

Technology of Molybdenum Ferroalloys

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Chapter Outline

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12.1 PROPERTIES OF MOLYBDENUM AND ITS COMPOUNDS

Molybdenum belongs to the subgroup **Vlb** of the periodic table, and its **atomic weight is 95.94** with an external electron shell configuration **$4d^5 5s^1$** . Its physical properties correspond well to its position between its analogs chromium and tungsten: **a body-centered cubic (BCC) crystal lattice ($a = 0.314$ nm)**, **a 2622°C melting point**, **a 4840°C boiling temperature**, and a density of **10.23 g/cm^3** .

Molybdenum has many important uses in **stainless steels, alloyed cast irons, and superalloys**. It provides **necessary hardenability in many heat-treatable alloys, such as pressure vessel steels**. Together with tungsten, it is an important component of **high-speed steels and other tool steels and hard metals**. Molybdenum also improves the corrosion resistance of stainless steels and brittle fracture resistance for steels and cast irons (Voronov et al., 2000).

The Mo-Fe system equilibrium diagram is shown in Figure 12.1. Iron and molybdenum form several intermetallic compounds: **FeMo (σ -phase)**, **Fe₇Mo₆**, **R-phase Fe₂₇Mo₂₆**, and solid solutions. In the figure, the melting point of

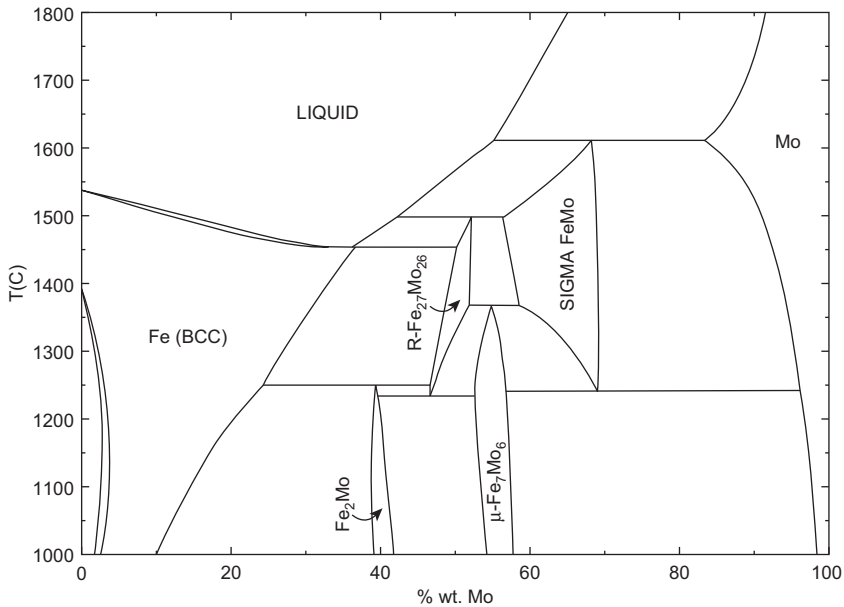


FIGURE 12.1 Equilibrium phase diagram of the system Mo-Fe.

iron-rich alloys is reduced up to ~37% wt. Mo, and after that it increases. The binary alloy with 55% to 58% wt. Mo melts at temperatures above 1650°C. The maximum solubility of iron in solid molybdenum is 15% Fe at 1610°C.

The equilibrium diagram of the Mo-C system is shown in Figure 12.2. Molybdenum with carbon forms two carbides, Mo_2C and MoC_{1-x} . These carbides have different phases, exhibiting coexistence at high temperatures. Small amounts of carbon are dissolved in the solid molybdenum with the formation of a solid solution. In the ternary system, the Mo-Fe-C formation of complex carbides $(\text{Fe},\text{Mo})_3\text{C}$, $(\text{Fe},\text{Mo})_{23}\text{C}_6$, η -phase $(\text{Fe},\text{Mo})_6\text{C}$, and $(\text{Mo},\text{Fe})_2\text{C}$ has been confirmed.

