

# DOBIJANJE FEROLEGURA TEŠKOTOPIVIH METALA METALOTERMIJSKIM POSTUPCIMA

## METALLOTHERMIC PROCEDURE FOR OBTAINING FERROALLOYS OF HARD SMELTING METALS

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### IZVOD

Oslanjajući se isključivo na domaće sirovine i sopstvenu tehnologiju, dobijene su u poluindustrijskim uslovima, metalotermijskim postupcima (aluminotermijski i silokotermijski) ferolegure: ferovolfram, ferobor, ferotitan i ferolegure složenog sastava. Optimizirani su kvalitativno-kvantitativni sastavi metalotermijskih mešavina i termodinamički uslovi procesa za svaku feroleguru. Dobijeni kvalitet ferolegura, opravdava masovnu proizvodnju, praktično bez ikakvih investicionih ulaganja.

**Ključne reči:** ferolegure, metalotermijski postupak.

### UVOD

Metalotermijski postupci proizvodnje ferolegura teško topivih metala naročito su dobili na značaju krajem drugog svetskog rata. Najčešće je korišćen postupak "na blok" bez izlivanja produkata reakcije. Ovaj postupak koristi se i danas. Niski tehno-ekonomski pokazatelji topljenja postupkom "na blok" usloveli su obimna istraživanja u oblasti iznalaženja progresivnijih metalotermijskih postupaka [1,2].

Cilj rada je prikazivanje rezultata istraživanja metalotermijskih postupaka dobijanja ferolegura "izlivanjem metala i troske". Ove legure su vrlo značajne za crnu metalurgiju naše zemlje i danas se isključivo uvoze. Rezultati ovih istraživanja predstavljaju osnovu za organizovanje industrijske proizvodnje

### 1. SIROVINE I NJIHOV KVALITET

Rudni koncentri sa visokim sadržajem metala i niskim sadržajem primesa predstavljali su osnovne sirovine za proizvodnju ferolegura teškotopivih metala.

Za dobijanje ferotitana korišćen je ilmenitski koncentrat, iz nanosnog ležišta "Žukovička reka" kod Knjaževca.

### ABSTRACT

Relying exclusively on domestic raw materials and own technology, and by applying metallothermic processes (aluminothermic and silicothermic), the following ferroalloys have been obtained under semi-industrial conditions: ferrowolfram, ferroboration, ferrotitanium and ferroalloys of complex composition. The quantitative and qualitative composition of the metallothermic mixes and thermodynamic conditions of the process have been optimized for each ferroalloy. The obtained quality of ferroalloys justifies their industrial production, which can be accomplished practically without any investment.

**Key words:** ferroalloys, metallothermic processes.

### INTRODUCTION

Metallothermic procedures for obtaining ferroalloys of hard smelting metals have particularly become significant at the end of WWII. "On block" procedure without casting reaction products was used. This procedure is used nowadays as well. Low techno-economical smelting indicators for "on block" procedure resulted in comprehensive researches in the field of finding more progressive metallothermic procedures [1, 2].

Goal of this paper is to show results of researching metallothermic procedures for obtaining ferroalloys "by casting metal and blast slag". These alloys are very significant for metallurgy of iron in our country and nowadays are solely imported. Results of these researches are grounds for organizing industrial production.

### 1. RAW MATERIALS AND THEIR QUALITY

Ore concentrates with high contents of metal and low contents of additives very primary raw materials for producing ferroalloys of hard smelting metals.

For obtaining ferrotitanium was used ilmenit concentrate from deposit bed "Žukovička reka" near Knjaževac.

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Osnovna sirovina za dobijanje **ferobora** je kolemanitska borna ruda iz detaljno istraženog ležišta "Baljevac na Ibru".

**Feromolibden** je proizveden na bazi pirolitički dobijenog  $\text{MoO}_3$ , u fabrici "Tesla" Pančevo, kao sporedni proizvod iz primarne proizvodnje.

Za dobijanje **ferovolframa** upotrebljen je zaostali industrijski uzorak šelitnog koncentrata iz ranije eksploataisanog ležišta "Blagojev Kamen".

