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RESEARCH INTO SPECIFICS OF RECYCLING THE SCALE OF NICKEL-MOLYBDENUM CONTAINING PRECISION ALLOYS BY THE METHOD OF HYDROGEN REDUCTION

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Досліджено кінетику водневого відновлення окалини нікель-молибденвмісного прецизійного сплаву. Ступінь відновлення 99% було досягнуто обробкою при 1273 К. Цільовий продукт металізації мав губчасту мікроструктуру і складався з γ -Fe, FeNi, фази Mo та залишку недовідновлених Fe_3O_4 та FeO. Дослідно-промислові випробування підтвердили ефективність використання нової легируючої добавки з паралельною утилізацією техногенних відходів

Ключові слова: окалина, прецизійний сплав, водневе відновлення, фазовий аналіз, мікроструктура, ресурсозбереження, легування

Исследована кинетика водородного восстановления окалины никель-молибденсодержащего прецизионного сплава. Степень восстановления 99% была достигнута обработкой при 1273 К. Целевой продукт металлизации имел губчатую микроструктуру и состоял из γ -Fe, FeNi, фазы Mo и остатка недовосстановленных Fe_3O_4 и FeO. Опытно-промышленные испытания подтвердили эффективность использования новой легирующей добавки с параллельной утилизацией техногенных отходов

Ключевые слова: окалина, прецизионный сплав, водородное восстановление, фазовый анализ, микроструктура, ресурсосбережение, легирование

1. Introduction

Demand for steel alloyed with rare and refractory elements, in particular, Ni and Mo, has been increasing over recent years.

At the same time, prices for appropriate alloying materials on the world market demonstrate a tendency to grow [1].

One of the alternative sources for obtaining the Ni and Mo alloying materials is the recycling of the alloyed tech-

nogenic wastes in order to bring them back to production. These include the scale of nickel-molybdenum containing precision alloys. The volumes of formation of the latter are relatively high and account for 3–4 % by weight of smelting and in the production of small-scale billets is 9–12 % by weight. A specific feature of this type of waste is a high degree of alloying. This necessitates taking into account a complex character of physical-chemical interaction between elements in the development of technological conditions for recycling.

Therefore, there is a relevant task to save resources and energy with a reduction in the losses of Ni and Mo during recycling and application of the scale of precision alloys in steelmaking industry. Strategic direction in solving this problem is to expand our understanding of the recovery mechanism of oxide nickel-molybdenum containing raw materials. Along with this, it is a significant task to improve ecological situation in industrial regions. Achieving positive results in addressing this problem is possible by replacing resource- and power-intensive smelting technology of refractory alloying materials with modern methods of solid-phase metallization in powder metallurgy.

2. Literature review and problem statement

When considering a list of techniques for a solid-phase recovery of oxide technogenic raw materials in powder metallurgy, it is possible to select the carbon-thermal and the hydrogen methods. Carbonothermia is technologically simpler and is more attractive economically. But the reduction products may contain residual carbon bound in the oxycarbide and carbide compounds [2]. Moreover, Fe and Mo (as the basic alloying element of many brands of precision alloys) are the carbide-forming agents. The formation of carbides of Fe [3] and Mo [4] was confirmed in parallel with the reduction of oxide materials in the process of carbonothermia. The nickel-molybdenum containing precision alloys such as 79 NM [5, 6] have, in turn, strict constraints on carbon. Given this, the application of carbonothermia for the reduction and recycling of the scale of precision alloys may result in technological complications while being impossible in some cases at all. In this case, it is more rational to opt for the hydrogen recovery.

A study into kinetics and mechanism of the MoO_3 hydrogen reduction, which can be present as a component of the scale of precision alloys, to MoO_2 is described in paper [7]. Research in a temperature range of 735–829 K has experimentally confirmed the possibility of formation of the intermediate oxide Mo_4O_{11} and parallel reduction reactions:

- 1) MoO_3 to Mo_4O_{11} ;
- 2) Mo_4O_{11} to MoO_2 .

