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IDENTIFYING REGULARITIES OF THE STRUCTURE AND PROPERTIES OF 13XFA PIPE STEEL SMELTED ON DIFFERENT CHARGES IN ELECTRIC ARC FURNACE

The problem of increasing the efficiency of 13XFA pipe steel for oil and gas wells by using selective selection of charges for smelting them in an electric arc furnace is considered. 4 batches of different chemical heterogeneity were studied. It was found that melt 1 from a purer charge 1 contains a smaller amount of harmful impurities in the form of surface-active substances (surfactants), which affect grain growth when samples are heated for quenching. Thus, melts 1 and 2, containing a smaller amount of surfactants in the charge, have a greater tendency to austenite grain growth and lower hardenability compared to melts 3 and 4, the charge of which is relatively heavily contaminated with surfactants. This is due to the low relatively free energy of melts 3 and 4. The study showed that at a relatively low tempering temperature (300 °C) there was an insignificant change in the mechanical properties of the samples (R_m, KC, etc.). Hydrogenation of steels significantly reduces the strength of steels from all melts, however, an increase in tempering time leads to an increase in long-term strength. In this case, the maximum impact strength (KC) of all melts is observed after normalization, but samples from melt 1 have a higher IC. When the samples were held (570 °C), the near-boundary layers of steel grains were enriched with P, Sb, Sn, As, leading to embrittlement and weakening of intergrain cohesion and a decrease in the energy of boundaries. In the process of testing at –80 °C, cracks along the grain boundaries are visible on the fractures of the samples after brittle tempering. By increasing the purity of metal waste for smelting pipe steel, it is possible to improve the complex of its properties, and hence the durability of seamless pipes for the oil and gas industry produced from it

Keywords: selection of metal waste, pipe steel, heat treatment, temper brittleness, cold resistance, oil and gas industry

Arif Mammadov
Corresponding author
Doctor of Technical Sciences, Professor-Advisor*
E-mail: ariff-1947@mail.ru
Agil Babaev
PhD, Associate Professor, Manager*
Nizami Ismailov
Doctor of Technical Sciences, Professor*
Mukhtar Huseinov
PhD, Associate Professor*
Faiq Guliyev
PhD, Associate Professor*
*Department of Metallurgy and Technology of Materials
Azerbaijan Technical University
H. Javid ave., 25, Baku, Azerbaijan, AZ 1073

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1. Introduction

The quality of products from any steel begins with the processes of smelting and casting steel. To date, steel smelting in an electric arc furnace and continuous casting of liquid steel are one of the most important elements of steelmaking and allow not only obtaining high-quality metal products, but also saving metal, energy resources, and improving the environmental situation [1, 2].

One of the most promising ways to improve the quality indicators of continuously cast headers is to improve the chemical composition of steels used for the production of seamless pipes.

The reduction of carbon content in steel, the introduction of microalloying elements that provide grain refinement and hardening of steel, along with other methods of influence, are effective measures to achieve the required quality indicators of continuously cast billets.

Reducing the carbon content will also reduce the level of chemical and structural heterogeneity, and, taking into account the addition of microalloying elements, it will also increase the level of ductile characteristics of pipe products while maintaining high strength [3, 4].

It is known that the quality of steel smelted in any furnace depends on the type and composition of the charge. At present, many plants, including Baku Steel Company LLC, work on the technology of steel smelting on metal waste. At the same time, the quality of the used charge from ferrous metal waste is of decisive importance, each batch of which can differ greatly from the other.

Therefore, when smelting steel on waste metal, it is necessary to carefully control the quality of the produced pipe steel, which is operated in very difficult oil and gas production conditions, and in many cases in extreme conditions, that is, in offshore conditions. In order to meet such stringent requirements for the quality of pipe steel, the enterprise must have scientifically based production recommendations and flexible product quality management.

So, for example, in steelmaking on waste metal, it is imperative to selectively select the charge used and find the relationship between the quality of the charge and the strength and performance properties of the products. However, such a scientific and technological approach is not practiced by enterprises producing special-purpose seamless pipes due to the lack of research on this issue. The lack of studies in this area makes it difficult to assess the quality of manufactured products from batch to batch. Pipes for oil and gas wells operate under the influence of dynamic loads, cold, aggressive hydrogen-containing environment, etc. It is precisely because of the lack of such scientific and technological recommendations that pipes often fail prematurely.

In this regard, research is required to determine the chemical composition and chemical heterogeneity of steels smelted on different metal wastes, the effect of heat treatment of such pipe steel on its quality, the study of a batch of steels from different metal wastes on the brittleness and cold brittleness of pipes after hydrogenation in a special solution.

Therefore, the study of the structure and properties of manufactured pipe steel, smelted on different charges, is of scientific and practical interest for the objective separation of defects between steelmaking and rolling industries, and will also serve as the basis for improving factory laboratory control to prevent defects.

2. Literature review and problem statement

The conducted literature analysis shows that at present, seamless pipes for the oil and gas industry are mainly produced using continuous casting technology, which is a more productive method. However, in this case, some defects of pipes of steelmaking, foundry and materials science nature are inevitable. For example, the work [5] shows that in order to avoid defects in tubular blanks in the process of continuous casting due to a decrease in their thermoplasticity, it is necessary to say that the content of carbon and alloying elements in steel is reduced to the very minimum. This work does not address the processes of formation of other defects and their relationship with other parameters of the technological chain of production. In addition, the problems of steelmaking on various metal waste, which have a direct impact on the formation of product quality, are not considered.

In [6], the problem of theoretical substantiation and implementation of a resource-saving technology for the production of electric alloying of steels and continuously cast billets from them is considered. Despite the wide range of studies, this paper lacks studies devoted to the selective selection of metal waste in the electric alloying of pipe steel, the relationship between heat treatment and hot deformation of pipes, and the features of specimen fractures after brittle tempering. In the absence of these studies, it is not possible to develop universal recommendations that ensure the production of high-quality pipe steel.

