Liquid-Phase Sintering of Aluminum-Based Alloys with Additive of Products of Direct Reduction of Iron Ore

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Abstract. The method of direct reduction by hydrogen for iron ores of the Lensk ore field were considered in the work, the particle size, bulk density, a corner of a natural slope of products of grind and reduction of ore were defined, morphological researches, the X-ray spectral microanalysis of particles of the reduced ore material were conducted. Aluminum-based sintered powder materials with the addition of the recovered ore are obtained. It is established that temperature increase of sintering leads to reduction of residual porosity of the compacts. Samples with additive of the reduced ore keep the correct geometrical form practically in all studied ranges of changes of temperature of sintering and content of additive. Measurement of hardness of the sintered composite aluminum-based alloys with additive of powders of the reduced demonstrate that higher values of hardness are observed at structures from 14.4 and 18.7 weight % of additive of the reduced ore.

1. Introduction

One of the priority directions of researches in the field of complex and deep processing of natural and technogenic mineral raw materials in the Russian Federation is creation of highly effective energy saving technologies of a ore preparation schemes, development in the field of dry technologies of enrichment [1]. Need of increase in efficiency, profitability and ecological purity of processes of enrichment has caused improvement of methods of processing of metal ores [2], application of methods of direct reduction of iron [3]. Process of direct reduction of iron of oxides proceeds according to the schemes Fe₂O₃ → Fe₃O₄ → FeO → Fe (above 570 °C), at the same time, from three gases-reducers (H₂, CO₂, CH4), technically the best is hydrogen [4]. Iron of direct reduction plays more and more important role in the steel-smelting industry [5]. Works on improvement of methods of direct reduction with use of gas-reducer as in the form of mixes of gases [6, 7], and pure hydrogen are conducted [8, 9]. Reduction of iron in the environment of hydrogen is applied to receiving nanodimensional particles for use as biologically active powders [10], catalysts [11], magnetic materials [8].

Melting in electric furnaces of products of direct reduction of iron in the form of the metallized pellets is widely applied to receive high-quality steel with the low content of harmful impurity, the increased physicomechanical properties [12]. Due to the increase in ecological and economic requirements to
processes of processing of iron ores continuous works are conducted on improvement of methods of direct reduction [13, 14]. At the same time, according to researches of the German experts, from the main innovative production technologies of steel, until 2050 the most perspective is the technology of direct reduction of iron ore by hydrogen. This conclusion was drawn on the basis of the multicriteria analysis of production technologies of steel with use of 12 various criteria from five categories ("Technologies", "Society and policy", "Economy", "Safety and vulnerability" and "Ecology") [15].

The method of direct reduction is widely used for receiving metal powders of iron. Use of products of direct reduction for complex alloying of powder alloys, including on the basis of aluminum is considered relevant. The research of regularities of sintering of systems on the basis of aluminum gains great practical value in connection with development of powder metallurgy of alloys on its basis. It is known that introduction of firm refractory particles of the second phase to plastic aluminum increases its durability, hardness, thermal stability and wear resistance at simultaneous decrease in coefficients of friction and thermal expansion [16]. Use of aluminide of intermetallic compounds of aluminum with transitional metals as the strengthening phase – is a perspective way of creation of new functional materials on the basis of aluminum.

In this regard the special relevance is acquired by studying of the processes happening at liquid-phase sintering, their contribution to volume changes of powder bodies to the interacting components. The research of processes of sintering of aluminum with additives of powders of transitional metals is represented the scientific problem which is closely connected with a practical problem of creation of new generation of composites on the basis of aluminum.

2. Samples and technique of tests

Samples from show of ferromanganesian ores in Munduruchchu riverheads (the left inflow of the Amga River) of the Lensk ore field of the Sakha (Yakutia) Republic were investigated. The texture of ores are massive and cavernous, is more rare colloform and oolitic. Ores are put by iron oxides - goethite, hydrogoethite and manganous oxides - manganous peroxide, psilomelane and manganin.