The MoO_3 hydrogen reduction at 1323 K was accompanied by the formation of the intermediate product MoO_2 and subsequent obtaining of the ultrafine Mo metallic powder of high purity [8]. In other words, in order to achieve a more complete reduction of MoO_3 during recycling of nickel-molybdenum containing oxide waste of precision alloys, it is advisable to maintain the above-mentioned temperature parameters.

In article [9], authors reported the possibility to obtain relatively pure powders of metallic Mo from the Mo oxides while treating with plasma using hydrogen. It should be noted that the application of plasma is accompanied by the ac-

tion of relatively high temperatures on the Mo oxides, which can cause its significant losses by sublimation. For these reasons, the choice of method for treatment with plasma is not appropriate for the reduction of molybdenum-containing oxide waste of precision alloys.

A study into reduction of NiO at temperatures 543–1593 K was performed by authors of paper [10]. It was determined that at 543–773 K the products of reaction comprised a mixture of Ni and NiO. At 1173–1593 K, the reaction rate significantly increased and a complete reduction to Ni was achieved. The structure is smelt, with fine pores. Taking the above-mentioned into account, it is more expedient for experiments to select a different interval of relatively high temperatures.

A solid-phase reduction of scale by hydrogen with obtaining iron powder is considered in paper [11]. The base of the scale consisted of Fe_2O_3 and FeO. A full reduction was achieved after treatment at 1000 °C. A reduction temperature of 1100 °C resulted in the activation of particle sintering. In other words, similar patterns can manifest themselves during reduction of the oxide iron-containing part of the scale of precision alloys. This should be considered when conducting experiments.

It follows from an analysis of the scientific literature that there are significant results reported in studies into hydrogen reduction processes of Ni and Mo on the example of separately taken oxides [7–10], as well as non-alloyed iron-containing oxide technogenic waste [11]. However, the mechanism of the course of the processes during hydrogen reduction of complex alloyed oxide technogenic raw materials, including the scale of nickel-molybdenum containing precision alloys, was not investigated sufficiently. A parallel participation in the process of oxide compounds of Ni, Mo, and Fe, as well as other impurities in the composition of highly-alloyed scale, can significantly affect the course of reduction. It can also affect the microstructure and phase composition of the resulting products of metallization. Research in this area could reduce the losses of Mo and Ni by the sublimation of oxide compounds during reduction of technogenic raw materials and subsequent application of a metallic alloying additive. Based on the above mentioned, it is expedient to conduct a comprehensive research into kinetics of hydrogen reduction of the scale of a nickel-molybdenum containing precision alloy, as well as the phase composition and microstructure of the products of metallization.

3. The aim and objectives of the study

The aim of present work was to study physical and chemical characteristics of recycling of the scale of nickel-molybdenum containing precision alloys employing a method of hydrogen reduction. This is necessary to define the parameters that reduce the losses of Mo and Ni during reprocessing of oxide technogenic waste and using the obtained metallized alloying additives in steelmaking industry.

To achieve the set aim, the following tasks have been solved:

- to examine kinetic regularities of hydrogen reduction of the scale of a nickel-molybdenum containing precision alloy at different temperatures;
- to study the phase composition and microstructure of the metallized scale of a nickel-molybdenum containing precision alloy with a varying degree of reduction, for deter-

mining a mechanism of the course of transformations during thermal treatment.

4. Materials and methods for examining the kinetics of reduction and metallization products of the scale of a nickel-molybdenum containing precision alloy

4. 1. Examined materials and equipment used in the experiment

The starting raw material is the scale of precision alloy with the following chemical composition, % by weight: C – 0.024; Si – 0.316; Mn – 0.712; S – 0.016; P – 0.016; Cr – 0.063; Ni – 63.040; Co – 0.080; Mo – 3.063; Cu – 0.16; O – 20.900; Fe – remainder.

Study into kinetics of reduction was performed on a universal thermogravimetric installation of the flow-through type (Fig. 1).