The paper [7] presents the results of studies on optimizing the structure and strength properties of special-purpose pipe steel. The characteristics of the microstructure of low-carbon tubular steel processed according to various heat treatment modes are given. These studies are aimed at increasing the cold resistance of seamless hot-worked oil and gas pipelines through combined heat treatment. It should be noted that the operating conditions of pipes for oil and gas wells are much more difficult than those of oil and gas pipelines. Therefore, the results of the study [7] cannot be used for pipes operated in oil and gas wells.

The study carried out in [8] is a continuation of the studies in [7]. In this paper, experiments were carried out simulating the operating conditions of pipes in oil and gas fields. However, in this work there are no studies on the metallurgical technology of pipe steel, that is, on the selective selection of metal waste and the study of material science issues and the processing of pipe blanks by pressure.

In [9], the effect of preliminary heat treatment on the hardness and impact toughness of 13XFA steel quenched from the intercritical temperature range (ICT) was studied. However, there are no studies in the work on the relationship between the selective selection of metal waste, the parameters of metallurgical technology, the technology of pressure treatment and heat treatment. Therefore, it is impossible to unequivocally determine the usefulness of the results of this study for the production of tubular steels operated in oil and gas wells.

In [10], the results of the creation of operational and reliable methods for non-destructive testing of the structure and level of mechanical properties of heat-hardened pipes for the oil and gas industry are presented. In this paper, no research was also carried out on the selective selection of metal waste, metallurgical technology for producing pipe steel and heat treatment technology, and the performance characteristics of pipes were not studied, and therefore these results cannot be considered complete for pipes operated in oil and gas wells, since these pipes often fail during operation due to violation of these technologies.

Since the technology of steelmaking in an electric arc furnace is based on the use of metal waste, a selective approach is required when choosing a charge, after which it is necessary to establish more flexible control over other operations in the technological chain of pipe steel production.

In this regard, in the production of pipe steel, it is necessary to carry out careful control when choosing one or another metal waste. This requires determining the chemical composition and chemical heterogeneity of steels smelted with different charges, assessing the effect of heat treatment of steels on their structure and properties, and studying the effect of the type of charge on the growth of austenite grains in the structure of steels and on their temper brittleness and cold brittleness. In addition, to determine the operational characteristics, it is required to conduct fractographic studies of fractures of samples and study their hydrogenation in a special solution that imitates the real operating conditions of pipes in oil and gas wells.

3. The aim and objectives of the study

The aim of the study is to find the relationship between the operations of the technological chain of production, the structure and properties of steel. This will make it possible to obtain high-quality seamless pipes using selectively selected metal waste.

To achieve this aim, the following objectives are accomplished:

– to determine the chemical composition and chemical heterogeneity of steels smelted from four different charges;

– to study of the influence of the type of charge on the growth of austenite grains in the structure of steels;

– to evaluate the influence of temperature and duration of tempering on the properties of 13XFA pipe steel;

– to study the influence of the type of charge on tempering brittleness, cold brittleness, after hot deformation, brittle tempering and normalization;

– to carry out fractographic studies of fractures of samples and to study their hydrogenation in a special solution.

4. Materials and methods of experiments

The object of the research is drill pipe steel, smelted with different charge loads in an electric arc furnace, its structure and properties.

The main hypothesis of the research is to identify the effect of selective selection of metal waste of different quality on the structure and properties of seamless pipes for the oil and gas industry.

When choosing the direction of this research, we proceeded from the fact that the quality of metal waste can play a serious role in the formation of the structure and properties of pipe steel, and hence its operational characteristics.

According to the standard, metal waste is very diverse and a large amount of experiments is required in such a wide range. In this regard, we regrouped them into 4 different charges, depending on the shape, size and specific gravity of metal waste.

For the research, charge number 1, consisting of 50 % of group No. 1 – 1A, 1B; 25 % from group No. 2 – 2A, 2B and 25 % from group No. 3 – 3A, 3B; charge number 2, consisting of 50 % of charge ingot 4A, 4B, 25 % of steel scrap of small sizes and waste No. 1 – 5A, 5B and 25 % of the same from group No. 2 – 6A, 6B; charge number 3, consisting of 50 % of a package of steel chips – 7A, 7B; 25 % from package No. 1 – 8A, 8B, 25 % from package No. 2 – 9A, 9B; charge number 4, consisting of 25 % of package No. 3 – 10A; 25 % from package No. 4 – 11A, 25 % from steel rope and steel wire 12A, 12B; 12.5 % each from steel shavings No. 1 – 13A and No. 2 – 14A, 14B were used.

For charge number 1, the scrap and waste used had the dimensions of the segments not more than 300×200×150 mm, and not more than 600×350×250 mm. The thickness of the metal was at least 6–8 mm. In the case of railway cars, the bulk density of the waste was at least 900–1,000 kg/m^3.

In the presence of pipes on the charge, their outer diameter was not more than 150 mm and the wall thickness was not less than 8 mm. For scrap and waste No. 3 – 3A, 3B, the dimensions of the scraps were no more than 800×500×500 mm, and the dimensions of the pipes – the outer diameter was not more than 150 mm. When using railway cars, the bulk density of the metal was at least 700 kg/m^3.

For charge number 2, ingots 4A, 4B and steel scrap and waste 5A, 5B were used with a metal thickness of at least 6 mm, as well as 6A, 6B with a section size of 3500×2500×1,000 mm with a metal thickness of at least 6 mm.

Charge number 3 consisted of packages of chips of steel 7A, 7B, 8A, 8V, 9A, 9B, the weight of the packages was in the range of 2–50 kg with a density of 4,500–5,000 kg/m^3 for packages 7A, 7B, for packages 8A, 8B the dimensions were 2,000×1,000×710 mm, with a density of 2,000–2,500 kg/m^3 and a weight of at least 100 kg, and for packages 9A, 9B, the dimensions were 2,000×1,000×710 mm, with a density of 1,800–2,500 kg/m^3 and a weight of at least 100 kg.