The diagram of the Mo-Si system includes several silicides (Fig. 12.3). Known silicides are Mo_3Si , Mo_5Si_3 , and MoSi_2 . MoSi_2 silicides exist in two modifications, and the temperature of the transformation $\alpha\text{-MoSi}_2 \leftrightarrow \beta\text{-MoSi}_2$ is ~1900°C. Molybdenum disilicide has an important application as a high-temperature heating element in different furnaces. The maximum solubility of silicon in Mo reaches 3.52% (at.) at 2053°C.

In the system Mo-Al, there are six known aluminides: MoAl_{12} , MoAl_6 , MoAl_5 , MoAl_4 , Mo_3Al_8 , and Mo_3Al (Fig. 12.4). Some of them might have composition homogeneity ranges.

With phosphorus and sulfur, molybdenum forms stable phosphides (Mo_3P , MoP_2) and sulfides (Mo_2S_3 , MoS_2 , and MoS_3). The first sulfide dissociates below 605°C, but MoS_2 is stable and forms mineral molybdenite, which is one

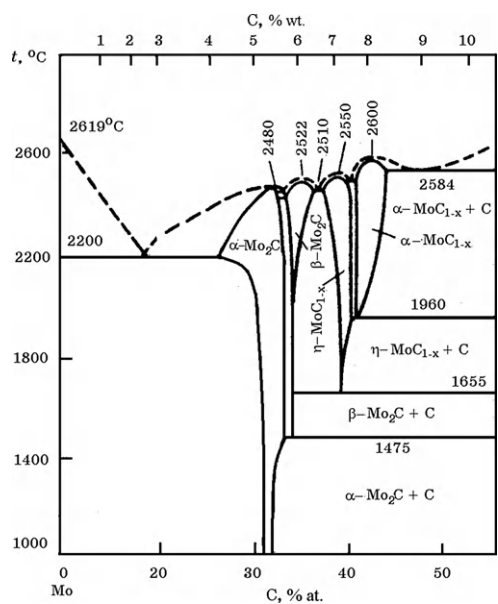


FIGURE 12.2 Equilibrium phase diagram of the system Mo-C.

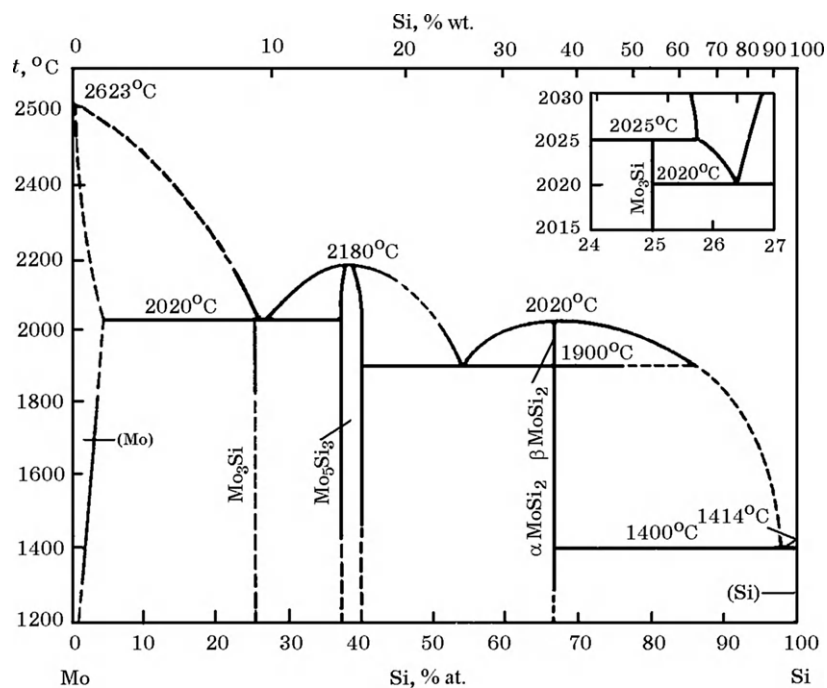


FIGURE 12.3 Equilibrium phase diagram of the system Mo-Si.

