Development of Technology for Extracting Titanium from Titanium-Magnetite Ore Concentrates

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Abstract— The article addresses the issues of metallurgical processing of iron- bearing ores of the republic. For the preparation of enriched minerals for metallurgical processing, agglomeration, rolling, etc., can be used. The dissertation analyses various methods of preparing iron-containing raw materials for metallurgical processing in order to choose an economically feasible method. The possibility of producing metallized concentrates from iron-containing ores with low iron content is considered in order to prepare them for metallurgical processing. It has been shown that the efficiency of the process of producing metallized concentrates is significantly influenced by the following factors: ore composition, physical and chemical properties of ore, the possibility of producing pellets, the type and consumption of reducing agent, etc.

Keywords— metallurgy, titanomagnetite, titanium, agglomeration, pellet, ore processing, recovery process, coke.

1. INTRODUCTION

The experience of the most developed countries in the world constantly reminds us of the well-known truth - the world does not stand still, the reforming and democratization of society, modernization and renewal of the country is not a one-time, one-time, continuously ongoing process. Especially considering that we live in the 21st century - the century of globalization and the Internet, when the level of intellectual work is of paramount importance, the scale and severity of competition in the world market is growing [1-5].

The ongoing crisis in the global financial and economic space, the growing decline in demand and the uncertainty of the situation on the commodity markets are reflected in the slowdown in economic growth in most countries, the reduction in investment activity and capital outflow - this is the reality that we see today.

The current situation in the world economy indicates that these processes will continue in the near future. Only the rejection of our outdated production facilities and enterprises, whose products already do not arouse any interest on the international level, and tomorrow will not cause any interest in our domestic market, the construction of modern enterprises and high-tech complexes-locomotives of economic growth and at the same time the consistent implementation of a deeply thought-out and balanced program modernization of the basic industries and the necessary infrastructure - this is the policy that is in demand, it is precisely the policy that is needed today, which can and should create for us a reliable access to the world export market, a stable financial and economic situation, a high level and quality of life of the country's population [6-12].

For centuries, the production of ferrous metals has been carried out in a two-stage scheme. a) reduction of oxides to metal with complete separation of waste rock and partial transfer of some elements into metal (carbon, manganese, silicon, phosphorus, sulfur, etc.); b) refining metal to obtain steel of a given composition. The first stage is realized mainly in blast furnaces, the second - in converter, open-hearth or electric arc steel-making furnaces. The two-stage process, in spite of its apparent complexity, has advantages that are unsurpassed in comparison with the direct production of steel from ore [13-20].

Currently, the production of metallized raw materials is growing in all continents of the globe, and for the Middle East countries this direction is predominant [21].

Scientific novelty:

- for the first time investigated the influence of the main technological parameters: temperature, composition and consumption of the reducing agent, pressure, etc.) on the rate and completeness of the reduction of titanomagnetite ores of the Tebinbulak deposit;

- considered the theoretical foundations, thermodynamics and kinetics of solid-phase reduction of iron oxides and other metals by various reducing agents;

- experimentally determined the main technological parameters of the process of reduction of titanomagnetite ores in Uzbekistan.

Protected provisions: - theoretical foundations of the process of solid-phase reduction of iron and other metals contained in the complex titanium-magnetite ores of Uzbekistan:

- determination of the influence of the main technological parameters on the recovery rates;

- determination of the main technological parameters of the process of solid-phase reduction of complex titanium-magnetite ores with various reducing agents.

Scientific and practical significance of research results [22-30]:

- it was found that titanium-magnetite ores of the Tebinbulak deposit can be processed by reduction methods with acceptable technical and economic indicators;

- theoretical foundations for the reduction of iron oxides and other materials from complex refractory polymetallic ores, such as titanium-magnetite ores of the Tebinbulak deposit, have been developed;

- investigated the influence of various factors on the speed and completeness of recovery processes;

- the optimal technological parameters for the recovery of complex polymetallic ores with various reducing agents have been determined;

- the implementation of theoretical research and practical recommendations in the industry will make it possible to obtain import-substituting and export-oriented steels from local raw materials on the basis of full localization of production. The reserves of ores at the Tebinbulak deposit will last for about 100 years, which will allow Uzbekistan to save significant currency funds. Moreover, given the needs of the Central Asian market and high prices for metals, this gives Uzbekistan the opportunity to receive significant foreign exchange from steel exports.

- theoretical developments and practical research results, as well as some methodological recommendations presented in the dissertation, are reflected in textbooks for bachelors in the courses "Introduction to the direction", "Waste-free technologies in metallurgy", "Steel production", "Direct production of iron from ore "," Electrometallurgy of steel and ferroalloys ".

2. ANALYSIS OF EXISTING TECHNOLOGIES

Considering the modern possibilities of obtaining metallized raw materials, one should keep in mind several of the following preliminary provisions [31-40].

