Ferromolybdenum Production according to Silicoaluminthermal Method: High Quality, Chemical and Granulometric Composition Stability

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The results of the thermodynamic analysis of silicoaluminthermal production process reactions using imported molybdenum roasted concentrate (MRC), ferrosilicium FeSi65, aluminum ferrosilicon FeSi55Al15 are stated. The key provisions through the production scheme of standard ferromolybdenum FMo60 first organized under PJSC “Dneprospetsstal” plant in a specially built workshop are presented.

Key words: *ferromolybdenum, molybdenum roasted concentrate, ferrosilicium, aluminum ferrosilicon, reaction crucible – furnace, technology, furnace slag, quality, ecology.*

PJSC “Dneprospetsstal” in Zaporizhzhia is one of the largest electric steel plants in Europe for the production of alloy and high-alloy steel and a wide assortment of different functionality. In total steel production a significant proportion is a corrosion-resistant, bearing, structural, tool steel, and heat-resistant, high-temperature steels and alloys, special steels and alloys (Table 1).

Table 1. Steel grades and chemical composition of electrical steel according to European norms (DIN EN) and international standards and GOST, melted at PJSC “Dneprospetsstal” with molybdenum content.

Standard designation DIN EN	Steel class	Steel grade acc. to GOST	Elements’ content, percentage by weight, %								
			Within limits			max					
			Cr	Mo	Ni	C	Si	Mn	P	S	N
DIN EN 10088-3	austenitic	07Х17Н12М2	16.5 18.5	2.00 13.00	10.00 13.00	≤0.07	≤ 1.00	≤2.00	≤ 0.045	≤ 0.030	≤0.11
DIN EN 10088-3	austenitic	05Х17Н13М3	16.5 18.5	2.50 3.00	10.50 13.00	≤0.050	≤ 1.00	≤2.00	≤ 0.045	≤ 0.030	≤0.11
DIN EN 10088-3	martensitic	39Х17М	15.5 17.5	0.80 1.30	-	0.33 0.45	≤ 1.00	≤1.50	≤ 0.040	≤ 0.030	-
DIN EN 10088-3 DIN EN 10272	martensitic	05Х13Н4М	12.0 14.0	0.30 0.70	3.50 4.50	≤.05	≤ 0,70	≤ 1.50	≤ 0.040	≤ 0.015	≤0.20
DIN EN 10088-3	ferritic	08Х17М	16.0 18.0	0.90 1.40	-	≤0.08	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.030	-

Along with those steels reported in Table 1, ferromolybdenum is widely used in the melting of corrosion-resistant nickel-chromium steels with nitrogen (15Х16Н2МВФБА), alloyed spring constructional steels (12ХНМДФ, 30ХНМФАб 40ХГНМ), tool steels (11Х4В2МФ3С2, Р12Ф5М, Р12Ф2Л8М3), heat-resistant and high-temperature steels and others.

Production of medium-alloy and especially high-alloy steels and iron-based alloys is accompanied by the consumption of large amounts of almost all kinds of ferroalloy [1], including the most expensive and scarce such as ferromolybdenum, ferrotungsten, ferrocolumbium and others. Domestic ferroalloy plants do not produce ferroalloys of the so-called small group, and the melting of the most groups of electro steels is produced using imported ferroalloys.

It should be noted that imported ferroalloys are not always characterized by stable chemical composition of the leading and doping elements, as well as granulometric composition [2]. However, in the last decade requirements on the quality of melted steel (stock material, rolled steel, forgings) have increased, including prescribed limit of the leading elements and permissible content of non-ferrous metals. The volatility of these ferroalloys characteristics of different suppliers creates certain difficulties in implementation of the relevant contract supply. A significant increase in prices for ferromolybdenum as the other ferroalloys was another factor that led to the technological and economic feasibility for organizing the ferromolybdenum production directly on the industrial site of PJSC “Dneprospetsstal”.