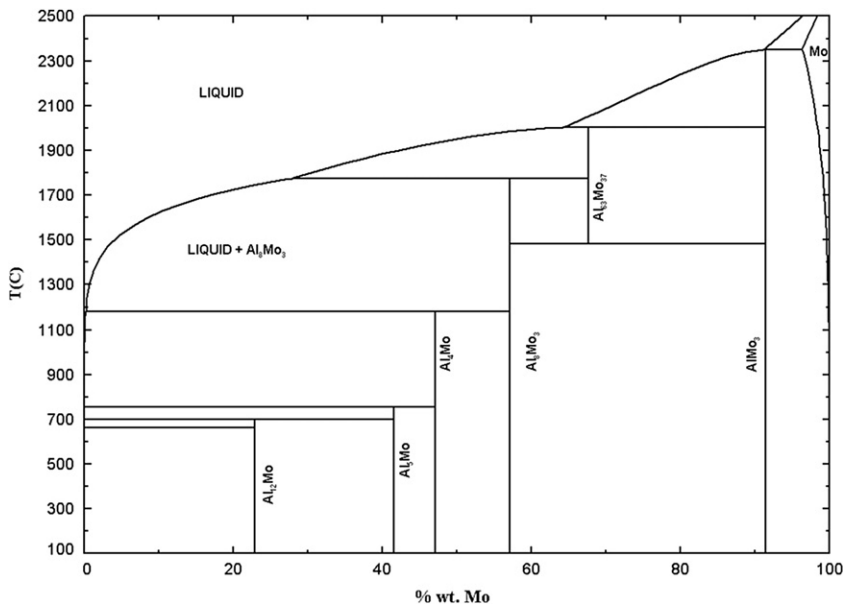


FIGURE 12.4 Equilibrium phase diagram of the Mo-Al system.

of the major molybdenum sources. Nitrogen does not dissolve in molybdenum in substantial amounts, so for nitriding it is possible for the ferroalloy used in powder form (Kirby and Fray, 1993).

Oxygen dissolves in solid molybdenum in small amounts, but like tungsten it forms many molybdenum oxides, of which the most known are yellowish white MoO_3 , brown MoO_2 , dark violet Mo_4O_{11} , black $\text{Mo}_{17}\text{O}_{47}$, violet $\text{MoO}_{2.8}$, dark blue Mo_8O_{23} , and Mo_9O_{26} (Fig. 12.5). When the O/Mo ratio increases, the melting temperature of the oxide drops and its vapor pressure increases; thus MoO_3 easily evaporates (sublimates) on heating before melting.

The evaporation of MoO_3 increases in the presence of water vapor; for example, at 690°C it is four times higher than in a dry atmosphere because of the formation of complex molecules $\text{MoO}_3 \cdot \text{H}_2\text{O}$. This has to be taken into account during the oxidative roasting of molybdenite MoS_2 concentrate. Oxide MoO_3 also tends to form trimer Mo_3O_9 , tetramer Mo_4O_{12} , and pentamer Mo_5O_{15} molecules in the gas phase near its melting point (Gasik et al., 2009).

Molybdenum has a relatively small affinity for oxygen and it can be reduced by carbon. However, the stability area of pure molybdenum is narrow, and thus molybdenum carbides also form during reduction (Fig. 12.6). As carbon content in ferromolybdenum is limited, the alloy should be produced by reduction with silicon or aluminum (Gasik et al., 2009).

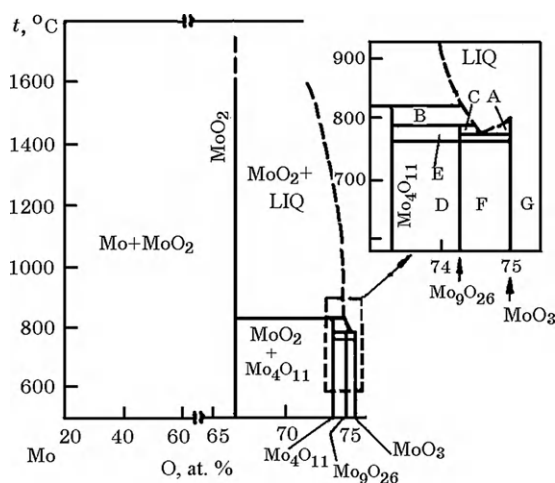


FIGURE 12.5 Equilibrium phase diagram of the system Mo-O. The insert shows details of phase areas: A = $\text{MoO}_3 + \text{L}$; B = $\text{Mo}_4\text{O}_{11} + \text{L}$; C = $\text{L} + \text{Mo}_9\text{O}_{26}$; D = $\text{Mo}_4\text{O}_{11} + \text{Mo}_9\text{O}_{26}$; E = $\text{Mo}_4\text{O}_{11} (\beta) + \text{Mo}_9\text{O}_{26}$; F = $\text{Mo}_9\text{O}_{26} (\gamma) + \text{MoO}_3$; G = $\text{Mo}_9\text{O}_{26} (\beta) + \text{MoO}_3$.