The recovery process outside the blast furnace is carried out for different purposes: often this process in the literature (especially in foreign) is called preliminary reduction, and the materials recovered in this way are partially recovered or previously recovered. This terminology is imprecise. For the further use of these materials (in blast-furnace, steel-smelting or other aggregates), the main importance is how much metal was formed during the preliminary reduction of oxides. Meanwhile, the magnitude of the reduction rate does not determine the amount of metallic iron formed during the reduction. Therefore, it is more correct to call such materials metallized or partially metallized, and evaluate their quality by a special value - the degree of metallization, which represents the ratio of the content of metallic iron in the material to the total (i.e., the sum of oxidized and metallic iron) iron content in it,% :

$$\eta_{met} = (Fe_{met}/Fe_{total})\ 100$$

Knowing the total iron content and the degree of metallization, one can always determine the amount of metallic iron (by weight) entering the unit.

Recently, the concept of the effective degree of metallization is also sometimes used.

$$\eta^{eff}_{met} = \eta_{met} = +6[C]$$

where [C] is the carbon content in the metallized material,%.

The formula is obtained empirically, but its meaning is clear. The carbon present in the metallized material can, during remelting, reduce the residual oxygen of iron oxides $FeO + C = Fe + CO$, and one part of iron requires $12/56 = 0.214$ kg C. Assuming that the amount of total iron is close to 100 %, every five parts of carbon gives an additional percentage of metallization.

Indirect recovery today can be applied in industry in four directions:

1) obtaining partially metallized iron ore materials for use in blast-furnace smelting;

2) obtaining metallized materials for their remelting into steel in steel-making and electric steel-making units;

3) metallization of iron for processing complex polymetallic ores;

4) reduction of iron oxides in order to obtain iron powder.

The latter direction is specific, special monographs are devoted to it, therefore it will not be considered here. The rest should be briefly discussed from the point of view of their prospects [41].

The idea of smelting metallized iron ore materials (mainly pellets, less often sinter and ore) in a blast furnace essentially contained one obvious idea: reducing the consumption of reducing carbon by reducing the amount of carbon going to direct reduction, and the resulting reduction in heat consumption on this process. It is known that, in addition to meeting the heat needs of the smelting (in this case, they say that coke is a source of carbon-heat carrier), coke also plays another important role - it participates in the formation of cast iron, that is, it restores hard-to-recover (practically not reduced by a reducing gas) oxides of silicon, manganese, and iron (in this case, they speak of a carbon-reducing agent).

However, iron can also be reduced with gas, and direct reduction (actively manifesting itself at high temperatures - above 900-1000 ° C) of iron takes place mainly only because iron is not completely reduced by gas to metal in the high temperature zone, but partially remains in the form of oxides (mainly FeO). For the conditions of modern smelting (a relatively low consumption of coke and, therefore, a relatively small amount of reducing gas - the product of combustion of coke carbon), this situation is apparently natural and evidence of this is the closeness to the equilibrium composition of the gas with respect to FeO in the temperature zone 800-1000 ° C [42].

The use of natural gas (as well as fuel oil and other additives), as a result of which the amount of reducing gas increases sharply, mainly due to hydrogen, significantly reduced the degree of direct reduction of iron rd. Several formulas have been proposed that relate the amount of natural gas blown into the furnace and the change in the degree of direct reduction. All these formulas are either based on the processing of experimental data, or built with some assumptions from theoretical premises. However, even in modern

blast furnaces operating with a high proportion of natural gas in the blast, 20-35% and more of all iron in the charge materials is reduced directly, that is, using solid carbon. Reserves for further decreasing rd. due to an increase in the proportion of natural gas, they are practically exhausted, since this growth is associated with a sharp violation of the gas-dynamic and thermal regimes of melting [43].

Perhaps the only major reserve for further reducing the degree of direct reduction of iron is the supply of pre-metallized materials to the furnace. In the 60s, in some research organizations (TsNIICHM, St. Petersburg Polytechnic Institute, Moscow Institute of Steel and Alloys in the CIS, IRSID in France, etc.), calculations were performed to determine the effect of penetration of metallized materials. Using the example of a simplified calculation, we will show their essence (the calculation is carried out per 1 ton of cast iron) [44].

3. THE NATURE OF THE PROPOSED TECHNOLOGIES

3.1 STATE OF THE ART BEYOND DOMAIN RECOVERY IRON ORE AND PIG IRON PRODUCTION

The initial data for the calculation (the removal of dust from the furnace is neglected): composition of cast iron: 4% [C]; 1% [Mn]; 1% [Si]; 0.1% [P]; original coke consumption 500 kg / t; carbon content in coke 85%; ash content in coke 10%; basicity of the slag $CaO: SiO_2 = 1.2$. The ratio between the carbon fired in the lances, C_f and the direct reduction carbon Cu is 3: 1. Carbon consumption 500-0.85 = 425 kg / t. The amount of carbon going into gas, i.e. minus carbon going into pig iron, 425-40 = 385 kg/t.

The amount of carbon consumed in direct reduction; 385 0.25 = 96kg / t; m of this carbon for the reduction of hard-to-reduce oxides (Mn, Si, P), carbon is consumed {[Mn] X12 / 55 + [Si] -24 / 28 + [P] -60/62} 10 * = (0.218 + 0.857 + 0, 1) 10 = 11.75kg~12kg / t. Therefore, the direct restoration of iron requires 96-12 = 84 kg / t [45-50].