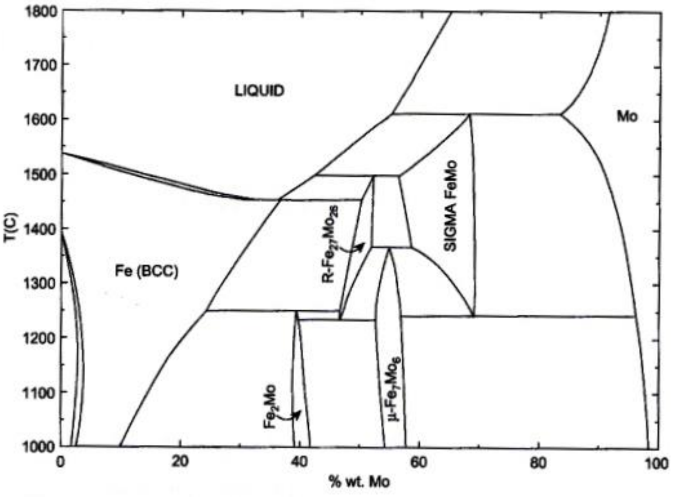
In early 2011 it was decided to build a shop for the production of ferromolybdenum from oxide molybdenic concentrate according to silika aluminumthermal technology. The shop construction and the successful development of technology enabled the company to ensure independently the production of high-quality and less expensive standard ferromolybdenum, thus significantly expanding the types and steel product range, as well as organizing commercialization of received ferromolybdenum.

Theoretical background of the chemical composition selection and melting technology of ferromolybdenum

In accordance with acting GOST 4759-89 ferromolybdenum is produced in six grades with Mo content min 60% in alloy of high grade ФМо60 and low grade ФМо50 min 50%. Doping elements in ferromolybdenum ФМо60 (W, Si, C, P, S, Cu, As, Sn, Sb, Pb, Zn, Bi) shall compose max tenths and basis point of a percentage. It is possible to analyze melting temperature, phase composition, at a first approximation based on binary system Fe-Mo.

Molybdenum refers to 4d- transition metal of Mendeleev's periodic law, has $4d^5 5s^1$ electron configuration and body-centered lattice (α=0,314 nm). Melting temperature is 2622°C and boiling point is 4840°C, density is 10,23 g/cm^2.

Diagram of system Fe-Mo balanced condition (computerised modeling) is shown in Fig. 1 [3].



Mo content, Percentage by weight, %

Fig. 1. Diagram of system Fe-Mo balanced condition [3].

As follows from the data, with increasing molybdenum content in the alloy solid solution of molybdenum in ferrum Fe(BCC) is initially formed followed by row of intermetallics Fe_2Mo, R-$Fe_{27}Mo_{26}$, μ-Fe_7Mo_6 and sigma phase of equiatomic composition of FeMo. At Mo content in alloys of 50-60% percentage by weight they correspond to ferromolybdenum of grades ФМо50-ФМо60, the microstructure in balanced condition is presented as intermetallic (μ-Fe_7Mo_6). Liquidus temperature of alloys with further increase in molybdenum content from 50 up to 60% percent by weight subsequent to the results of retrospective multipurpose instrumental analysis [4], increases up to 1550-1600°C, that is lower compared to the melting temperature of alloys of such composition according to the data of computerised modeling.

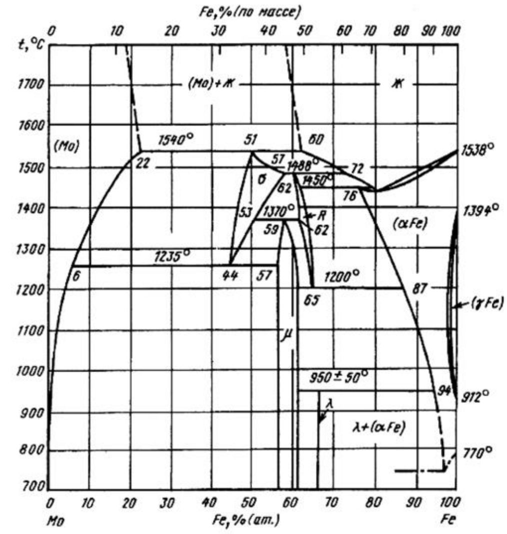


Fig. 2. Diagram of system Fe-Mo balanced condition (built by computational method according to metallographic, X-ray analysis and thermal study together with thermodynamic data [4].

Knowledge of molybdenum phase state makes possible to choose science-based refrigeration mode of ferromolybdenum ingot (block) and granulating characteristics with resulting commercial dimensional sizes. Out-of-furnace metallothermic ferromolybdenum melting technology provides usage of silicon molybdenic concentrate as one of the regenerator in the form of rich ferrosilicium FeSi65.

In the system of Mo-Si (Fig. 3) there are silicide phases: Mo_2Si (t_{sq}=2020°C), Mo_5Si_2 (t_{sq}=2180°C), $MoSi_2$ (t_{sq}=2020°C). In triplex system Fe-Mo-Si phase composition, concentrated fields of phases coexistance and oxides melting temperature will differ from alloys characteristics of Mo-Fe binary system. In this system FeSi amounts to 50-60%.