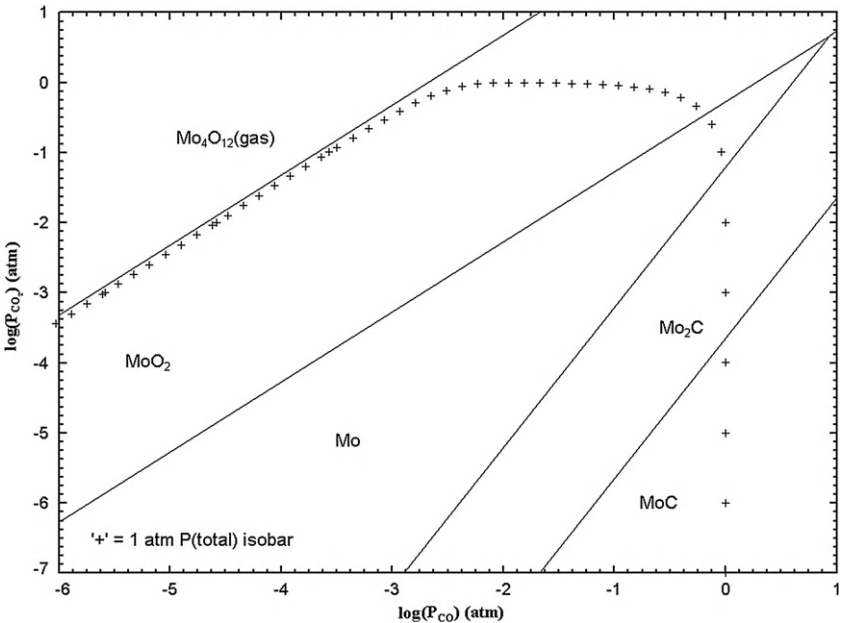


FIGURE 12.6 Phase dominance diagram in the Mo-O-C system at 1200°C.

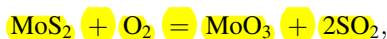
12.2 MINERALS, ORES, AND CONCENTRATES OF MOLYBDENUM

Known molybdenum minerals are molybdenite (MoS_2), povellite (CaMoO_4), wulfenite (PbMoO_4), molybdate (ferrimolybdate) ($\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$) ($n = 7-8$), and molybdenum scheelite (Ca(W,Mo)O_4). The most common mineral is MoS_2 , which is the main mineral of molybdenum in concentrates used to produce ferroalloys (Kummer, 1979). It is derived as primary ore (United States, Canada, China) or as a by-product of the extraction of other metals (copper) (United States, Chile, Mongolia). Various molybdenum ores are being recovered also in Russia, Kazakhstan, Uzbekistan, and the Caucasus region. Molybdenite (MoS_2) traditionally occurs in quartz veins, often in conjunction with scheelite (CaWO_4), wolframite ($(\text{Fe,Mn})\text{WO}_4$), cassiterite (SnO_2), chalcopyrite (CuFeS_2), and other minerals such as those containing arsenic and bismuth. The ores are classified into simple (quartz-molybdenum), copper-molybdenum, and molybdenum-tungsten. Ordinary quartz-molybdenum ores contain about 0.1% to 1% Mo (Kummer, 1979; Gasik et al., 2009). The use of other minerals such as ferrimolybdate for direct smelting of ferromolybdenum from lean concentrates has been also reported by Pattnaik et al. (1981).

Polycrystalline (formed via substitution of other minerals) ores of molybdenum and tungsten contain molybdenite with scheelite (CaWO_4), pyrite (FeS_2), and chalcopyrite, although concentrations of the last two are usually minor (e.g., ores from Northern Caucasus). Molybdenite is normally removed first by flotation, but as scheelite (CaWO_4) and povellite (CaMoO_4) form an isomorphic mixture, molybdenum concentrates always have some tungsten. Depending on the grade, enriched concentrates have 45% to 60% wt. Mo, below 5% to 9% WO_3 , <0.03% to 0.07% As, <0.01% to 0.7% Sn, and <0.01% to 0.05% P. Major impurities, which vary significantly with ore-dressing degree, are silica (from <0.2% to 12%) and copper (from <0.01% to 2.5%). Because these concentrates have up to 35% sulfur, they have to be roasted to oxidize molybdenite (Voronov et al., 2000).