**Ferolegure složenog sastava** dobijene su na bazi navedenih koncentrata. Hemijski sastav korišćenih koncentrata prikazan je u tabeli 1.

Tabela 1. Hemijski sastav (tež.%) osnovnih sirovina za dobijanje ferolegura )

Komponenta	NAZIV SIROVINE			
	Ilmenit	Šelit	Mo-konc.	B. ruda
FeO	40.23	8.76	-	-
TiO <sub>2</sub>	42.55	-	-	-
WO <sub>3</sub>	-	61.55	1.26	-
MoO <sub>3</sub>	-	-	95.70	-
B <sub>2</sub> O <sub>3</sub>	-	-	-	38.50
SiO <sub>2</sub>	2.25	3.34	-	11.37
CaO	1.68	16.28	-	19.20

Kao reducent upotrebljen je Al-prah, sa preko 99% Al. Jedini proizvođač Al-praha je "Sinter" Užice, te su industrijske probe rađene sa njihovim proizvodom. Pored Al praha, redukcion procesi odvijali su se primenom ferossilicijuma sa 75% Si.

Kao topitelji korišćeni su kreč sa sadržajem CaO od 90%, i fluorit iz Krupnja, flotacijski obogaćen, sa 89,4%  $\text{CaF}_2$ .

Železonošna komponenta bila je specijalno pripremljena kovarina iz Tople valjaonice iz železare Smederevo, sa 70% Fe. Za povećanje egzotermnog efekta reakcije, korišćen je natrijum nitrat sa 95%  $\text{NaNO}_3$ .

## 2. POSTUPAK DOBIJANJA FEROLEGURA

Za dobijanje ferolegura primenjeni su aluminotermijski i silikotermijski postupci.

Uslov za intenzivno odvijanje redukcionih reakcija u celokupnoj metalotermijskoj mešavini, koji treba ostvariti u cilju potpunog razdvajanja metala i troske je:  $Q_{egz} > Q_{pr} + Q_g$ , odnosno toplotni efekat egzotermne reakcije redukcije ( $Q_{egz}$ ) treba da bude najmanje jednak ili veći od količine toplote koja je neophodna za rastapanje produkata reakcije ( $Q_{pr}$ ), i toplotnih gubitaka ( $Q_g$ ).

Primary raw material for obtaining **ferroboron** is colemanit boron ore from thoroughly explored bed "Baljevac na Ibru".

**Ferromolybdenum** is produced based on  $\text{MoO}_3$ , obtained in pyrolitic manner in factory "Tesla" Pančevo, as a secondary product from primary production.

For obtaining **ferrowolfram** was used residual industrial sample of scheelite concentrate from previously exploited bed "Blagojev Kamen".

**Ferroalloys of complex composition** were obtained based on named concentrate. Chemical composition of used concentrate is given in Table 1.

Table 1 Chemical composition (wt.%) of primary raw materials for obtaining ferroalloy)

Component	RAW MATERIAL			
	Ilmenit	Scheelite	Mo. conc	B. ore
FeO	40.23	8.76	-	-
TiO <sub>2</sub>	42.55	-	-	-
WO <sub>3</sub>	-	61.55	1.26	-
MoO <sub>3</sub>	-	-	95.70	-
B <sub>2</sub> O <sub>3</sub>	-	-	-	38.50
SiO <sub>2</sub>	2.25	3.34	-	11.37
CaO	1.68	16.28	-	19.20

As a reductor was used Al-powder with over 99% Al. Sole manufacturer of Al-powder is "Sinter" Užice, therefore industrial testing were performed with their product. In addition to Al powder, reduction processes were performed using ferrosilicon with 75% Si.

As welding flux were used lime with 90% contents of CaO and fluorite from Krupanj, enriched by flotation with 89.4%  $\text{CaF}_2$ .

Ferro component was specially prepared swarf from Warm Rolling Mill from Iron Works Smederevo with 70% Fe. For increase of exothermic reaction effect was used sodium nitrate with 95%  $\text{NaNO}_3$ .