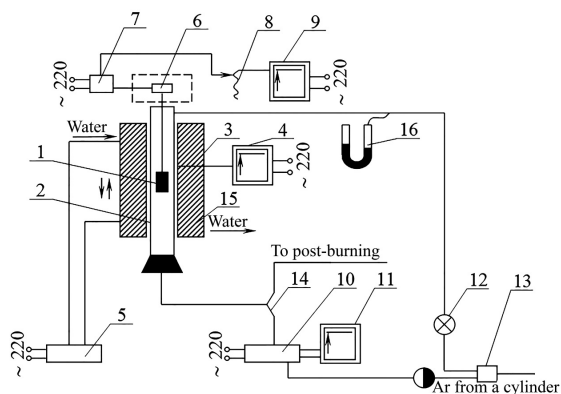


Fig. 1. Schematic of the thermogravimetric installation:

- 1 – sample; 2 – reaction pipe; 3 – thermocouple;
- 4 – potentiometer KSP2-003; 5 – furnace control unit;
- 6 – mechanotron 6MH8B; 7 – electronic unit; 8 – regulating supports MKL-49; 9 – potentiometer KSP-4;
- 10 – chromatograph LHM-80; 11 – potentiometer KSP-4;
- 12 – control valves; 13 – gas reducer; 14 – tee;
- 15 – resistance furnace; 16 – manometer

We used drained H_2 as a reducing agent, which was obtained from the hydrogen generator “Hydrogen-1” (Ukraine), and which was fed to the reaction zone through control valves (Fig. 1). Protective gas to purge the system is Ar in line with GOST 10157-79.

X-ray phase analysis of the samples was carried out on the diffractometer “DRON-6” (Russia).

Images of the microstructure of samples were obtained on a raster electron microscope “REM-106I” (Ukraine).

4. 2. Procedure for conducting experiments and determining indicators of the sample properties

A temperature interval of kinetic studies is 673–1573 K; duration is 360 minutes; hydrogen consumption is 9 l/h; linear gas flow rate is 8×10^{-3} m/s. Continuous measurement of changes in the mass of the samples was carried out over the duration of experiments. To check for the absence of sublimation, we calculated a mass of oxygen of the scale, having reacted with hydrogen, and compared it to a change in the mass of the sample during experiment.

In order to run a phase analysis and to study the microstructure, the samples were exposed to the isothermal

treatment at a temperature of 1273 K in the atmosphere of hydrogen. The experiments were terminated at preset intervals to receive product with a varying degree of reduction.

Phase composition of the examined samples was determined by the method of X-ray structural analysis using monochromatic radiation of Co K_{α} ($\lambda=0.178897$ Å) with a Fe filter. The measurements were performed at a voltage on the pipe of $U=30$ kV and anode current $I=10$ mA. The composition of phases was determined using the software PDWin 2.0 (Russia).

Study of the microstructure of samples was carried out at accelerating voltage 20 kV and at a current of the electronic probe of 52–96 μ A. Working distance to the examined surface was 10.6–10.8 mm.

5. Results of research into hydrogen reduction of the scale of a nickel-molybdenum containing precision alloy

Treatment at 673 K provided the degree of recovery at 16 % (Fig. 2, curve 1). At 773 K, minute 105 of the thermal treatment, a degree of reduction was 22 % (Fig. 2, curve 2). Over the subsequent period, the reduction rate was decreasing. After 360 minutes of the process we achieved a degree of reduction of 25 %.

Treatment at 1273 K yielded a faster reduction rate. At minute 115, the degree of reduction was 96 % (Fig. 2, curve 3). The process proceeded further in the diffusion region with a pronounced decrease in the rate of reduction. The resulting degree of reduction amounted to 99 %.

At 1523 K and 1573 K (Fig. 2, curves 4, 5), the initial period of removing oxygen proceeded at a relatively high rate. At minute 35, the samples were reduced by 73 % and 69 %, respectively. The process proceeded further at a much lower rate, relative to the results obtained in the previous case. Over 360 minutes of thermal treatment, the degree of reduction was 79 % and 73 %, respectively.

