1. Introduction

One of the alternative sources for obtaining alloying materials containing W, Mo, Cr, V is the processing and return-
plex compounds. That necessitates taking into consideration the complex character of the physical-chemical interaction between elements when developing the technological conditions for processing.

Thus, it is a relevant task in metallurgy to save resources and energy with reducing the losses of alloying elements when processing and using the slag from aluminothermic production and the scale from rapid cutting steels. For this purpose, it is necessary to study the phase composition and microstructure of technogenic raw materials that contain, along with the slag-forming components and iron, expensive refractory alloying elements.

2. Literature review and problem statement

Reduction with carbon [1], as well as with a complex of C and Si [2] during the reducing smelting, has positive practical results as a technique for processing oxide technogenic raw materials. This is especially true for scale and other fine-disperse technogenic waste contaminated with mineral oils and emulsions that require refining from harmful impurities.

Based on the research results by authors of work [3], the iron scale consists of FeO, Fe2O3, FeO. Similar results were obtained by authors of paper [4] in the study of the rolling iron scale. The possibility of the presence of a Fe phase, along with the oxide phases, in the scale is indicated by authors of work [5]. When investigating scale of steel P18 in paper [6], in contrast to the non-alloyed raw materials, the authors did not rule out the possibility of the presence of oxide compounds with the content of refractory alloying elements. This is important, since the higher Mo and W oxides have, at a temperature increase, a relatively high susceptibility to sublimation. Such a feature might cause significant losses of refractory elements when processing technogenic raw materials.

Based on research results in [7], slag from the ferrochrome production has 3.5% Cr2O3 in its composition and can additionally contain about 9% by weight of metallic Cr. Other components are represented by Al2O3, MgO, SiO2, CaO, FeO and SiC. In paper [8], authors determined using an X-ray phase analysis that the slag from aluminothermic ferrochromium production consists mostly of the phases of Al2O3 and metallic Cr. Moreover, the diffraction peak of Cr had a relatively high intensity. This indicates the possibility of the presence of a significant residual content of Cr in the slag; hence the expediency for the further extraction of the refractory element.

The authors of work [9] studied the removal of V from the vanadium converter slag using the reducers C and Si. It was stated in work [9] that slag could consist of V oxides along with SiO2, FeO, MnO, and TiO. During reduction, the formation of carbide and silicide phases is not excluded. The reduction of vanadium slag using C and Si for the purpose of extracting V was investigated in practice by authors of work [10]. The amount of oxide V2O5 in the slag was 4.35% by weight. The oxides of FeO, CaO, Al2O3, MgO, SiO2, MnO, TiO, Cr2O3 and P2O5 were also present. The achieved degree of removal of V was larger than 95%. It should be noted that the higher oxide compounds of V in the slag have a relatively high susceptibility to evaporation. This is confirmed by studying the losses of V in the evaporation of oxides from the samples of vanadium-containing slag in the system CaO–MgO–Al2O3–SiO2 by authors of work [11]. That indicates the expediency of reduction with the transfer of oxide compounds of V to carbides and silicide that are not susceptible to evaporation.

The authors of work [12] analyzed the slag formed in the aluminothermic smelting of ligatures of grade AVTU (Al–V–Ti–C), AHMK (Al–Cr–Mo–Si) and ACMO (Al–Zr–Mo–Sn) by using an X-ray phase analysis. The main phases of slags AVTU and AHMK are Al2O3, CaAl2O19, CaOAl15O40. In all samples of the slag, F2 was identified, and a relatively small amount of KCl was present in the slag from the smelting of AVTU. CaAl2O19, CaZrO3, CaZr2O5, Al2O3 and Al2O3 were found in the slag from smelting the ligature ACMO. Based on the results from paper [13], the slag from AVTU smelting could contain elemental carbon, metallic carbide phases. That is, the presence of compounds and metallic impurities of refractory and expensive elements is possible in the slag from the aluminothermic production of ligatures, with the prospect for their further extraction and return to production.