## 2. PROCEDURE OF OBTAINING FERROALLOYS

For obtaining ferroalloys were used aluminothermic and silicothermic procedures.

Condition for intensive reduction reactions in entire metallothermic mixture which is to be achieved for complete separation of metal and blast slag is:  $Q_{egz} > Q_{pr} + Q_g$ , i.e. thermal effect of exothermic reduction reaction ( $Q_{egz}$ ) should be at least equal or larger than quantity of heat necessary for reduction reaction product smelting ( $Q_{pr}$ ), and thermal losses ( $Q_g$ ).

Za ispunjenje navedenog uslova i određivanje međusobnih odnosa polaznih komponenti metalotermijskih mešavina, za svaki zadati kvalitet gotovog proizvoda, odnosno ferolegure, korišćeni su, za ovu svrhu urađeni programi za PC računar [3]. Ovi programi baziraju se na osnovama materijalnog i toplotnog bilansa metalotermijskih procesa. Ulazni podaci predstavljaju karakteristike polaznih komponenti mešavine i zadati kvalitet ferolegure. Program omogućava dobijanje velikog broja rezultata i međurezultata, od kojih treba izdvojiti: međusobni odnos (receptura) polaznih komponenti, koji je neophodan za ostvarivanje zadatog kvaliteta

Na osnovu dobijene recepture izrađivane su aluminotermijske i silikotermijske mešavine. Osnovne komponente su prethodno pripremljene (oksidaciono žarenje, usitnjavanje na određenu klasu krupnoće). Proces se odvijao u specijalnom livnom lonacu, zapremine 30l, sa čeličnim plaštom, debljine 10 mm. Sa unutrašnje strane plašt je obložen sinter magnezitom. Izrađene mešavine su šaržirane u reaktor, a reakcija je aktivirana smešom  $\text{NaNO}_3$  i Mg-praha. Na kraju reakcije, metal i troska su izlivani istovremeno u kalupe od magnezitnog peska. Nakon završetka reakcije, troska, koja prva očvršćava, lako se razdvajala od ferolegure., koja se, posle hlađenja u vodi, drobila na zahtevanu granulaciju.

Tehnološki tok procesa metalotermijskog postupka dobijanja ferolegura prikazan je na slikama od 1 do 6.



Slika 1.- Oksidaciono žarenje sirovina  
Figure 1.- Oxidation annealing of raw materials

For meeting the condition and determining interrelations of initial components of metallothermic mixtures for each set quality of final product, i.e. ferroalloys, were used PC softwares created for this purpose [3]. These softwares are based on material and thermal balance of metallothermic processes. Input data are features of initial components of the mixture and set quality of ferroalloys. The software enables generation of vast number of results and inter-results out of which should be highlighted: interrelation (formula) of initial components necessary for achieving set quality of ferroalloys; quantity of metal and blast slag; chemical composition of blast slag, specific heat of the process, temperature of products (metal and blast slag) etc.

Based on obtained formula were formed aluminothermic and silicothermic mixtures. Primary components were pre-prepared (oxidation annealing, pounding to determined size). Process was performed in special casting pot, capacity of 30l, with 10 mm thick steel shell. On inner side, shell is coated with sinter magnesite. Formed mixtures are batched into reactor, and reaction triggered by mixture of  $\text{NaNO}_3$  and Mg-powder. At the end of reaction, metal and blast slag were simultaneously cast into moulds made of magnesite sand. After reaction completion, blast slag which solidifies the first easily separated from ferroalloys which after cooling down in water granulated to required size.

Technological course of metallothermic process of obtaining ferroalloys is shown in Figures 1 through 6.



