



# University-based Research Studies aided by FactSage Simulation Program



NaF - NaCI - CaF,

## **Bora Derin and Onuralp Yucel**



Istanbul Technical University Metallurgical and Materials Engineering Department Maslak, Istanbul, 34469, Turkiye



GTT-Technologies 10<sup>th</sup> Annual Workshop, June 4-6, 2008

# Some Studies of Extractive Metallurgy Division

- 1. A Process Designed for The Ancient Copper Smelting Slags
- 2. Calcination Studies of West Anatolian Dolomite Ores
- 3. Magnesium Production via Pidgeon Process
- 4. Self Propagating High Temperature Synthesis (SHS) Studies
- 5. Carbothermal Studies for Titanium diboride Synthesis
- 6. Modeling of Sulfide Capacities of Binary and Multicomponent Slags





















An approximate amount of **2 million tons** of copper smelting slag has been lying on the northern part of Turkiye-Kastamonu/Küre, dating back Genoese times ( A.D. 958-1528).

Chemical composition of the ancient Küre copper slags

		11 0	
Components	Wt. %	Components	wt. %
Co	0.4	SiO <sub>2</sub>	26.1
Cu	0.82	Al <sub>2</sub> O <sub>3</sub>	6.8
Zn	0.15	CaO	0.7
Fe	47.8	MgO	1.0
S	1.5	NiO	0.02



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#### **EAF Studies for Ancient Copper Slags**



- o Different EAF crucibles for 25, 30 and 150 kg-weight samples of Küre slag with or without additives were charged into for reduction smelting.
- o Coke as reducing material (78.5 % fixed carbon, 3.64 % volatile substances, and 17,6 % ash
- o CaCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> as fluxing additives
- o Tap to tap time was selected as at most 50 min.
- o At selected intervals, submerged type of Pt-PtRh10 thermocouple was introduced to the crucible to measure the temperature of the molten slag.
- o In the taping stage, the metal and slag temperatures were also measured with an optical pyrometer.







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Case 1

Table II. The chemical compositions and phases of metallic matters for various reduction temperatures<sup>[8]</sup>.

Cuanula	Reduction	Cher	nical co	mpositio	n of	
No	Temp.	m	etallic a	lloys, (%	)	Phases identified by X-ray diffaction
110	(°C)	Co	Cu	s	С	
1	1380	2.38	3.51	3.1	0.21	Fe, Cu, Co, Cu <sub>2</sub> S, FeS, Fe-C, CuO <sub>0.75</sub> Fe <sub>0.58</sub> S <sub>2</sub>
2	1440	1.96	3.00	2.9	0.26	Same
3	1550	2.34	2.10	2.72	0.31	Fe, Cu, Co, FeS, Fe-C
4	1630	1.47	2.14	2.26	0.42	Same
5	1710	1.42	1.35	1.82	0.46	Same
6	1790	1.36	1.31	1.32	0.53	Same



#### FactSage for reduction behaviour at different temperature







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Aim: to prepare calcined dolomite for Mg production via Pidgeon process.

- Dolomite (Mg,Ca)CO<sub>3</sub> (1000 g)
- Different temperatures (800-1100 °C)
- Different times (0-300 min)







Samples of about 10 g each were extracted from the hot zone at different intervals.



- Ruhstrat rotary drum furnace (1400 °C max., ±5 °C)
- One or both end open stainless steel tubes
- Both end open ceramic tube
- Rotation rate: 2 rpm.

COMPUTATIONAL SOLUTIONS IN METALLURGICAL PROCESSES

#### Bora Derin\*, Onuralp Yücel\*, Klaus Hack\*\*

\*Department of Metallurgical and Materials Engineering, Istanbul Technical University, Maslak, Istanbul, 34469, Turkiye E-mail: bderin@itu.edu.tr, yucel@itu.edu.tr \*\*GTT-Technologies Kaiserstrasse 100 D-52134 Herzogenrath Germany E-mail: kh@gtt-technologies.de

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Chemical analysis of some calcined dolomite samples showed that

- 1000 1100 °C
- Interaction with Stainless Steel reaction tube
- Green particles on calcined dolomite grains





In order to collect these green particles for the characterization, some of samples withdrawn at different time and temperature were sieved for 30 min using a sieve shaker equipped with 106  $\mu$ m screen.