It should be noted that there are significant results in studying the composition of scale from the non-alloyed grades of steels, reported in papers [3–5]. In addition, there are certain results in studying the scale of a tungsten rapid cutting steel, which are reported by authors of work [6]. However, the demonstration of the refractory elements of W and Mo in the composition of phases and compounds in the scale of tungsten-molybdenum grades of rapid cutting steels is studied insufficiently. One of the most common of them is the grade R6M5. There are also significant achievements in the research into the composition of slag from metallurgical production for the purpose of further processing, reported by authors of studies [7–11]. The slags of aluminothermic production of ligatures of refractory elements are one of the most promising for processing and extraction of high-cost components; results of studying them are given in papers [12, 13]. However, at the same time, the nature of the phases and compounds in which there are refractory elements, is studied insufficiently. Research in this field can help reduce the losses of Mo, W and other alloying elements through sublimation with an elevated temperature when processing technogenic waste. In other words, it is expedient to conduct a comprehensive study into the phase composition and microstructure of slag from the aluminothermic production of the ligatures of refractory elements of various grades and the tungsten-molybdenum scale from a rapid cutting steel of grade R6M5. Using a raster electron microscopy with an X-ray microanalysis will make it possible to significantly expand our understanding of the structure and composition of separate sections of the microstructure in the examined materials.

3. The aim and objectives of the study

The aim of this work was to study the features of the physical-chemical properties of slags from the aluminothermic production of ligatures, as well as scale from the tungsten-molybdenum rapid cutting steel R6M5, as the alloyed technogenic secondary raw materials. This is necessary to determine the parameters that reduce the losses of Mo, W and other elements through the sublimation of oxides in the processing of alloyed technogenic waste.
To achieve this goal, the following tasks were set:

– to determine the phase composition and microstructure of slags from the aluothermic production of ligatures of various grades regarding the nature of presence of the alloyed elements;

– to investigate peculiar properties of the phase composition and microstructure of scale from the tungsten-molybdenum rapid cutting steel R6M5 as the alloyed technogenic secondary raw materials.

4. Materials and methods to study the alloyed technogenic secondary materials

4.1. Examined materials and equipment used in the experiment

The slags from the aluothermic production (TU 48-0514-34-87), obtained after smelting of ligatures of the refractory elements AMVT (TU 48-4-308-88), MFTA (TCU48-4-365-88) and AHM-50 (TU 48-4-365-88).

Requirements in the technical specifications TU 48-0514-34-87 to the content of components in slag, % by weight:
- aluminum oxide – not less than 68.0;
- silicon oxide – not larger than 2.0;
- iron oxide – not larger than 0.2;
- the sum of oxides of refractory elements (Mo, W, Cr, V, and others) – not larger than 8.0;
- calcium oxide – the rest. Grain size, mm – not larger than 80.0.

The scale from the rapid cutting steel grade R6M5 of the following composition, % by weight: C – 0.75; Si – 0.15; Mn – 0.21; Cr – 3.85; Mo – 4.81; V – 1.65; W – 5.75; Co – 0.07; Ni – 0.24; Cu – 0.12; S – 0.009; P – 0.027; O – 27.0; Fe – the rest.

An X-ray phase analysis of the samples was performed at the diffractometer “DRON-6” (Russia).

Photographs of the microstructure of samples were acquired at raster electron microscopes “REM-106I” (Ukraine) and “JSM 6360LA” (Japan). The microscopes are equipped with the system of an X-ray microanalysis to determine the chemical composition of separate plots of the samples’ surface.

4.2. Procedure for conducting the experiments and determining the indicators of samples’ properties

Phase composition was determined using the method of an X-ray phase analysis, employing the monochromatic radiation of Co Kα (λ=0.178897 Å). Measurements were made at a voltage at the tube of U=30 kW and at an anode current of I=10 mA. The composition of phases was examined using the software package PDWin 2.0 (Russia).

We examined the microstructure of samples at the accelerating voltage of 20–25 kW and a current of the electronic probe of 52–96 µmA. Working distance to the examined surface was 10.8–12.3 mm. Phase composition was determined by the non-reference method for calculating fundamental parameters.

