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ON THE ISSUE OF ALLOYING AND MODIFICATION OF ALLOYS: USING THE WASTE PRODUCTS FOR CREATION OF NOVEL MATERIALS

At the large and powerful industrial (private or state) enterprises of the world, particularly, Kazakhstan, RF, and some other post-Soviet (and not only) countries, the products are manufactured using obsolete technologies with high wastes' generation. At that, the storage and warehousing are unorganized and technically unreasonable (wastes of different chemical compositions and hazard class are mixed) that does not allow their further efficient recycling. Increased processing of many industrial and household wastes is not only economical, but also considerably improves the environmental situation, significantly reduces the consumption of natural raw materials, and reduces the use of scarce lands for waste storage [1]. The authors of this article carried out a literary review on this topic and attempted to use microsilica, as a waste of silicon production, to create new materials with special properties. This refers to the field of experimental study of structures, phases, structural components for understanding the processes of alloying, modification, diffusion, *etc.* Understanding physical thinking from the metal physics point of view in the study of the nature and kinetics of the phase transformations, alloying, and modification processes enables using the physical research methods to solve research and technological problems in metallurgy and materials science in order to predict and change the required set of properties. The method of research in this article is electron microscopy as the simplest and fastest method of obtaining information about the microstructure, elemental composition, and distribution of components in the bulk.

Keywords: alloying, microalloying, modification, modifier, alloying element, production waste.

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1. Introduction

Alloying has become purposefully applied relatively recently in the history of the world. This was partly due to technological difficulties. The alloying additives simply burned out using traditional steelmaking technology.

It is noteworthy that the first steels that a person met were natural alloyed steels. Even before the beginning of the Iron Age, meteoric iron was used, containing up to 8.5% nickel.

Naturally, alloyed steels made from ores originally rich in alloying elements were also highly valued. The increased hardness and toughness of Japanese swords with the ability to provide a sharp edge is possibly due to the presence of molybdenum in the steel.

Modern views on the influence of various chemical elements on the properties of steel began to take shape with the development of chemistry in the second quarter of the 19th century.

Apparently, the first successful use of targeted alloying can be considered the invention in 1858 by Muchette of steel containing 1.85% carbon, 9% tungsten and 2.5% manganese. The steel was intended for the manufacture of cutters for machine tools and was the prototype of the modern line of high-speed steels. The industrial production of these steels began in 1871.

It is believed that the first alloy steel of mass production was the Hadfield Steel, discovered by the English metallurgist Robert Abbott Hadfield in 1882. The steel contains 1.0–1.5% carbon and 12–14% manganese, has good casting properties and wear resistance. This steel has survived to this day without any significant changes in its chemical composition [2].

Microalloying is the introduction into a metal or alloy of a small amount of alloying additives, the total weight of which should not exceed 0.1% of the weight of the original metal or alloy. It is used to improve the performance properties of structural, heat-resistant, stainless steels, non-ferrous alloys and to modify the parameters of many semiconductor materials.

Microalloying can be applied both on the surface and in the bulk. If the microalloying is carried out on the surface, it is called implantation.

The main microalloying additives (impurities, dopants) are vanadium, titanium, boron, niobium, zirconium, many rare-earth elements (cerium, yttrium, lanthanum, *etc.*), their mixtures, misch metal, aluminium, nitrogen, barium, calcium, magnesium. The microalloying technique is similar to the alloying methods.

As a rule, microalloying is mainly reflected in the structure and energy state of grain boundaries. During microalloying, selective adsorption occurs along the boundaries, low-melting impurities (tin, sulphur, lead, bismuth) are bound by alloying additives to form refractory compounds. Thus, recrystallization is delayed, heat resistance, corrosion resistance, cold resistance increases, and the tendency to crack formation in steels and alloys decreases [3].

Analysis of the current state of metallurgical technologies shows that, at the moment, in metallurgy, to a very small extent, they use the huge opportunities contained in the microalloying and modification of steels and alloys. It is difficult to find the most economically profitable technological operations that give a large economic effect at low cost [4], especially if you carry out microalloying or modification with elements from industrial waste.

2. The Main Industrial Varieties of Alloying and Modification

There are different methods for changing the structure of a substance in order to create the required set of properties, which include alloying and modification. Traditionally alloying, microalloying and modification are referred to steels, cast irons, non-ferrous metals. At the same time, some countries do not have their own mineral resource base for the production of alloying materials or modifiers, especially based on rare and refractory elements. The need for them is met by imports from abroad. This problem has become especially aggravated in recent years in connection with the rapid rise in prices on the world market as a result of the developing trend of depletion of mineral resources.