Slika 2.- Homodenizacija komponenti aluminotermijskih mešavina  
Figure 2.- Homogenization of components of aluminothermic mixtures



Slika 3.- Metalotermijska reakcija  
Figure 3.- Metallothermic reaction



Slika 4.- Izlivanje u kalup  
Figure 4.- Casting into mould



Slika 5.- Kontakt produkata reakcije (troska-feroledura)  
Figure 5.- Contact of reaction products (sand blast-ferroalloy)



Slika 6.- Gotov proizvod  
Figure 6.- Final product

### Dobijanje ferolegura u poluindustrijskim uslovima i njihov kvalitet

**Ferotitan-** Titan sa železom obrazuje dva intermedijarna jedinjenja:  $TiFe_2$  (30%Ti) i  $TiFe$  (46,2%Ti). Za dobijanje ferotitana korišćena je mešavina, koja se sastojala iz tri dela: inicijalne mešavine, osnovne mešavine i mešavine za umirivanje šarže. Osnovne komponente mešavine bile su: ilmenitni koncentrat, Al-prah, kovarina, ferossilicijum, kreč, fluorit i natrijum nitrat.

Za odvijanje aluminotermijske reakcije, prema podacima iz programa za određivanje uslova odvijanja procesa, specifična toplota procesa je 2300 kJ/kg mešavine. Pri redukciji čistog  $TiO_2$  specifična toplota reakcije iznosi 1350 kJ/kg, što je nedovoljno za odvijanje procesa topljenja i razdvajanja metala i troske. Zbog toga je mešavini dodavana lakoreduktivna kovarina, u količini koja je proistekla iz programa za projektovanje sastava mešavine i termodinamičkih uslova procesa. Ova količina obezbeđuje povećanje specifične toplote procesa na 2762 kJ/kg. Proces se odvija na temperaturi od 1980°C, i dovoljan je da obezbedi adekvatno razdvajanje troske i metala.

### Obtaining ferroalloys in semi-industrial conditions and their quality

**Ferotitanium-** Titanium with iron form two intermediary compounds:  $TiFe_2$  (30% Ti) and  $TiFe$  (46.2% Ti). For obtaining ferrotitanium was used mixture which consisted of three parts: initial mixture, primary mixture and mixture for stabilizing batch.

Primary components of the mixture were: ilmenit concentrate, Al-powder, swarf, ferrosilicon, lime, fluorite and sodium nitrate.

According to data from software for determining conditions under which aluminothermic reaction occurs, specific heat of the process is 2300 kJ/kg of mixture. With reduction of pure  $TiO_2$  specific reaction heat is 1350 kJ/kg, which is insufficient for smelting and separation of metal and blast slag. Due to this reason, to mixture was added slightly reductive swarf in quantity deriving from software for determining mixture content and thermodynamic conditions of the process. This quantity enables increase of specific heat of the process up to 2762 kJ/kg. The process occurs at the temperature of 1980°C, and is sufficient to provide adequate separation of blast slag and metal.

Poznato je da Si obrazuje sa Ti stabilnija jedinjenja u odnosu na Al. Zato je mešavini dodavan ferosilicijum i na taj način je sadržaj Al u leguri sveden na minimum. Istovremeno, iskorišćenje Ti je veće, jer Si pomera reakciju u pravcu prelaska Ti u metal.

Inicijalna mešavina koja je šaržirana u reaktor, aktivirana je smešom Mg-praha i  $\text{NaNO}_3$ . Po otpočetoj reakciji, dodavana je osnovna mešavina i to ravnomerno po celoj površini, da bi metalno ogledalo obrazovane troske bilo pokriveno tankim slojem mešavine. Nakon okončanja topljenja dodavana je mešavina za umirivanje šarže. Na slici 1. prikazan je makroskopski snimak dobijenog ferotitana.

Hemijski sastav izlivenog ferotitana kreće se u sledećim granicama: Ti 25÷ 30 %; Si 3÷5%; Al 3÷7 %; C max. 0,2 %; S max. 0,03 % i P max. 0,07%.

Hemijska analiza troske dala je sledeće rezultate.:  $\text{Al}_2\text{O}_3$  69,5%;  $\text{TiO}_2$  13,56%;  $\text{SiO}_2$  1,6%; CaO 0,3%. Petrografskom analizom troske konstatovano je da glavnu mineralnu fazu čine prizmatični i tabličasti kristali korunda, kao i sitnozrni pervoskit. Cementnu fazu čini staklo. Bez obzira što se troska može ponovo redukovati u cilju iskorišćenja Ti, mineralni sastav troske omogućava njenu primenu, kako u industriji abrazivnih materijala, tako i u cementnoj industriji za dobijanje deficitarnog visokovatrostralnog cementa. Iskorišćenje titana iznosilo je 60 - 75%.

