University-based Research Studies aided by FactSage Simulation Program – Part II

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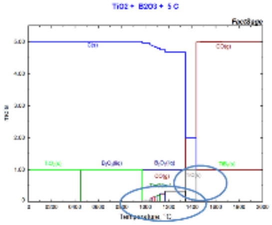
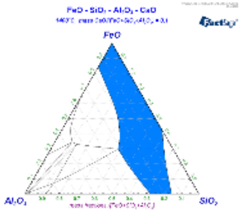
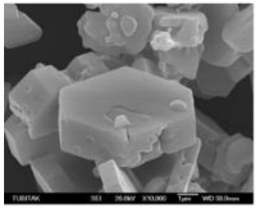
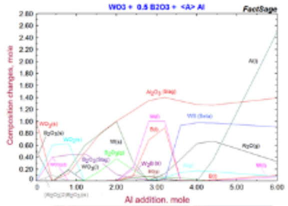








Case 1:

Canadian Metallurgical Quarterly

Investigation of effect of colemanite addition on copper losses in matte smelting slag

A. Ruşen[1], A. Geveci[1], Y. A. Topkaya*[1] and B. Derin[2]

The aim is to reduce copper losses to slag in copper production by using a boron compound, called colemanite ($2CaO.3B_2O_3.5H_2O$), as flux, besides silica.

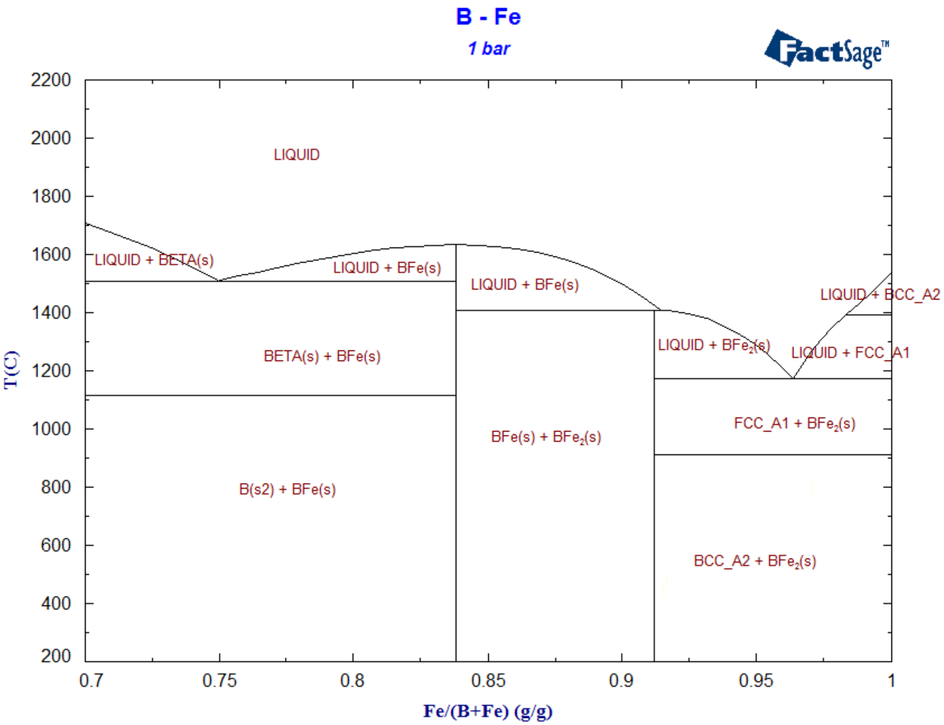
Table 1 Chemical analyses of all samples (FFM, FFS, MM and MS), wt.%

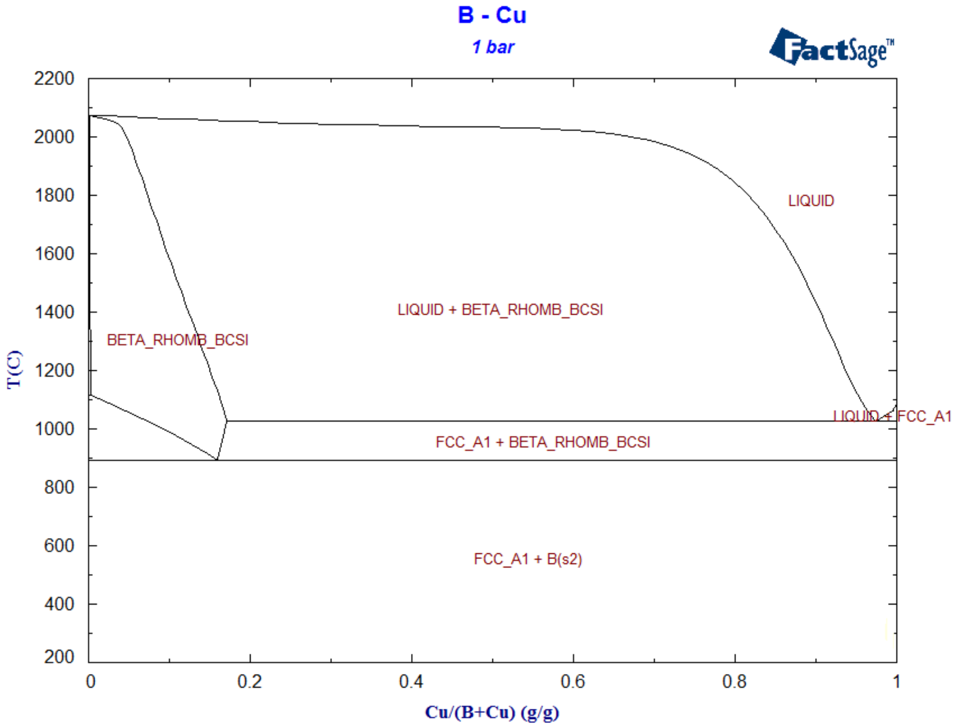
Sample/Constituent	Cu*	SiO_2	Fe_{Total}	S	Zn	Pb	Fe_3O_4	FeO‡	CaO	Al_2O_3
FFM	50·18	...	27·4	19·8	2·0	0·6	...	...	...	...
FFS	0·88	36·1	36·7	0·8	3·3	0·1	5·3	43·9	0·6	2·2
MM	51·56	...	24·4	24·0	...	...	...	...	...	...
MS	†	37·6	49·2	...	...	...	3·5	60·0	...	...