Scientists from many countries are developing scientific and industrial solutions of a man-made nature, the novelty of which lies in the advanced use of industrial waste of various nature using modern technologies and equipment. By alloying, microalloying and modifying metals and alloys with industrial waste, not only metal alloys are created, but also new materials for special purposes.

Therefore, the authors have worked through many literary and electronic sources, which provide technological solutions to a similar problem. For example, one of the methods of smelting steel is carrying out smelting of steel without oxidation and is used mainly in smelting alloyed and high-alloyed steels in order to maximize the use of alloying elements contained in production wastes. Smelting in this case is carried out with the restriction of oxidative processes, without the supply of iron ore and oxygen. At the same time, they try not to remove the slag or remove only after the restoration of alloying elements with ground ferrosilicon, which makes it possible to maximize the assimilation of alloying elements from production wastes. The negative aspect of steel melting without oxidation is the impossibility of removing carbon, phosphorus, and hydrogen from the melt.

Currently, scarce tungsten-containing hard alloys, the cost of which is constantly increasing, are mainly used for electrospark alloying of metal surfaces. In Ref. [5], when analysing the problem of electrode materials, a hypothesis was put forward about the possibility of processing tin-containing wastes and creating new electrode materials for electrospark alloying of metal surfaces.

Vanadium is also one of the most important alloying elements, but also one of the most expensive. Therefore, the development of resource-saving technologies that ensure the maximum involvement of secondary materials containing vanadium in the form of oxide compounds in metal circulation is relevant today. The solution to this problem was considered in [6], the authors of which showed the possibility of using vanadium-containing wastes to obtain steels and alloys with a given content of this component, which will reduce vanadium losses and reduce the cost of steels by using cheaper alloying materials contained in oxides.

In the work [7], the efficient use of waste for alloying high-speed alloys at Ukrainian enterprises is proposed: a resource-saving technology of molybdenum- and tungsten-containing alloys and master alloys has been developed. This solution provides a significant increase in the concentration of these alloying elements and, at the same time, increases the degree of utilization of alloyed non-mobile waste (high-speed steel scale).

One of the alternative sources for the production of alloying materials is the processing and returns to production of alloyed technogenic waste, large volumes of which in practice do not find sufficient effective application. So in work [8], the authors considered the technology of carbon reduction (carbothermy) wastes of alloyed heat-resistant, heat-resistant, corrosion-resistant and other grades of steels and alloys, the operation of which may be accompanied by the influence of aggressive media, temperature and mechanical factors, contain expensive elements (nickel, chromium, tungsten , molybdenum and others). Indeed, such wastes contain these alloying elements, but in the form of oxide and complex compounds; a significant part is made up of oxide and finely dispersed waste (scale, grinding dust).

Modern trends in metallurgy are aimed at increasing demand for steel alloyed with rare and refractory elements, which include chromium. There is a gradual depletion of raw material deposits, which causes a tendency for the world market prices to rise for refractory alloying elements. Traditional technologies for producing alloying materials based on chromium (ferroalloys) using carbon-silicothermal and alumothermal melts are characterized by significant temperatures and processing times, which causes high environmental pollution by reaction products and solid waste, significant resource and energy consumption. The existing problems of resource conservation are most relevant for special metallurgy, where expensive alloying additives are used, which, due to their physicochemical properties, pass into slag, scale and other metallurgical waste. In the work, the authors of [9] propose replacing standard ferroalloys with spongy alloying materials with qualitatively new advantageous properties by obtaining them by the method of powder metallurgy by solid-phase reduction of the above metallurgical waste.

At machine-building enterprises, the method of electrical discharge machining of parts made of complex alloyed steels and alloys is widely used, as a result of which wastes are formed containing a significant amount of alloying elements: nickel, chromium, tungsten, molybdenum, titanium, *etc*. Thus, the authors of [10] propose a technology for obtaining complex alloying additives (ligatures) from such wastes by the most complete reduction of metal oxides (thermal reduction). This will allow the return of valuable elements to production, reduce the cost of pig iron production, improve its mechanical properties and reduce the environmental burden on the environment.

The works [11, 12] present the results of developments on the creation of foundry materials from metal-containing industrial waste and intermediate products of related industries by reducing metals, in particular titanium, from titanium-containing powder materials. The introduction of titanium into the melt by the direct alloying method provides savings in expensive and scarce ferroalloys. The modifying effect is achieved due to the chemical interaction of the introduced additives with individual elements of the crystallizing substance. In contrast to the known methods for modifying cast iron from ferrotitanium, when the modifying effect is explained by the deoxidizing effect of titanium, and with direct alloying and the presence of such a strong reducing agent as atomic carbon, carbide inclusions have a decisive modifying effect. In industrial conditions, titanium-containing production wastes are used for microalloying rail steel with titanium. The degree of assimilation of titanium from waste is at the level of assimilation from ferroalloys and is 40–50%. The resulting rails in all respects meet the requirements of regulatory documents.