With the degree of metallization of the blast furnace charge η_{met} = 40% and assuming (with a small error) that the decrease in the consumption of carbon used for the direct reduction of iron is proportional to the degree of metallization of the charge, we obtain a decrease in the consumption of carbon: 84-0.4 = 33.6kg / s. Coke savings due to this will amount to 33.6: 425-100 = 7.9% [51].

Along with this, there is a saving of heat due to the endothermic effect of the reaction of the reduction of iron oxide with carbon (we will conventionally assume the reduction of free iron oxide):

$$FeO + C = Fe + CO-152.67 \text{ MJ, or } 12.72 \text{ MJ / kg C.}$$
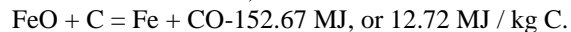
With a decrease in carbon consumption by 33.6 kg, the heat saving will be 12.72-33.6-0.001 = 428 kJ / kg of cast iron. Typically, the heat balance of blast furnace smelting (calculated taking into account the actual heat consumption for the process) ranges from 5.5 to 6.7 MJ / kg. Assuming a heat consumption of 6.3 MJ / kg, we obtain a heat saving 428: 6300-100 = 6.8%.

Finally, there is one more reason for saving coke - a decrease in the slag yield due to a decrease in the supply of ash with coke. The total coke savings are not yet known to us. Having set the approximate value of saving 15%, we get a decrease in the amount of ash 500-0.15-0.1 = 7.5 kg / t. In addition, there is no need to introduce flux for slagging this amount of ash: 7.5-1.2 = 9 kg. We get a total reduction in the amount of slag of 16.5 kg. According to the data, for every 1 kg of slag it is necessary to spend 0.2 kg of coke. Consequently, the savings in coke due to a decrease in the amount of slag will be 16.5X X 0.2 = 3.3 kg of coke, or 3.3: 500-100 = 0.7%. And so, the total saving of coke will be 7.9 + 6.8 + 0.7 = 15.4%, or, as it is commonly believed, 3.85% of coke for every 10% of the metallization of the charge.

The above calculation is, of course, approximate and allows one to obtain only the order of the required value. The calculations performed in the works were carried out according to the complex method of A. N. Ramm, however, they could not give more accurate results, since unknown indicators were taken as the initial data and, above all, the degree of indirect reduction of Ri, the degree of use of the chemical energy of the gas and heat losses. Therefore, these calculations gave approximately the same results as those given by us.

Experimental melts carried out in the CIS, USA, Canada, Japan have shown that for every 10% of the metallization of the charge within the range of 0-50%, the increase in productivity under various conditions is 4-7%, and the decrease in coke consumption is 5-7%. The efficiency of using metallurgical raw materials in blast furnaces is mainly associated with the search for a rational method of their production [52].

Two conclusions can be drawn from the above results: 1) in most cases, the predicted coke savings turned out to be less than those achieved in practice; 2) with an increase in the degree of metallization (especially above 30-50%), the "specific" savings in coke (ie, savings attributed to 10% metallization of the charge) monotonously decreased. The second circumstance cannot be explained at all from the point of view of the accepted structure for calculating the coke economy, since regardless of the previously achieved degree of metallization of the charge, a new portion of metal should result in the same, as before, saving carbon and heat due to a further decrease in the degree of direct reduction [53].

When using the Ackerman - Pavlov principle, with an increase in the metallization degree, the "specific" saving of coke does not decrease, but increases, since with the perfection of melting and an increase in the heat efficiency of the process, a greater amount of heat is saved.

Until now, a decrease in the specific saving of coke in a blast furnace with an increase in the degree of metallization of the charge has not found a real explanation. Meanwhile, it becomes clear if we take into account other factors accompanying the smelting of metallized raw materials in a blast furnace. Let us consider this issue in more detail [54].

Metallization of raw materials leads to a significant increase in the "cold" (ie, during storage and transportation) and especially "hot" (ie, during heat recovery treatment) strength of the charge. The main destruction of iron ore materials during reduction corresponds to the hematite - magnetite phase transition. Less often, destruction occurs when FeO is reduced to metal. The formation of metallic iron significantly reduces the destructibility of the iron-ore charge, sharply reduces the formation of fines in the furnace and thus contributes to a noticeable increase in the furnace productivity. The increase in productivity varies for different melting conditions from 0.5 to 1.0% for each percentage of fines removed from the furnace. The effect of productivity growth when metallized materials are used in the charge therefore depends on a decrease in the amount of fines in the charge and is difficult to estimate in advance. The strength of metallized materials depends not only on the degree of metallization, but also on the technology of their production, which will be discussed below [55].

Productivity gains can be driven by other factors as well. When melting metallized materials, the heat exchange between the gas and the charge improves and intensifies, and, consequently, the heating of the charge. Mention should also be made of a possible change in the bulk density of materials and a subsequent change in the ore load on coke. Depending on the technology of preliminary metallization of the charge, the type of reducing agent and the achieved degree of metallization, the density of the particles of the metallized material may increase, decrease, or not change. When iron ore materials are reduced with gas, their density is the higher, the higher the degree of metallization. In the case of reduction with solid carbon, this tendency persists; however, the absolute density values are usually lower and may even be lower than that of oxidized iron ore materials. Finally, metallized pellets generally have a slightly higher density and bulk density than metallized agglomerate, and from this point of view, they more affect productivity than metallized agglomerate [56].

