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DEGRADATION OF SPARINGLY ALLOYED STEEL

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Introduction.

Sparingly alloyed steels gain the lead according to usage in the chemical industry. This is due to the fairly high strength and plasticity characteristics at a relatively low price. In future their use will spread. Much of the equipment and pipelines has been in service for a long time. During the operation a metal of any pipeline or device deteriorates, degrades and subjects to corrosion and mechanical damages of various types. Frequently damages are local in nature, due to the specific conditions of a specific device area, but steel degradation is caused by processes that are common, so it is the one that determines the remaining lifetime of the entire transport system or equipment. Degradation is dangerous and irreversible process, which lasts continuously since the beginning of service. The equipment parts, which work under considerable mechanical stresses in hostile environment, undergo particularly intense degradation processes. Currently, controversial is the issue of the choice of sensory characteristics, which are able to adequately evaluate the degree of steel degradation. According to the literature data the key factor of steel degradation of major pipelines is their stress aging in the process of which the strength usually increases, the ductility and impact strength decrease. However, if the service life comes up to 20 ... 30 years, volume damageability expands in the metal, which causes a number of peculiarities in the mechanical behavior of the material. In the oil refining and chemical industries reliability substantially depends on the corrosive action of technological environments and is caused by processes of the corrosion-fatigue fracture [1]. In addition to the environment static and cyclic stresses influence on the resource, which have an effect on the equipment during the scheduled time, the steel chemical composition, thermal and mechanical processing, equipment operation temperature, hydrogenation and steel degradation degree [2, 3]. Due to the fact that most part of the equipment and pipelines have come up to depletion of the resource or have worked a scheduled time, it makes conditions for emergencies. Therefore, it is important to identify the changes tendencies in the mechanical characteristics and to forecast the residual life of equipment based on the obtained results. The mechanical properties are the most important for structural materials, they often determine the possibilities and conditions for the further usage of certain equipment.

We investigated the structural low temperature carbon ASTM A333 Grade 6 steel from which the pipes of ammonia pipe Toliatti - Odessa were made, which had worked in a range of operating temperatures of 0 ° C - +21,5 ° C for about 262,800 hours (30 years) in conditions of liquid ammonia transportation. According to the chemical composition the investigated ASTM A333 Grade 6 steel is close to the 20G domestic steel. The JIS G3458 STPA22 steel was also studied, from which the pipes of synthetic ammonia vaporization plant 1-Б JSC "Sieverodonetsk Association Azot" were manufactured. JIS G3458 STPA22 steel is sparingly alloyed structural steel which is used for the production of steam heaters, steam pipes and collectors, flanges which has operated for a long time at temperatures up to 500 ° C. According to the chemical composition the studied steel is close to the national 15XM steel (GOST 4543-71). Vaporization system is included in the steam reforming unit and is designed to produce steam under pressure not more than 109 kg/cm2 (excess) at the temperature 480-482 ° C required for steam condensing turbine with controlled steam extraction, which is a drive of triple-effect centrifugal compressor of nitrogen hydrogen mixture. Until begin of the study the pipeline has been in operation for 162,904 hours (30 years).

Basics of methodical approach.

The strength properties have been determined for the original and degraded steel samples. The blanking of exploited steel was performed by oxy-fuel gas cutting, providing the allowances for zone with modified properties when heated. In the manufacture of samples preventive measures (cooling, the corresponding processing modes) were made, excluding the possibility of metal properties changing by heating or defamation arising from mechanical processing.

The mechanical researches on stretching were carried out on standard samples by P-5M machine according to GOST 1497-84 at 20 ° C. The researches at the elevated temperatures were carried out according to GOST 9651-84. The unit for researches at elevated temperatures consisted of: machines on stretching P-5M, tubular furnace with rotary guide, potentiometer with the TXA thermocouple, autotransformer to regulate the temperature in the furnace. Metallographic studies of metal macrostructure were fixed by МБS microscope at low magnification (up to 10 times) and the microstructure was studied by metallographic microscope MIM-8M by increasing by 150 times or more. Straight pipe sections were only researched, areas containing curves work in substantially different conditions. The correlation of changes in the mechanical characteristics and identification of common tendencies in the run of the steels service represents the work objective.

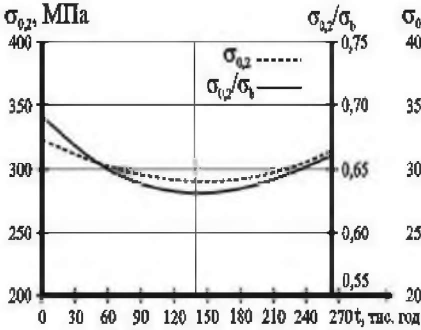
Research results and discussion.

The structure of ASTM A333 Grade 6 metal is fine-grained, which is typical for rolled sparingly alloyed steels with colorful elongated ferritic and pearlitic component and colorful elongated sulfide inclusions (2 - 3 grade GOST 1778-82), mainly concentrated in ferritic tapes (Fig. 1).