The main obstacle to the widespread use of titanium and its alloys is the high cost, first of all, of titanium sponge. A promising direction for reducing the cost of titanium products is the use of waste, which makes it possible to reduce the cost of secondary alloys by 30 percent or more while maintaining the basic structural properties inherent in titanium alloys.

As known, in the prime cost of titanium ingots, up to 90% of all costs are the costs of expensive components of the charge. Every 10% of waste reduces its cost by 5–8%. When 10% of waste is involved in the charge per 1 ton of smelted titanium-based ingots, an average of 100 kg of sponge and 10 kg of alloying elements is saved [13]. Accordingly, in the production of semi-finished products and products from titanium alloys, all traditional types of waste are generated: lump waste, shavings, sheet trim. The total amount of waste generated annually in the production and use of titanium alloys is very large, it is about 70% of the charge consumed during smelting, and this figure changes very little over time [14]. Currently, unlike most metals, titanium waste is used to a limited extent in the production of titanium alloys. Industrial titanium alloys are mainly obtained by alloying titanium with the following elements: Al, V, Mo, Mn, Sn, Zr, Cr, Cu, Fe, W, Ni, Si; doping with Nb and Ta is used less frequently. The variety of alloys and the ratios of their amount make it difficult to smelt cheap secondary titanium alloys with regulated strength properties on an industrial scale, since, according to current practice, the properties of titanium alloys, including strength, are mainly determined by their chemical composition and within the narrow limits of the content of specific alloying elements. The invention [15] relates to the field of obtaining α-, pseudo-α-, $\alpha + \beta$-titanium alloys from secondary raw materials with regulated strength properties, namely, ultimate tensile strength (tensile strength), mainly for the manufacture of sheet semi-finished products, structural products and structural armour, and can be used in defence and civilian industries.

It is known that at present there are a large number of steels alloyed with titanium, which improves the performance properties of the alloy. At the same time, the concentration of titanium in steels varies in the range of 0.01–1.0%, that is, within the fairly narrow framework. Therefore, an urgent task in the technology of producing titanium-containing steels is the guaranteed provision of such titanium concentrations with a minimum consumption of alloying materials. The main difficulty in alloying steel with titanium is its high reactivity with respect to oxygen, which leads to the formation of titanium oxides, which pass into the slag. This significantly increases the consumption of alloying materials and negatively affects the cost of production.

In Ref. [16], the following methods of alloying steel with titanium are considered that makes it possible to solve three problems following below.

(i) The use of complex alloys (ligatures obtained by alloying ores, production waste in electric furnaces) containing highly active elements (titanium, chromium, aluminium, calcium, magnesium, *etc*.). However, this method does not allow obtaining complex alloys with high titanium content, there is a significant waste of highly active elements and strong segregation, and the resulting product is characterized by a high content of impurities and high cost.

(ii) Production of complex alloys with titanium for alloying steel by the self-propagating high-temperature synthesis (SHS). This process takes place without the participation of oxygen due to the heat of chemical reactions of synthesis, does not require the supply of energy from external sources, it is ecologically safe. However, with this technology, the products obtained from pure metals also have a very high cost.

(iii) On the basis of the above, the authors [16] propose a developed metallurgical SHS-process, in which production wastes or cheap ferroalloy powders are used as initial components. The silicotitanium alloys obtained by this method are characterized by high titanium content, low impurity content, and the presence of elements highly reactive with respect to oxygen, which protect titanium from oxidation. Their use will help solve the problem of obtaining the required titanium concentrations in steel within narrow limits, reduce the consumption of alloying materials and improve the quality of the finished steel sheet.

In Ref. [17], the technology of creating new compositions of oxide alloys obtained based on industrial waste with specified service properties (wear resistance, corrosion resistance, heat resistance) is presented. These alloys are intended for the production of cast parts for units operating under conditions of abrasive wear, aggressive media and sharp temperature changes. The use of new oxide alloys enables to increase by 4–5 times (as compared with similar metal parts) the service life of parts and equipment operating under conditions of abrasive wear and corrosive environments, and to reduce the cost of castings by 2–3 times as compared with the existing stone-cast products. The alloys will be used to produce slag-cast products in the projected slag-stone casting workshop.