Charge number 4 consisted of packages No. 3 – 10A, No. 4 – 11A and steel ropes and wires No. 12A, 12B, steel chips No. 1 – 13A and No. 2 – 14A –14B. At the same time, for package No. 3 – 10A, the dimensions were 2000×1000×710 mm with a density of at least 1,200–2,500 kg/m^3 and a weight of at least 100 kg.

Package No. 4 – 11A differed from package No. 3 – 10A only in density, in which the density was at least 2500 kg/m^3, i.e. it was packed more tightly. Steel ropes and wire No. 12A, 12B consisted of a coil (for wire) with a diameter of 800 mm, a length of 500 mm and a weight of at least 20 kg. The cross section of the rope was at least 20 mm with a length of 800 mm. Steel chips No. 1 – 13A and No. 2 –14A, 14B were not packaged. The length of the loop and the section of chips No. 1 was no more than 50 mm, and No. 2 – no more than 100 mm. The length of the chip loop is allowed up to 100–200 mm, not more than 2 % or not more than 0.5 % of the weight of the chips.

Comparative studies of the physical, mechanical and special properties of 13XFA steel smelted using these four charges, various sizes, shapes and compositions of waste were given. Melting was carried out in a 50 ton electric arc furnace.

The technologies for smelting melts, their out-of-furnace treatment, continuous casting and further metal pressure treatment and thermal hardening of seamless pipes were identical.

To determine the chemical inhomogeneity of steels from all melts, X-ray microanalysis was performed on a Camsan analyzer.

The tendency to austenite grain growth was determined according to GOST 5739-82 ASTM E112-2013 on samples with a diameter of 15 mm after vacuum etching carried out at 900, 950, 1,000 1,050, 1,100, 1,150 °C for 1 h, followed by accelerated cooling, which prevents interfacial etching of grains.

The hardenability was determined by the terc test method according to GOST 5657-69 ASTM A255-2014 and by the bulk hardening method.

To determine the effect of the degree of contamination with microimpurities on the mechanical properties of steels, tensile tests (GOST 1487-84 EN ISO6892.1-2016), impact bending tests (GOST 9454-78 EN ISO148-2016, ASTM E23-2012) were carried out, and the hardness of the samples was measured after the following heat treatment: quenching from 930 °C with cooling in water using a sprayer, tempering at 150, 250, 350, 450, 600, 650 °C for 2 hours, followed by cooling in air. For each type of test, five samples of each melt were used.

Tensile tests were carried out on cylindrical specimens with a diameter of 5 mm, impact strength tests – on specimens with a notch ((τ_H=1 mm), hardness on impact specimens (measurements were carried out at five points).

To determine the temper brittleness temperature, a series of samples were tested after heat treatment, consisting of hardening (T=930 °C) and tempering at 530, 550, 570, 590, 610, 630, 650, 670, 700 °C for 2 hours after blowing slow cooling in a furnace for 3 hours. After tempering, the steel had a sorbitol-troostite structure.

Samples 16 mm in diameter were hydrogenated in an aqueous solution of 4.5 % H_2SO_4+2.5 % NH_4CNS at normal temperature with cathodic polarization at a current density of 60 A/m^2 on a lever setup under conditions of single-base tension at a constant load.

5. Results of the study of the structure and properties of pipe steel smelted with different charges in an electric arc furnace

5. 1. Determination of the chemical composition and chemical heterogeneity of steels smelted from four different charges

Experimental melts obtained from different batches of metal waste had a similar chemical composition (Table 1).

The structure of steel smelted from various charges after hot deformation and cooling in air was ferrite (grain No. 10) and thin-lamellar pearlite.

With the help of special etching of thin sections ($FeCl_2$+HCl picric acid), the chemical inhomogeneity of steels in terms of carbon and alloying elements was revealed.

X-ray microanalysis confirmed the chemical inhomogeneity in chromium and vanadium, which in the cross section of the samples was 0.1–0.2 % and was almost the same in all four melts, since they were introduced during the melting of the charge specifically in the form of ferrochrome and ferrovanadium. However, the studied steels still differed from each other in terms of the content of microimpurities of some non-ferrous metals (As, Sb, Cu, Zn) (Table 2).

Table 1

Chemical composition of 13XFA steel, smelted from different charges

No.	Charge number	Melt number	Content of elements, wt %						
			C	Mn	Si	Cr	V	P	S
1	1	1	0.11	0.65	0.20	0.70	0.08	0.025	0.025
2	2	2	0.13	0.52	0.25	0.65	0.06	0.026	0.022
3	3	3	0.15	0.51	0.30	0.70	0.06	0.030	0.023
4	4	4	0.17	0.41	0.35	0.69	0.05	0.029	0.024

Table 2

Content of trace impurities of some non-ferrous metals in 13XFA steel

No.	Charge number	Melt number	Content of trace impurities, wt %					
			As	Sb	Zn	Pb	Cu	Sn
1	1	1	0.0004	0.002	0.001	0.001	0.019	0.0009
2	2	2	0.0008	0.008	0.002	0.002	0.018	0.005
3	3	3	0.002	0.013	0.003	0.003	0.017	0.008
4	4	4	0.006	0.014	0.004	0.003	0.019	0.009

Melt 1 from batch 1 contained the least amount of surface-active substances (surfactants) compared to other melts. To elucidate the effect of microimpurity segregation on the state of austenite grain boundaries, the relative free energy of the boundaries was determined.

The results of the study showed that the boundaries of the austenite grains of melt 4 had the lowest relative free energy compared to melts 1, 2 and 3, which indicates the highest degree of their contamination with surfactants. The amount of microimpurities and their distribution should affect the technological properties of the studied steels: the tendency to austenite grain growth and hardenability [11, 12].

