of the latter at the grain boundaries. Effect of molybdenum, as noted authors [3, 6, 16], the most effective in co-introduced with metal carbide elements [18]. In addition, from the literature [3, 5, 7, 12, 15, 16], the authors of many studies do not have a clear answer regarding the effect of molybdenum on the microstructure [19], composition and condition of non-metallic inclusions [20, 21, 22], which mainly determine the corrosion-mechanical and technological properties of welding joint [23].

In addition, it should be noted that in the literature there are no data on the use of molybdenum as alloying modifier in the main type of electrode coatings for welding low carbon steels used in the construction of pipeline construction as heat-power transport communications sector, industrial production, and urban heat networks [24, 25, 26]. Therefore, the study of the influence of molybdenum on the nature of the micro-structure, in particular non-metallic inclusions, with the aim of improving the reliability of welds, is an urgent task.

Investigation of the effect of molybdenum on the microstructure of weld metal welded joints made of primary electrodes on low carbon steel.

METHODOLOGY OF RESEARCH

The objects of study were samples cut from welding joints, in particular from different zones — weld metal, fusion zone, thermal impact zone and the parent metal adjacent to the surrounding area. The main material was the boiler steel brand 20 K, which is widely used for the production of pipes [10, 11], intended for water supply pipelines, steam, high temperature and pressure, and other objects at agricultural and food production enterprises [27, 28]. Welding was performed with electrodes with the main type of coating with a diameter of 4 mm from the VDU-504 rectifier in modes: \( U_d = 23-24 \text{ V} \); \( I_d = 180 \text{ A} \) (DC, reverse polarity). Molybdenum was introduced into the mixture in the amount (in%): 1.0 (M1); 2.5 (M2); 3.0 (M3); 4.0 (M4) in the manufacturing process of the electrodes. Before welding, the electrodes were calcined in a thermal furnace at 400°C for 1 year.

The structure of the weld metal and the surrounding area was studied using a scanning electron microscope model “JSM-35CF” (Jeol, Japan). X-ray microanalysis structure of joints studied in microanalyzer system “ORTEC” (USA). Fractographic analysis of the fractures of the samples was performed using a microscope "JSM-35CF". The composition of the non-metallic inclusions was determined on a Link-860 energy dispersion spectrometer (Link, UK).

RESULTS OF RESEARCH

The results of studies of the microstructure of the weld metal are shown in Fig. 1-10. The results of the studies showed that the structure of the base metal (Fig. 1a) and the weld metal (Fig. 1b) of the M1 electrodes is characterized by the following features. The non-equilibrium grain upper bainite (200-600 micron diameter and 0.5-1.6 mm long) surrounded by polycrystalline ferritic preeutectoid fringe width of 15-25 mm, not containing discharge phases, but with non-metallic inclusions and pearlitic colonies along its borders. In the body of the grains there are plates of carbides (mainly iron carbides) with a thickness of 10-15 microns, small pearlite colonies and non-metallic inclusions, usually spherical in diameter of 0.5-2.5 microns.

![Fig. 1 Structure of base metal:](image-url)

- **a)** boiler steel, brand 20K, x400;
- **b)** weld metal, steel 20K, x500

The doping of the weld metal with molybdenum in the amount of 0.2-0.4% causes the following changes in the microstructure of the metal — Fig. 2-4 (central weld zone): 

a) the size of both bainite grains (Fig. 2a, b) and its carbides (Fig. 4) decreased significantly, in particular: grain diameter — 100-200 microns (0.2% Mo) and 200-300 microns (0.4% Mo);  

b) the width of the pre-eutectoid ferrite decreased (Fig. 3a, b) — 4-6 microns (0.2% Mo) and 6-9 microns (0.4% Mo);
c) the thickness of bainitic carbides decreased (Fig. 4) – 3-6 microns (0.2% Mo) and 5-8 microns (0.4% Mo). In addition, when doping with molybdenum metal in the amount of 0.25%, the fragmentation of the pre-eutectoid ferrite was subdivided into subgrain – Fig. 6 (8-12 microns in diameter).

Figure 2 Structure of bainitic grain of weld metal: 
\[ a) \quad \text{molybdenum doped 0.25\% x540; b) molybdenum is absent x500. 20 K steel} \]

Figure 3 Structure of pre-eutectoid weld ferrite: 
\[ a) \quad \text{molybdenum is absent x2000; b) molybdenum 0.25\% x2000 20 K steel} \]

Figure 4 Iron carbides in weld: 
\[ a) \quad 0\% \text{ Mo; b) } 0.25\% \text{ Mo; a, b – x3000} \]

Figure 5a shows a cross-section of a welding joint on 20K steel, and Figure 5b, c shows the microstructure of the transition zones: from the base metal to the center of the weld metal (Fig. 5b, c); then shows the structure of the heat affected zone (Fig. 5d, e). Moreover, Fig. 5d shows the sub-stratum (trunk) structure, which is a continuation of the same structure around the weld zone. Figure 5 (e) shows the microstructure of the fusion line zone, ie the direct transition from the base metal structure to the weld structure. Figure 5f shows pearlite grains surrounded by crushed ferrite core, and, as follows from Fig. 5c, the pearlite package consists of a mixture of finely dispersed ferrite and cementitious grains, indicating a beneficial effect of molybdenum as a modifier on the microstructure of the weld metal. This is also confirmed by the data shown in Fig. 6a, b, which shows the fine ferrite-pearlite structure of the weld metal doped with 0.25% molybdenum.