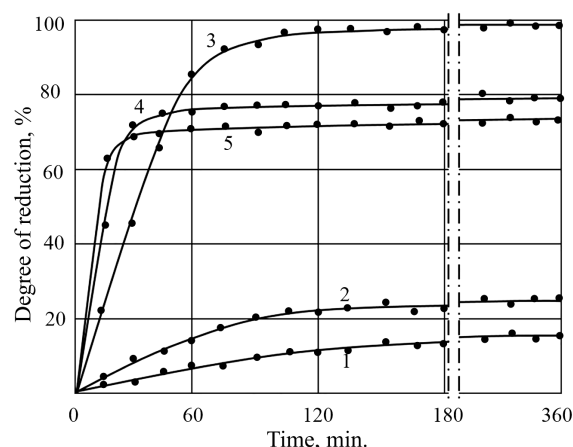


Fig. 2. Kinetics of hydrogen reduction of the scale of a nickel-molybdenum containing precision alloy at different temperatures: 1 – 673 K; 2 – 773 K; 3 – 1273 K; 4 – 1523 K; 5 – 1573 K

The mass of removed oxygen in all experiments was practically equal to a decrease in the weight of sample during the experiment, which indicates the absence of sublimation of the alloying elements under conditions of conducting the experiment.

The scale is represented by MoO_3 , Fe_2O_3 , Fe_3O_4 with, possibly, the Ni atoms dissolved there (Fig. 3). At a 20 % reduction, we observed the emergence of phases $\gamma\text{-Fe}$, FeO , FeNi and MoO_2 , and the disappearance of Fe_2O_3 and MoO_3 . With an increase in the degree of reduction from 20 % to 95 %, the intensity of manifestation of Fe_3O_4 and FeO decreased. MoO_2 was detected at a reduction of 20–60 %; the phase of Mo – within 20–95 %. The resulting product of treatment with a reduction of 95 % consisted of FeNi , $\gamma\text{-Fe}$, the phase of Mo, and a solid solution of atoms of Ni and Mo in $\gamma\text{-Fe}$. Part of a non-reduced oxide component is represented by FeO and Fe_3O_4 .

The microstructure of samples is not uniform with the presence of particles of different size (Fig. 4). After a treatment at 673 K, the processes of particle sintering were of a relatively low level (Fig. 4, a). The samples reduced at 1273 K had a sponge microstructure (Fig. 4, b), with a clearly manifested certain degree of particle sintering.