In work [18], a technology for obtaining an exothermic briquette from metallurgical waste is presented. The modification of low-grade cast irons at low temperatures (1300–1350 °C) with heat release completely eliminates the chill of the castings and increases the tensile strength. Graphite is substantially refined, and the matrix is predominantly pearlite. Composition of briquettes: 60% aluminium shavings and 40% scale. The consumption of the modifier is within 0.9–1.1% of the mass of the liquid metal with modification effect for at least 20 minutes.

Constantly rising energy prices, together with stricter environmental regulations, are driving the development of modern recycling technologies for aluminium waste (aluminium alloy shavings and slags). Currently, in many countries, low-waste and non-waste technologies, clean technological processes and industrial production that ensure the integrated use of all types of raw materials are becoming priority in state industrial policy. Therefore, in Ref. [19], the authors propose a technological solution, namely the introduction of aluminium shavings with contamination of 6 and 25% as components of the charge, aluminium slags with a content of 50–68% of aluminium and sieving of aluminium slag with a fraction of more than 10 mm. An increase in the proportion of slag from 22 to 30% leads to an increase in the metallurgical yield from 71 to 83. In addition, such a waste-free technology makes it possible to obtain pig grade alloys such as AK5M2 and AB87, which eliminates the need for disposal of secondary aluminium slags and payment of environmental tax, and increases the profitability of production.

The work [20] shows the possibility of manufacturing a porous material on an aluminium basis by implementing the most rational scheme for processing industrial waste chips, excluding their remelting. It is based on the techniques typical for the processes of powder metallurgy and pressure treatment, as well as the basic principles inherent in the technology of producing foam aluminium.

In work [21], the authors investigated a diffusion-alloyed alloy from waste cast iron shot in a mobile powder medium and obtained a wear-resistant coating from this alloy using induction surfacing. A large amount of dispersed waste (iron-containing dust, scale, shavings, sludge, scrap from the production of hardware and processing of rolled products, sawdust, scrap, chips, foundry waste, wire, *etc.*) is generated annually at the production facilities. Some types of the listed waste are successfully used as secondary raw materials for the production of powders. However, the waste from the production of shot has not found use and is mainly sent to remelting, although this is impractical; there is a waste of alloying elements, at the same time this waste is almost ready-made metal powder.

The work [22] proposes the development of cheap modifiers for cast iron, the introduction of which significantly improves the structure and increases the mechanical characteristics of such an alloy. The implementation of this method allows you to saturate effectively cast irons with carbon instead of the traditional dilution method; at the same time, high-quality carbon black is obtained from waste of high-polymer compounds, and also to extract expensive and scarce metals from waste in the oxide phase (industrial scale, grinding waste, *etc.*) and effectively alloy melts with them.

At titanium–magnesium enterprises, chlorination of titanium slags produces 0.2–0.3 tons of solid chloride waste containing elements that can work as good deoxidizers, modifiers, microalloying elements for all casting alloys. These valuable elements are irretrievably lost with chloride waste. At the same time, such waste is not processed at the enterprise and, as hazardous emissions, is transported to dumps, polluting the land and the environment. In Ref. [23], the authors developed and proposed a technology for modifying cast irons with chloride wastes from titanium–magnesium industries in Russia and Ukraine. As a result, the mechanical and special properties of ductile iron are increased; the content of sulphur and gases is reduced.

The work [24] proposes a resource-saving technology for processing 100% of foundry waste of the heat-resistant alloy ZhS32-VI, which ensures the quality of cast bar billets in terms of the content of impurities, gases and mechanical properties in accordance with the requirements of TU, a stable chemical composition of alloys for the main alloying elements, a decrease in cost and reducing the consumption of scarce and expensive alloying metals such as Ni, Co, Mo, W, Re, Ta and others. The developed technology serves as the basis for solving another important problem of the production of cast heat-resistant alloys, namely, the full use of all waste generated at engine building and repair plants. Resource-saving waste processing technology allows creating a closed cycle of returning expensive and scarce alloying metals to production, ensuring their economy and reducing the cost of alloys without compromising quality.

It is known that the modification of large masses of liquid metal with various additives significantly increases the quality of products and their service life. The work [25] proposes a technology for the modification and microalloying of reducing coatings using secondary raw materials or industrial waste. This can affect the quality of the restored surface of parts made of various materials operating under conditions of wear, high temperatures, loads, as well as a reduction in the cost of the finished product.

