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DETERMINING THE PHYSICAL-CHEMICAL CHARACTERISTICS OF THE CARBON-THERMAL REDUCTION OF SCALE OF TUNGSTEN HIGH-SPEED STEELS

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Визначено фізико-хімічні перетворення при вуглецевотермічному відновленні техногенних оксидних відходів виробництва швидкоріжучої сталі Р18. Виявлено протікання хімічних реакцій відновлення та карбідоутворення за участю заліза та легуючих елементів. Відсутність фаз схильних до сублімації, підвищена відновна здатність, губчаста мікроструктура забезпечують відносно високий ступінь вилучення тугоплавких елементів при використанні отриманого матеріалу як легуючої добавки

Ключові слова: леговані техногенні відходи, швидкоріжуча сталь, вуглецевотермічне відновлення, мікроскопічне дослідження, карбідоутворення

Определены физико-химические превращения при углеродотермическом восстановлении техногенных оксидных отходов производства быстрорежущей стали Р18. Обнаружено протекание химических реакций восстановления и карбидообразования при участии железа и легирующих элементов. Отсутствие фаз склонных к сублимации, повышенная восстановительная способность, губчатая микроструктура обеспечивают относительно высокую степень извлечения тугоплавких элементов при использовании полученного материала в качестве легирующей добавки

Ключевые слова: легированные техногенные отходы, быстрорежущая сталь, углеродотермическое восстановление, микроскопическое исследование, карбидообразование

1. Introduction

One of the alternative sources for obtaining alloying materials containing W, Cr, V is the recycling of alloyed tech-

nogenic wastes for their subsequent use in the production. These include the scale of tungsten high speed steels. A specific feature of this type of waste is a high degree of alloying with W and other refractory elements. This necessitates

taking into account the complex character of physical-chemical interaction between elements when developing technological conditions for disposal.

Therefore, it is an important task to save resources and energy by lowering the losses of alloying elements during processing and using the scale of tungsten high speed steels in steelmaking. This requires studying the mechanism of reduction of the technogenic raw materials, which, together with Fe oxides, contain oxide compounds of W, Cr and V as alloying elements. It is possible to improve environmental safety by replacing the regenerative melting with the newest methods of powder metallurgy that employ solid phase reduction.

2. Literature review and problem statement

Advantages of refractory alloying materials, obtained by the methods of powder metallurgy, relative to the melted, are specified in paper [1]. The main one among positive sides is the possibility to reach a much higher speed of dissolution and the degree of assimilation of the target elements by the molten metal. Solid phase reduction by carbon has demonstrated practical positive results as a technique for processing oxide ore and technogenic raw materials [2]. The choice of a technique for solid phase reduction instead of reducing smelting process for obtaining tungsten-containing ligature [3], in terms of environmental pollution by waste and reaction products, is safer environmentally. At the same time, the process requires lower temperatures, less energy resources, and is accompanied by significantly smaller losses of the target element [4].

The results of study reported by authors of paper [5] show that the iron scale is composed of Fe_3O_4 , Fe_2O_3 , FeO . Important role of participation of the gas phase of CO , CO_2 in the reduction of Fe by carbon was specified in article [6]. The formation of CO from carbon occurs at temperatures above $1,000^\circ\text{C}$ and causes intense gas exchange. Authors of work [5] studied the reduction of iron scale at temperatures from 750°C to $1,050^\circ\text{C}$. They determined that the greatest degree of reduction is achieved at $1,050^\circ\text{C}$ with the content of Fe in reduction products of 98.40 % by weight. After different temperatures of treatment, along with Fe, reduction products revealed Fe_3C and C. These technological aspects should be considered when developing parameters for the reduction of scale of a high-speed steel. At the same time, the presence of W, Cr and V in the scale of tungsten high speed steels necessitates research into carbon-thermal reduction of oxide systems with these elements.