Fig.1. Sulphide inclusion fracture, ×150.

The non-uniform corrosion was observed on the inner and outer surface of the pipe with the maximum depth of up to 0,20 mm on the outer surface and up to 0,16 mm on the inside that is covered with a thin layer of corrosion products. Moreover, zoned ripping of metal was observed on surface layers.

In general metallographic studies bring us to the conclusion that in accordance with the rule of ferrite-pearlitic structure the pipe metal subjected to non-uniform corrosion with the depth up to 0,2 mm, but during the operation porosity formation and decomposition of sulfide inclusions began. The major issue is comparison and rating of characteristics during service. Mostly, researchers compare the characteristics only with their values at the start of service. However, the mechanical characteristics can show various tendencies to changes during prolonged service, so it is necessary to measure them at regular intervals and track tendencies to changes throughout the whole operation [4]. It is desirable to take as output values the characteristics values for pipes metal from the same batch, which were studied but were not in operation (pipe batch in reserve). It is often problematic to achieve during a long time service for decades. In this case, the mechanical characteristics were studied after 140160 and 262800 hours of the pipeline service. The characteristics were selected on the basis of passport data of metal pipes at the start of ammonia pipeline service. 5 pipes were under study, which had the following geometrical characteristics: pipes No. 1, 2, 4 - Ø323,8×17,4 mm; pipe No. 3 - Ø273×10,31 mm; pipe No. 5 - Ø317×17,4 mm. The samples from all the pipes were made with the orientation of fibers parallel to the pipe longitudinal axis, conventional liquid limit $\sigma_{0,2}$ and power border σ_b were determined, a composite index $\sigma_{0,2}/\sigma_b$ was defined based on these data (Fig. 2). The samples from transverse direction of the fibers were studied for the pipe No. 4. Also 5 additional samples were made from the pipe No. 5, which consisted welded joint.



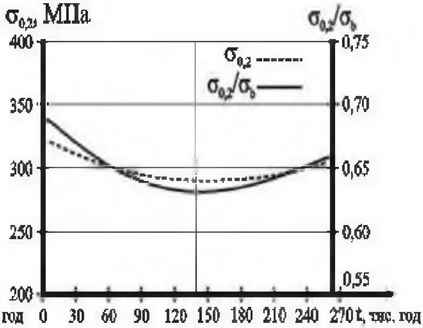


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Fig. 2. Variation characteristic of conventional liquid limit and composite index: a - pipes No.1; б - pipes No. 2.

The use of composite index $\sigma_{0,2}/\sigma_b$ to some extent allows to eliminate disadvantage of comparison of characteristics which is associated with the lack of samples made from steel of the same batch of delivery, but not being in service. In addition, for some metals this index may be more sensitive as for detection of variations in the mechanical characteristics.

It is established that according to the temporal changes nature of conventional liquid limit $\sigma_{0,2}$, the pipe material of pipes No. 1, 2, 4, 5 underwent weakening at the first stage of service and it was characterized by steel hardening vice versa at the second stage. Pipe material No. 3 showed a strong tendency to weakening in service. A possible reason for differences in pipe No. 3 characteristics is its smaller geometric dimensions.

As a result of experimental data processing it was established that a change in time of conventional liquid limit $\sigma_{0,2}$ could described by the equation:

$$\sigma_{0,2} = k - mt + nt^2,$$

where k, m, n – constant values;

t – time, thous. hrs.

During the JIS G3458 STPA22 steel study the samples made from the pipes which had worked 38880, 70000, 108460 and 162904 hours, were studied, respectively. At the baseline of service the characteristics were chosen based on certificate of the manufacturer. The microstructure of the base metal of pipes is ferrite-pearlitic. Perlite is granular. Perlite spheroidizing corresponds to 2-3 grade. Microdamages of pipes metal and welded joints were not detected. According to results of carbide analysis, based on the results after 38880 hours of service, 4,6%-7,9% of chromium and molybdenum were transferred from the solid solution to carbides.

Metallographic studies of metal blanking were conducted at six microsections cut from two coils of the base metal and 9 macro and microsections cut from three welded joints. After operation for 162904 hours spheroidizing and partial coagulation of cementite spheroids in a matrix and on the grain boundaries were detected. Spheroidizing of perlite corresponds to 2 - 3 grades after scale E OCT 34 - 70 - 690 - 96.

To conduct the tests on stretching the samples were manufactured with the orientation on fibers parallel to the longitudinal axis of the pipe. The time resistance σ_b (Fig. 3a), conditional liquid limit $\sigma_{0,2}$ (Fig. 3б) were determined.