Chemical analysis of the collected green sleved residue (<106µm	nical analysis of the collected green sieved residue (<106	um)
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		Wt. %	1	
Cr	Fe	Ni	MgO	CaO
9.65	1.09	0.06	24.06	37.92

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# *FactSage* for simulation of interaction between stainless steel retort and dolomite









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# **Magnesium Production via Pidgeon Process**

#### Aim:

Production of magnesium metal from Turkish calcined dolomite (43.20 % MgO and 47.46 % CaO) via the Pidgeon process was studied under the pressure of 1 mbar.

Lab. Scale

**Semi-pilot Scale** 

1 lt retort





#### **11 It retort**





**Pilot Scale** 

100 lt retort





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#### FactSage for simulation of Mg reduction





# Self Propagating High Temperature Synthesis (SHS) Studies

#### <u>SHS</u>

- Advanced ceramics,
- Intermetallics,
- Organic and inorganic compounds,
- Oxygen free single crystals
- Polymers

After initiation, reaction becomes self-sustaining and propagates in the reactant mixture.

A high amount of heat which is generated during the process accelerates the reaction rate and thus it makes the process highly productive and economically feasible for different production scales.



Photo of SHS process



Schematic of SHS process

#### Case 4

#### **TiB<sub>2</sub> Synthesis via SHS + HCl leaching**



## The SHS product = TiB<sub>2</sub>+MgO



Power Supply, 2. Electricity Cable, 3. Crucible,
 MgO lining, 5. SHS Mixture, 6. CrNi heating wire,
 Steel Cover, 8. Argon gas inlet, 9. Gas hose,
 Flowmeter, 11. Gas manometer, 12. Argon Gas

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 $TiO_2 + B_2O_3 + 5Mg = TiB_2 + 5MgO$ 

#### Different stoichiometric Mg (90-110%) and B<sub>2</sub>O<sub>3</sub> (100 and 110%) additions were examined

Reaction Powders	Purity, wt %	Particle Size, µm
TiO <sub>2</sub>	98.84	33 (mean)
Mg	99.95	< 150
H <sub>3</sub> BO <sub>3</sub>	99.50	-
B <sub>2</sub> O <sub>3</sub>	99.00	< 53





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 $MgO + 2HCI = Mg^{2+} + 2CI^{-} + H_2O$ 

In the leaching step,

the SHS product was leached by HCI solution (0 - 9.25 M HCI)

- 1/5, 1/10, 1/20 S/L ratio,
- 30 minutes,
- 10 g of specimens.
- 20 °C
- 400 rpm stirring rate,

## Filtering Step







## **TiB<sub>2</sub> product**





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XRD analysis of the SHS products collected on the steel cover and remained in the crucible (100 % stoic. Mg and  $B_2O_3$  additions)  $\bullet$ :TiB<sub>2</sub>,  $\blacksquare$ :MgO, O:Mg,  $\triangle$ : Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>,  $\checkmark$ :Mg<sub>2</sub>TiO<sub>4</sub>

 $\begin{array}{l} B_2O_3 + 3MgO = 3MgO.B_2O_3\\ TiO_2 + 2MgO = 2MgO.TiO_2 \end{array} \qquad \textit{Minor phases} \end{array}$ 

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#### **Tungsten boride synthesis via SHS method**

## $CaWO_4 + XB_2O_3 + YAI$

## FactSage

#### • What is Tad?

• Which composition gives the best result?







 $WO_3 + XB_2O_3 + YAI$ 







# **Carbothermal Studies for Titanium diboride Synthesis**



#### High-Temperature Ruhstrat-Nernst Tammann tube furnace



•Temperature (1400 - 1700 °C) and time (0 - 60 min.) were selected as experimental parameters.

•At the end of the experiments, the sample was left to soak in the crucible keeping flow of argon gas up to below  $300 \ ^{\circ}C$ .