FFS-flash furnace slag
FFM-flash furnace matte
MS-master slag
MM-master matte

Eti Bakır Co. Samsun Plant is the only plant in Turkey where copper cathode is produced from ore.

Samsun Plant has a flash smelter, sulphuric acid, converter, anode casting and electrolysis facilities.



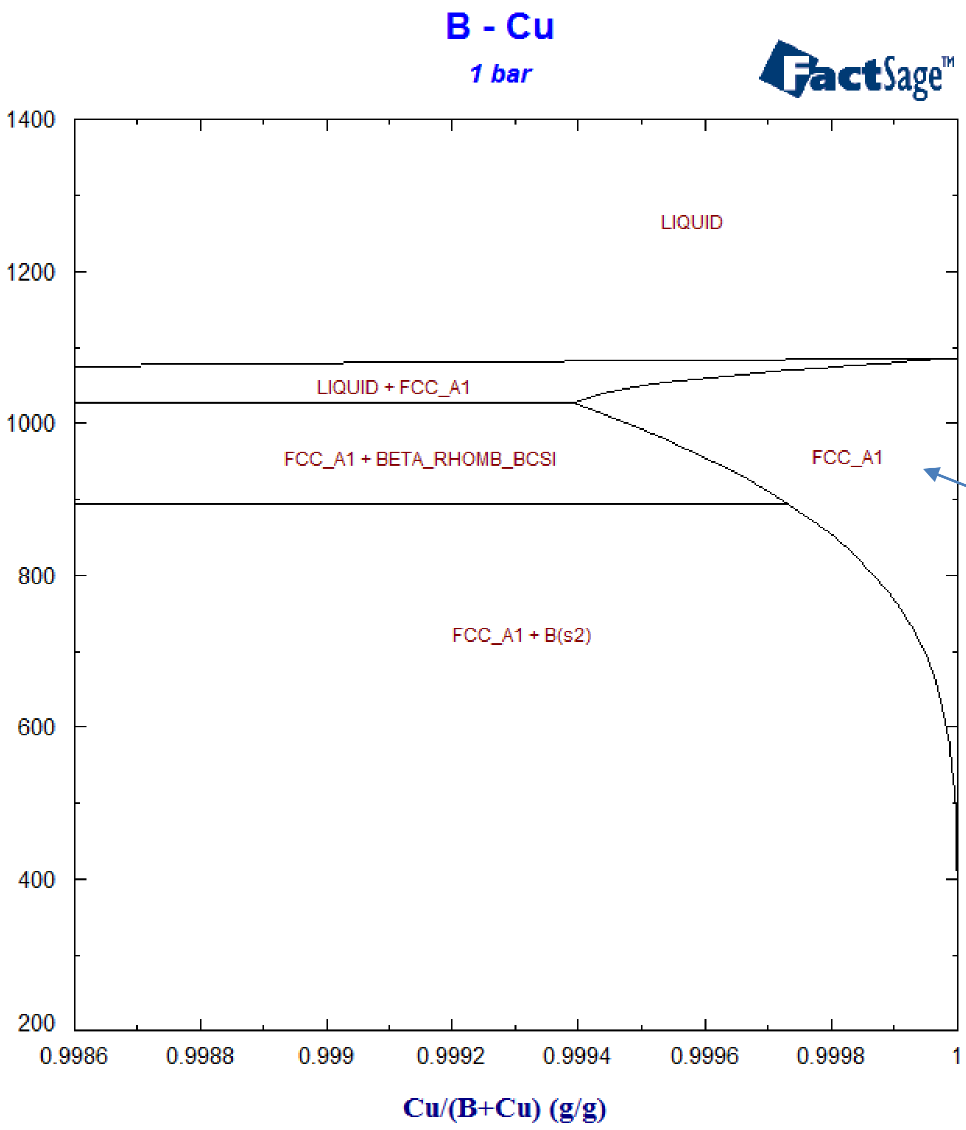


Boron-Iron Phase Diagram