12.3 OXIDATIVE ROASTING OF MOLYBDENITE CONCENTRATES

During oxidative roasting of molybdenite concentrates, molybdenum sulfide transforms to MoO_2 and MoO_3 . The oxidation of the sulfur proceeds first with the formation of MoO_3 :



followed by the reaction of MoO_3 with molybdenum sulfide:



The oxidation of MoS_2 to MoO_3 is highly exothermic, so external heating is required only at the end of the firing process, when the amount of molybdenum sulfide is getting too low. Sulfides of other metals (FeS_2 , Cu_2S , ZnS , NiS , etc.) present as impurities in commercial molybdenum concentrates oxidize at the same time.

The roasting process is carried out in an oxidizing atmosphere in a vertical furnace with eight levels at a maximum temperature of 680° to 750°C to avoid evaporation losses of MoO_3 with gases. Despite the seeming simplicity of roasting of molybdenum concentrate, industrial realization of the process to get concentrate suitable for smelting of standard ferromolybdenum is a complex process. The quality and yield of the concentrate depend on many factors: mineralogy, particle size and composition of source concentrate, temperature distribution, oxidation potential of the gas phase, the duration of firing, and so on. The identification of a rational and optimal combination of factors is an important technological challenge. Voronov et al. (2000) describe this process in more detail.

Residual sulfur content in the concentrate should not exceed 0.05% to 0.15% S. This calcined (roasted) molybdenum concentrate should have at least 50% to 55% Mo, $<0.03\%$ to 0.05% P, $<0.05\%$ As, $<0.6\%$ to 1.5% Cu, 5% to 7% SiO_2 , $<0.05\%$ Sn, and $<0.1\%$ C (Gasik et al., 2009). Additionally, roasted concentrate contains 14% to 16% CaO, $<3\%$ FeO, $<1.5\%$ MgO, $<0.7\%$ Al_2O_3 , and 0.15% to 0.5% W. About one tenth of all molybdenum in this concentrate is present as MoO_2 , and the rest is present in the form of MoO_3 .

12.4 TECHNOLOGY FOR PRODUCING FERROMOLYBDENUM

Standard ferromolybdenum alloy has about 60% Mo, although grades with 50% to 58% Mo have been also produced on request. Also, ferromolybdenum with increased silicon content ($<15\%$ to 20% Si, $>45\%$ to 50% Mo) has been produced (Voronov et al., 2000). As the Mo-Fe phase diagram shows (see Fig. 12.1), such an alloy has a liquidus temperature of over 1800°C , but the first liquid phase forms around 1540°C (decomposition of FeMo sigma phase). A high melting temperature and high density of the alloys (9 to 9.3 g/cm^3) represent a challenge of the addition of FeMo lumps into molten steel, although this challenge is less critical than it is for ferrotungsten. Gourtsoyannis et al. (1984) reported on the dissolution of molybdenum and ferromolybdenum in liquid steel. Pure Mo dissolves in stagnant steel baths at 1600°C at a rate of 0.4 mm/min, whereas the rate measured in an inductively stirred bath was 0.7 mm/min. By extrapolation it was calculated that ~ 1.2 min is needed for the dissolution of a 2" FeMo lump in a stirred steel bath at 1600°C .

Other impurities in ferromolybdenum are usually tungsten (0.3% to 0.8%), silicon ($<0.5\%$ for the highest grade and $<3\%$ for the lowest grade), copper ($<0.5\%$ and $<2\%$, respectively), phosphorus ($<0.05\%$), and sulfur ($<0.15\%$).

Nonferrous metals accompanying molybdenum in minerals and concentrates (As, Sn, Sb, Pb, Zn, Bi) normally should not exceed 0.005% to 0.01% each (Gasik, et al., 2009; Voronov et al., 2000). **Carbon** content is limited to 0.05% for the highest grade and 0.5% for the lowest grade of the ferroalloy.