In connection with the constant rise in prices for imported materials used to obtain wear-resistant coatings, research related to the recycling of metal production wastes is increasingly developing. The work [26] provides a technology for producing diffusion-alloyed alloys for induction surfacing from metal production wastes in the form of cast shot and shavings (formed during shot blasting of products, during mechanical processing of parts during their manufacture) in mobile powder media for the purpose of surfacing protective coatings working in conditions of intense abrasive wear. First, metal production waste is subjected to diffusion alloying (saturation with boron) in a rotary electric furnace, and then, to surfacing with ready alloyed waste. Protective coatings after this technology had an increased hardness, a reduced wear rate.

Due to the high level of alloying with scarce expensive components, the new alloys are distinguished by an increased cost, which hinders their introduction into serial production. An effective solution to reduce the cost of finished products in the production of cast heat-resistant alloys is to involve in the production cycle waste generated in the manufacture of semi-finished products and parts from these alloys. In work [27], a multistage technology for producing wrought heat-resistant nickel alloys from industrial wastes (shavings, skull, beads, scrap) is presented, which consists in the preliminary preparation of these wastes (cleaning from impurities and contaminants, *i.e.*, refining), smelting in a vacuum induction furnace with a branded mixture with using substandard waste and smelting of VZh175 and VZh172 brand alloys. This technology makes it possible to reduce the cost of new alloys without deteriorating their quality.

Steel, resistant to abrasion and corrosion, is of considerable interest in industrial applications as a means of minimizing the costs associated with product failure and/or short replacement. These grades of steels contain alloying elements that increase their resistance to abrasion and corrosion. However, their benefits are currently at a potentially prohibitive cost; thus, high-performance steel products are more technically complex and more expensive to manufacture.

While these methods have proven effective in improving the performance of more expensive, high-performance steel components, they are not economically feasible for relatively inexpensive steel products. The development of new technologies is needed. Therefore, in work [28], the technology of using wastes of the automobile industry for the formation of a ceramic coating on the surface of a steel product is given. This solution as an innovative and effective way allows us to obtain products with low cost, with improved properties while reducing the need for raw materials for coatings or alloying, as well as reducing the environmental burden on the environment.

In order to organize large-scale production of highly melted composite materials, cheap and affordable fillers are needed. In Refs. [29–31], the authors point out that in addition to traditional mineral fillers (chalk, kaolin, *etc.*), production wastes can be used for this purpose, the disposal of which is not only cost-effective, but also contributes to solving the problem of environmental protection. Among cheap mineral fillers, one of the leading places belongs to the carbonate type filler. On the territory of Kazakhstan, on the Mangyshlak Peninsula, there are large deposits of shell rock, developed on an industrial scale. Currently, shell rock is used mainly in construction. When it is cut into blocks and slabs, up to 40% of fine waste is formed that is carried by the wind, clogging up the soil and air. In addition, millions of tons of filter cake sludge with a high content of calcium carbonate accumulate in the form of sugar production waste, and only a small part of it is used in agriculture as fertilizer. Therefore, a promising solution to the problem of environmental protection can be the use of finely dispersed waste from the stone-cutting production of shell rock and marble as well as carbonate waste from other industries as a modifier, filler to obtain new composite materials.

The development of technology at the present stage requires the development of new or modification of already known materials with the necessary functional and operational properties. Currently in Russia, there are no economically viable industrial technologies for recycling highly dispersed waste from electrometallurgical and blast furnace industries, which are characterized by a high iron content (up to 40%). As a result, the disposal of sludge is carried out by moving them to dumps. The paper [32] considers the possibility of processing industrial waste of metallurgical production in order to obtain new iron-containing materials that can be used as a feedstock for electrometallurgical and blast-furnace production. The result of this research is the final products: powder, granular and briquetted materials, which can be used as raw materials for metallurgical production.

Microsilica, *i.e.*, a waste of silicon production, is actively used in the production of dry building mixtures, concrete, foam concrete, cement, ceramics, facing slabs, paving slabs, curbs, tiles, refractory masses, rubber, and coatings. Such cast iron obtains good abrasion resistance, increased cohesion in the layers, high strength, increased anti-corrosion resistance, durability and frost resistance. It is used in bridge construction, road construction, in the construction of residential and industrial facilities, dams and dams, drilling platforms and wells, collector routes [33].

3. Description and Results of the Study

In connection with the above, the authors of this article focused on microsilica (microsilica) as a modifying additive for aluminium alloys.