Sometimes, an increase in the iron content in the charge is taken as an independent factor influencing the indicators of blast-furnace smelting, equating the effect on the melting of metallized materials and metal additives. This approach is erroneous, since, unlike metallized materials, metal additives practically do not introduce slag-forming elements, and metallized materials have an increased content of not only iron, but also waste rock [57].

It should be noted that the increase in the productivity of the blast furnace is affected by a sharp decrease in the amount of fines in the charge and an increase in ore load due to coke saving. To take into account the increase in productivity when evaluating the efficiency of smelting metallized charge in blast furnaces, we will use production data. As follows from the above data, at a charge metallization degree of 20–40%, an increase in furnace productivity by 15–25% is achieved [58].

An increase in productivity associated with an increase in the hot strength of the charge manifests itself only at low degrees of metallization of the charge, since with a further increase in the degree of metallization, the strength of the charge materials changes little. The subsequent increase in productivity is associated only with the removal of solid fuel from the charge and this explains the decrease in the "specific" increase in productivity with an increase in the degree of metallization.

The increase in productivity affects the consumption of coke by reducing heat losses. Taking heat losses equal to 20% (calculated using the true heat balance method) and a productivity gain of 25%, we obtain the maximum reduction in heat consumption (and, consequently, coke consumption savings): 5 or 1.25% for every 10% of the metallization of the charge. Along with this, we will take into account a slight decrease in the temperature of the blast furnace gas during melting of metallized raw materials (by 30-40 ° C), which can also lead to a coke saving of 1%. Then the total saving of coke when melting a metallized charge, having $\eta_{met} = 40\%$, will be 5.0-5.5% for every 10% of metallization of the charge, which, apparently, is close to the limiting value of coke economy. It is important to note a decrease (with an increase in the degree of metallization above 30-40%) in the share of coke savings associated with an increase in the productivity of the blast furnace. This is illustrated in Figure 1, which shows the lines of change in coke savings and its components associated with various determining factors.

Curve 1 corresponds to a decrease in coke consumption as a result of a decrease in the degree of spinning and calculations, the coke saving is proportional to the degree of metallization of the charge.

Curve 2 corresponds to a decrease in coke consumption as a result of a decrease in heat losses through the walls and the top.
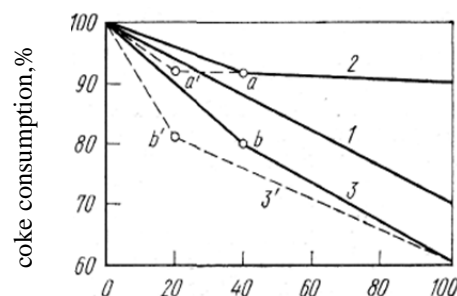
metallization degree, %
Figure 1. Influence of the degree of metallization of the charge on the consumption of coke in a blast furnace.

Practice shows that a decrease in the temperature of the blast furnace gas tends to decrease only at the initial degrees of metallization and, reaching a sufficiently low value, then practically does not change. This makes it possible to summarize the savings in coke caused by a decrease in losses through the top and walls, one indicator, although their reasons are different: in the first case, it is an increase in the water equivalent of the charge; in the second, it is an increase in the productivity of the furnace. Curve 2 has two sections: the first section is a noticeable decrease in coke consumption and the second is a small savings in coke. Curve 3 is the sum of curves 1 and 2. It is easy to see that the inflection point in curve 3 (b ') corresponds to the corresponding point a on curve 2, and the position of point a can vary depending on the technological conditions of melting in the furnace, mainly from hot strength of charge materials and their bulk density [59].

Apparently, a shift of the point, and to the ordinate line, is possible, i.e., obtaining materials with high hot strength at a zero degree of metallization (for example, obtaining wustite pellets). With a large fuel shortage, it may be advantageous to reduce the fuel consumption for metallization to a minimum with obtaining strong wustite pellets upon reduction and corresponding savings in coke in the blast furnace.

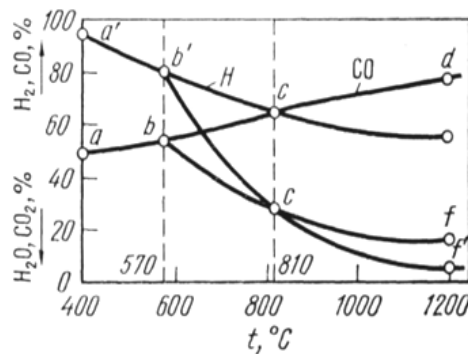Equilibrium conditions are graphically shown in Fig.2.

Figure 2. Equilibrium diagrams Fe-O-CO and Fe-O-H_2

Naturally, the one shown in Fig.2 the diagram is simplified. With an increase in the degree of metallization, the technical and economic results of blast furnace smelting change according to a more complex law and straight lines are transformed into curves, but the trends do not change. The most important conclusion, following from the diagram, about the presence of two sections characterizing the efficiency of melting of metallized materials, of which the initial one has higher melting rates, remains valid under any melting conditions. The point, or, more precisely, the inflection area, in accordance with the above reasoning, can move, but most often it is in the range of metallization values of 30-40%. Therefore, from the point of view of penetration efficiency, it is advisable to use metallized materials with a metallization degree of 30-40% [60-62].