Cracking and crushing of ore were made with application of a hydraulic press of IP-500 and disk laboratory mill of Fritsch Pulverisette 13. Division according to fineness of mechanical mixes of grains was made according to GOST 27562-87 by a dry method on a screen grate of Fritsch Analusette 3 set with sizes of openings 2; 1; 0.5; 0.25; 0.125 and 0.063 mm (the module sit 2). Direct reduction of the crushed fineness class ore less than 0.063 mm was carried out in the environment of hydrogen at a temperature of 950 °C within 40 min. [17]. The reduced material was exposed to a doizmelcheniye and enrichment by method of magnetic separation [18].

The humidity of ore material was defined according to GOST 12764-73. The X-ray spectral quantitative element analysis was carried out by means of a X-ray fluorescent spectrometer of SRS-3400 Bruker. The bulk density of ore material was defined according to GOST 25732-88. The main properties of the processedore material are given in table 1.

| Property                  | Crushed ore | The reduced and enriched product |
|---------------------------|-------------|----------------------------------|
| Size of grain, mm         | less 0.063  |                                  |
| Real density, g/sm3       | 3.05        | 3.50                             |
| Bulk density, g/sm3       | 0.84        | 1.27                             |
| Humidity, %               | 2.2         | 2.1                              |
| Corner of a natural slope, | 48          | 39                               |
| Content of iron, weight % | 34.44       | 42.81                            |
3. Studying of morphology of particles of the reduced product

Morphological researches of particles of ore material were conducted on samples of the reduced and enriched fineness material less than 0.063 mm by means of a raster electronic microscope of JEOL JSM - 7800F.

As it shown in the figure 1, a, particles have the splintered form caused by a receiving method - mechanical crushing in a disk mill. At bigger increase (figure 1, b) is observed the expressed relief of a surface of particles, formation of a spongy surface in the course of reduction in hydrogen. Particles have high porosity owing to evaporation of vapors of water from their volume at reduction of oxides of iron.

At increase by 10 000 times, it is visible (figure 1, c), that particles consist of the accrete sintered components, the surface of subparticles has a lamellar structure of various degree of development, thickness of plates varies from tens to 100 nanometers.

![Figure 1. Morphology of particles of the reduced ore material of a class of fineness less than 0.063 mm. Increase: a – 300; – 5000; b – 10000.](image)

4. X-ray spectral microanalysis of particles of ore material

The X-ray spectral microanalysis of particles of ore material of a class of fineness less than 0.063 mm was carried out by means of a power dispersive spectrometer of Swift ED 3000 Oxford Instruments of the scanning electronic microscope of Hitachi TM3030.

The general view of ore material of a class of fineness less than 0.063 mm with sites of scanning by the microprobe before reduction is shown in the figure 2. It is established that before reduction of ore material the content of iron is 36.24 weight %, content of oxygen 34.45 weight %. After reduction the maintenance of elements made: iron 45.76 weight. %; oxygen 29.02 weight % (figure 3, table 2).

![Figure 2. General view of ore material: a - before reduction; b - after reduction.](image)
Figure 3. Power dispersive range of particles of ore material. a - before reduction; b - after reduction.

Table 2. The maintenance of elements in particles of ore material.

| Chemical element | Compound, weight % |
|------------------|--------------------|
|                  | Before reduction   | After reduction |
| Fe               | 36.24              | 45.76           |
| O                | 34.45              | 29.02           |
| C                | 7.36               | 6.02            |
| Si               | 13.01              | 12.9            |
| Al               | 8.34               | 6.29            |
| K                | 0.6                | -               |

Rather high content of oxygen can be explained with the increased content in ore of hardly reparable oxides of aluminum and silicon. Individual particles have non-uniform chemical and mineral composition, are put from grains of various phases. Heterogeneity of structure, existence of inclusions of oxides of other elements complicates process of reduction and enrichment of ore raw materials [19].

5. Liquid-phase sintering of aluminum-based alloys with additive of powder of the reduced iron ore
In the process of receiving the sintered composites on the basis of aluminum it was used standard powder of aluminum of the ASD-1 brand (TU 48-5-226-87), powder of the reduced iron ore of a class of fineness less than 0.063 mm.