•The product was discharged, ground and sieved. The phase compositions of the product were examined by XRD

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#### **Factsage software calculation**





Many complex reactions occur until a complete  $TiB_2$  formation, as in agreement with the literature.

Intermediate Phases are: Magneli phases  $(Ti_nO_{2n-1})$  and TiC





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Mass loss of the experimental products after carbothermal synthesis at different temperature and time





1600 °C 1-h



1700 °C 1-h





Sulfur is considered undesirable in steel because of the deleterious effect on the mechanical properties. So sulfur removal in the production stage is a necessary step in order to produce clean steel.

In copper, nickel and lead smelting, sulfur may also lead to metal losses in both forms entrained and chemical dissolution in the fayalite slags.

*Sulfide Capacity* is a measure of ability of a slag to remove sulfur from metal.

Cs = (wt.%S)
$$(\frac{PO_2}{PS_2})^{1/2}$$



#### **REDDY-BLANDER MODEL**

The Reddy-Blander Model predicted that sulfide capacity can be calculated *a priori*, based on a simple solution model and on knowledge of the chemical and solution properties of sulfides and oxides.

In Reddy-Blander Model, slag component is divided into two groups -"Acid" Components: SiO<sub>2</sub>, AlO<sub>1.5</sub>, TiO<sub>2</sub>, FeO<sub>1.5</sub> -"Basic" Components: CaO, FeO, MgO, MnO, NaO<sub>0.5</sub>, CuO<sub>0.5</sub>



Case 6

#### **REDDY-BLANDER MODEL**

Formulation of Equations for Binary Acid Melts  $(0.33 \le XSiO_2 < 1)$ 

$$Cs = 100 * W_{S} * K_{M} * a_{MO} * \frac{X_{SiO2}}{\overline{W}} \left( \frac{\Phi_{S}}{a_{MS}} \right)$$

Formulation of Equations for Binary Basic Melts (0≤XSiO₂≤0.33) (Such as CaO-SiO₂, MgO-SiO₂)

$$Cs = 100 * Ws * K_M * a_{MO} \left[ \frac{1 - 2X_{SiO2}}{\overline{W}} \right]$$

 $K_{M} = \left(\frac{P_{O2}}{P_{S2}}\right)^{1/2} \frac{a_{MS}}{a_{MO}}$ 

 $W_s =$  Molecular weight of sulfur

 $\overline{W}$  = Average molecular weight of the solution

 $a_{MO}$  = Activity of MO in the solution

#### Formulation of Equations for Multicomponent Slags

For a multicomponent system MO-NO-...-SiO<sub>2</sub>, which contains only one acid component, such as FeO-CaO-SiO<sub>2</sub> system, Flood-Grjotheim approximation (electrically equivalent fractions) is applied.

 $\ln C_{s} = N_{M} \ln C_{sM} + N_{N} \ln C_{sN} + \dots$ 

Where

$$N_{M} = (\frac{X_{MO}}{X_{MO} + X_{NO} + \dots}) \qquad \qquad N_{N} = (\frac{X_{NO}}{X_{MO} + X_{NO} + \dots})$$

 $\rm C_{S,M}$  and  $\rm C_{S,N}$  are sulfide capacities in the sulfide capacity of ternary MO-NO- ... -SiO\_2 system



For a multicomponent system containing more than one acid component such as MO-NO-....-SiO<sub>2</sub>-AlO<sub>0.5</sub>-TiO<sub>2</sub> system

$$XSiO_{2}+XAIO_{0.5}+...\leq 0.33,$$

$$Cs = 100 *W_{S} *K_{M} *a_{MO} \left[ \frac{1-2X_{SiO_{2}}-2X_{AIO_{1.5}}-2X_{TO_{2}}}{\overline{W}} \right]$$

$$XSiO_{2}+XAIO_{2}+... > 0.33$$

$$Cs = 100 * Ws * K_{M} * a_{MO} \left[ \frac{X_{SiO2} + X_{AIO0.5} + X_{TiO2}}{\overline{W}} \right] \left( \frac{\phi_{S}}{a_{MS}} \right)$$
$$\ln C_{S} = \sum N_{MO} \ln C_{SMO}$$