Let us note in conclusion that the legitimacy of the reasoning about the very important contribution of the increase in the hot strength of the charge materials to the value of the resulting economy of coke was confirmed by the melting of iron-wustite cakes, carried out by employees of the Moscow Institute of Steel and Alloys at the plant. Petrovsky. Due to the long-term storage of metallized pellets in the open air, the degree of their metallization decreased from 20 to 1-2%. However, when the YUGOK sinter was replaced with iron-wustite cakes, a 7% coke saving was obtained due to the higher hot strength of the latter.

A few words should also be said about the reduction processes during the melting of metallized materials in a blast furnace.

When metallized materials are used in a blast furnace, the amount of higher iron oxides, which are easily reduced by furnace gas, is sharply reduced in the charge. When the degree of metallization of the charge is 30-40%, trivalent iron is practically absent in the charge, and all oxygen is in the lowest, most difficult to reduce iron oxide. In addition, the amount of furnace gas sharply decreases with an increase in its reduction potential, this entails certain changes in the course of the reduction process.

3.2 DETERMINATION OF THE DEGREE OF METALLIZATION IN THE PROCESSING OF IRON-CONTAINING RAW MATERIALS

Smelting an agglomerate containing 55% Fe in the form of magnetite; coke consumption 500 kg, carbon content in coke 85%, in cast iron 4%.

II. Melting of metallized agglomerate containing 62% Fe, including 24.8%. Fe_{met}h (η_{met} = 40%) and 47.5% FeO. Higher iron oxides are absent. Coke consumption 400 kg.

Option I. The content of magnetite is 55: 0.724 = 76%, the oxygen content of iron oxides in the agglomerate is 76-55 = 21%. Sinter consumption 94: 55 = 1.7 t / t of pig iron. The amount of oxygen in iron oxides is 1.7·0.21·22.4 / 32 = 260 m³ / t. The amount

of gasified carbon of coke is 500-0.85-40 = 385 kg / t. The amount of CO generated in the furnace is 385-22.4 / 12 = 730 m^3 / t. The amount of reducing agent per unit of oxygen of iron oxides 730: 260 = 2.8 m^3 / t.

Option II. The consumption of metallized raw materials is 94: 62 = 1.52 t / t, the oxygen content in iron oxides is 47.5-16 / 72 = 10.3%. The amount of oxygen of iron oxides in the charge is 1.52-0.103-22.4 / 32 = 110 m^3 / t. The amount of gasified coke carbon is 400X X0.85-40 = 300 kg / t. The amount of CO generated in the blast furnace is 300-22.4 / 12 = 560 m^3 / t. The amount of reducing agent per unit of oxygen of iron oxides in the charge is 560/110 = 5 m^3 / t.

Thus, when melting metallized raw materials, the "specific" amount of reducing gas increases in comparison with melting under normal conditions, almost twofold. This is due to the fact that the amount of oxygen in iron oxides decreases to a greater extent than the consumption of coke. This leads to a well-grounded conclusion about the inexpediency of smelting metallized raw materials in blast furnaces using natural (raw or converted) gas, fuel oil and other hydrogen-containing additives. At the same time, the use of carbon-containing substances (powdered coals) is quite acceptable [63].

Indirect reduction during the melting of metallized raw materials is, therefore, associated with the reduction of iron oxide FeO by a gas containing a large proportion of CO at low and moderate temperatures, and in order to obtain maximum coke savings, it is necessary that no less the amount of FeO than under normal melting conditions. This is facilitated by the improved gas-dynamic conditions in the furnace shaft due to the higher hot strength of the charge and the higher "specific" yield of the reducing gas, and is hindered by the higher density of the metallized charge.

In any case, a decrease in the amount of gasified oxygen in the charge inevitably means a significant decrease in the amount of carbon dioxide in the blast furnace gas and a corresponding drop in the degree of utilization of the reducing ability of the gas in the blast furnace. This objectively follows from the equilibrium conditions for the reduction of iron oxide FeO with carbon monoxide:

$$FeO + nCO = Fe + (n - 1) CO + CO_2.$$
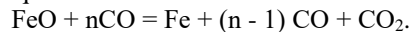
At 800 ° C, the equilibrium of this reaction corresponds to the content of 70% CO and 30% CO_2 in the gas phase. Then (n-1): 1 = 70:30; n = 31 / 3.

Consequently, the limiting degree of CO utilization at 800 ° C will be

$$\eta_{co} = \frac{1}{2.1/3+1} = 0,3$$

With an increase in the reduction temperature, the equilibrium degree of CO utilization will be even lower. The real degree of utilization of the restorative capacity will, of course, be lower.

Some experts consider a noticeable decrease in the degree of use of the reducing ability of gas to be a significant disadvantage of the technology for melting metallized raw materials in a blast furnace, which prevents the introduction of this technology. In no case can one agree with this. The degree of utilization of the reducing ability of gas is neither the only nor the main indicator of the efficiency of blast-furnace smelting. The main goal of the blast-furnace process is to obtain the maximum amount of high-quality metal with the minimum consumption of raw materials and energy. Operation with unsaturated values of the degree of gas utilization can be considered optimal for these conditions, if the maximum productivity and minimum coke consumption are achieved. In this case, you should think about the most rational ways to use the top gas. One of such solutions, for example, may be the tandem technology proposed at TsNIICHM, a process in which two blast furnaces, one of which melts metallized and the other a conventional charge, operate in one block, and the top gas of the first furnace is rich in reduction. components, after cleaning from oxidants or without it, is blown into the second furnace [64].