Thermodynamic calculations of WO_3 carbon-thermal reactions were performed by authors of work [7]. The greatest probability in the range of $1,500$ – $3,500$ K were demonstrated by the processes of transition of WO_3 into W_2C and WC , followed by W. The possibility of existence in the products of reduction of residual carbon, bound in oxycarbide and carbide compounds, was also confirmed by authors of paper [8]. The study of carbon-thermal reduction of W oxides, conducted by authors of article [9], showed that this process undergoes the stages of transition of WO_3 into $\text{WO}_{2.72}$, WO_2 and W. At 950°C , the formed oxides are reduced to W. At the same time, there occurred the processes of carbide formation. The carbide tungsten-containing component of WC was obtained by authors of paper [10] after treatment at $1,323$ K. Susceptibility to carbide formation, along with reduction

during carbon-thermal treatment, was also confirmed in the study reported by authors of work [11]. However, it should be noted that the oxide technogenic waste of high speed steels, in addition to W compounds, contain Fe and alloying elements. In this case, the form of presence can be more complex and be different from pure oxides taken separately. This can significantly affect the processes of reduction, as well as the phase and structural features of derived products.

The importance of participation of the gas phase of carbon oxides during reduction processes in the system Fe–Cr–O–C is specified in [12]. Authors of papers [13, 14] noted a possibility of the progress of parallel reduction and the formation of Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 , at temperatures $1,273$ – $1,773$ K. We should emphasize the course of carbide formation and the unavoidable presence of carbides in reducing carbon-thermal processes.

The reduction process of iron-vanadium component of FeV_2O_4 from ore raw material by carbon is described by authors in paper [15]. The most effective indicators of reduction were achieved at a temperature of $1,350^\circ\text{C}$ over 60 min. The extraction of Fe and V was achieved at the level of 95.07 % and 71.60 %, respectively. The reduction of $\text{FeO}\cdot\text{V}_2\text{O}_3$ and $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ oxides at different ratios of C/Fe and at temperatures from $1,250$ to $1,100^\circ\text{C}$ was examined in paper [16]. It was determined that an increase in C/Fe from 0.8 to 1.4 led to the increase in degree of extraction (%) of V and Cr from 10.0 to 45.3 and from 9.6 to 74.3, respectively. A rise in temperature to $1,250^\circ\text{C}$ led to an increase in the formation of carbides. At C/Fe below 0.8, the authors observed a significant decrease in the degree of extraction of V and Cr and a decrease in carbide formation. The formed Cr and V carbides dissolve in γ -Fe. It appears that in order to achieve an increase in the degree of extraction of V and Cr during reduction, a certain excess amount of carbon, relative to oxygen, is needed in the composition of charge.

One should note the presence of significant results of research into the mechanism of carbon-thermal treatment of iron scale. There are also substantial achievements in the reduction of separately taken oxides of basic alloying elements of the scale of tungsten high speed steel. However, insufficiently investigated is the mechanism of transformation of complex alloyed oxide technogenic raw material, which is the scale of high speed steels. Research into this issue could reduce the loss of W and other alloying elements by the sublimation of oxide compounds during thermal treatment and further use of a metallized alloying additive. Thus, it is appropriate to study comprehensively the phase composition and microstructure of the tungsten scale of high speed steels and products of carbon-thermal treatment with a different degree of reduction. The use of raster electron microscopy with an x-ray microanalysis will make it possible to elucidate the understanding of the structure and composition of separate sections of microstructure in the examined materials.

3. The aim and objectives of the study

The aim of present study was to examine the physical-chemical patterns of the carbon-thermal reduction of scale of tungsten high speed steels. It is necessary to determine parameters that reduce the loss of W and other elements by the sublimation of oxides during processing of oxide technogenic waste and the use of metallized alloying additives.

To accomplish the aim, the following tasks have been set:

- to determine the features of phase composition and microstructure of scale of the tungsten high-speed steel R18 as the starting raw material for metallization;
- to examine the phase composition and microstructure of metallized scale of the tungsten high-speed steel R18 with a different degree of reduction in terms of influence on the reduction in losses of alloying elements by the sublimation during alloying.

4. Materials and methods for examining the carbon-thermal reduction of scale of high-speed steel

4.1. Examined materials and equipment used in the experiment

The starting raw material was scale of the high-speed steel R18 that contained, % by weight: C – 0.75; Si – 0.24; Mn – 0.22; Cr – 3.75; Mo – 0.20; V – 1.05; W – 16.70; Co – 0.12; Ni – 0.20; Cu – 0.09; S – 0.007; P – 0.025; O – 26.0; Fe – remainder. Reducing agent was the dust of carbon-graphite production. Estimated ratio O/C – 1.33.