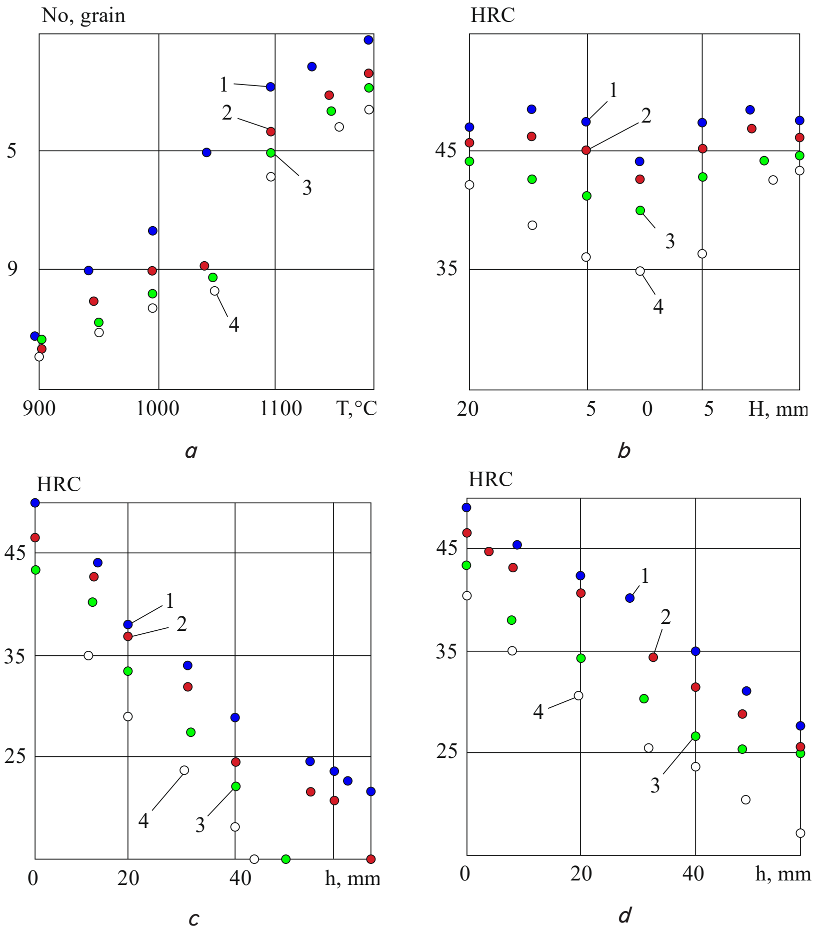
5. 2. Study of the effect of the type of charge on the growth of austenite grains in the structure of steels

It was found that melts 1, 2 have a greater tendency to grain growth than melts 3 and 4 (Fig. 1, *a*).

However, at 1,000 °C and above, when the mechanism of grain growth changes and the diffusion mobility of microimpurities increases, all melts behave in the same way. At 1,050 °C, a large inequigranularity was observed, there were giant grains formed due to the coalescence (merging) of small ones. At 1,100 °C, the grain size was equalized in all four melts, although some grain inconsistency was still preserved.

The hardenability was determined by the terc test method according to GOST 5657-69 ASTM A255-2014 and by the bulk hardening method. Steels from melts 1 and 2 had the highest hardenability, and steels from melt 4 had the lowest hardenability. Steel from melt 3 occupies an intermediate position in hardenability (Fig. 1, *b*).

With an increase in the heating temperature for quenching from 900 °C to 950 °C, the hardenability of steel increases, although the difference in the hardenability of steels smelted on different charges remains approximately the same (Fig. 1, *c*, *d*). Such an increase in hardenability can be explained by a decrease in the rate of austenite-pearlite transformation due to the growth of austenite grains with an increase in the heating temperature for quenching [13, 14].



a *b* *c* *d*

Fig. 1. Dependence of the growth of austenite grains of 13XFA steel and its hardenability after heat treatment on the type of melts 1, 2, 3, 4 — obtained from the corresponding charges (Table 1): *a* — growth of austenite grains; *b* — hardenability after end hardening; *c* — hardenability after volumetric hardening from 930 °C; *d* — hardenability after volumetric hardening from 900 °C; *H* — distance from the center; *h* — distance from the end

5. 3. Evaluation of the influence of temperature and duration of tempering on the properties of 13XFA pipe steel

Fig. 2, *a–c* show that up to 300 °C tempering temperature, there is a slight change in the mechanical properties of the samples, with a further increase in tempering temperature. There is a noticeable softening and increase in plasticity. The mechanical properties of steels smelted on different charges were practically the same. Only melt 1 after quenching and tempering at 550 °C had a higher impact strength (Fig. 2, *b*) and relative narrowing (Fig. 2, *c*). With an increase in tempering temperature, there is an increase in the long-term strength of steels from all melts, but still a higher long-term strength is observed for steel from melting (Fig. 2, *d*). Hydrogenation of steels significantly reduces the long-term strength of steels from all melts. Nevertheless, with an increase in the duration of tempering of steels, the long-term strength somewhat increases (Fig. 2, *e*), but its value after reheating is almost five times less than that of non-hydrogenated samples.