Metallized charge for blast furnace smelting can be obtained by various methods: reduction with gas in a shaft furnace, reduction with a solid reductant on a conveyor roasting machine, combined reduction with solid and gas reductants in a tube furnace. In this case, you should pay attention to the following circumstances:

1) any iron ore material can be metallized - ore, agglomerate, pellets, as well as combine agglomeration processes with metallization, creating a reducing atmosphere in the charge layer;

2) for metallization, you can use both solid and gaseous reducing agent, as well as a combination thereof;

3) it is economically feasible to use as a reducing agent non-scarce and inexpensive fuels;

4) the efficiency of metallization increases with a decrease in the amount of waste rock in iron ore material.

Let us concretize these provisions.

Apparently, one should not prove that it is preferable to combine agglomeration of small ores with metallization of the product than to obtain oxidized not only materials, and then to reduce them. And the reason is that the two processes are combined in one, the recovery of the previously obtained agglomerate or pellets is associated with certain diffusion resistances, since a sufficiently dense final structure of the agglomerate and pellets significantly slows down the recovery process and increases the consumption of the reducing agent.

3.3 OPPORTUNITIES FOR USING RECYCLED MATERIALS IN THE CHARGE OF STEEL-MAKING FURNACES

The emergence of a second (after cast iron) source of primary iron in the form of metallized pellets for a given volume of steel smelting and full consumption of scrap leads to displacement from the balance of the basic materials of the cast iron industry, a change in the structure of steelmaking processing and, consequently, to a change in the cost of smelting all steel in the industry. In

this case, the effect of factors that make steel smelting cheaper and more expensive cannot be assessed by a simple comparison of costs according to the calculation items of the corresponding redistribution, since they are functions of the complex impact of changes in the technological regimes of steel smelting and structural shifts in the industry [65].

In the last decade, this direction has been widely implemented on an industrial scale and is most often defined as "direct production of iron." Its attractiveness is caused by the simultaneous influence on the development of metallurgy, at least, four factors.

1. A sharp decline in world reserves of coking coal.

Certain regions are almost completely devoid of deposits of coking coal, and even countries that had large enough reserves of this fuel are expressing concern about the decrease in these reserves. In blast-furnace smelting, it is impossible to completely replace coke with another type of fuel; therefore, a process involving non-blast metal production is of interest. A new scheme for obtaining metal, metallized materials - steel allows you to completely do without coal coke [66].

2. Significant increase in requirements for steel quality. Industry experience convincingly shows that steel smelted using metallized materials (most often instead of scrap) has better properties. There are still no comprehensive explanations for this phenomenon. The main reason is seen in the fact that metallized materials, unlike scrap, practically do not contain undesirable impurities, especially impurities of non-ferrous metals. In this sense, one speaks of the "original properties" of metallized materials or "original charge", emphasizing that metallized materials have not previously passed the stage of metallurgical remelting.

From this point of view, apparently, it should be added that metallized materials also practically do not contain gas dissolved in the metal and non-metallic inclusions.

3. The rise of metallurgy in developing countries has caused the need to create cost-effective low-power plants that would be able to flexibly change the production program and the range of metal. At the same time, aggregates typical for the traditional scheme are generally more economical the larger they are. The new scheme of metallurgical production made it possible to solve the problem of creating economical "mini-factories" with a productivity of 0.1-1.0 million tons. In some cases, it is advisable to build such factories not only in small, but also in large industrial countries [67].

4. Significant environmental benefits. In contrast to the traditional scheme, the new version guarantees complete safety for the environment.

For melting in steel-making furnaces, it is believed that metallized materials should have a metallization degree of at least 80%, i.e. the degree of recovery is quite high. The efficiency of metallization in this case will strongly depend on the recovery method and the unit used. Extensive industrial research has been carried out to date in three types of units: a) mine installations of continuous and periodic (retorts) action; b) apparatus with a fluidized bed; c) tubular rotary kilns and combined installations such as conveyor machine - tubular kiln. For the first two methods, gas is used as a reducing agent - the product of the conversion of natural gas or liquid fuel, or the product of gasification of solid fuel. The latter method is characterized by the combined use of solid and gaseous reducing agents. To date, tube furnaces have not found widespread use. Most of the metallized materials are currently produced in shaft-type furnaces. A significant number of different methods of obtaining metal in these units (Midrex, Proofer, Agmso and others) do not differ in principle (perhaps, except for the method of obtaining spongy iron in periodically operating retorts). The general laws of the process are as follows.

1. Recovery is carried out in the solid-phase region. There are no liquid products from the process. Consequently, the waste rock from the metal is not separated, and all the resulting material is sent to the steelmaking unit. Based on the conditions for the economy of the steel-smelting process (the minimum amount of slag), strict requirements are imposed on the content of waste rock in the initial iron ore raw material - its amount in the metallized material should not exceed 5%, and, therefore, in the initial oxidized material should be less than 3%. It is easy to determine that the iron content in the original1 iron ore concentrate, for example magnetite, must be at least 0.724 - 70%, where 0.724 is the iron content in magnetite, equal to 168: 232.