Powders were mixed up in the "mixer a drunk barrel" during 2 h. Previously they were dried in the vacuum dryer SNVS on the mode: 1.5 h at 150 °C in the conditions of a forevacuum. Formation of cylindrical samples with the diameter of 10 mm high was made in a steel compression mold, the initial porosity was 20%. Sintering was carried out in the SNVE furnace in a vacuum with a pressure of 0,1*10⁻³ Pa and temperature from 700 to 900 °C.

Density of the pressed samples was defined by a geometrical way. In case of loss or distortion of the correct geometrical form the method of hydrostatic weighing was applied.

Hardness according to Brinell was estimated according to GOST 9012-59 on the Omag Affri 206RTD device.

According to results of the researches of powder systems conducted earlier, aluminum – transitional metal (Al–Ni, Al–Ti, Al–Fe, Al–Cu), the area of concentration of metal-additive to 20 at % is of the
greatest scientific and practical interest. Taking into account it, alloys with the content of additive to 26.8 weight % were investigated.

The great influence on volume changes of powder bodies is exerted by the sintering mode. For the studied Al-Fe system allocation of a large amount of heat at formation of intermetallids is in evidence. Thermal explosion at emergence of a liquid phase can cause sharp changes of volume of pressing and loss of a form of a briquette. Besides, elimination of influence of the gases adsorbed and being in a time on process of sintering requires decontamination of a briquette.

Regulation of speed of heating and carrying out solid-phase annealing are necessary for prevention of loss of a form at a temperature that is lower than temperature of emergence of a liquid phase. At solid-phase annealing on a surface of particles of iron due to diffusion of atoms of aluminum the refractory intermetallic layer is formed. At further sintering this layer slows down process of alloy formation and reduces the speed of allocation of warmth at the time of emergence of a liquid phase. At enough particles of refractory additive during solid-phase annealing the solid-phase skeleton of pressing providing constancy of a shape of a powder body at liquid-phase sintering is formed.

Proceeding from the aforesaid, sintering of samples on the basis of powder of aluminum of the ASD-1 brand was carried out on the mode with vent solid-phase annealing at $t = 500$ °C within 30 min. then temperature of the furnace rose up to the sintering temperature with a speed of 15 °C/min.

It is established that samples experience shrinkage in all range of temperatures of sintering from 650 to 800 °C and keep the correct geometrical form practically in all studied ranges of changes of temperature of sintering and content of additive. Growth of volume of powder bodies was observed among the sintered briquettes with the content of additive of 26.8% at a temperature of sintering of 650 °C. Sweating of a liquid phase on a surface of samples is observed that demonstrates low wettability of particles of a firm phase liquid, and as a result, it leads to difficulty of process of liquid-phase sintering. Temperature increase of sintering up to 700 °C leads to reduction of residual porosity of the compacts, to elimination of sweating of a liquid phase by surfaces of samples and that demonstrates the best wettability of a firm phase liquid that it is possible to explain by aluminothermal reaction of a postreduction surface oxide films on particles of the reduced ore.

At the same time, increase in concentration of additive up to 22.8 and 26.8 weight % leads to increase in residual porosity of the sintered composites at a temperature of sintering of 750 °C with the subsequent its decrease at a temperature of sintering of 800 °C. For structures with the content of additive from 9.8 to 18.7 weight % at a temperature of 800 °C occurs distortion of a form of the compacts.

![Figure 4. Dependence of residual porosity p the sintered alloys from sintering temperature.](image-url)
Figure 5. Dependence of hardness of the sintering alloys on sintering temperature.

The residual porosity of the sintered alloys is one of the major factors influencing structure and mechanical properties of powder materials. Results of measurement of hardness of the sintered samples are given in figure 5. Rather high residual porosity of the sintered alloys leads to decrease in hardness.

The increase of content in alloy of the strengthening intermetallic particles depending on amount of the alloying additive brings to increase in hardness. But at the same time, there is an increase in residual porosity of alloys. Mutual influence of these factors leads to the fact that higher values of hardness were revealed among structures with 14.4 and 18.7 weight % of additive of the reduced ore.

With increase in temperature of sintering the hardness of the sintered alloys of all structures increases and that is connected with reduction of residual porosity of alloys.