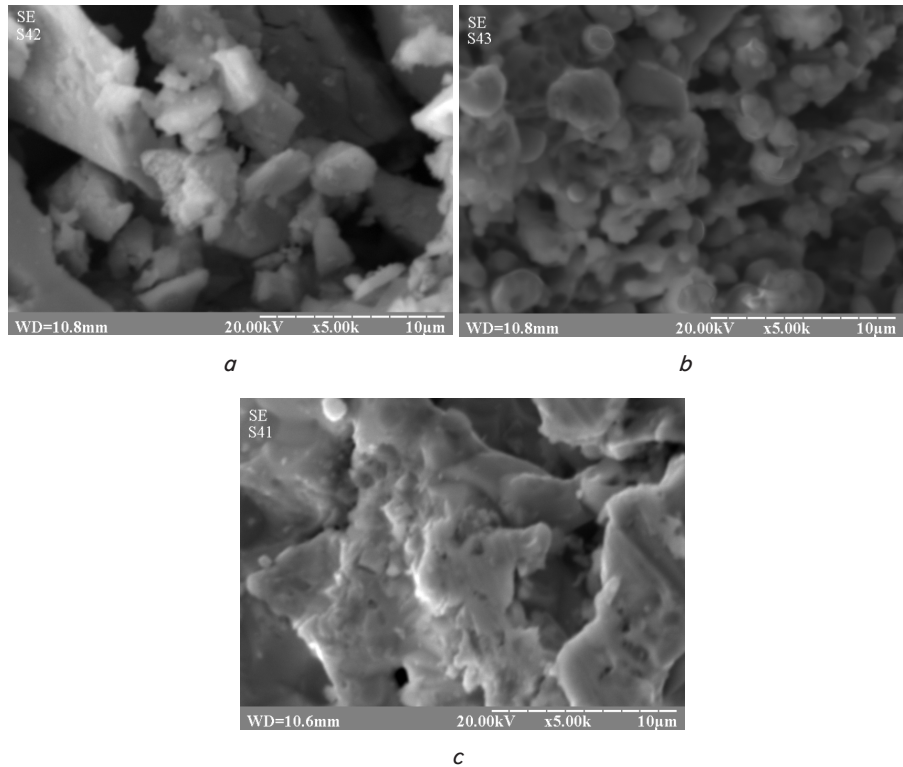


Fig. 4. Images of microstructure of the metallized scale of a nickel-molybdenum containing precision alloy after hydrogen reduction at different temperatures with a magnification of $\times 5000$: a – 673 K, b – 1273 K, c – 1573 K

Reduction at 1573 K leads to the formation of the smelt structure of surface layer (Fig. 4, c). In contrast to two previous cases, it is difficult to distinguish between separate particles – one observes an almost solid smelt layer.

6. Discussion of results of research into hydrogen reduction of the scale of a nickel-molybdenum containing precision alloy

The kinetic research conducted (Fig. 2) indicates that treatment at 673 K and 773 K does not provide high enough degree of reduction. Of practical interest is the thermal treatment at 1273 K enabling a degree of reduction of 99 %. This agrees well with the results of papers [7, 15, 16], where authors under similar conditions achieved the most effective indicators of reduction. Increasing the temperature of treatment to 1523 K and 1573 K is accompanied by a decrease in the degree of reduction of samples to 79 % and 72 %, respectively. This may be caused by the formation of surface “block-layers” of sintered particles clearly confirmed by microscopic studies (Fig. 4). The result of this is the complicated gas exchange, which shifts reduction process from the kinetic region to the diffusion region. It becomes apparent that a further increase in temperature plays a negative role in achieving an increase in the rate and degree of reduction. Similar patterns are noted in article [16], in which a rise in temperature from 1273 K to 1373 K was accompanied by a substantial intensification of smelting.

It was determined that the scale of a nickel-molybdenum containing alloy, in contrast to the unalloyed scale [16], is small in its composition of the phase of Fe_3O_4 and MoO_3 . Atoms of Ni could possibly partly substitute the atoms of Fe in oxides. The presence of alloying elements predetermined

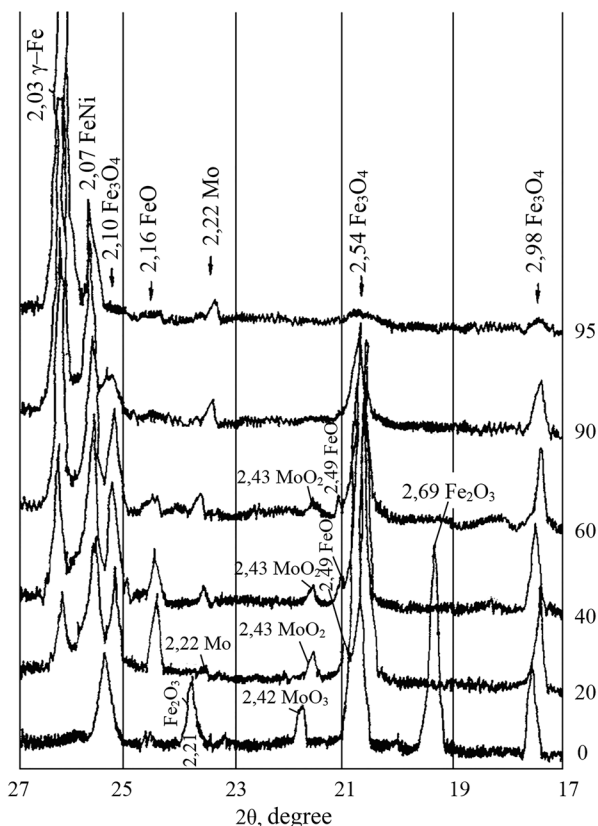


Fig. 3. Plots of diffractograms of the sample of scale of a precision nickel-molybdenum containing alloy with a varying degree of reduction. Figures next to the diffraction maxima correspond to parameters of the crystal lattice