Thus, the first condition for the feasibility of the process under discussion is the presence of an easily enriched iron ore material, which makes it possible to obtain a concentrate containing at least 69-70% iron [68].

2. When reducing in the solid-phase region, the removal of harmful impurities (P, S, As, Cu, etc.) practically does not occur. Meanwhile, to obtain high-quality steel in electric furnaces without a significant waste of energy, low initial contents of these impurities are required. Therefore, the second condition for carrying out the process of obtaining steel from metallized materials is a low (less than 0.01-0.02%) content of harmful impurities in the original iron ore concentrate.

3. The product of the reduction of iron ore materials in shaft furnaces (iron ore pellets are mainly used as raw materials for reduction) is the so-called spongy iron, so named because of its peculiar appearance. Fresh-reduced metallic iron is actively sintered, forming bunches and conglomerates, which negatively affects the process in shaft furnaces (mainly, the movement of material in the furnace is hampered and the uniformity of its heat and reduction treatment is disturbed). Since the intensity of metal sintering increases with increasing temperature, the maximum process temperature should not be, as a rule, higher than 750-900 ° C. If the process temperatures are low, then the recovery rates decrease and the technical and economic indicators deteriorate.

4. In shaft furnaces, the reducing gas is supplied to the layer from the periphery. The larger the transverse dimension of the shaft furnace, the more difficult it is to achieve uniform gas distribution over the bed cross section and, consequently, uniform heat and reduction treatment of the bed. With a certain cross-section of the furnace, this becomes generally impossible. Therefore, shaft furnaces have a limit on productivity, amounting to 400-600 thousand tons / year.

5. Freshly reduced spongy iron has an increased tendency to oxidizability and pyrophoricity, and the lower recovery temperature, the more these properties. Therefore, in the production of metallized pellets special measures should be taken to suppress oxidation and self-ignition.

Thus, the process of obtaining steel from metallized pellets can be carried out only under certain conditions: the presence of readily-milling and non-harmful iron-ore materials; inexpensive sources of reducing gas; cheap electricity; the feasibility of building mini-factories.

### 3.4   THE RATE OF OCCURRENCE OF CHEMICAL REACTIONS AT REDUCTION OF OXIDES

For practical purposes, it is not enough to know that the investigated reaction is fundamentally possible, as thermodynamics tells us about. It is equally important to have information about the time (rate) of this reaction. Reduction of oxides, as a rule, is a complex and multi-stage process, which includes a variety of independent phenomena with all the laws inherent only to them. The interweaving of these patterns creates a rather complex overall picture, which is often extremely difficult to decipher.

In the general case, when considering any reduction, it is necessary to solve two main questions: 1) in which medium an act of chemical interaction takes place, leading to the removal of oxygen from the oxide; this or that sequence of separate stages of the process depends on it; 2) depending on the scheme of the process, which stage is the slowest, which determines the overall rate of the recovery process as a whole [69].

In the general case, the interaction, accompanied by the removal of oxygen from the metal oxide, can occur in the gas phase, at the metal - oxide or lower oxide - higher oxide interface.

Sometimes the main place of interaction changes during the course of the reaction, making it even more difficult to analyze it. However, it is most often assumed that the place of oxygen removal from the oxide is unchanged. The main theories for the reduction of metal oxides are based on this basic assumption.

A. Baikov, apparently, was one of the first to propose an integral scheme of the mechanism for the reduction of oxides:

$$MeO = Me + 1/2O_2$$

$$\frac{B + 1/2O_2 = BO}{MeO + B = Me + BO}$$
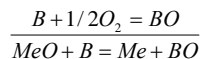
The process consists of two stages: the dissociation of the metal oxide MeO and the oxidation of the reducing agent from the oxide with oxygen. The undoubted advantages of this model are simplicity and convenience for calculations. The time of the emergence of the theory is the first twenty years of our century, but even now this scheme is widely used in calculating heat consumption during recovery processes and compiling heat balances of these processes.

The accumulation of experimental data led to the conclusion that the dissociation of oxides plays a minor role in the reduction process, since the real elasticities of the dissociation of oxides, which are known to be a measure of their strength, are so small that they can be neglected. The lower the dissociation elasticity, the stronger the oxide.
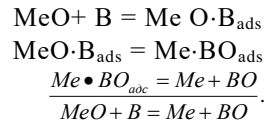
So, the logarithm of the dissociation elasticity of FeO at 700 and 1700 ° C is - 20.8 and - 6.9, respectively, MnO - 32.7 and - 12.3, etc. Most of the oxides that are important in metallurgy have the same properties, with the exception of some higher oxides of some metals. For example, upon dissociation $3Fe_2O_3 = 2Fe_3O_4 + ½ O_2$, the equilibrium partial pressure of oxygen becomes equal to atmospheric at 1383 ° C, during dissociation $6Mn_2O_3 = 4Mn_3O_4 + O_2$ - at 940 ° C, and during dissociation of $4MnO_2 = 2Mn_2O_3 + O_2$ - even 460 ° C. However, there are very few such oxides.

