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Changes in material characteristics of pyrolysis furnace tube coils

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1. Introduction

Traditional methods of structure change analysis of composite alloyed pollycrystalline materials during farce and temperature deformation do not allow to reveal the peculiarities resulting in operating defects. The application of multifractal parametrization methods for structure analysis by metallographs allows to study purposefully the changes occurring during the evolution of secondary phase ensemble [1]. Information about deformation mechanism change can be obtained from the relationship of order parameter on material service time. Characteristic extrema of this relationship are connected with the change of the main deformation mechanism as noted in the paper [2].

Multifractal analysis of separate phase distribution can point to the most probable time intervals for microcrack formation. Fractal dimentionality approximation "two" can facilitate new surface formation, i.e. cracks.

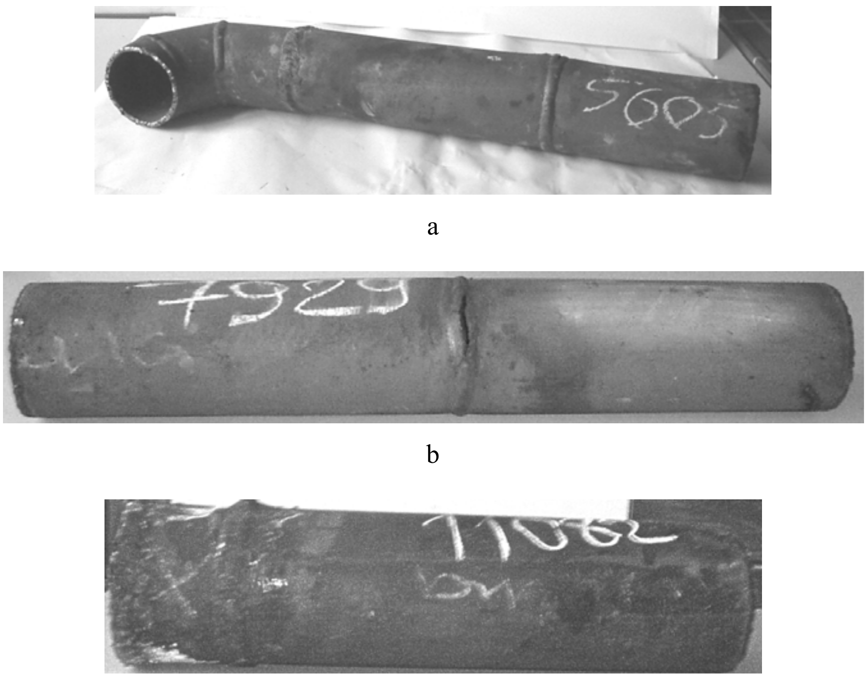
2. **Experimental**

At present the tendency for developing pyrolysis high temperature decomposition process of hydrocarbon stuff, is directed at decreasing residence time of raw material in the reaction zone and increasing the process temperature [3]. So, steel out of which furnace coils are made must retain structure and mechanical properties under high operating temperature (up to 850ºC), as well as under thermal cycling conditions (start-ups, shut-downs and vapour burning-out).

For making coils of pyrolysis furnace tubes in Russia steel containing 0.20% of carbon, 23% of chrome, 18% of nickel is mostly used. In a number of papers [4, 5] it was shown that during the use of corrosion-strength steel containing 0.20% of carbon, 23% of chrome, 18% of nickel under operation conditions of pyrolysis process the change of its phase composition and mechanical properties occurs resulting in various defects formation in tubes: cracks, local geometry change, burn-out. Metallographic and x-ray phase studies revealed [4, 5]:

- -σ-phase availability in the vicinity of through cracks;
- -magnetization effect along the crack boundary;
- -carburisation of internal tube surface.

For regularities revealing in the structure and multifractal parameter change metallografic studies, mechanical tests of steel specimens and multi-fractal parameterization were carried out.



a

b

c

Fig. 1 Pyrolysis furnace tube defects produced in service: a- τ=5605 h; b - τ=7929 h; c - τ=11082 h

To conduct the studies coil tube sections of one furnace were selected after different service time under operating conditions of pyrolysis process 5605 h, 7929 h, 11082 h and a tube in the supply state-0 hours (Fig. 1).