a more complex nature of phase transformations (Fig. 3). The resulting reduction product consisted of γ -Fe, FeNi, the phase of Mo, and a certain part of residual oxides of Fe_3O_4 and FeO. At the intermediate stages, MoO_2 formed, but in the target product the dominant amount of Mo, judging by the diffractograms, was in a solid solution of γ -Fe and the Mo phase. Similar patterns in the reduction with the formation of the intermediate Mo oxides are reported in papers [6, 7].

The results of phase X-ray structural studies (Fig. 3) indicate a lack of formation in the process of reduction of the compounds and phases inclined to sublimation. In other words, there is no need to create special conditions that prevent evaporation and the loss of alloying elements with a gas phase. This also predetermines an increase in the degree of use of alloying elements.

A possible shortcoming is the lack of an X-ray microanalysis. Employing it would make it possible to better uncover the nature of phases and inclusions in the photographs of the microstructure.

Experimental-industrial testing of the metallized scale, as a charge additive, during smelting of precision alloys of the 79 NM type, was carried out in the induction furnace "IST-7" at the steel works PAT "Dniprospsstal" (Ukraine). The total amount of the melted alloy was 110 tons. The loading was conducted on the bottom of the furnace "under the filling". The additive was in briquettes of round shape with the following dimensions: length and width is 60 mm, thickness is 40 mm. The temperature of crucible of the furnace at loading (after draining the previous melting) was equal to 1450–1500 °C. The temperature of the melt during dissolution of the metallized alloying additive was 1540–1600 °C. The metallized scale was used in the amount from 30 to 175 kg/t, which enabled reduction of the consumed metallic Ni and Mo by 35–40 % of the weight of appropriate alloying materials. Slag is basic. Basicity is 2.5–2.6. Content of Al_2O_3 is 5–10 % by weight, MgO – 1–2 % by weight. Ni and Mo are present in slag in

the form of oxides in the amount of 0.5–1.5 % by weight. The assimilation of the alloying elements from the metallized alloying material was over 96 %. A relatively high degree of the assimilation was provided by the absence of compounds inclined to sublimation and a sponge structure, which predetermines faster dissolution of alloying additive in metal melt.

7. Conclusions

1. It was established in the course of kinetic research that the highest degree of hydrogen reduction of a nickel-molybdenum containing precision alloy (99 %) is achieved by thermal treatment at 1273 K. This is predetermined by the intensification of reduction processes and a sufficient level of porosity, which enables satisfactory gas exchange in the regions of reactions.

2. It was found that with an increase in the degree of reduction of a nickel-molybdenum containing precision alloy to 95 %, the basic phases underwent transformations from Fe_3O_4 , Fe_2O_3 , MoO_3 to γ -Fe, FeNi, Mo. Part of the non-reduced oxide component in the resulting product is represented by Fe_3O_4 and FeO. We revealed a presence of MoO_2 at a degree of reduction from 20 % to 60 %. A microstructure of the products of metallization of the scale is heterogeneous, made up of particles with different size, level of sintering, depending on the temperature of treatment.

The formed phases in the examined temperature range do not demonstrate a noticeable inclination to sublimation, which makes it possible to bring down the losses of alloying elements when obtaining the highly-alloyed metallized scale. Testing the latter while smelting of precision alloys confirmed their manufacturability and efficiency of recycling the alloying elements. At the same time, disposal of industrial wastes enables a reduction in the technogenic load on industrial regions and improves ecological situation.

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