5. Results of studying the properties of the alloyed technogenic secondary materials

Based on the results of the phase study, the slag samples from the aluothermic production of ligature AMVT mostly contained the oxide CaAl₄O₇ and the vanadium-containing compound AlV₂O₄ (Fig. 1). The compound CaAl₄O₇ was also identified in the slag samples from the production of ligature AHM-50. A chrome-containing component is represented by the oxide CrO₂ (Fig. 2). Slag samples from the production of ligature MFTA mostly consisted of the complex compounds Al₇5Mo₂0W₅ and Mo(Si, Al)₃ (Fig. 3).
The scale of rapid cutting steel grade R6M5 is represented by the oxides of Fe₃O₄, Fe₂O₃ and FeO (Fig. 4). Along with this, we identified the demonstration of the complex oxide FeWO₄. Molybdenum–containing compounds are represented by the oxide MoO₂ and carbide Mo₂C. Demonstration of the carbide WC was observed as well.

The microstructure of the examined technogenic materials is disordered, it consisted of the particles with different size and shape (Fig. 5). The content (% by weight) of W and Mo in the examined plots of scale from steel R6M5 was within 3.45–10.73 and 2.17–6.65, respectively (Fig. 6, Table 1). We also identified a plot with the content (% by weight) of Cr and V – 1.23 and 1.18, respectively.

The content of oxygen in the examined plots was within 8.52–23.16 % by weight. Fe formed the base.

Table 1
Results of the X-ray microanalysis of reduced products according to Fig. 5, d

<table>
<thead>
<tr>
<th>Sample plot</th>
<th>Content of elements, % by weight</th>
<th>Total</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>O</td>
<td>Al</td>
</tr>
<tr>
<td>1</td>
<td>15.84</td>
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<tr>
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<td>8.52</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>23.16</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>18.67</td>
<td>0.00</td>
</tr>
</tbody>
</table>

6. Discussion of results of studying the properties of the alloyed technogenic secondary materials

The study into slags from the aluminothermic production of smelting the ligatures AHM-50 and AMVT shows that the base consisted of CaAl₄O₇ (Fig. 1, 2). This agrees well with the results in study [12]. At the same time, the difference is in the detection of compounds with refractory elements: AlV₂O₆, CrO₂ (Fig. 1, 2). According to a research reported in paper [14], CrO₂ decays at a temperature of about 783 K, and it is stable at lower temperatures. That indicates the possibility of CrO₂ formation when cooling the slag within temperatures below 783 K and the presence in the respective samples, which were examined using an X-ray phase analysis.
The samples of slag from the production of ligature MFTA contained the phases of Al$_2$Mo$_{20}$W$_5$, Mo(Si, Al)$_3$, which could be present in the form of metallic inclusions (Fig. 3). The respective examined samples probably had the clusters of inclusions of these phases. This is consistent with the results of papers [7, 8, 13], which noted in the examined samples the presence of a metallic component. The microstructure of the examined slags is heterogeneous, consisting of disordered particles (Fig. 5).

The research conducted indicates that the phase composition of scale from steel R6M5 is mostly represented by Fe$_3$O$_4$, FeO$_2$, FeO (Fig. 4). This agrees well with the results in papers [3–6]. The difference is the detection in the composition of compounds with the participation of refractory elements: FeWO$_4$, MoO$_3$, WC, Mo$_2$C, due to the increased degree of W and Mo doping. The presence of particles with a relatively high content of alloying elements in the scale is confirmed by the results of an X-ray microanalysis (Fig. 5, d, Table 1). At plot 2, the content of W and Mo reached 10.73 % by weight and 6.65 % by weight, respectively. At plot 3, the content of Cr and V content 1.23 % by weight and 1.18 % by weight, respectively. It is not excluded that a certain part of the atoms in the alloying elements, including Cr and V, could be included as the replacement atoms in Fe oxides. The microstructure of scale was characterized by the disordered particles of different size and shape (Fig. 5, d).