3. Metallographic studies

For etching and polishing of steel specimen the methods of electrochemical polishing with the following conditions were used [4]:

- -solution - 73 ml of H_2SO_4, 7 ml of HF, 20 ml of H_2O;
- -cathode-stainless steel, stress-10-12V;
- -current density-15 A/dm^2;
- -temperature-60ºC.

When sharp grain structure boundaries appeared electrochemical polishing was stopped. Thus for each service time of the steel its etching time was different. The structure was surveyed on a digital electron microscope "Axiovert-100A". For indicating geometry number and arrangement changes the structure of the formed second phases the magnification of ^{x}1700 was used.

Fig. 2 presents steel containing 0.20% of carbon, 23% of chrome, 18% of nickel structure. It is seen that at grain boundaries and in the grain body the second phases of dark tone are present; with increase in service time their arrangement, geometry in steel structure as well as the number change. During the service time from 0 to 7929 h the second phases are present in the structure as "micro-grids" along the grain boundaries. In Fig. 2, d it is seen that at service time 11082 h phases of dark tone are present as large conglomerates along the grain boundaries (in triple joints) and as smaller phases in the grain body.

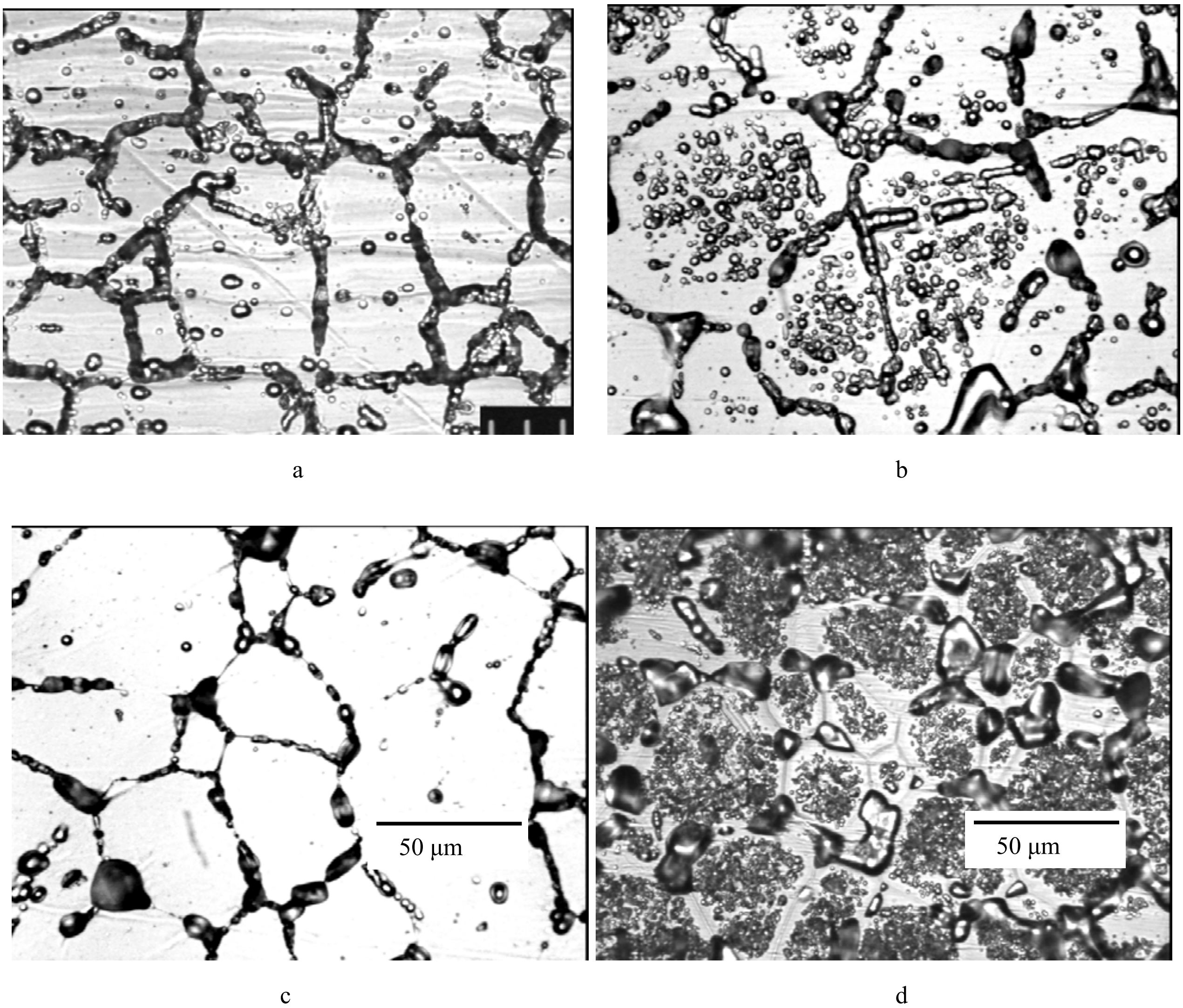


Fig. 2 Steel sample structure containing 0.20% of carbon, 23% of chrome, 18% of nickel, ^{x}1700: $\tau = 0$ h; $\tau = 5605$ h; $\tau = 7929$ h; $\tau = 11082$ h

Etched sample survey in the polarized light showed that all phases of dark tone are of grey colour which allows speaking about their indentical nature; in the steel structure a small number of small-size phase groups of yellow colour and regular geometric form (triangles, squares, ect.) are present as well. According to reference data [6] yellow phases were identified as titanium carbides. With the increasing service time their number, arrangement and size in the structure did not change.

X-ray phase studies showed that besides austenite-matrix base, the second phases (phases of dark tone)(Fig. 2, a, b, c, d) with tetragonal crystalline grid CrNi, Cr_5Fe_7, FeCr (σ-phase) are contained.