X-ray diffraction phase analysis of the samples was performed using the diffractometer «DRON-6» (Russia).

Photographic images of the microstructure of samples were obtained using the raster electron microscope «REM-106I» (Ukraine). The microscope is equipped with a system of x-ray microanalysis to determine chemical composition of separate areas at the surface of samples.

4.2. Procedure for conducting the research and for determining the indicators of sample properties

Temperature of reduction is 1,523 K; isothermal aging duration is 60 min. The protective environment is the atmosphere of argon with a linear gas flow rate of $2.5 \cdot 10^{-3}$ m/s. Mass of the examined samples before thermal treatment is 80 g.

The phase composition was determined using the method of x-ray structural analysis employing the monochromatic radiation of Co, K_{α} ($\lambda=0.178897$ Å), and Mo, K_{α} ($\lambda=0.07093$ Å). The measurements were performed at a voltage on the tube of $U=30$ kV and anode current $I=10$ mA. The composition of phases was determined applying the software package PDWin 2.0 (Russia).

The microstructure of samples was investigated at an accelerating voltage of 20–25 kV and a current of electronic probe of 52–96 μ A. Working distance to the examined surface was 10.1–29.8 mm. The phase composition was deter-

mined using a reference-free method for the calculation of fundamental parameters.

5. Results of research into the carbon-thermal reduction of scale of high-speed steel

Phase composition of the scale of steel R18 is composed of oxides of Fe_3O_4 , Fe_2O_3 , FeO (Fig. 1). Compounds of alloying elements did not manifest themselves explicitly. The structure is disordered with the presence of particles of different size. We detected in the chemical composition of examined area, % by weight: Fe – 63.57, W – 16.34, Cr – 2.68, V – 1.82, Mo – 0.18, Al – 0.09, O – 15.32 (Fig. 2).

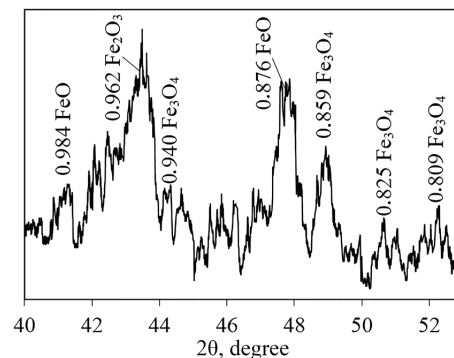


Fig. 1. Plot of diffractogram of the scale of steel R18

Phase transformations during carbon reduction proceeded through the formation of α -Fe, as well as carbide compounds of Fe_3C , Fe_2C (Fig. 3). The content of alloying elements manifested itself by the detection of phases of $FeWO_4$, Fe_3W_3C , $(Fe, Cr)_7C_3$, W_2C , V_2C at intermediate stages with a degree of reduction in the range of 36–77 %.

At an increase in the degree of reduction from 36 % to 84 % we observed the manifestation of sintering processes, the formation of reduced particles of different shape, and a spongy microstructure (Fig. 3). We revealed areas with an elevated content of Fe and W, % by weight: to 96.30 and 30.27, respectively (Fig. 3, Table 1).

Some of the reduced particles were characterized by a relatively high content of Cr and V, % by weight, to 33.24 and 19.90, respectively. Indicators of the O content for the examined areas ranged from 1.63 to 12.44 % by weight (Fig. 3, Table 1).

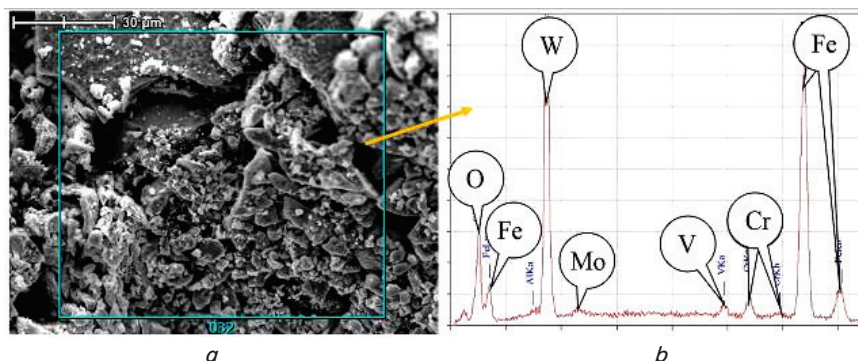


Fig. 2. Area of the microstructure with an x-ray microanalysis of the scale of steel R18: *a* – photographic image with at magnification $\times 1,000$; *b* – spectrogram of x-ray microanalysis