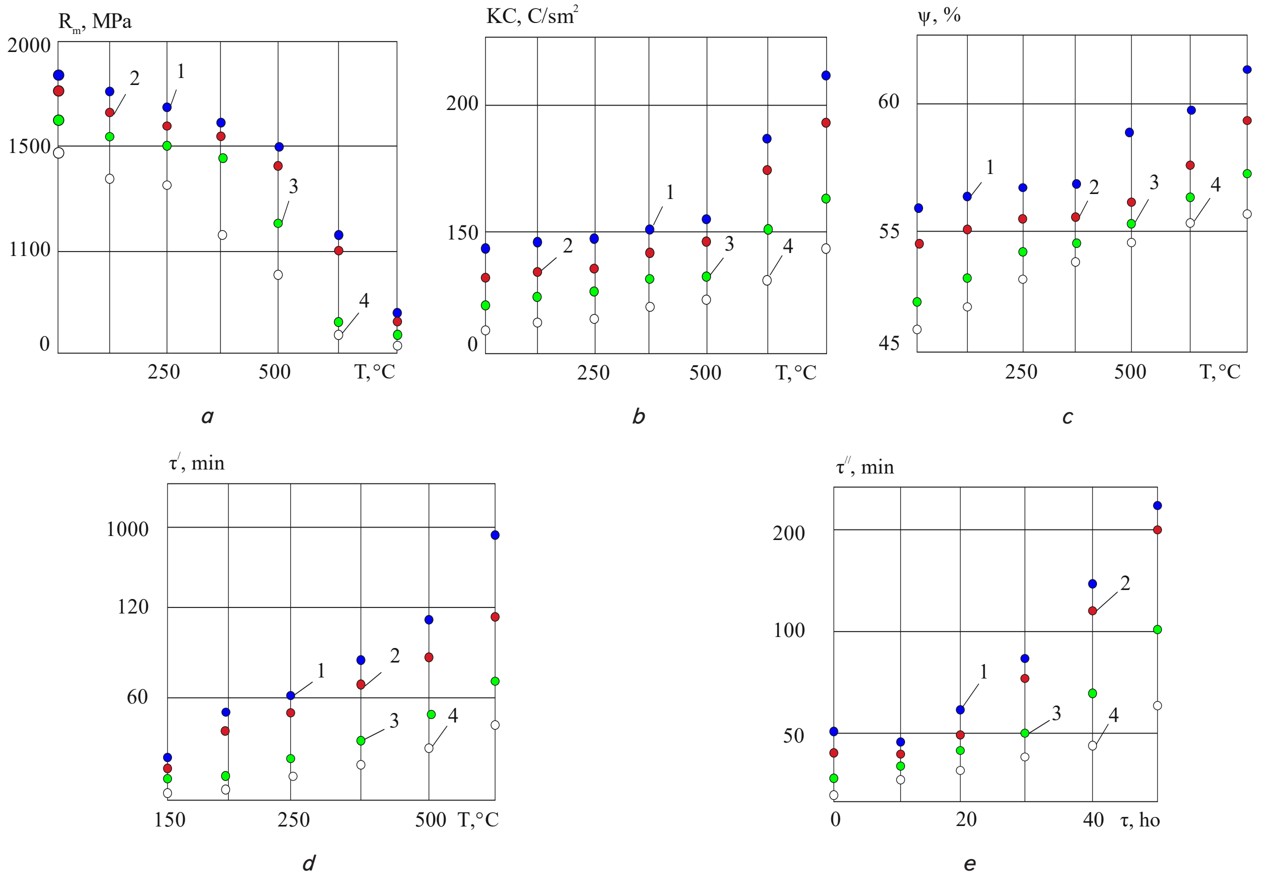
Thus, the operating conditions of pipes in a highly aggressive environment, that is, when exposed to a hydrogen-containing environment, require a more careful approach when choosing a charge for steelmaking. Therefore, the use of a charge containing a large amount of microimpurities in the smelting of steel for pipes of oil and gas wells is unacceptable.

5. 4. Study of the effect of charge type on temper brittleness, cold capacity after hot deformation, brittle tempering and normalization

Based on the results of tests on the impact strength of samples after tempering at 530–700 °C.

The curves indicate the numbers of melts, the temperature of tempering brittleness was determined – 570 °C (Fig. 3, *a*). The microstructure of the studied steels melted with different batches after quenching and tempering at 570 °C was the same. The absolute values of the impact strength of melt 1, at all tempering temperatures in the range of 530–700 °C, are higher than that of melts 2, 3 and 4 (Fig. 3, *a*), which can be explained by the greater contamination of the grain boundary of melts 2, 3 and 4 with surface-active impurities.

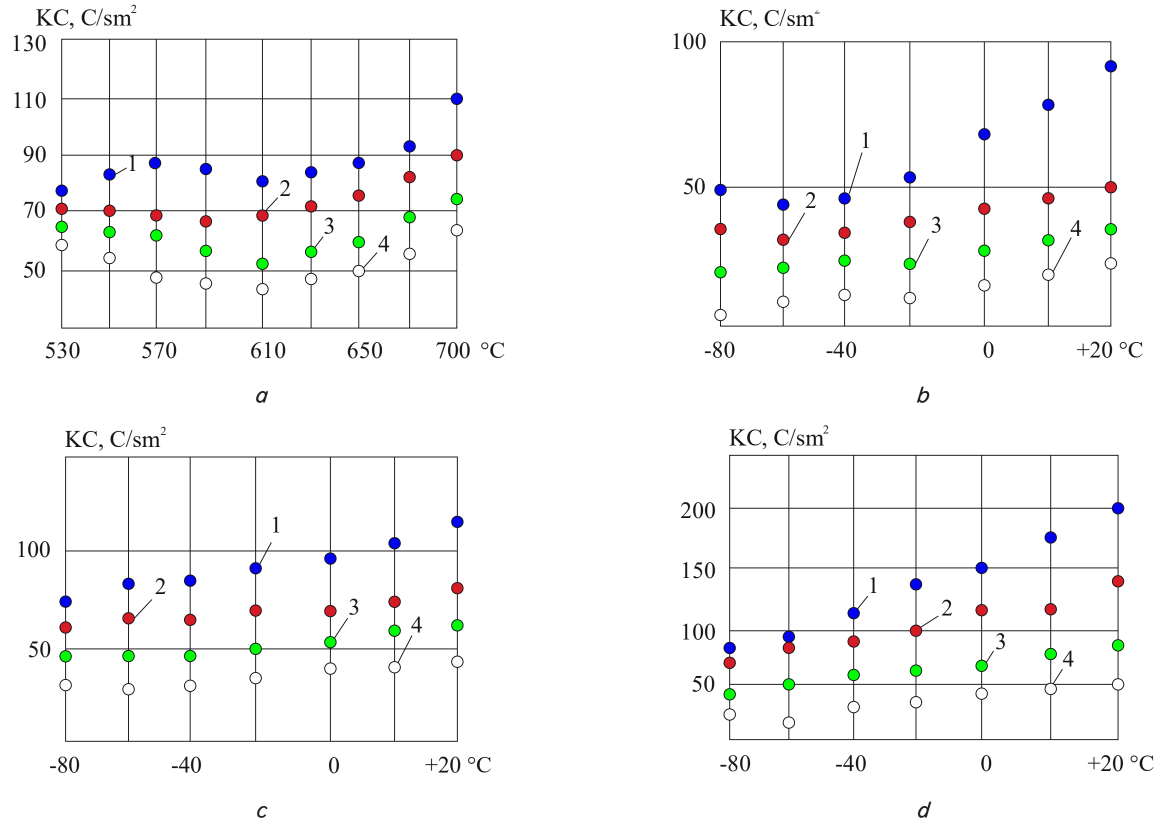
We also studied the cold brittleness of steel after hot deformation, coarse tempering at 570 °C for 50 h, and normalization (Fig. 3, *b–d*). In all four melts, a monotonic decrease in impact strength was observed with decreasing test temperature. The temperature at which the reduced viscosity was 40 C/cm^2 was taken as the conditional threshold of cold brittleness of 13XFA steel; melt 1 had the highest in all three states, and melt 4 had the lowest. The maximum impact toughness was observed after normalization.