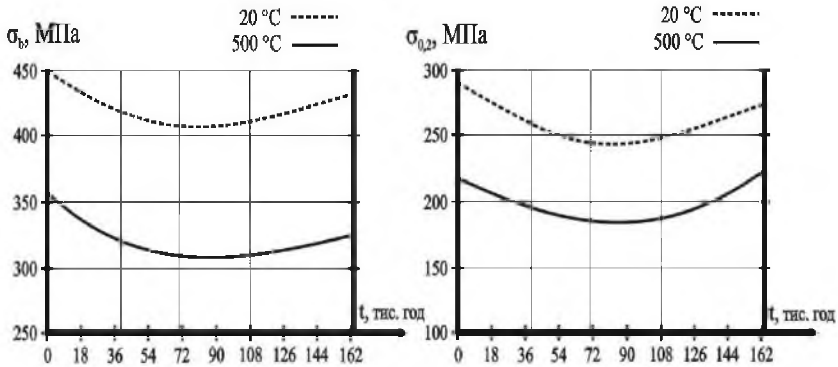

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Fig. 3. Variation characteristic: a – ultimate stress σ_b; б - conventional liquid limit $\sigma_{0,2}$.

It has been established that the pipe material under study underwent weakening at the temperature of 20 °C and 500 °C at the first stage of service and the second stage was marked by steel strengthening vice versa. Common to the power characteristic is the service lowering at the first stage of operation up to 70000 labour hours and some strengthening at the final stage of operation. After 162904 hours of operation at the test temperature of 500 ° C the value of conventional liquid limit $\sigma_{0,2}$ is still 2% as much in comparison with the value of the same quantity at the beginning of the operation.

As a result of experimental data processing it has been established that the variation in time of tensile strength σ_b, $\sigma_{0,2}$ and $\sigma_{0,2}/\sigma_b$ is described by the equation which are similar to the corresponding equations for steel ASTM A333 Grade 6. The difference lies in the specific values of constant quantities k, m, n, a, b, c. But the general changes tendencies in time of mechanical characteristics turned out to be common: weakening at the first stage of the operation and the strengthening at the second one. Moreover, all studied characteristics demonstrated the ability to use them for evaluation of the degradation degree under long-term service. The obtained dependencies of the changes of mechanic quantities make it possible to forecast their values at least for the coming years.

The original approach to the evaluation of the responsiveness of the mechanic characteristics and determination of the residual life has been suggested in the theory of dissipated in the metal damageability elaborated by scientific school of Professor G. Nykoforchyn [6, 7]. At present, the theory has been well confirmed for pipe steels used in the composition of oil and gas pipelines. This theory considers the article made of metal as macro object and microdamages formed as a result of various factors, distributed in the volume of body under probability law. The action of intensifying factors, such as hydrogenation or high temperature on the dynamics of degradation is taken into account. According to this theory the point of minimum relative narrowing is considered as a criterion for its application (Fig. 4).

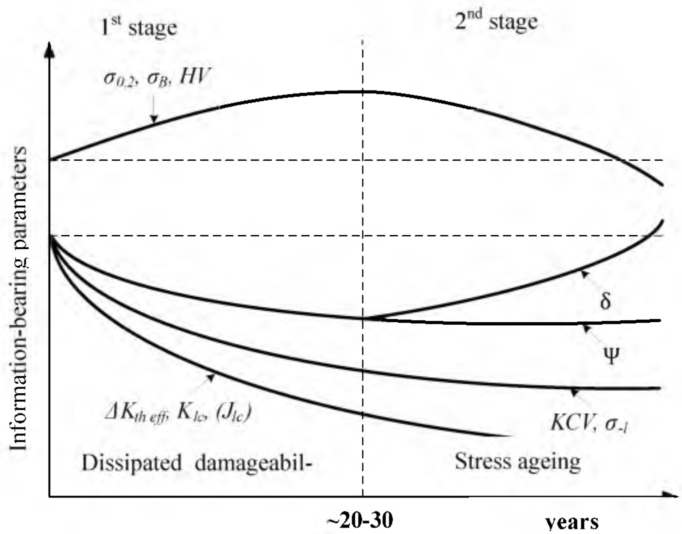

Fig. 4. General variation scheme of commonly used mechanical characteristic of pipe steels in service.

When passing to this stage the authors propose not to consider the relative elongation as a sensitive value because of numerous micro cracks in the metal volume. Professor G. Nykyforchyn also was the first to develop the approaches to correlation of changes in mechanical and electrochemical characteristics during continuous operation in hostile environment [8]. Thus, when passing through the point of maximum or minimum of mechanic characteristics it is worth considering the crucially different degradation mechanism. It is essential in the operation of equipment being in service for a long time.

Conclusions. The stated regularities of power characteristics changes make it possible to forecast their value from now on. There are determined the functional dependences of temporal changes of conventional liquid limit $\sigma_{0,2}$, σ_b and composite index $\sigma_{0,2}/\sigma_b$. The rapid response of conventional liquid limit $\sigma_{0,2}$ to constructional steel degradation has been confirmed[5]. There is proved the efficiency of $\sigma_{0,2}/\sigma_b$ composite index usage for the estimation of steel degradation degree. In whole the results of the conducted study may be useful for the estimation of metal degradation degree of the equipment and forecasting of the remaining lifetime. The obtained data are confirmed by the study results of other researches [6, 7] in the tendency of constructional materials of equipment under conditions of corrosive medium prior to the strengthening through long-term usage.

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