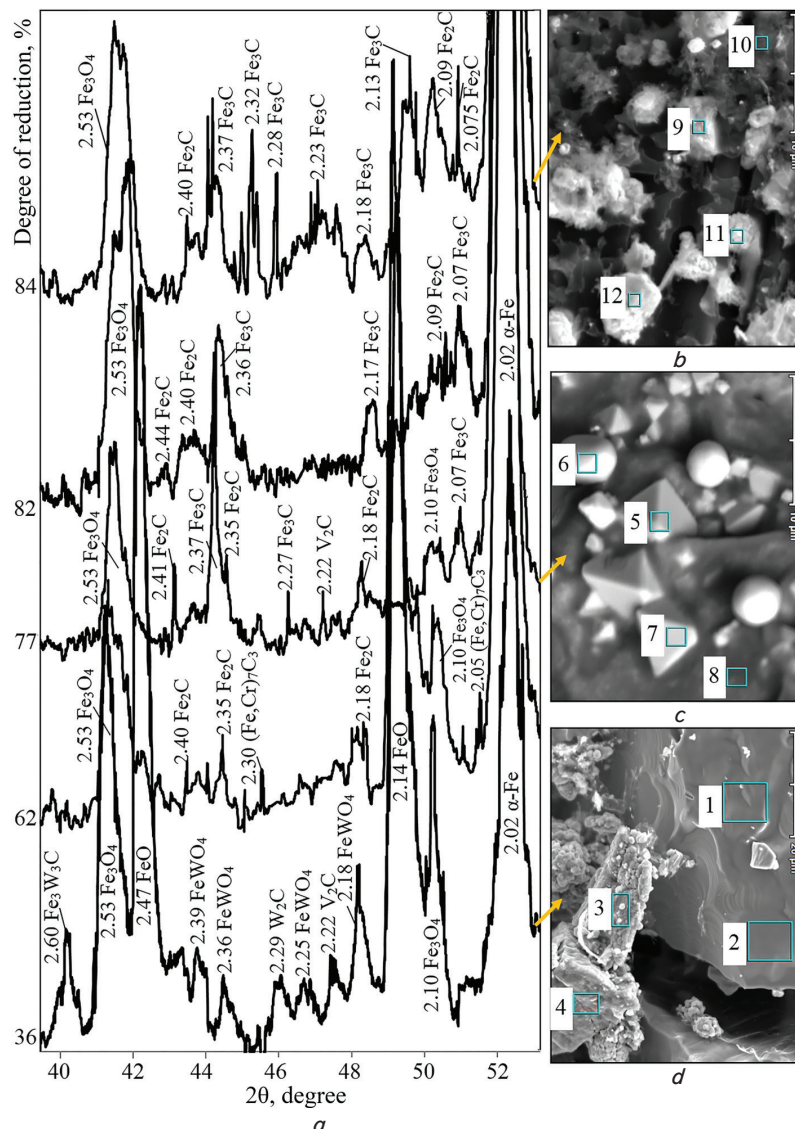


Fig. 3. Phase x-ray structural study of the products of scale reduction of steel R18 and respective images of microstructure at different magnification: *a* – plots of diffractograms; *b* – $\times 2,000$, *c* – $\times 5,000$, *d* – $\times 4,500$; 1–12 – areas of x-ray microanalysis of the samples

Table 1
Results of x-ray microanalysis of the reduction products according to Fig. 2