a *b* *c*

d *e*

Fig. 2. Influence of temperature and duration of tempering on the properties of 13XFA steel, obtained from melts 1, 2, 3, 4 — smelted from the corresponding charges: *a* — dependence of tensile strength on tempering temperature; *b* — dependence of impact strength on tempering temperature; *c* — dependence of relative narrowing on tempering temperature; *d* — dependence of long-term strength on tempering temperature; *e* — dependence of destruction time on tempering duration; $\tau^{/}$ — long-term strength at R=0.6R_v, $\tau^{//}$ — time to failure with hydrogenation R_m=600 MPa after tempering at 650 °C



a

b

c

d

Fig. 3. Dependence of temper brittleness and cold brittleness of 13XFA steel on the type of melts 1, 2, 3, 4 – obtained from the corresponding charges: *a* – temper brittleness; *b* – cold brittleness after hot deformation; *c* – cold brittleness after brittle tempering; *d* – cold brittleness after normalization

The lower cold brittleness vapor for all four melts is located at a temperature below room temperature –80 °C with slow cooling. During holding at 570 °C, the near-boundary layers were enriched with P, Sb, Sn, and As, leading to embrittlement and weakening of the intergrain cohesion and a decrease in the energy of the boundaries [15–17].

Since the amount of phosphorus is approximately the same in all melts, the reason for the decrease in impact strength should probably be sought in a larger amount of surface-active elements and microimpurities segregating along the grain boundaries.

5. 5. Fractographic studies of fractures of samples and the study of their hydrogenation in a special solution

Fractographic studies carried out on a Stereoscan-180 electron microscope made it possible to determine the features of the fracture substructure of the samples tested at +20 °C after a brittle piece. When comparing fractures, it was found that in melts 3 and 4, which are most contaminated with microimpurities, there is a large proportion of brittle intergranular fracture, fewer brittle fracture elements in melt 2, and even less in melt 1 (Fig. 4) with a decrease in the test temperature in fractures, an increase in the proportion of brittle intergranular fracture was observed, especially in melt 4.

In the process of testing at –80 °C, microfractograms of samples of all four melts after coarse tempering clearly show cracks along grain boundaries, which indicates the dominant effect of the state of boundaries on intergranular fracture [18–20].

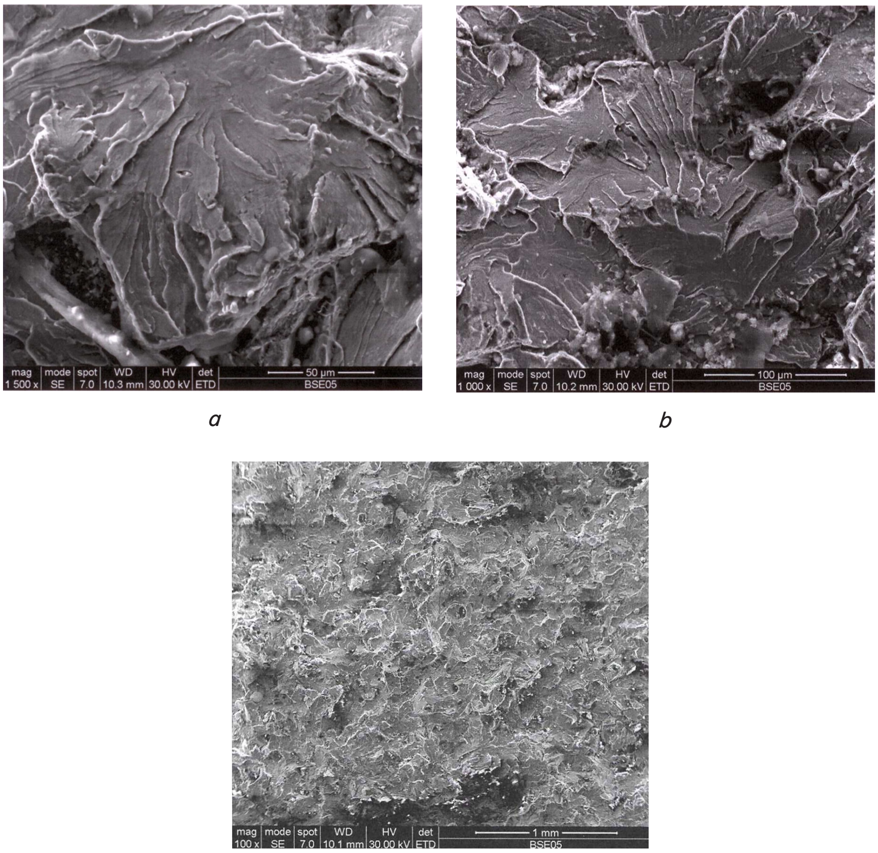
To determine the effect of the degree of impurity contamination of the grain boundaries of steels smelted in an electric arc furnace on the durability of seamless pipes made from them during operation under the influence of aggressive media, tests were carried out on the bottom strength in a hydrogen-containing medium [21].