 $a_{MO}$  is the activity of MO in the MO-SiO<sub>2</sub>-AlO<sub>1.5</sub>-TiO<sub>2</sub> system  $\overline{W}$  is the is the average molecular weight of MO-SiO<sub>2</sub>-AlO<sub>1.5</sub>-TiO<sub>2</sub> system



Case 6

# **FactSage** for close approximations of activity values (a<sub>MeO</sub>) in multi-component slags





	Luit	нер								
3	2			T(C) P(atm) Ene	rgy(J) Mass(g)	Vol(litre)		11 🖳	3	<b>7</b> :
+	Code	Species	Data	Phase	Mole	Fraction	Activity	Range	T	v 4
	100	N-0	ETavid	ET - GIRLAGA	4 000000 000	2 20705-02	4 50005-00			
	101	Mgu	FIOXID	FTOXICSLAGA	4.9622E-02	3.2870E-02	4.5908E-03			
	181	FeU	Floxid	FT oxid-SLAGA	0.6193	0.4102	4.4863E-01		-	
	182	5102	Floxid	FT oxid-SLAGA	0.5509	0.3649	2.1205E-01			
	183	Lau	Floxid	FT OXID-SLAGA	0.2283	0.1512	3.7726E-04			
	184	NIU	Floxid	FT OXID-SLAGA	4.0673E-02	2.6942E-02	8.1321E-02		+ +	
	185	Fe2U3	FIOXID	FT0xid-SLAGA	2.0916E-02	1.3854E-02	7.2079E-03			
	180	MaD	FToxid	FToxid-SLAGA‡	0.0000	3.2421E-02	4 5908E-03			
	181	Fe0	FToxid	FToxid-SLAGA‡	0.0000	0.4046	4.4863E-01			
	182	SiO2	FToxid	FToxid-SLAGA‡	0.0000	0.3599	2.1205E-01			
	183	CaO	FToxid	FToxid-SLAGA‡	0.0000	0.1491	3.7726E-04			
	184	NiO	FToxid	FToxid-SLAGA‡	0.0000	2.6574E-02	8.1321E-02			
	185	Fe203	FToxid	FT oxid-SLAGA‡	0.0000	1.3665E-02	7.2079E-03			
ih	w				For	nat — — —	Order	_		
S	ecies-	100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100		1	( n	ole				
~	gas	0 🔽 dup	licate		C g	ram	C amount			
~	liquid		eted 146		<u>S</u> =	ound	C fraction			
Г	aquec	us 0 i seid	JUCU 140		66	ata	activity			
~	solid	134 AIV	Clear		P	Celevilete				
1	solutio	n 12 — —		re properues	Pos	-calculate		Cofronk		1

Ma	ass(g)	Species	Phase	T(C)	P(total)**	Stream# Da
47.5	FeL			<u> </u>		
•  33.1	SiO	2		<u>~</u>		
12.8	CaC			<u>~</u>		
+ 4.6	NiO			~		
+ 2	Mgl			¥		







Cs(R-B)

6.87x10<sup>-2</sup>

2.87x10<sup>-2</sup>

7.71x10<sup>-2</sup>





Yazawa<sup>[4]</sup> and Roghani et al<sup>[6]</sup>

(1)

50

40

Slag Composition (%)

FeO

22.8

32.0

36.0

SiO<sub>2</sub> CaO

21.0 24.5

14.0

22.0

12.3 17.5

Slag

(°C)

1225

1200

1300

PbO

2.8

2.8

1.1

ZnO

17.3

19.9

8.7

**Comparison of pressure ratios for the matte** grades from different smelting plants: (1) INCO (2) Rio-Tinto (3) Tamano (4) Norddeutsche (5) Phelps (6) Outokumpu

Cu grade in matte, wt pct.