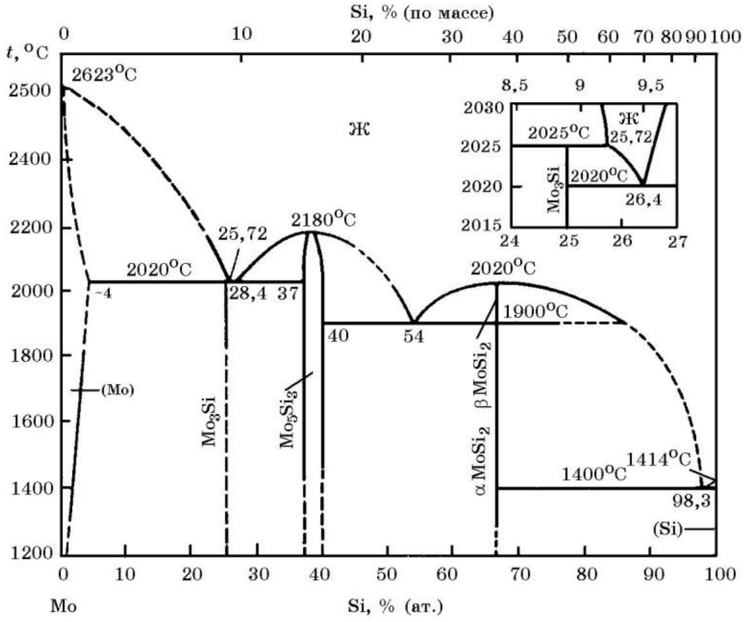


Fig. 3. Diagram of system Fe-Mo balanced condition [4].

At ferromolybdenum melting in PJSC “Dneprospetsstal”, together with rich ferrosilicium base regenerator the aluminium in the form of aluminum ferrosilicon alloy (FeSiAl, 55-60% Si, 15-20% Al, residual Fe) may be used. In this connection Mo-Al system analysis may be of interest [4].

Peculiarity of Mo-Al phase composition is six molybdenum aluminide from Al_2Mo (36% Al, 64% Mo) up to $AlMo_2$ (12% Al, 88% Mo). Practically all aluminides are subject to peritectic transformation, which temperature increases with an increase in molybdenum concentration in appropriate aluminides.

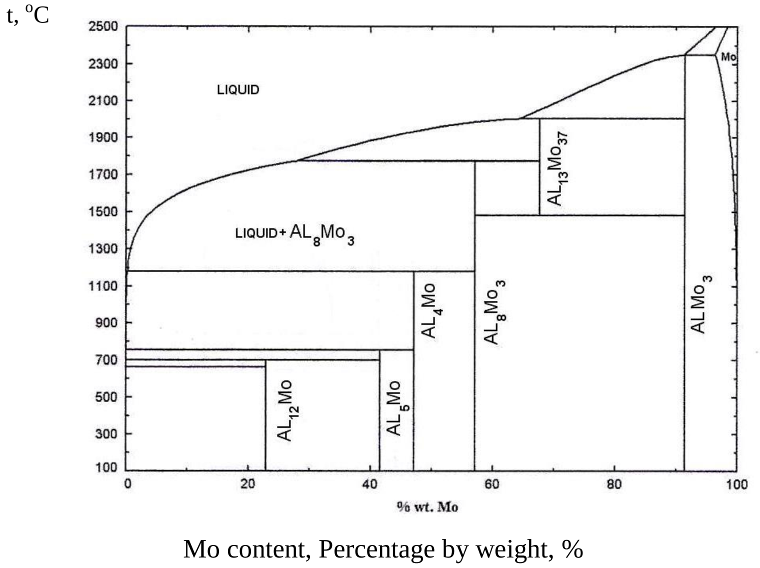


Fig. 4. Diagram of system Mo-Al balanced condition [3].

It follows from represented data that silicon and aluminium reduce melting temperature of alloys of the two binary systems. However, because of low content of Si and Al in ferromolybdenum of engineering grade melting temperature of ferromolybdenum is defined by molybdenum content.

Thermodynamic analysis of reduction reaction of molybdenum from MoO_3, MoO_2 oxides by silicon and aluminium

Molybdenum oxides characteristics.

Industrial production of ferromolybdenum of standard chemical composition, as mentioned above, is based on usage of molybdenic roasted concentrate (MRC)*[1] (90% MoO_3, 10% MoO_2) as molybdenum-containing material.

In binary system Mo-O there is a row of oxides: MoO_3 MoO_2, MoO, $Mo_{17}O_{47}$, $MoO_{2,80}$, $Mo_{80}O_{23}$. The extreme members of this row (basic oxides) are MoO_3, MoO_2. Most significantly, both oxides are thermodynamically-unstable and at elevation of temperature they may boil off (sublimate) and disproportionate.