Thus, the studies conducted showed that thermal cycling loads under operating conditions of pyrolysis process affects the geometry, number and distribution of the second phases in steel structure.

4. Mechanical tests

To define mechanical properties of steel tensile and impact bending tests were carried out at room temperature. For service time three specimens of each steel were made.

The tensile tests were carried out on a direct stress machine Y10 under the deformation rate v_{def}=2 mm/min. Values of the following steel mechanical properties $\sigma_{0,2}$, σ_u, ψ, δ were calculated with the obtained stress-strain diagrams according to GOST 1497.

The impact bending tests were carried out on the specimens with a "U"- shaped concentrator on a pendulum impact testing machine RPSW 150/300 SCHNEK TREBEL. According to the results of specimens subjected to the impact bending test the impact test values were calculated. Mechanical tests results are given in Table 1.

Table 1

Mechanical properties of steel containing 0.20% of carbon, 23% of chrome, 18% of nickel

Steel service time, h	$\sigma_{0,2}$, MPa	σ_u, MPa	δ, %	ψ, %	*KCU*, J/cm^2
0	356	677	32	43	119
5605	344	604	26	19	60
7929	322	591	26	30	53
11082	358	651	19	3	57

From the data given in Table 1 it follows that at service time of 11082 h strengthening and embrittlement of steel proceeded simultaneously-conventional ultimate strength and yield strength values increased, relative steel elongation and relative reduction of area have minimum values.

5. Multifractal parametrization

To evaluate the effect of second phase geometry, number and distribution in steel structure on the mechanical properties the method of multifractal parametrization was used.

Classical methods of the ordered microstructure description are related to the use of such parameters as the sizes of grains, phases and size distribution. Many of the mechanical properties of steel change in service due to the processes proceeding at phase boundaries which process fractal character. They are described by additional structure indices, such as multifractal dimensionality. The latter one allows to carry out the parametrization capable of differentiating structure features which are inaccessible with conventional methods of analysis.