The smelting of FeMo is based on the reduction of molybdenum oxides with silicon and aluminum off-furnace, as the process is exothermic and the alloy ingot is solidified at the end of the smelting hearth. The following charge compositions have been employed commercially for FeMo processing (Table 12.1).

At the Chelyabinsk Electrometallurgy plant in Russia, the alloy is produced from the charge consisting of roasted molybdenum concentrate (50% to 55% Mo), granulated aluminum, iron ore and chips, and lime. The main reductant is FeSiAl alloy (60% to 65% Si and 10% to 12% Al), especially designed for this type of process to provide optimal heat release during reactions. The smelting hearth is charged and covered and the charge is ignited. This process of ferromolybdenum smelting consists of two periods: the first includes the reaction progress and gas and solid separation; the second consists of the separation of reaction products (metal and slag). The duration of the first period is regulated according to the specific heat release of the charge (kJ/kg of charge) based on industrial practice. It usually varies between 10 min (~2100°C) and 50 min

TABLE 12.1 Examples of Charge Compositions for FeMo Smelting (per 100 kg of MoO₃ in the Concentrate with 60% Mo)

Component	Al Reduction	SiCa Reduction	Al and Si Reduction	Si Reduction
Fe-75%Si	31.5	21–23		38
Granulated Al	9			5
FeSiCa		17–18		
Fe-45%Si-10%Al			65	
FeMo scrap				5.5
CaF ₂			7	7.5
Lime				2.5
Iron (steel) chips	5–6	18		
Iron mill scale	29	16–18	35	51
MoO ₃ captured dust				9.5

(~1760°C). Temperature of the melt in the first period determines the time of the second period (30 to 50 min) and the final result of melting. This time is needed to allow metal droplets to coagulate and to precipitate at the bottom of the hearth.

The liquid slag is tapped at the end of the process into the slag ladle via skimmer. Even though slag has a much lower density than ferromolybdenum alloy, metal droplets are not easily separated because of the high slag viscosity (Ivanov et al., 1984; Voronov et al., 2000) when slag has 60% to 70% SiO₂, 9% to 13% Al₂O₃, 7% to 11% FeO, and 6% to 9% CaO. The highest metal content in the slag is in the skimmer and stuck to the walls of the smelting hearth (slags with >0.3% Mo are recycled back to the process with ferromolybdenum scrap).

When processing low-grade concentrates (25% to 40% Mo), there is not enough exothermal heat to achieve reasonable amounts of reductant (Al and Si); in this case the process should be carried out in an electric furnace (Voronov et al., 2000). The charge is formed from low-grade concentrate, recycled slags, FeMo scrap, lime, and 65% Si ferrosilicon. Smelting in a 3.5 MVA furnace is carried out for 90 minutes (first period) with 30 minutes soaking for droplets removal. The best results were obtained with slags having CaO/SiO₂ = 0.85, giving <0.25% Mo in the slag and 50% to 51% Mo in the alloy. Although the molybdenum content is lower than in standard alloy, the process was reported to be efficient, as more expensive aluminum or FeSiAl alloy is not used.

All smelting processes release a substantial amount of fumes (~3% of used concentrate) containing MoO₃ and nonferrous metals; therefore, collected dust recycling is important. Typical dust composition as captured by electric filters has 10% to 15% Mo, <4% Bi, <10% Pb, <10% Zn, <0.5% Cu, 15% to 18% SiO₂, 10% to 12% FeO, <2% CaO, <5% MgO, and <7 Al₂O₃ as well as other impurities (As, Sn, Re, Cd, Se, Te, Ag, Au, etc.). Rhenium and noble metals have their special extracting technology. Collected dust was pelletized with coke, lime, and fluorspar and fed into a small furnace (0.5 MVA). The addition of lime combines molybdenum into CaMoO₄, decreasing losses with vapors and increasing the reduction temperature (so molybdenum retains in the slag phase). The slag contains 10% to 13% Mo, <2% Pb, <6% Zn, and <0.1% Bi. The by-product alloy has essentially bismuth (40% to 43% Bi) and lead (57% to 60% Pb) with little molybdenum (<0.01% Mo). In this way both slags and dust from the FeMo smelting are recycled.

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