The results obtained are shown in Table 3, from which it can be seen that the samples after hot deformation had the highest resistance.

The resistance of samples against hydrogen agglomeration after normalization decreased by an order of magnitude compared to the resistance in the hot-rolled state and by three orders of magnitude after quenching and low tempering. Depending on the resistance to hydrogen embrittlement, steels obtained from various charges can be arranged in the following sequence: melt 1 – melt 2 – melt 3 – melt 4.

The results of studies of the resistance of steels in a hydrogen-containing medium depending on the tempering temperature, given at the same stress level – $\sigma=0.6r_m$, made it possible to evaluate the effect of residual stresses, structure and microimpurities on the kinetics of hydrogen embrittlement (Fig. 2, *d*, *e*). In the tempering temperature range of 150–650 °C, the resistance of melts 1 and 2 increases more intensively than that of melts 3 and 4.

The gas analysis of samples carried out by the vacuum heating method, both in the initial state and at various stages of the hydrogen embrittlement test, showed that melt 4 contains more hydrogen than melts 1, 2, and 3. In turn, microimpurities and hydrogen, which is also a surfactant, significantly reduce local stresses that cause the initiation and development of microcracks, which leads to brittle fracture [22].



a *b*

c

Fig. 4. Microfractograms of 13XFA steel after tempering at 660 °C (x500): *a* — melt 1; *b* — melt 2; *c* — melt 4

Table 3

Results of hydrogenation of samples in an aqueous solution of 4.5 % H_2SO_4+2.5 % NH_4CNS

Melt	Sample condition	τ, min. at stress σ, n/mm^2			
		300	400	500	600
1	After hot deformations	8,560	5,430	6220	3450
2		7,420	3,760	2640	2860
3		6,130	3,020	1530	1960
4		5,525	2,560	1220	1750
1	After normalization	5,410	2,250	689	455
2		2,920	1,020	320	435
3		610	860	308	85
4		520	310	125	73
1	After quenching and low tempering	41	25	15	9
2		25	23	14	8
3		20	18	8	7
4		20	8	6	5

This process appeared most clearly in the decrease in the long-term strength of steels at 650 °C (Fig. 2, *d*), corresponding to the temper brittleness. A further increase in the duration of tempering at 650 °C led to a redistribution of microimpurities – a decrease in their concentration along the grain boundaries, which caused a significant increase in resistance to hydrogen embrittlement (Fig. 2, *e*). Thus, by increasing the purity of steel in terms of microimpurities, it is possible to achieve an improvement in the complex of its physical and mechanical properties, and, consequently, the durability of seamless pipes made from them for the oil and gas industry.

6. Discussion of the results of studies of the structure and properties of pipe steel smelted with different charges in an electric arc furnace

The studies carried out made it possible to determine that the chemical compositions of steels smelted on different charges are almost similar (Table 1). However, with the help of special etching of thin sections, the chemical inhomogeneity of steels in terms of carbon and alloying elements was revealed. Chemical inhomogeneity in chromium and vanadium was revealed, and it was practically the same in all four melts, since they were removed in the process of melting the charge in the form of ferrochromium and ferrovanadium. However, steels smelted on different charges differed from each other in the content of trace impurities of some non-ferrous metals, such as As, Sb, Cu, Zn (Table 2). Melt 1 from batch 1 contained the least amount of surfactants compared to other melts. Consequently, microimpurities and their distribution have an effect on the technological properties of steels.

It was found that melts 1 and 2 have a greater tendency to grain growth than melts 3 and 4 (Fig. 1, *a*). The mechanism of austenite grain growth is strongly influenced by the heating temperature. So, at 1,000 °C and above, the mechanism of grain growth changes due to an increase in the diffusion mobility of microimpurities, that is, in this case, all melts behave in the same way. At the same time, a higher hardenability of steel is observed in melts 1 and 2, the lowest – in melt 4 (Fig. 1, *b*) in the case of an increase in the temperature for hardening from 900 to 950 °C, the hardenability of the steel increases, but the difference in the hardenability of steels obtained from different charges remains (Fig. 1, *c*, *d*). An increase in the hardenability of 13XFA steel is associated with a decrease in the rate of austenite-pearlite transformation due to the growth of austenite grains.

These results differ from each other due to the difference in charge materials, that is, metal waste, which is not the same from batch to batch. They are inherited along the technological chain of pipe steel production.

An assessment of the effect of temperature and duration of tempering on the properties of 13XFA pipe steel showed that the strength properties of steels obtained from different charges are almost the same, with the exception of steel from melt 1, which, after quenching and tempering at 550 °C, has a higher relative narrowing and impact strength (Fig. 2, *b*, *c*). Increasing the tempering temperature above 300 °C leads to a noticeable softening and increase in plasticity (Fig. 2, *a*–*c*). An increase in the tempering temperature leads to an increase in the long-term strength (τ^1) of steels from all melts, yet higher values for this characteristic are recorded in steel from melt 1 (Fig. 2, *b*). Hydrogenation of samples sharply reduces the long-term strength (τ^{11}) of steels, and in this case, steel from melt 1 has higher values (Fig. 2, *e*).