The experience of using multifractal formalism for structure analysis in materials (microstructure, structure of fractures, ect.) [1, 7] showed informationality of the following multifractal structure indices – D_0, D_1, D_2, D_q, f_q, Δ_q obtained during multifractal parametrization:

1) D_0 – Hausdorf-Bazikovich dimensionality characterizing a uniform fractal;

2) D_1 – informational dimensionality;

3) D_2- correlational dimensionality;

4) $D_{+\infty}$ and D_{∞} - extremum values of D_q corresponding to rarefaction degree of multifractal aggregate set;

5) degree of uniformity $f_\infty \approx f_q$, q>>1. The higher is $f_\infty \approx f_q$, the more uniform is the structure for the canonical spectra and vice versa, for the pseudospectra. By the degree of structure uniformity is meant not the conventional qualitative characteristics of the external structure appearance, but a character index of unit element distribution of the structure considered in noneuclidean space covering this structure;

6) multifractal parameter of latent structure periodicity of the set $\Delta_q= D_1- D_q$. The more (by modulus) is the latent periodicity value, the more ordered is the structure. The values of Δ_q are obtained from the canonical and pseudospectra account for somewhat different degree of order. This index obtained from the cononical spectra and calculated on large scales accounts for the degree of order and violation of symmetry for the general configuration of the studied structure as a whole. According to informational interpretation the multifractal formalism Δ_q meets a multifraction information extremum and accounts for the symmetry violation degree of the studied structure measure with respect to multifractal transformation. Thus an increase means that the system is loaded with information and the degree of violated symmetry increases in it. For pseudomultifractal calculation (on small scales) the index accounts for the local symmetry violation degree of the studied structure measure with respect to multifractal transformation averaged over the whole structure. Great modulus values of this index in the latter case imply greater degree of local symmetry violation.

To provide white and black colour (black colour – intermetallides, white colour – austenite) of steel structure representation the program Contour was used; black and white structure is shown in Fig. 3.

For the calculation 100%, 99%, 98% coverage of representation area was applied. Comparison of the obtained roof – mean-square deviation values of the multifractal parameters and adequecy parameter showed the greatest information content of the multifractal parameters obtained at 100% coverage of the representation area.

The values of multifractal structure parameters are presented in Fig. 4 as the relationships of variation f_{200} and Δ depending on steel service time.

Below in Table 2 the results of some mechanical property values and corresponding values of multifractal order parameter (Δ) are presented.

Table 2

Results of mechanical property

Steel service time, h	$\sigma_{0.2}$, MPa	σ_u, MPa	*KCU*, J/cm$_2$	Δ
0	356	677	119	0.204
5605	344	604	**60**	**0.333**
7929	322	591	53	0.272
11082	358	651	57	0.231

In the relationships presented in Fig. 4, a the minimum value of multifractal order parameter takes place. According to Ivanova V.S. the maximum value of this parameter implies the change of steel deformation mechanism [2]. In case of steel containing 0.20% of carbon, 23% of chrome, 18% of nickel the maximum value of the given parameter is in the area Δ_{max}=0.30 - 0.33 and points to the change of steel destruction mechanism: transition from a tough destruction mechanism to a brittle one. This is supported as well by the fact that impact strength value at steel service time up to 5605 h decreases to 60 J/cm^2 and hereinafter practically does not change. However in this case the decrease in order parameter values occurs – steel adapts itself to operating conditions of the process, an order system becomes predominant with respect to a chaos system. The changes on the structural level occurs hereinafter due to the change of geometry and the number of phases in the system.