Reaction	N, kJ	kJ /mol of gas
$SiO_2=SiO_2(г)$……………………………………..	588	588
$SiO_2=Si +O_2$…..………………………….…..	911	911
$SiO_2=Si + 2O$………….……..………......................	1407	704
$2SiO_2=2SiO + O_2$………….……..………………..	790	790
$2SiO_2=SiO + O$………….……..…………………	643	643
$SiO_2=Si_r + 2O$…..………….……..…………………	1861	620
$SiO_2=Si_r + O_2$…..………….……..…………………	1365	683
$SiO_2=Si_r + O$…..………….……..…………………	1058	529
$2SiO_2=2SiO_r + O_2$………….……..………………	1621	540
$2SiO_2=Si_{r(2)} + 2O_2$………….……..……...………	2415	805
$2SiO_2=Si_{2(r)} + 4O$…..………….……..…..…………	3406	681

Taking into account that the most likely reaction is characterized by a minimal thermal effect, attributed to a mole of a gaseous product, the eighth reaction is preferable, and not the second, as is usually accepted.

This new interpretation of the role of dissociation has not yet been sufficiently developed, but calculations show that at temperatures below 1300 ° C, the dissociation of lower oxides of iron and manganese does not play any significant role.

In the mid-30s, a new concept of the mechanism of the reduction of oxides appeared, known as the adsorption-autocatalytic theory. G. I. Chufarov, O. A. Esin, P. V. Geld, S. T. Rostovtsev took an active part in its development. It is expressed by the following scheme:

$$MeO + B = Me\ O \cdot B_{ads}$$
$$MeO \cdot B_{ads} = Me \cdot BO_{ads}$$
$$\frac{Me \bullet BO_{adc} = Me + BO}{MeO + B = Me + BO}.$$

The reduction reaction takes place in three stages: adsorption of a reducing gas on the surface of the reduced oxide, a chemical reaction on the surface of the oxide, and desorption of the reduction product. In the adsorption-autocatalytic theory, the place of interaction is considered to be the gas - oxide surface interface; autocatalysis was found in some cases at an early stage of reduction.

The new theory was, first of all, valuable because it laid the basis for a real circumstance - the need for direct contact of the reducing gas with the reduced metal oxide. This made it possible to use the regularities known from physical chemistry, physics and surface chemistry to assess the mechanism and kinetics of reduction. Some experimental results were explained, such as the data of Stalhane and Malmberg, on the disproportionately significant effect of the addition of oxidizing agents ($CO_2 > 2$ and H_2O) on the rate of reduction reactions; The new theory confirmed in this case the role of adsorption; it was shown that the molecules of gaseous products of reduction, being more active adsorbents, occupy the most active sites on the surface of the reduced oxide, sharply reducing the degree and rate of reduction. Other examples can be cited.

However, obtaining new experimental data, especially with the help of the latest research methods, continuously revealed the limitations of the adsorption-autocatalytic theory. It is known that the adsorption capacity of substances decreases with increasing temperature. To obtain reliable results, experiments were carried out at low temperatures, but this did not correspond to the real conditions of metallurgical processes. The role of the processes of delivery of the reducing gas to the surface of the iron ore material and the removal of reduction products has not been denied, but has not been sufficiently evaluated. There were some methodological errors in the experiments. We add that the phenomenon of autocatalysis is also rarely observed.

Modern ideas about the mechanism of recovery of pieces of iron ore material distinguish, first of all, the variety of processes that occur during recovery. Among them, it should be emphasized, unfortunately, the underestimated until now role of solid-phase processes - reactions and diffusion in solids. As will be shown, for almost all conditions (starting with a reduction of 50 - 60%), the processes in the solid phase are limiting.

4. CONCLUSION

For centuries, the production of ferrous metals has been carried out in a two-stage scheme. a) reduction of oxides to metal with complete separation of waste rock and partial transfer of some elements into metal (carbon, manganese, silicon, phosphorus, sulfur, etc.); b) refining metal to obtain steel of a given composition. The first stage is realized mainly in blast furnaces, the second - in converter, open-hearth or electric arc steel-making furnaces. The two-stage process, despite its apparent complexity, has advantages that are unsurpassed in comparison with direct production of steel from ore.

Firstly, in this way it is possible to obtain a metal of a given grade from any iron ore material, regardless of the content of rocks and harmful impurities in it. This makes it possible to involve in the metallurgical redistribution practically all rocks related to the concept of "iron ore".

Secondly, the units used in the two-stage scheme have a very high unit performance. The daily productivity of a modern large blast furnace is 10-12 thousand tons of pig iron.

Thirdly, the presence of some elements in cast iron is favorable for steelmaking processing.

In parallel with the significant improvement of the two-stage process, there is a continuous search for effective methods for the direct production of metal from iron ore material. Hundreds of patents have been registered worldwide for the production of steel and iron from ores. Some of them have found a certain distribution in industry over the past 15-20 years. In a number of publications of scientific, technical and popular science, there is an increased interest in out-of-blast-furnace production methods for the direct production of metal from ore.

At present, the production of metallized raw materials is growing in all continents of the globe, and this direction is predominant for the Middle East countries.

5. ACKNOWLEDGMENT

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