Change dependency of reactions Gibbs energy the oxides formation MoO_3(1), MoO_2(2) of temperature is given below by formulas:

$$4Mo_{(r)} + 11/2O_{2(r)} = Mo_4O_{11(r)}$$

$$\Delta G^0_T = -2743000 + 853\ T,\ J/mole\ (T = 1000 – 1340K) \qquad (1)$$

$$Mo_{(r)} + O_2 = MoO_{2(r)}$$

$$\Delta G^0_T = -571800 + 166{,}2\ T,\ J/mole\ (T = 1070 – 1320K) \qquad (2)$$

MoO_3 oxide is a powder with green colour which becomes yellow at heating. Density of MRC powder is 4,69g/cm^3. Powder is melting at 795°C, boiling at 1155°C. Temperature dependence of general pressure of fumes under $MoO_{3(r)}$ has the form (MPa)

$$lgP_{gen}= -1545/T+0{,}526.$$

Pressure boost of fumes under MoO_3 increasing with temperature rise in the following sequence:

Dependence of dissociation tension according to reaction $MoO_2 \rightarrow Mo + O_2$ from temperature is described by the formula of MoO_2oxide

$$lgP_{O2}=-2564/T + 0{,}618\ (MPa)$$

Temperature, °C	734	785	814	851	892	955	1083	1151	
$P_{MoO3,}$ mm of mercury		1,0	2,0	10	20	40	100	400	760

Sublimation of MoO_3 takes place $(MoO_3)_{(T)} \rightarrow (MoO_3)_{(gas)}$ and is described in dependence on the temperature in the following formula (in atm):

$$lgP_{MoO3}\ (sublimation)= -15{,}11/T + 1{,}46\ lgT- 1{,}32\cdot 10^{-3}T+0{,}071.$$

The volatilization of MoO_3 oxide increases in the presence of water steam. Thus, at a temperature of 690°C and water steam of 798 kPa steam pressure MoO_3 increases approximately by 4 times because of formation of complex molecules $MoO_3{\cdot}H_2O$. With these properties of MoO_3, the increase in volatilization and possible losses of molybdenum oxides are connected.

According to data of R. Durrer, G. Folkert [5] the processes of deoxidation of molybdenum oxides by silicon and aluminium may be presented by reactions (3) and (4), respectively (cal/mole):

$$2/3\ MoO_3+Si=2/3Mo+SiO_2 \qquad (3)$$

$$\Delta G^0_{<1700^oC} = -95940 + 3{,}07TlgT – 8{,}800T,\ cal/mole$$

$$2/3MoO_3+4/3Al = 2/3\ Al_2O_3+2/3Mo \qquad (4)$$

$$\Delta G_{T\,=} - 150390 + 0{,}57TlgT + 11280T,\ cal/mole$$

By contrast, the reaction of ferrum deoxidation by silicon from FeO (5) is presented below (cal/mole):

$$2FeO + Si = 2Fe + SiO_2 \qquad (5)$$

$$\Delta G_{T\,=} - 159210 + 265TlgT + 396820T,\ cal/mole$$

In another sources, the cooperation of MoO_3 and MoO_2 is presented by reaction with silicon (6) and (7):

$$2/3MoO_3+Si = 2/3Mo + SiO_2 \qquad (6)$$

$$\Delta G^0_T = -469870 + 65{,}6T,\ J/mole,$$

$$MoO_2 +Si= Mo+SiO_2 \qquad (7)$$

$$\Delta G^0_T = -334040 + 19{,}5T + 11280T,\ J/mole,$$

with aluminium (8) and (9)

$$2/3MoO_3 + 4/3Al = 2/3Mo + 2/3\ Al_2O_3 \qquad (8)$$

$$\Delta G^0_T = -683660 + 51{,}16T,\ J/mole$$

$$MoO_2 + 4/3Al = Mo + 2/3\ Al_2O_3 \qquad (9)$$

$$\Delta G^0_T = -519140 + 5{,}15T,\ J/mole.$$

In these data, deoxidation of molybdenum oxides by aluminium is accompanied with higher thermal effect.