Na slici 7. prikazan je makro snimak komada ferotitana usitnjenog nakon naglim hlađenja u vodi.

It is known fact that Si forms more stable compounds with Ti than with Al. This is the reason why to the mixture is added ferrosilicon and in this way, contents of Al in alloy is reduced to minimum. At the same time, utilization of Ti is larger, because Si shifts reaction toward transformation of Ti into metal.

Initial mixture which is batched into reactor was triggered by mixture of Mg-powder and  $\text{NaNO}_3$ . After initiated reaction, primary mixture was added equally along entire surface, so metal glass of formed blast slag would be covered with thin layer of mixture. After smelting end was added mixture for batch stabilization. In Figure 1 is shown macroscopic view of obtained ferrotitanium.

Chemical compound of casted ferrotitanium is within the following ranges: Ti 25÷30 %; Si 3÷5%; Al 3÷7 %; C max. 0.2 %; S max. 0.03 % and P max. 0.07 %.

Chemical analysis of blast slag gave the following results:  $\text{Al}_2\text{O}_3$  69,5%;  $\text{TiO}_2$  13,56%;  $\text{SiO}_2$  1,6%; CaO 0,3%. Petrographic analysis of blast slag showed that the main mineral phase consists of prism and table-shaped crystals of corundum, as well as fine grained the fact that blast slag can be reduced for utilization of Ti, mineral contents of blast slag enables its implementation, both in abrasive material industry and cement industry for obtaining deficit high temperature-resistant cement. Utilization of titanium was 60 - 75%.

In Figure 7 is shown macro view of ferrotitanium piece pounded after sudden cooling down in water.



Slika 7.- Makro izled ferotitana  
Figure 7.- Macro view of ferrotitanium

**Ferobor-** Na osnovu dijagrama stanja "železo-bor", železo obrazuje boride:  $\text{Fe}_2\text{B}$  (8,94%B) i  $\text{FeB}$  (16,42%B). Za metalotermijsko dobijanje ferobora, prema podacima iz programa za određivanje uslova odvijanja procesa, potrebna je značajna količina termitnih dodataka, jer se redukcijom anhidrovanog  $\text{B}_2\text{O}_3$  izdvaja svega 3268 kJ/kg oksida. Za optimalno odvijanje reakcije, specifična toplota procesa, pri optimalnom odnosu borne rude, kovarine i aluminijuma 1,7:1:1, iznosi 5363 kJ/kg mešavine. S obzirom da borna ruda sadrži molekulsku vodu, neophodno je podvrgnuti procesu žarenja. Ovaj postupak treba pažljivo sprovesti, jer u protivnom, tokom žarenja, može doći do značajnih gubitaka bora i do 20%. Isto tako, od kvaliteta sprovedenog žarenja zavisi stepen iskorišćenja metala u toku aluminotermijskog procesa. U cilju kompenzacije toplote, dodata je tačno utvrđena na programu, količina termitnih dodataka ( $\text{NaNO}_3$  i Al- praha). Postupak topljenja, koji je sličan postupku kojim se dobija ferotitan, obuhvatao je obrazovanje rastopa, redukciju oksida i obradu šljake. Nakon završetka procesa, metal i troska su izlivani u kalupe. S obzirom na veliki afinitet bora prema kiseoniku i azotu, izlivena legura držana je duže u kalupu, u cilju obezbeđivanja minimalnog sadržaja ovih gasova u leguri.

Na slici 8. prikazan je makrosnimak dobijenog ferobora, sa uočljivom gasnom poroznošću, koja je posledica neadekvatnog žarenja borne rude.