Aluminium alloys are widely used in industry and intensively analysed [34–43]. The above mentioned aluminium alloy was chosen as the object of study, since the main component of the alloy (Al) is characterized by a high prevalence and in terms of production it takes the second place after iron used for the production of iron and steel, and, accordingly, has a low cost. In addition, aluminium and its alloys are characterized by low specific gravity, high thermal and electrical conductivity, which is up to 60% of copper electrical conductivity [44]. The mechanical properties of pure aluminium are not high; it is very ductile and easy to roll, stamp and extrude. However, the aluminium alloys themselves are hardened by heat and deformation. In addition, a distinctive feature of aluminium alloys is their high corrosion resistance. All of these factors contribute to wide using aluminium alloys in me-

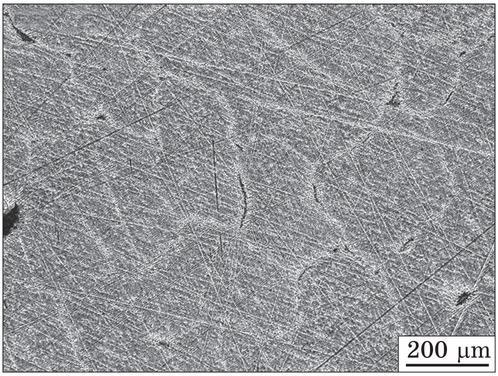


Fig. 1. Microstructure of the original aluminium alloy AD31 (×100) [45]

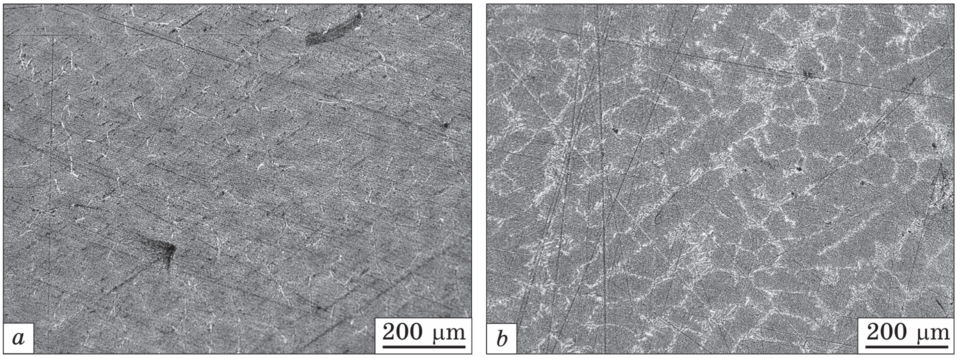
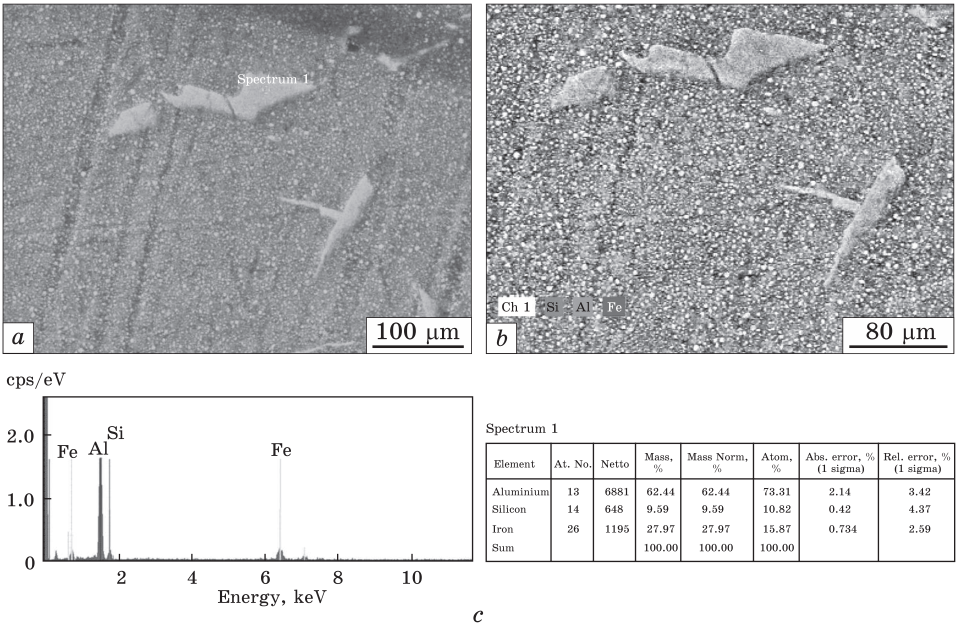


Fig. 2. Image of the microstructure of an AD31 aluminium alloy modified with 1% (×100): silica fume (*a*); corundum Al_2O_3 (*b*) [45]