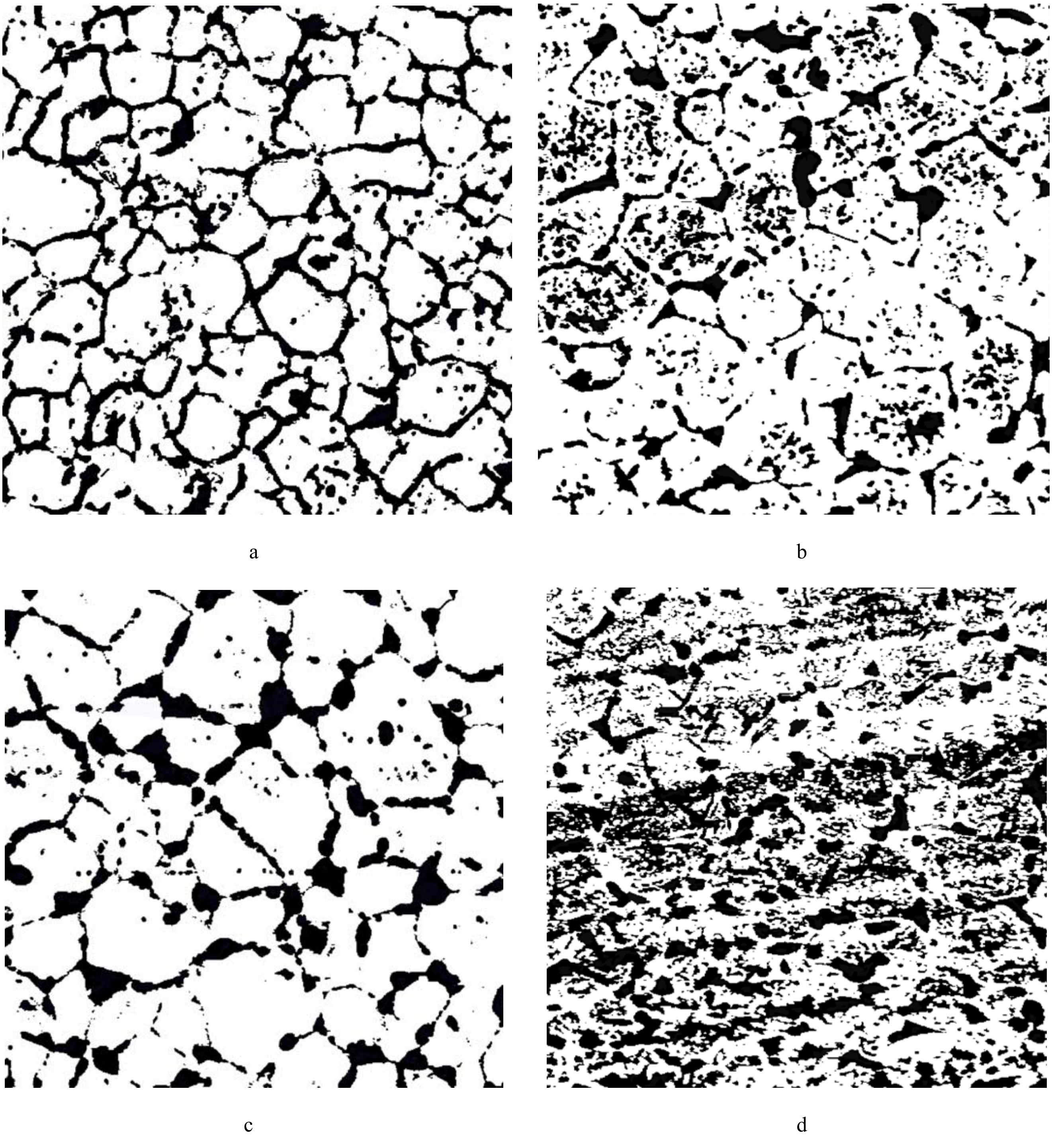
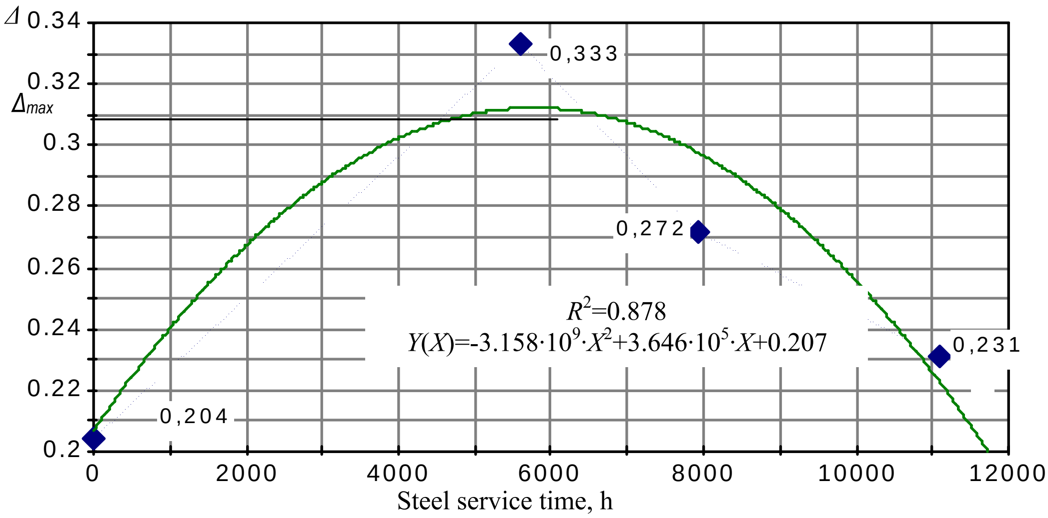