*Slika 8.- Makroizgled komada ferobora*  
*Figure 8.- Macro view of ferroboron piece*

Dodavanjem kreča i fluorita mešavini regulisana je viskoznost troske. Iskorišćenje bora iznosilo je 45-60 %, a najviši stepen iskorišćenja ostvaren je pri odnosu  $\text{CaO}$  i  $\text{Al}_2\text{O}_3$  u troski od 0,20-0,25 [4].

**Feroboron-** Based on diagram of condition "iron-boron", iron forms borides:  $\text{Fe}_2\text{B}$  (8.94% B) and  $\text{FeB}$  (16.42% B). According to data from software for determining conditions under which process occurs, for metallothermic obtaining of ferroboron is required significant quantity of thermo additives, because by reduction of anhydrated  $\text{B}_2\text{O}_3$  is separated only 3268 kJ/kg of oxide. For optimal reaction, specific heat of the process, with optimal ratio of boron ore, swarf and aluminum 1.7:1:1, is 5363kJ/kg of mixture. Since boron ore contains molecular water it is necessary to conduct annealing process. This procedure should be carefully conducted, because if not during annealing can occur significant losses of boron, even up to 20%. Similarly, quality of conducted annealing affects level of metal utilization during aluminothermic process. For heat compensation is added precise quantity of thermal additives ( $\text{NaNO}_3$  and Al- powder) determined by the software. Smelting procedure, which is similar to procedure used for obtaining ferrotitanium included formation of cast, oxide reduction and blast slag processing. After process end, metal and blast slag were casted into moulds. Considering large aptitude of boron to oxygen and nitrogen casted alloy was kept longer in the mould for securing minimal content of these gases in alloy.

In Figure 8 is shown macro view of obtained ferroboron with visible gas porosity which is result of inadequate annealing of boron ore.

By adding lime and fluorite to the mixture is regulated viscosity of blast slag. Utilization of boron was 45-60 %, with the highest level of utilization with  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  ration in blast slag of 0.20-0.25 [4].

Dobijena legura sadržavala je 10-13%B; 4-7%Si i do 10 % Al. Hemijski sastav troske bio je:  $\text{Al}_2\text{O}_3$  68,6%;  $\text{CaO}$  19,13%;  $\text{MgO}$  2,1%;  $\text{B}_2\text{O}_3$  7,4%. Od mineralnih faza, pored korunda, kao osnovne faze, značajno je zastupljen magnezijski spinel. Prisutani su hercinit i oldamit.

**Ferovolfram-** Volfram i železo obrazuju sledeća stabilna jedinjenja:  $\text{WFe}_2$  (62,2%W) i  $\text{W}_2\text{Fe}_3$  (68,7%).

Izdvojena toplota aluminotermijske reakcije je sasvim dovoljna za prevođenje komponenti mešavine u rastop i za dobro odvajanje metala od troske. Upravo zbog toga je deo Al-praha, kao reducenta, zamenjen jeftinijim ferossilicijumom.

S obzirom da je šelitni koncentrat bio izrazito sitnozrn (veličina zrna manja od  $0,075 \mu\text{m}$ ) isti je briketiran sa 20 % aluminijumskog praha. Topljenje je izvedeno sa donjim aktiviranjem reakcije. Karakteristična je likvacija elemenata po dubini izlivene legure, naročito W. Razlika ponekad prelazi 10%. Hemijski sastav dobijenog ferovolframa, čiji je makrosnimak prikazan na slici 9, bio je: W 73,34%; Si 0,45%; Al 0,93%; S 0,07%; P 0,03%. Iskorišćenje volframa iznosilo je 95-97%.

Obtained alloy contained 10-13%B; 4-7% Si and up to 10% Al. Chemical compound of blast slag was:  $\text{Al}_2\text{O}_3$  68.6%;  $\text{CaO}$  19.13%;  $\text{MgO}$  2.1%;  $\text{B}_2\text{O}_3$  7.4%. In terms of mineral phases, in addition to corundum as basis of the phase, magnesite spinel was significantly present. Hercinite and oldamite were also present.

**Ferowolfram-** Wolfram and iron form the following stable compositions:  $\text{WFe}_2$  (62.2%W) and  $\text{W}_2\text{Fe}_3$  (68.7%).