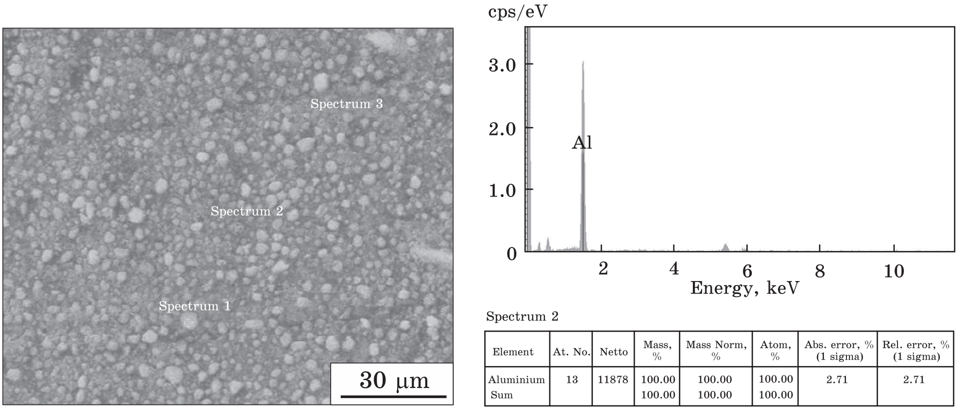
Spectrum 1

Element	At. No.	Netto	Mass, %	Mass Norm, %	Atom, %	Abs. error, % (1 sigma)	Rel. error, % (1 sigma)
Aluminium	13	6881	62.44	62.44	73.31	2.14	3.42
Silicon	14	648	9.59	9.59	10.82	0.42	4.37
Iron	26	1195	27.97	27.97	15.87	0.734	2.59
Sum			100.00	100.00	100.00		

Fig. 3. Sample of AD31 aluminium alloy modified with silica fume: image of the microstructure, ×1513 (*a*); distribution of elements on the investigated surface, ×1513 (*b*); energy dispersive analysis of the alloy and quantitative analysis (*c*) (Ch 1 is the scanning channel of the energy dispersive detector for studying the microstructure) [45]

Table. **Composition of a sample of aluminium alloy at point *1* (spectrum *1* — the place of investigation with an energy dispersive etector according to Fig. 3, *a*) [45]**

Element	Al	Si	Fe	Total
Mass.%	62.44 ± 2.14	9.59 ± 0.42	27.97 ± 0.73	100.00
At.%	73.31 ± 3.42	10.82 ± 4.37	15.87 ± 2.59	100.00



Spectrum 2

Element	At. No.	Netto	Mass, %	Mass Norm, %	Atom, %	Abs. error, % (1 sigma)	Rel. error, % (1 sigma)
Aluminium	13	11878	100.00	100.00	100.00	2.71	2.71
Sum			100.00	100.00	100.00		

a *b*

Fig. 4. Microstructure of the new alloy basis (×4847) (spectra *1–3*) [45]

chanical engineering (for bearing alloys, as semiconductor materials used in the production of atomic energy *etc.*).

Thus, studies were carried out on the effect of modifying additives of microsilica on the structure and phase composition of the aluminium alloy AD31. The melting of the aluminium alloy AD31 (Fig. 1) was carried out with the addition of 1% of waste powder of silicon production ‘Silicium Kazakhstan’ (microsilica grade MK-85) and fine powder of corundum Al2O3 as modifiers (emery waste of cutting discs) in a chamber electric resistance furnace in corundum crucibles (at a temperature of ≈900 °C). We revealed the positive effect of modifying additives from industrial waste on the structure and properties of the alloy: the grain is refined, the phase composition changes, and the properties of modified aluminium alloys improve.

The samples of modified aluminium alloy obtained as a result of melting were subjected to sample preparation: grinding, polishing, and etching in a reagent to reveal the structure of aluminium alloys. Further, the samples were examined on a Leica optical microscope (Fig. 2) and a Zeiss scanning electron microscope (Fig. 3) [45].

The waste of silicon production ‘Silicium Kazakhstan’ used to modify the sample of aluminium alloy AD31, as shown by the results of energy dispersive analysis, consisted of silicon dioxide, which, in turn, contained a small amount of impurities, and, in general, was microsilica grade MK-85. The modifying addition of the second sample of the AD31 aluminium alloy was the waste of cutting discs, *i.e.*, corundum powder Al_2O_3.

As can be seen from the photo of the microstructures of the initial sample of the AD31 aluminium alloy (Fig. 1) and the modified aluminium alloy samples (Fig. 2), as a result of the modification of the microstructure, they are refined (visually) by 4–6 times.

As a result of modifying an aluminium alloy with microsilica, the alloy composition changes slightly, Fe and Si impurities appear (see Table).