Fig. 3 Steel containing 0.20% of carbon, 23% of chrome, 18% of nickel structure: a - 0 h; b - 5605 h; c - 7929 h; d - 11082 h

Linear interrelation (Fig. 5) of yield limit $\sigma_{0,2}$ and multifractal characteristic D_0 is seen.

From the relationship given in Fig. 5 follows that the geometry of the second phase boundaries influences the value of steel yield strength. In this case it is suggested that at D_0=2 the yield strength value will have the maximum value and the probability of brittle destruction will increase.



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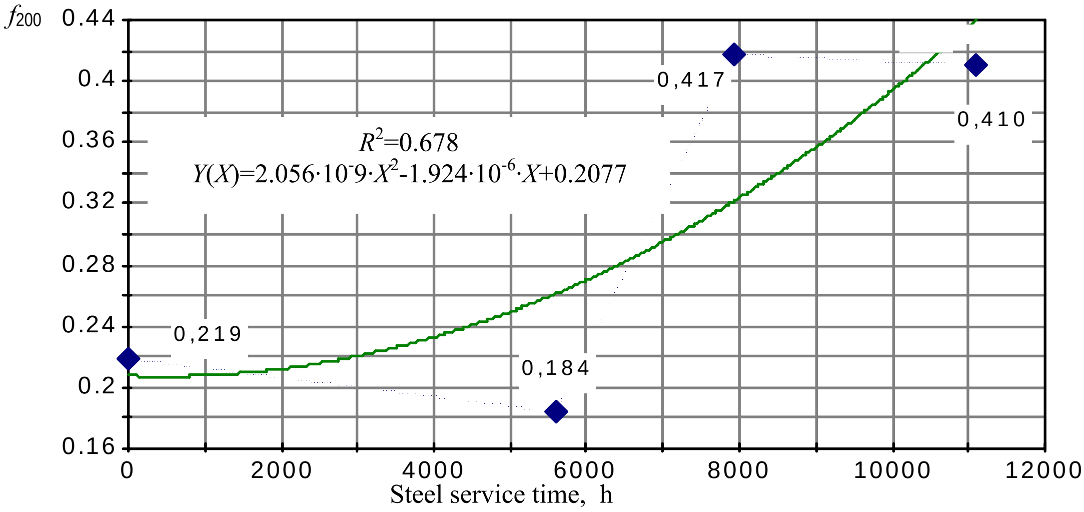

b

Fig. 4 The relationships of changing multifractal parameters depending steel service time: a - order (Δ); b - uniformity (f_{200})