Figure 5 Microstructure of weld metal on 20K steel alloyed with 0.25\% Mo: 
\[ a) \quad x450, \ b) \quad x450; \ c), d), e); \ f) \quad x600 \]

Note: Explanations for Figure 5 are provided in the text.

Figure 6 Structure of perlite grain of weld metal on 20K steel The molybdenum content is 0.25\%. x400

It is also established (see Fig. 7) that sulfides, oxysulfides and silicates in molybdenum-doped welds consist of sulfur and oxygen compounds with manganese, iron and titanium, and have a globular shape of \( \sim 4-6\ \mu m \) in diameter. Therefore, in this case, the binding of sulfur to the MnS compound reduces the likelihood of the formation of fusible Mo-MoS eutectics, which is known to enhance the resistance of welds against the formation of hot cracks [7, 12, 14, 17].

X-ray microanalysis performed on an ORTEC (USA) microanalyzer showed that molybdenum is almost unrelated to non-metallic inclusions, ie the formation of Mo\(_2\)C type molybdenum carbide is unlikely but forms a solid solution with ferrite. Manganese carbides and oxidesulfides, which include molybdenum, are also observed. In addition, a significant effect of molybdenum on chemical heterogeneity was observed, which is manifested in the expansion of the ligation bands of phosphorus and manganese and in the reduction of the degree of uneven distribution of elements such as silicon and sulfur, which is in good agreement with the results of the works [1, 7, 12, 13, 14, 29, 30].
Comparison of structural and micro-X-ray spectral analysis data suggests that the improvement of plastic properties of molybdenum-doped metal is due to the fact that molybdenum narrows the width of the γ–α transformation region, obtaining a sufficiently fine and homogeneous structure of the lower bainite with a minimum width of pre-eutectoid ferrite rim. As is known [2, 6, 7, 9, 16], this structure contributes to the high mechanical properties of the weld metal, in particular the toughness [31]. The data of fractographic analysis of specimens on impact (in the temperature range – 30...+20°C) showed the following:

To establish the structures responsible for the destruction, the fractures of the specimens were deeply etched in the nickel. As a result, it was possible to establish that the weld metal, not doped with molybdenum, is destroyed by the pre-eutectoid ferrite, as the ferrite structure is etched on the chips facets (Fig. 8a, c, e). Fractures of specimens of molar metal doped with molybdenum are viscous sections of the pit type (Fig. 8b, d). In this case, the proportion of the viscous component in such samples is 95% or more, and samples without molybdenum content – 45-50%.

Molybdenum-doped (0.25% Mo) seam metal is destroyed by the sub-grain of the lower bainite (Fig. 8b, d, e). Therefore, due to this type of fracture, the viscosity of the weld metal is increasing sharply.

The microstructure of fracture of 0.1% molybdenum-welded welds is shown in Fig. 9. Microcracks arise mainly from non-metallic inclusions – sulfides, oxides and silicates of Fe and Mn, and their growth and propagation occurs along grain boundaries (Fig. 9a, b).

From the data shown in Fig. 10, it is seen that the doping of the weld metal with molybdenum in the amount of 0.25% can dramatically reduce the size and number of non-metallic inclusions, which contributes to the improvement of the mechanical properties of weld metal, which is confirmed in [3, 6, 15, 16].
The increase in visco-plastic characteristics of welds when alloyed with molybdenum is due, in our opinion, not only to the improvement of the structure of the deposited metal, but also to the plasticizing effect of molybdenum on the properties of the introduction phase and the matrix [3, 6, 15, 16]. Molybdenum, being a part of carbides, reduces their hardness due to the increase of dislocation motion, which is caused by the decrease of the energy of interaction of its atoms with dislocations, thereby facilitating plastic deformation [15, 18].

Plasticizing the grain matrix with molybdenum is confirmed by fractographic studies of specimen fractures. Thus, in the metal of the weld doped with molybdenum (0.25%), there is a viscous fracture by the mechanism of the origin and confluence of micro-voids near non-metallic inclusions (Fig. 3a, c, e, and Fig. 4b, d). The destruction of quasisol, which is observed in non-doped molybdenum samples, occurs, as a rule, in the body of ferrite segments near large non-metallic inclusions (1-2 microns in diameter), which serve as a stress concentrator (Fig. 4a, c). Micro-voids, which merge to form a critical-length binder crack, from which fracture begins, can occur both around non-metallic inclusions and as a result of stratification along the boundaries of ferrite grains [4, 8, 9, 14]. Mechanical testing of the samples showed that the most stable and high toughness values and characteristics of crack resistance of the weld metal boiler steel 20 K are achieved when the concentration of molybdenum in the weld metal within 0.1-0.3%. This range of molybdenum content in the metal weld on introduction of electrode coatings molybdenum powder in an amount of 1.5-3.5% by weight. Accordingly, was chosen the best chemical composition of weld metal (in %): C ≤ 0.17-0.19; Si 0.30-0.35; Mn 0.7-0.9; Mo 1.5-2.5.

CONCLUSIONS
Metallographic studies, using laboratory equipment with high identifying ability, found that alloying weld metal molybdenum in the amount of 0.2-0.4% causes fragmentation of ferrite-pearlite structure, including carbides Mn and Fe, and does not reduce the number and size – sulfides, oxides and silicates. Moreover, non-metallic inclusions have a dispersed appearance, which promotes plasticization of the structure, which directly increases the viscous-plastic characteristics and resistance of the metal joints to crack formation.

Based on the results of metallographic research, the optimum content in the weld metal of the alloyed element – molybdenum, which is 0.2-0.4%, is determined.

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