Figure 4 (*a*, *b*) shows a photo of the base of the new modified alloy, the spectrum and numerical values of the elements [45].

As the analysis of the AD31 aluminium alloy modified with silica, the fume has shown:

(1) iron impurities in the aluminium alloy form $FeAl_3$ compounds (dark purple precipitates in the photo of microstructures);

(2) light structural components that have a characteristic form of broken (trapezoidal) curved lines (Fig. 3, *a*) in the presence of silicon and iron, triple phases α (Al–Fe–Si) and β (Al–Fe–Si) are formed;

(3) silicon in a small amount forms a solid solution with aluminium (Fig. 3, *b*), while, as literature sources show, it dissolves in solid aluminium only in a limited amount [46];

(4) with a sufficient content of impurities, a skeletal eutectic Al + α (Al–Fe–Si) appears; a protective film is formed on the surface of the modified alloy, containing Al_2O_3 and SiO_2 in its composition, and is characterized by relatively good resistance in many corrosive environments, especially in oxidizing ones; as the authors of Ref. [47] point out, only alkalis (1) and hydrofluoric acid (2) can destroy an oxide film of the indicated composition:

$$SiO_2 + 2NaOH \rightarrow Na_2OSiO_2 + H_2O; \tag{1}$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O. \tag{2}$$

Aluminium alloy AD31, modified with Al_2O_3 corundum powder (Fig. 2, *b*) also changed the phase composition and structure:

(1) due to the introduced Al_2O_3 impurities, a large amount of Al + α skeletal eutectic is formed;

(2) in an insignificant amount (due to the presence of impurities in the composition of the original AD31 alloy phases α and β are formed as light structural components with a characteristic form of broken (trapezoidal) curved lines.

Thus, as a result of modification by industrial waste with microsilica, aluminium alloys change their structure and phase composition. The microstructure is refined, the mechanical properties are improved (the strength properties are increased), which can be further regulated using various regimes of the heat treatment [48, 49]. This concerns not only aluminium alloys, but also a wide spectrum of both three-dimensional [50–54] and two-dimensional [55–58] materials.

4. Conclusion

Mechanical engineering, metallurgy are the most metal-consuming industries. The economy, reliability and durability of the manufactured products predetermine the consumption of metal, energy and labour costs. Therefore, in science there has appeared a direction of using industrial waste to obtain traditional and non-traditional materials.

The use of microsilica as a modifying additive to metal alloys leads to the creation of new materials with special properties that differ from world analogues in improved performance characteristics and meet the needs of science-intensive industries in the modern materials [59, 60].

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ДО ПИТАННЯ ПРО ЛЕГУВАННЯ ТА МОДИФІКУВАННЯ СТОПІВ: ВИКОРИСТАННЯ ВІДХОДІВ ВИРОБНИЦТВА ДЛЯ СТВОРЕННЯ НОВІТНІХ МАТЕРІАЛІВ

На великих і потужних промислових (приватних або державних) підприємствах світу, зокрема, Казахстану, РФ і деяких інших пострадянських (і не лише) країн, випуск продукції все ще здійснюється за застарілими технологіями з високим утворенням відходів. При цьому неорганізованим і технічно необґрунтованим є складування та зберігання їх (змішуються відходи не лише різного хімічного складу, але й класу небезпеки), що унеможливлює подальше ефективне перероблення їх. Підвищене ж перероблення багатьох промислових і побутових відходів є не лише економічним, але й значно поліпшує екологічну обстановку та істотно понижує витрати природньої сировини, а також зменшує застосування для зберігання відходів дефіцитних земель [1]. Автори даної статті провели літературний огляд з даної тематики та зробили спробу використання мікрокремнезема (мікросиліки) як відходу кремнійового (силіційового) виробництва для створення нових матеріалів із спеціальними властивостями. Це відноситься до області експериментального дослідження структур, фаз, структурних складових задля розуміння процесів легування, модифікування, дифузії тощо. Усвідомлення фізичного міркування з точки зору металофізики у вивченні природи та кінетики процесів фазових перетворень, легування та модифікування уможливлює застосування фізичних методів дослідження для вирішення дослідницьких і технологічних завдань у металознавстві та матеріалознавстві з метою прогнозування та зміни необхідного комплексу властивостей. Методом дослідження у даній статті слугує електронна мікроскопія як найбільш простий та швидкий метод черпання інформації про мікроструктуру, елементний склад і розподіл компонентів в об'ємі зразка.

Ключові слова: легування, мікролегування, модифікування, модифікатор, легувальний елемент, відходи виробництва.