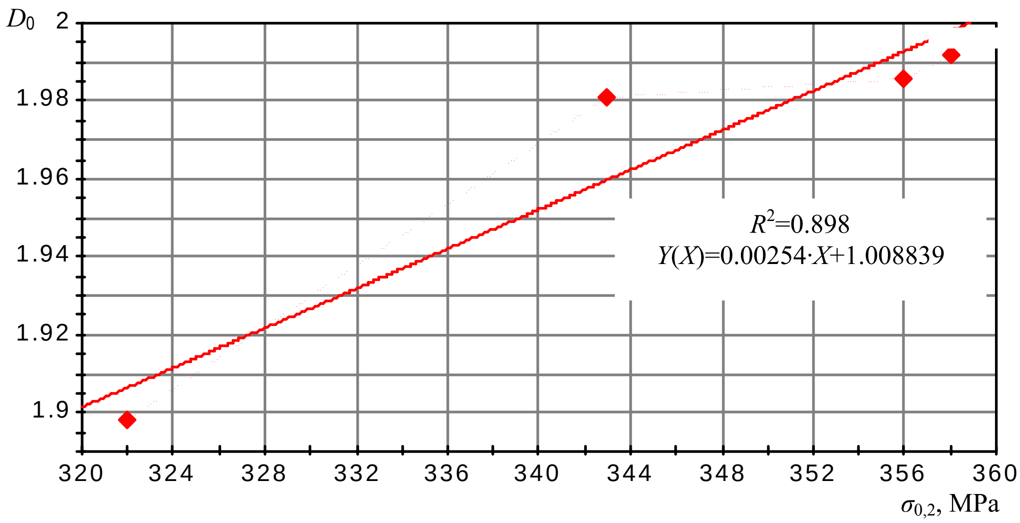

Fig. 5 Correlation of relative change of yield strength value with multifractal characteristic D_0 of steel containing 0.20% of carbon, 23% of chrome, 18% of nickel structure with various service time

6. Conclusions

1. The regularity of changing the structure of steel containing 0.20% of carbon, 23% of chrome, 18% of nickel is revealed.

2. The geometry of the second phases - intermetallides, influences the values of steel yield strength; the relationship between the second phase geometry and the

yield strength is linear in character.

3. The maxima of the order distribution in time are in the area Δ=0.3. This correlates with the data of the paper [2] and supports that Δ_{max} is the fundamental characteristic when changing steel deformation mechanism.

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PIROLIZĖS SPIRALINIŲ VAMZDELIŲ PAVIRŠIAUS MEDŽIAGOS CHARAKTERISTIKŲ PASIKEITIMAS

R e z i u m ė

Straipsnyje nagrinėjamas hidrokarboninės pirolizės spiralinių vamzdelių paviršius, turintis įtakos agregato suirimui. Parodyta, kad plyšio atsiradimui nemagnetiniame labai legiruotame Cr-Ni pliene turi įtakos magnetinės savybės. Nagrinėjama, kaip keičiasi mechaninės savybės, kol formuojamas spiralinis vamzdelis, ir nustatoma ekstreminė formavimo trukmė. Metalo struktūros pasikeitimui nagrinėti taikyti multifraktūriniai parametrizuoti suirimo metodai. Įrodyta, kad mechaninių savybių pasikeitimas susijęs su sigma fazės evoliucija ir kitais tarpmetaliniais junginiais, atsirandančiais apdirbimo metu.

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CHANGES IN MATERIAL CHARACTERISTICS OF PYROLYSIS FURNACE TUBE COILS

S u m m a r y

Tube coil of hydrocarbon pyrolysis furnace resulting in aggregate failures have been considered. It is shown that with the appearance of the cracks non-magnetic high-alloyed grade of Cr-Ni steel reveals magnetic properties. Changes in mechanical properties coil during operation have been studied and extreme operation time relationships have been obtained. To analyse the changes in metal structure involving failures multifractal parameterization methods were applied. It is shown that the changes in mechanical properties are connected with the evolution of sigma-phase and other intermetallic compounds arising in service.

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ИЗМЕНЕНИЕ ХАРАКТЕРИСТИК МАТЕРИАЛА ПОВЕРХНОСТИ СПИРАЛЬНЫХ ТРУБОК ПИРОЛИЗА

Р е з ю м е

В статье исследуется поверхность гидрокарбонных спиральных трубок пиролиза, влияющая на разрушение агрегата. Показано, что на образование трещины в немагнитной высоколегированной Cr-Ni стали имеют воздействие магнитные свойства. Изменение механических свойств исследуется во время формирования спиральной трубки и определяется экстренное время формирования. Мультифрактурные параметризированные методы исследования использованы для изучения изменения структуры метала. Показано, что изменение механических свойств связано с эволюцией сигма-фазы и другими межметалическими строениями, которые образуются во время обработки.

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