6. Conclusion
The scheme of grinding and crushing of ore was developed. The technique of reduction of ore in the environment of hydrogen was fulfilled. The particle size distribution, bulk density, a corner of a natural slope of products of processing of iron ore were defined. By morphological researches, it was revealed that initial particles have the splintered form caused by way of crushing. Products of reduction of ore showed the expressed relief of a surface of particles, formation of a spongy surface. Particles consist of the accrete sintered smaller components, the surface of the sintered subparticles has a lamellar structure, thickness of plates varies from tens to 100 nanometers.

The X-ray spectral microanalysis of particles of the reduced ore material showed basic suitability of a method of direct reduction by hydrogen in relation to iron ores of the Lensk ore field.

The sintered powder materials on the basis of aluminum with additive of powder of the reduced ore were received. It was established that temperature increase of sintering leads to reduction of residual porosity of the compacts, elimination of sweating of a liquid phase on a surface of samples that demonstrates the best wettability of a firm phase by liquid. Samples with additive of the reduced ore kept the correct geometrical form practically in all studied ranges of changes of temperature of sintering and content of additive.

Measurement of hardness of the sintered composite aluminum-based alloys with additive of powders of the reduced ore demonstrate that higher values of hardness are observed at structures about 14.4 and 18.7 weight % of additive of the reduced ore.
At completion of a technique, it is perspective to apply the method of direct reduction by ore hydrogen for receiving a concentrate with its subsequent application as the alloying additive for receiving the sintered aluminum-based alloys.

7. References
[1] Chanturia V A and Weisberg L A and Kozlov A P 2014 Enrichment of Ores vol 2 p 3
[2] Gil A Pillared 2010 Clays and Related Catalysts (New York: Springer)
[3] Robert Hunter 2005 Handling and shipping of «DRI/HBI» (VATECH, Moskau)
[4] Baykov A A 1961 Chosen works (Moskau.: Metallurgizdat)
[5] Kirichenko I S and Aleksakhin A V 2016 Young scientist vol 2 p 85
[6] Yi Ling-yun and Huang Zhu-cheng and Li Tie-hui and JIANG Tao 2014 Journal of Central South University vol 21 p 506
[7] Hai-bin Zuo and Cong Wang and Jie-ji Dong and Ke-xin Jiao and Run-sheng Xu 2015 International Journal of Minerals, Metallurgy, and Materials vol 22 p 688
[8] Oznur Karaagac 2013 Journal of Superconductivity and Novel Magnetism vol 26 p 1707
[9] Lei Guo and Han Gao and Jin-tao Yu and Zong-liang Zhang and Zhan-cheng Guo 2015 International Journal of Minerals, Metallurgy, and Materials vol 22 p 12
[10] Kirichenko S and Aleksakhin A V 2016 Young Scientist vol 2 p 85
[11] Shinkarev (ml) AA and Starshinova V L and Gnevashnev S G and Abdullin I Sh 2015 The Bulletin of the technological university T 18 vol 13 p 122
[12] Muscolino F and Martinis A and Ghiglione M and Duarte P 2016 Metallurgia Italiana vol 4 p 25
[13] Skorianz M and Mali H and Pichler A and Plaul F and Schenk J and Weiss B 2016 Steel research international vol 87 n 5 p 633
[14] Dì Cecca C and Barella S and Mapelli C and Ciuffini A F and Gruttadauria A and Mombelli D and Bondi E 2016 Metallurgia Italiana vol 4 p 33
[15] Weigel M and Fischedick M and Marzinkowski J and Winzer P 2016 Journal of cleaner production vol 112 n 1 p 1064
[16] Tarasov P P and Syromyatnikova A S 2015 News of higher educational institutions. Powder metallurgy and functional coverings vol 3 p 4
[17] Tarasov P P and Pryadeznikov B Yu and Petrov P P and Stepanova K V and Sleptsov O I 2017 Chemical technology vol 3 p 129
[18] Tarasov P P and Pryadeznikov B Yu and Petrov P P and Stepanova K V and Tarasov I P 2017 Science and education vol 2 (86) p 76
[19] Tarasov P P and Pryadeznikov B Yu and Petrov P P and Stepanova K V 2016 Science and education vol 3 (83) p 67