Areas of samples	The content of elements, % by weight						Total
	O	V	Cr	Fe	Mo	W	
1	3.35	0.00	0.00	96.30	0.00	0.35	100.00
2	5.24	0.00	0.00	94.40	0.00	0.36	100.00
3	3.24	0.00	0.00	86.33	0.00	10.43	100.00
4	12.44	0.00	0.00	57.29	0.00	30.27	100.00
5	2.28	19.90	33.20	40.60	0.00	4.02	100.00
6	1.96	0.38	0.66	90.01	0.79	6.20	100.00
7	1.90	16.98	33.24	45.41	0.11	2.36	100.00
8	5.08	9.71	16.31	58.12	0.00	10.78	100.00
9	1.63	0.70	0.90	67.57	0.48	28.72	100.00
10	2.59	0.00	0.97	92.67	0.00	3.77	100.00
11	1.80	0.51	0.97	87.67	0.65	8.40	100.00
12	2.74	8.97	13.99	66.45	0.00	7.85	100.00

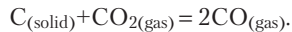
6. Discussion of results of the carbon-thermal reduction of scale of high-speed steel

The study conducted indicates that the base of phase composition of the scale of steel R18 is composed of Fe_3O_4 , Fe_2O_3 , FeO (Fig. 1), which agrees well with the results of paper [5]. The alloying elements probably were mostly located, as the replacement atoms, in the oxides of Fe. This is also evidenced by the results of x-ray microanalysis for determining the content of Cr, W, V, and other elements in the examined area of the microstructure, which was characterized by the disorder and non-uniformity (Fig. 2).

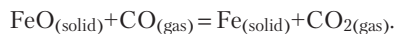
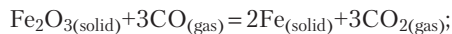
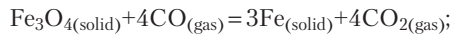
We also do not rule out the presence of separate oxides of alloying elements, though their manifestation, based on the x-ray structural analysis, was fragmented, and was characterized by low intensity.

A spongy structure of reduction products predetermines satisfactory gas exchange during heat treatment in the zone of reaction. That is, as noted in papers [6, 12], of essential importance are the chemical reactions involving a gaseous

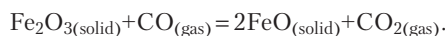
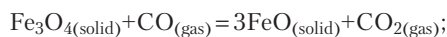
reducer of CO. The role of $C_{(solid)}$ implies the constant regeneration of $CO_{(gas)}$ according to reaction:



An increase in the degree of reduction of the scale led to a decrease in the intensity of manifestation of iron oxides with the detection of α -Fe (Fig. 3). That is, the following chemical reactions are likely to occur:

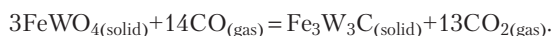
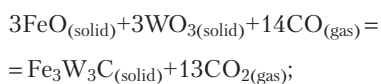
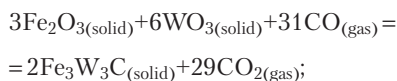
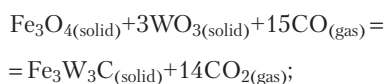
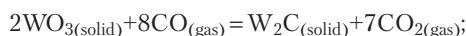


In parallel, there is a possibility of reactions when higher oxides of iron transfer to the lower oxides:



At a relatively low degree of reduction (32 %) we discovered the complex oxide $FeWO_4$ ($FeO \cdot WO_3$). The presence of this phase is not also ruled out in the starting scale, though the respective diffractogram manifested it implicitly. This can be due to using different wavelengths of monochromatic radiation during an x-ray structural analysis of the scale and the products of its reduction.

In contrast to the carbon-thermal treatment of unalloyed scale, which was investigated by authors of paper [5], there were the manifestations of tungsten-containing carbide compounds of W_2C and Fe_3W_3C . Certain chemical reactions, which can initiate possible formation of these compounds, take the following form:

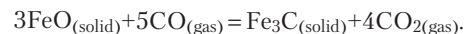
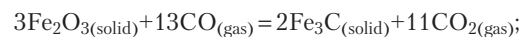
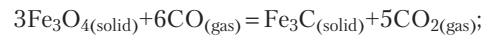


We also revealed carbides $(Fe, Cr)_7C_3$, V_2C whose formation reactions take a similar form.

The formation of carbide compounds of W agrees well with the results of papers [7, 9–11]. The difference is in detecting Fe_3W_3C , due to the reduction of the complex of oxides of W and Fe.