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[1] Molybdenum is represented by MoS_2 molibdenite in commercial ores

Ferromolybdenum melting technology

Ferromolybdenum is produced in crucible furnaces using imported molybdenum roasted concentrate (MRC) as molybdenum-containing material. Names of charge components and discharge intensity per heat in tones:

Ferromolybdenum concentrate (de-agglomerated)	(60-65% MoO_3)	4.940
Iron-ore pellets	min 65% Fe	1.480
Chip scrap or pimples hot working 2A		0.390
Ferrosilicium FeSi65 (de-agglomerate)	DSTU 4127)	1,470
Ferrosilicium FeSi55Al15	(55-60 % Si; 15-20 % Al)	0.500
Lime milled (hydrate of lime)	(mesh size max 3,0 mm)	0,413
Fume of gas cleaning nonorganic		0.413
Total		10.443

Burden constituents with humidity over 1% are subject to drying separately in drum kiln driers (length of 7 mm, diameter of 0,8 m) with the capacity of 7 t/h. In drying process the material humidity declines up to 0,5%. Smoke fumes with temperature 400°C discharge through the chimney (height of 45 m, diameter of 2,2 m). Dried concentrate, ferrosilicium, aluminum ferrosilicon and iron-ore pellets are subject to ball milling up to mesh size max 1 mm. De-agglomerated components pass to collecting bin of preparation room. From the collecting bins each component enters a self-discharging bucket resting on platform scale of driveless truck moving under the whole bin trestle.

After that each component from the corresponding bucket unloads to stirred tank (cylindrical closed container on the supports with off-gravity centered) where burden constituents are carefully stirred. Once-through charge in stirred tank executes according to weight 1/5 parts (2,0 t) of the whole material charge for one heat (10,0 t).

Metallothermic ferromolybdenum melting of beneficiated burden is carried out in crucible furnace of melting compartment of the build shop for ferromolybdenum production. The crucible furnace is a steel cylindrical pipe shell 2000 mm in diameter and 2000 mm in height, 20 mm in width. The crucible furnace is bushed with chamotte brick and furnished with taphole for flushing of slag. It is mounted on breezing, having a deepening in central part for acceptance of liquid ferromolybdenum originated during melting.

Once-through charge in furnace (material charge) is 1/5 of once-through multicomponent charge with adding of chip scrap (15.6 kg) on top of each charge. Batch charging in stirred tank and charge (25 furnace charges) is carried out until full filling of crucible furnace of all charge calculated for melting (10 t). After crucible covering with lined crown with dust and gas withdrawal the igniting charge is burned-up by spark ignition, that is noted as melting beginning of ferromolybdenum production by aluminum ferrosilicon method. The duration of melting is from 30 to 40 min. Physico-chemical processes which take place in crucible furnace were examined above at analysis of molybdenum reduction from MoO_3 and MoO_2 by silicon and aluminum using ferrous additions.

Received ferromolybdenum is characterized by a high stability according to input member content Mo and residual non-iron metals (Percentage by weight %):

Mo	Si	Cu	Sb	Sn	C	S	P
59,5-61,0	0.15-0.9	0.4-0.6	0.04-0.05	0.04-0.05	0.04-0.10	0.06-0.08	0.03-0.04

Slag of crucible furnace flushes through the taphole disposed closer to lower flange of crucible. Slag is characterized by stability of chemical composition (Percentage by weight %):

$Mo_{(gen)}$	SiO_2	FeO	Al_2O_3	CaO	MgO
0.06-0.15	62-68	7-11	9-13	6-8	1-3

Extracted block of ferromolybdenum (5 t) is cooled in the water cistern resulting in thermal stresses to the block fractures (0-10 mm).

Defined commercial mesh sizes of ferromolybdenum are received after granulating using the corresponding breaking machines СМД-106 (mesh size 2-10 mm), СМД-109 (mesh size 0-50 mm), and as packaged in big-bags 1 t in size ferromolybdenum send to the customer.

The equipment catching dust and gas in baghouse with self-pulsing ФРИР-1800 erected from the design provides purification efficiency of 98% and does not adversely affect the environment.

Conclusions

1. On the basis of theoretic generalization of data stated in literature and industrial experience melting of ferromolybdenum concentrate with ferromolybdenum roasted concentrate the thorough flow diagram and manufacturing processes of standard FeMo of highest quality level according to molybdenum leading element content and impurities of nonferrous metals were developed.
2. For the first time in Ukraine in PJSC “Dneprospetsstal” the production shop of ferromolybdenum by silicoaluminthermal production process using ferrosilicium ФС65 and aluminum ferrosilicon FeSi55Al15 was built according to designed project. Introduction of technology provides ferromolybdenum production with the extraction of molybdenum in alloy of 98%.

3. Annual output of ferromolybdenum provides needs of the works in fully and overstock is for sale that improves essentially the technical-and-economic indexes of molybdenum-containing steels production in terms of PJSC "Dneprospetsstal".

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