The study of the effect of the type of charge on tempering brittleness, cold brittleness after hot deformation, brittle tempering and normalization of 13XFA steel showed that the absolute value of the impact strength of steel of melt 1 at all tempering temperatures (530–700 °C) was higher than that of steels from melts 2, 3 and 4 (Fig. 3, *a*). This is due to the greater contamination of the surfactant boundary of the grains of steels from melts 2, 3 and 4.

We also studied the cold brittleness of steel after hot deformation (Fig. 3, *b*), brittle tempering at 570 °C for 50 hours (Fig. 3, *c*) and normalization (Fig. 3, *d*). With a decrease in the test temperature, a decrease in impact strength is observed on all samples. The lower threshold of cold brittleness for all steels from four melts is located at a temperature below room temperature, that is, at –80 °C. The maximum impact strength of steels from all melts was observed after normalization (Fig. 3, *d*). The decrease in the impact strength of 13XFA steel is explained by the enrichment of the near-boundary layers with P, Sb, Sn, As grains, which leads to embrittlement of the intergranular coupling and a decrease in the energy of the boundaries.

Fractographic studies of steel samples from all melts and the study of their hydrogenation in a special solution were carried out. In steels from melts 3 and 4, which are most contaminated with microimpurities, there is a large proportion of intergranular fracture, fewer brittle fracture elements in melt 2, and even less in melt 1 (Fig. 4).

We also tested the durability of seamless pipes during operation in oil wells under the influence of a hydrogen-bearing aggressive environment (aqueous solution of 4.5 % H_2SO_4+2.5 % NH_4CNS). The results obtained show that pipe specimens after hot deformation have the greatest resistance (Table 3).

The resistance of hydrogenated pipe samples during normalization decreased by an order of magnitude compared to the resistance in the hot-rolled state and by three orders of magnitude after quenching and tempering: in terms of resistance to hydrogen embrittlement, steels from various charges can be arranged in the following sequence: melt 1 – melt 2 – melt 3 – melt 4.

Gas analysis of the samples by vacuum heating in the initial state and at various stages for hydrogen embrittlement showed that steel from melt 4 contains more hydrogen than steel from melts 1, 2 and 3. Therefore, microimpurities and hydrogen, which is also a surfactant, significantly reduce local stresses that cause the initiation and development of microcracks, which leads to brittle fracture.

This is confirmed by a decrease in the long-term strength of steels at 650 °C, (Fig. 2, *d*) corresponding to tempering brittleness, and a further increase in the duration of tempering at 650 °C leads to a redistribution of microimpurities, that is, a decrease in their concentration along grain boundaries, which causes a significant increase in resistance to hydrogen embrittlement (Fig. 2, *e*).

The originality of the proposed method of selective selection of metal waste makes it possible to increase the purity of steel in terms of microimpurities, significantly improves the complex of its physical and mechanical properties, as well as the performance of seamless pipes for operation in oil and gas wells.

However, the proposed method of selective selection of metal waste for the production of pipe steel has certain limitations, consisting in the absence of a special program for the mechanization and automation of the steelmaking process. This, in turn, reduces the productivity of the process of manufacturing high-quality tubular blanks.

Therefore, the conducted studies may have specific purposes in the case of using selectively selected metal waste, and for other cases, additional studies are required.

For further development of this research, it is necessary to develop a special computer program to control the processes of selective selection of metal waste and heat treatment of pipe steels used in oil and gas wells.

7. Conclusions

1. Melt 1 from a purer charge 1, which has the lowest quality of surfactants compared to other melts, has the smallest segregation of micro-mixtures, which affects the state of the boundaries of austenite grains. The amount of microimpurities and their distribution at the boundaries of austenite affect the tendency to austenite growth and the hardenability of steel.

2. It was found that melts 1, 2 have a greater tendency to austenite grain growth than melts 3 and 4. At higher temperatures of steel heating for hardening, the diffusion mobility of microimpurities increases, so all melts behave almost the same. An increase in the heating temperature for hardening from 900 to 950 °C increases the hardenability of pipe steel, which is associated with a decrease in the rate of austenitic-pearlite transformation due to the growth of austenite grains.

3. An increase in the tempering temperature of steel up to 500 °C contributes to a slight decrease in its strength, while impact strength, relative narrowing and long-term strength, on the contrary, increase. A further increase in the tempering temperature above 500 °C significantly changes the strength, ductility and long-term strength indicators. With an increase in the duration of tempering at 650 °C, the time to destruction of hydrogenated samples under a load of 600 MPa increases significantly. Other things being equal, steel smelted from charge 1 shows higher performance compared to charges 2, 3, 4.

4. A research of the cold brittleness of steel after hot deformation, brittle tempering at 570 °C for 50 hours and normalization for all 4 melts showed a decrease in impact strength with decreasing test temperature. When exposed to 570 °C, the boundary layers of P, Sb, Sn, and As crystals are enriched, which leads to embrittlement and weakening of the intergranular cohesion and a decrease in the energy of the boundaries. The lower threshold of cold brittleness for all melts is at a temperature of –80 °C. Compared to melts 2–4, steel smelted from charge 1 has the best performance in terms of temper brittleness and cold brittleness after hot deformation, brittle tempering and normalization.

5. The study of fracture fractograms showed that melts melted on charges 3 and 4, which are most contaminated with microimpurities, have a large share of brittle intergranular fracture, and in melts 1 and 2 there are fewer elements that cause brittle fracture. The results of studying the resistance of steels in an aqueous medium depending on the tempering temperature made it possible to evaluate the effect of residual stresses, structure, and the amount of microimpurities on the kinetics of

hydrogen embrittlement. With an increase in tempering temperature (in the range of 150–650 °C), the resistance of melts 1 and 2 increases more intensively than that of melts 3 and 4.

Conflict of interest

The authors declare that they have no conflict of interest in relation toi this research, whether financial, personal, authorship or otherwise, that could sffect the research and its results presented in this paper.

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Data availability

The manuscript has no associated data.

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