The presence of chromium-containing carbide agrees well with data from papers [13, 14, 16]. However, similarly to the case of W, the formation of $(Fe, Cr)_7C_3$ is predetermined by the complex reduction of iron–chromium-containing oxides. The manifestation of V_2C and $(Fe, Cr)_7C_3$ creation at the

intermediate stages of reduction matches the results of paper [16]. Its authors indicate the possibility for V and Cr carbides formation at a temperature of 1,523 K, which satisfies the criteria of the performed research. Similarly to ref. [5], one of the products of carbon-thermal treatment was Fe_3C . The difference is in detecting Fe_2C as well (Fig. 3). Some of the possible chemical reactions of the formation of carbide compounds of iron can be represented in the following form:



Chemical reactions with the formation of Fe_2C take a similar form. An increase in the degree of reduction leads to the prevalence of manifestation of α -Fe, Fe_3C , Fe_2C relative to the compounds of alloying elements. This is probably caused by the dissolving of these compounds in α -Fe, which agrees well with the research work [16] for the case with V and Cr carbides. We also do not rule out partial replacement of Fe atoms with the atoms of alloying elements in Fe_3C and Fe_2C carbides.

Micro-structural studies indicate the presence of particles with a relatively high content of both Fe and alloying elements (Fig. 3, Table 1). Areas 3 and 4 in Fig. 3 with a relatively high content of Fe and W are in a good agreement with the detection of complex carbide Fe_3W_3C . Parts of a pyramidal shape in areas 5, 7 are probably the complex carbide compounds of V, Cr and Fe, and in area 6 – W and Fe. At a relatively high degree of reduction (Fig. 3), the most pronounced is the manifestation of a spongy structure with a manifestation of the reduced particles containing Fe and alloying elements.

According to research results, there is no formation, in the process of reduction, of compounds and phases with a relatively high susceptibility to sublimation. That is, there is no need to create special conditions that prevent the evaporation and the loss of alloying elements from the gas phase. This also predetermines an increase in the degree of use of alloying elements. Residual carbon in the form of carbides provides for an increased reducing capability and the degree of assimilation of alloying elements with the post-reduction of the residual oxide component in a liquid metal during alloying. The spongy structure contributes to the faster dissolution, relative to the corresponding standard ferroalloys. This ensures a reduction in the total time of melting and, consequently, reduces the energy expenditure, as well as technogenic emissions to the environment, which creates more environmentally-friendly production conditions.

We consider to be a shortcoming of present study the lack of research results for the dependence of phase composition and microstructure of metallization products on the content of carbon reducer in the charge.

This research could be developed in the direction of extending the range of grades of steel whose oxide wastes would be disposed of using the method of a solid-phase reduction. The most promising are the high alloyed steels for cutting tools.

We conducted experimental-industrial tests using the metallized scale during high-speed steel smelting at the induction furnace with a crucible capacity of 4,000 kg at the plant PAT «Dniprospeksstal» (Ukraine). Heating and melting of the metallized scale in packets along with a metal charge in the crucible with a loading of 150–320 kg/t did not cause any technological complications. This provided

the degree of disposal of refractory elements from scale at the level of 92–94 %. At smelting, we observed a slightly elevated slag formation compared to the standard melting method for the production of high-speed steel, however, it met the requirements of technological instruction. The proposed method for the disposal of alloying elements from scale in the production significantly reduces the expenditures of standard ferroalloys and metallic alloying materials.

7. Conclusions

1. It was determined that scale of the high-speed steel R18 is comprised mostly of phases of Fe_3O_4 , Fe_2O_3 , FeO ,

with the presence of alloying elements as the replacement atoms. The microstructure is disordered and non-uniform. In the examined area, in addition to Fe, we revealed the presence of, % by weight: W – 16.34, Cr – 2.68, V – 1.82, and others. The content of O was 15.32 %.

2. It was established that the reduction of scale of the high-speed steel R18 proceeds with the formation of α -Fe and carbides $\text{Fe}_3\text{W}_3\text{C}$, $(\text{Fe}, \text{Cr})_7\text{C}_3$, W_2C , V_2C , Fe_3C , Fe_2C . Manifestation of carbides of alloying elements decreased with an increase in the degree of reduction. The microstructure of reduction products is heterogeneous, containing particles with a different content of alloying elements. An increase in the degree of reduction led to the formation of a spongy microstructure.

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