Separated heat aluminothermic reaction was quite sufficient for transforming mixture components into cast and for separation of metal from blast slag. Due to this reason, part of Al-powder as reductor was replaced with cost-efficient ferrosilicon.

Since scheelite concentrate was extremely fine grained (grain size smaller than  $0.075 \mu\text{m}$  micrometer), it was coal-caked with 20% of aluminum powder. Smelting was performed with lower triggering of reaction. Element diffusion in depth of casted alloy is very characteristic, particularly W. Sometimes the difference exceeds 10%. Chemical composition of obtained ferrowolfram, whose macro view is shown in Figure 9 was: W 73.34%; Si 0.45%; Al 0.93%; S 0.07%; P 0.03%. Utilization of wolfram was 95-97%.



Slika 9.- Izgled komada ferovolframa

Figure 9.- Piece of ferrowolfram

**Feromolibden-** Sa železom molibden obrazuje jedinjenja, praktično u svim odnosima. Kada je sadržaj Mo 36% obrazuje eutektikum, čija je tačka topljenja  $1440^\circ\text{C}$ . Pri sastavu 60% Mo i 40%Fe, tačka topljenja iznosi  $1800^\circ\text{C}$ . Za optimalno odvijanje postupka dobijanja feromolibdena specifična toplota procesa treba da iznosi  $2300\text{kJ/kg}$  oksida, što se lako postiže korišćenjem ferossilicijuma kao reducenta (specifična toplota redukcije  $\text{MoO}_3$  sa Si iznosi  $2930 \text{ kJ/kg MoO}_3$ ).

**Ferromolybdenum-** Molybdenum with iron forms compounds, practically in all relations. When contents of Mo is 36% it forms eutektikum with smelting point at  $1440^\circ\text{C}$ . With contents of 60% Mo and 40% Fe smelting point is at  $1800^\circ\text{C}$ . For optimal development of procedure of obtaining ferromolybdenum, specific process heat should be  $2300\text{kJ/kg}$  of oxide, which is easily achieved by using ferrosilicon as reductor (specific reduction heat of  $\text{MoO}_3$  with Si is  $2930 \text{ kJ/kg MoO}_3$ ).

Vlažnost korišćenog molibdenovog koncentrata bila je i do 15%, zbog čega je on najpre osušen pa žaren. Kao topitelj korišćeni su kreč i fluorit.

Međusobni odnos komponenti mešavine i termodinamički uslovi procesa definisani su tako da sadržaj Si u feromolibdenu bude ispod 0,5%. Normalan tok procesa topljenja feromolibdena praćen je izdvajanjem gasova i prašine u obliku obilnog gustog dima, zbog čega je neophodno raditi procesa izlivanja je feromolibden u peščane kalupe, hlađen vodom i usitnjavan na potrebnu granulaciju (+5 -50 mm).

Hemijski sastav feromolibdena bio je: Mo 64,67%; Si 0,21%; Al 0,1%; S 0,06%; P 0,03%. Troska se karakterisala sledećim hemijskim sastavom: SiO<sub>2</sub> 66,5%; Al<sub>2</sub>O<sub>3</sub> 12,56%; MoO<sub>3</sub> 0,64%, CaO 6,45%, CaF<sub>2</sub> 2,35%. Na slici 10. prikazan je makrosnimak feromolibdena.

Moisture of used molybdenum concentrate was up to 15%, and due to this it was dried first, and then annealed. As welding flux were used lime and fluoride.

Interrelation of mixture components and thermodynamic conditions of the process were defined in way that content of Si in ferromolybdenum is under 0.5%. Normal course of smelting process of ferromolybdenum is followed by separation of gas and dust in form of abundant dense fume, due to which is necessary to work with systems for removing dust. After process completion, ferromolybdenum was casted into sand moulds, cooled down with water and pounded to required granulation (+5 -50 mm).