When comparing the results of research into the properties of slags from the alumothermic production and the scale of steel R6M5, it should be noted that they are similar in the presence of refractory elements in the composition of compounds. In this case, refractory elements were bound in oxide or complex compounds, which predetermines the application of additional reduction processes and the recycling for reuse. According to the research results, the examined materials contain no compounds with a relatively high susceptibility to sublimation. In other words, there is no need to create special conditions that prevent the evaporation and loss of alloying elements with the gas phase. That also predetermines an increase in the degree of using alloying elements and reduces certain restrictions for the addition of the examined slags to slag-forming mixtures and temperature limitations for melting regimes.

As a shortcoming, we should note the absence of results from an X-ray microanalysis of plots in the microstructure of slags from alumothermic production. This study might be developed in the direction of expanding the range of examined slags from the alumothermic smelting of ligatures for further processing, such as niobium or zirconium-containing.

The slag of alumothermic production and the scale of rapid cutting steel were used as components of the charge to smelt the alloying and deoxidizing alloy in accordance with TU 14-146-87-90. Introduction of scale to charge makes it possible to ensure the specified degree of alloy doping by refractory elements when disposing of fine-disperse oxide waste. At the same time, shavings from the power grinding of the surfaces of commodity billets and metal-abrasive dust containing silicon carbide were introduced to the charge. The slag-forming mixture consisted of the flux AN-295, fluoric spar, and slag from the alumothermic production of ligatures. Testing the specified slag-forming mixture in the composition of charge during smelting of the alloying and deoxidizing alloy was conducted in the three-tones electric arc furnaces SKB-6069 with a coal lining. The ignition was conducted in a furnace bath with the loaded charge, followed by melting and finishing to a temperature of 1,813–1,833 K. Aging at a predefined temperature was conducted to average and stabilize the chemical composition throughout the entire volume of the furnace bath. The discharge was performed on a roller into metal pallets or on a booth with molds. The alloy was obtained in pieces with a weight not exceeding 180 kg (typically, 20–30 kg). The obtained alloy complied with TU 14-146-87-90 with a mass share of elements: C – 2.0–4.5; Si – 1.0–4.5; Cr – 1.0–6.0; Mo – 2.0–5.0; V – 1.0–2.0; W – 3.0–6.0; Mn – not larger than 0.6; Mn – not larger than 0.6; Co – not larger than 0.6; S – not larger than 0.03; P – not larger than 0.03; Fe – the rest. The practical significance of introducing slag from the alumothermic production is to ensure the refining capacity of the slag mixture, the possibility for additional extraction of refractory elements from slag and to lower the cost of the alloy. Introduction to the charge composition of slag from the alumothermic production according to TU 48-0514-34-87 in the range of 4.5–14.5 % by weight ensured the increased doping of the alloy. We have achieved an increase in the content of refractory elements through the reduction from oxides and the removal of metallic inclusions from slag within 1.89–6.09 kg/t. There was also a somewhat increase in the alloy desulphurization.

7. Conclusions

1. It was determined that the base of slags from the alumothermic production of ligatures AHM-50 and AMBT is CaAl$_2$O$_4$. At the same time, a compound was detected with the refractory elements AlV$_2$O$_4$ and CrO$_2$. The phases of Al$_2$Mo$_{20}$W$_5$ and Mo(Si, Al)$_3$ were identified in the slag samples from smelting the MFTA ligature. The microstructure was heterogeneous, and consisted of the disordered particles.

2. The phase composition of scale of steel R6M5 mostly consisted of Fe$_3$O$_4$, FeO$_2$ and FeO. In addition, compounds with the refractory elements FeWO$_4$, MoO$_3$, WC, Mo$_2$C were detected. The plots of microstructure with a relatively high content of W and Mo were found, as well as the plots with the presence of Cr and V. The replacement of part of Fe atoms with the atoms of the refractory alloying elements is possible in oxide compounds. The microstructure of scale was characterized by the disordered particles of various size and shape.

References