Sridhar et al<sup>(2)</sup>

60

70

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80



#### Journal & Proceeding Papers

#### Thermochemical Calculations with FactSage

- 1. Derin B., Yucel O., Reddy R.G., "Modeling of Sulfide Capacities of Binary Titanate Slags" EPD Congress 2004, TMS Annual Meeting, March 14-18, (2004) North Carolina-USA, 155-160
- 2. Yucel O., Yigit S., Derin B., "Production of Magnesium Metal from Turkish Calcined Dolomite using Vacuum Silicothermic Reduction Method" Magnesium – Science, Technology and Applications, Materials Science Forum, Vols. 488-489 (2005) 39-42.
- 3. Onuralp Yücel, Selen Yiğit ve Bora Derin "Production of Magnesium Metal using Vacuum Silicothermic Reduction Method" Proceedings of the International Metallurgy and Materials Congress, (2005), Istanbul,.
- 4. "Bora Derin.,Onuralp Yucel, Ramana G. Reddy, "Sulfide Capacities of PbO-SiO2 and PbO-SiO2-AlO1.5 (Sat) Slags" Lead&Zinc 2005 Proceedings of the International Symposium on Lead and Zinc Processing, Kyoto, Japan, October 17-19, (2005) Vol II. pp: 1279-1287.
- 5. Derin B., Yucel O., Reddy R.G., "Predicting of Sulfide Capacities of Industrial Lead Smelting Slags" Sohn International Symposium on Advanced Processing of Metals and Materials: Principles, Technologies and Industrial Practice, August 27-31, 2006 Catamaran Resort. San Diego, California, USA
- 6. U. Demircan, B. Derin and O. Yücel. " Effect of HCl concentration on TiB<sub>2</sub> separation from a self-propagating high-temperature synthesis (SHS) product" Materials Research Bulletin (2006)
- 7. B. Derin U. Demircan, T. Uzunoglu, and O. Yücel. "Semi-Pilot Scale Calcination Study of Turkish Dolomite for Magnesium Production" International Magnesium Conference, China, (2006)
- 8. Derin B, Demircan U, Uzunoğlu T, Yücel O, "Decomposition of Turkish Dolomite Using Semi-Pilot Scale Rotary Furnace" 13th Proceedings of the International Metallurgy and Materials Congress, (2006), Istanbul, Turkiye.
- 9. Derin B, Yucel O, Klaus Hack "Computational Solutions in Metallurgical Processes" 13th Proceedings of the International Metallurgy and Materials Congress, (2006), Istanbul, Turkiye
- **10.** B. Derin, U. Demircan, O. Yucel, The Synthesis of TiB<sub>2</sub> Powder by a Self-Propagating High-Temperature Synthesis (SHS) and HCl Leaching Technique, Proceedings of the 10th International Conference of the European Ceramic Society, June 17 21, (2007), Berlin, 447 450.
- 11. B.Derin, M. Alkan and O. Yücel, "Effects of Charge Components on Ferromolybdenum Production by Aluminothermic Process" EuroMAT 2007, 10 13 September 2007, Nürnberg, Germany.
- 12. Filiz Sahin, Kutluhan Kurtoglu, Bora Derin, Onuralp Yücel. An Investigation of TiB2 Synthesis Using TiO2/B4C/C Powder Mixture, EPD Congress 2008 TMS Annual Meeting, March 9-13, (2008), New Orleans, USA, 355-360.
- 13. Bora Derin, Kutluhan Kurtoglu, Filiz Sahin, Onuralp Yücel. Titanium Diboride Synthesis by Carbothermal Reduction of TiO2 and B2O3, EPD Congress 2008 TMS Annual Meeting, March 9-13, (2008), New Orleans, USA, 379-383.
- 14. Derin B., Demircan U., Uzunoglu T., Yücel O,. "A Study on Thermal Decomposition of Dolomite from West Anatolia Region using semi-pilot Scale Rotary Furnace" The International Journal of Mineral Resources Engineering, Vol. 12, No.3 (2007) 205-214.



## Workshop on Computational Thermochemistry in Istanbul









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# Conclusion

*FactSage* is an invaluable tool for our experimental/modeling studies since it helps us for understanding and optimizing the existing /new processes.



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# THANK YOU FOR YOUR ATTENTION









**Bora Derin and Onuralp Yücel** 

Department of Metallurgical and Materials Engineering, Istanbul Technical University, Maslak, Istanbul, 34469, Turkiye

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