Chemical composition of ferromolybdenum was: Mo 64.67%; Si 0.21%; Al 0.1%; S 0.06%; P 0.03%. Blast slag had the following chemical composition: SiO<sub>2</sub> 66.5%; Al<sub>2</sub>O<sub>3</sub> 12.56%; MoO<sub>3</sub> 0.64%, CaO 6.45%, CaF<sub>2</sub> 2.35%. In Figure 10 is shown macro view of ferromolybdenum.



Slika 10.- Izgled komada feromolibdena

Figure 10.- Piece of ferromolybdenum

**Ferolegure složenog sastava-** Poslednjih godina koriste se legure složenog sastava, čime se umanjuje cena, a povećava efekat legiranja.

Kao osnovne komponente korišćeni su koncentri Mo i Ti, kao i hromitni koncentrat sa 52% Cr<sub>2</sub>O<sub>3</sub>, koji se koristi u livnicama.

Izrađene su legure Mo- Cr, zatim Cr- Ti, kao i Al-Mo-Ti. Dobijeni hemijski sastav navedenih legura prikazan je u tabeli 2.

**Ferroalloys with complex composition-** In recent years, alloys with complex composition have been used, which reduces their price and increase alloying effect.

As primary components were used concentrates of Mo and Ti, as well as chromite concentrate with 52% Cr<sub>2</sub>O<sub>3</sub>, used in foundries.

In this way were formed the following alloys Mo-Cr, then Cr-Ti, and Al-Mo-Ti. Obtained chemical composition of named alloys is shown in Table 2.

Tabela 2.: Hemijske osobine legura složenog sastava

Table 2.: Chemical properties of alloys with complex composition

	Mo	Cr	Ti	Si	Fe	Al
MoCr	55.87	46.43	-	0.33	0.85	0.39
CrTi	-	56.34	22.40	9.12	2.19	1.30
AlMoTi	48.40	-	8.67	0.40	0.90	ostalo



### 3. ZAKLJUČAK

Prikazani rezultati poluindustrijskih ispitivanja mogućnosti dobijanja ferolegura teškotopivih metala, ukazuju da potpuno odvijanje redukcionih procesa oksida metala i reducenata, pored termodinamičkih karakteristika procesa, u značajnoj meri zavisi i od kinetičkih uslova odvijanja reakcija. Iskorišćenje metala, takođe zavisi od navedenih parametara, ali pre svega od uslova raspodele produkata reakcije, odnosno metala i troske. Domaće sirovine, minimalna ulaganja, kao i kvalitet dobijenih ferolegura opravdavaju dalja istraživanja, koja treba nastaviti u pravcu ostvarivanja što ekonomičnije proizvodnje. S tim u vezi, istraživanja su usmerena u kompenzaciju skupih termitnih dodatka, koji su neophodni za povećanje specifične toplote procesa nekih reakcija.

Treba istaći da metalotermijski postupci pružaju mogućnost sinteze materijala koja se drugim postupcima ne može ostvariti. S obzirom na dokazivanje adekvatnosti izrađenih programa (matematičkih modela) kroz prognozu osobina ferolegura, kao i kroz mogućnost upravljanja njihovim osobinama, sasvim su opravdana, već otpočeta istraživanja i u ovoj oblasti.

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### 3. CONCLUSION

Shown results of investigation options for obtaining hard smelting metals under semi-industrial conditions, show that complete realization of reduction processes of metal oxide and reductive elements, in addition to thermodynamic properties of the process, significantly depend on kinetic conditions for reaction realization. Utilization of metal also depends on named parameters, but foremost due to condition of reaction product diffusion, i.e. metal and blast slag. Domestic raw materials, minimal investments, as well as quality of obtained ferroalloys justify further researches, which should be continued for achieving the most cost-effective production. In regards thereof, researches have been directed toward investigating implementation of electric energy for compensation of expensive thermo additives which are necessary for increase of specific heat of the process with some reactions.

It should be pointed out that metallothermic processes enable synthesis of material which cannot be achieved in other processes. Considering proving of adequacy of created softwares (mathematic models) through prognosis of ferroalloy properties, as well as ability of managing their properties, already started researches in this field are fully justified.

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