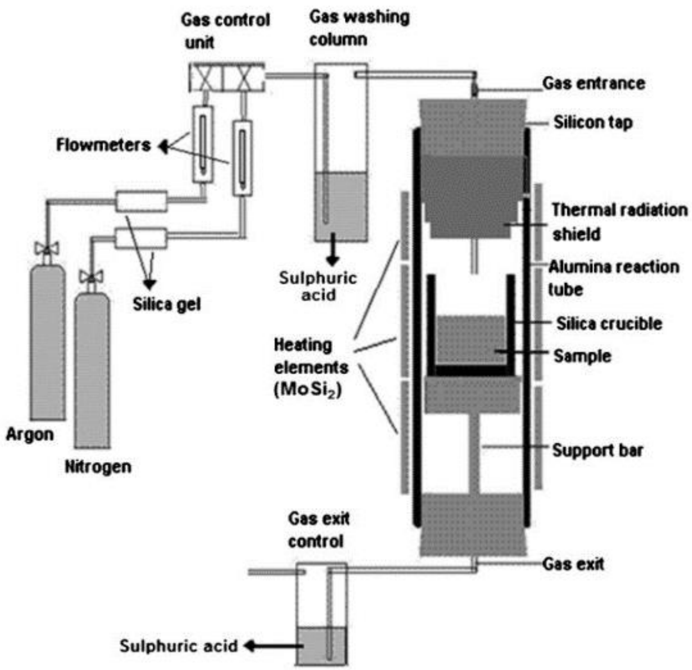
Boron compounds in Iron and Steel Slags could be deleterious for the steel.

Boron-Copper Phase Diagram

It seems boron has no solubility in copper in a macroscopic scale.

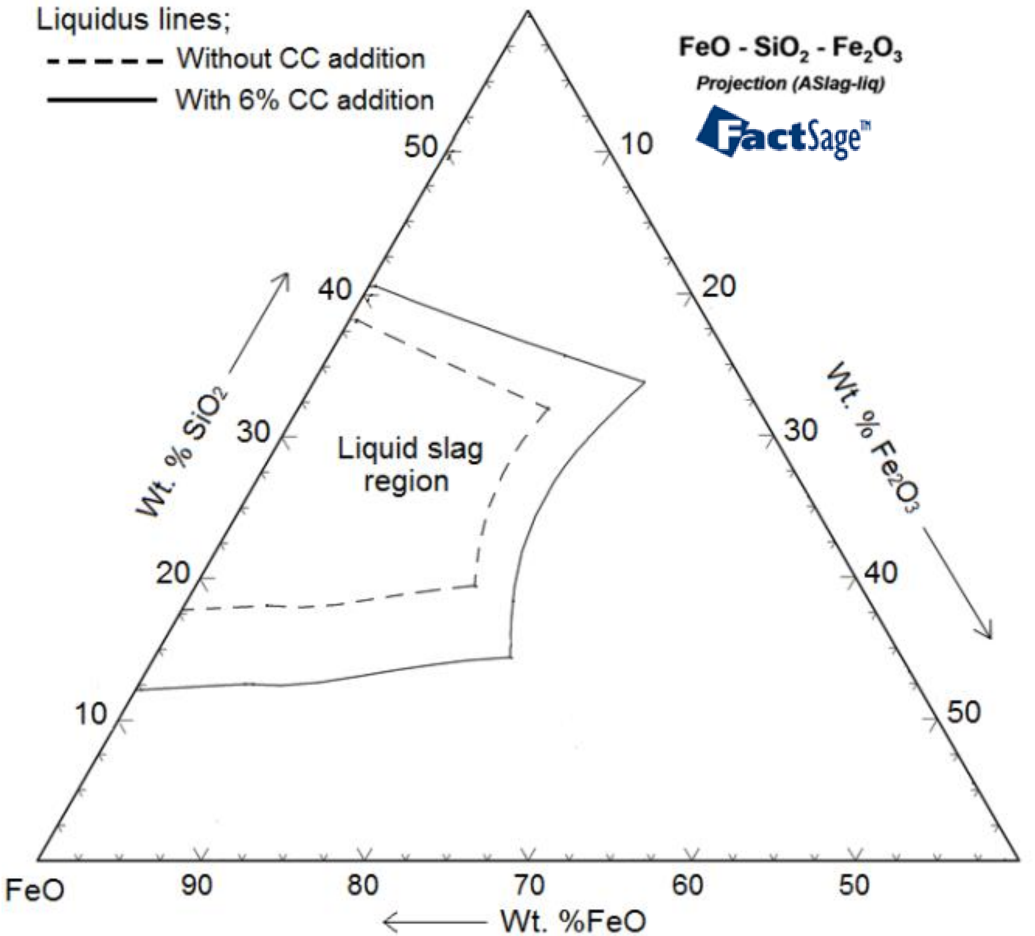


Copper has a negligable boron solubility at a certain temperature interval.

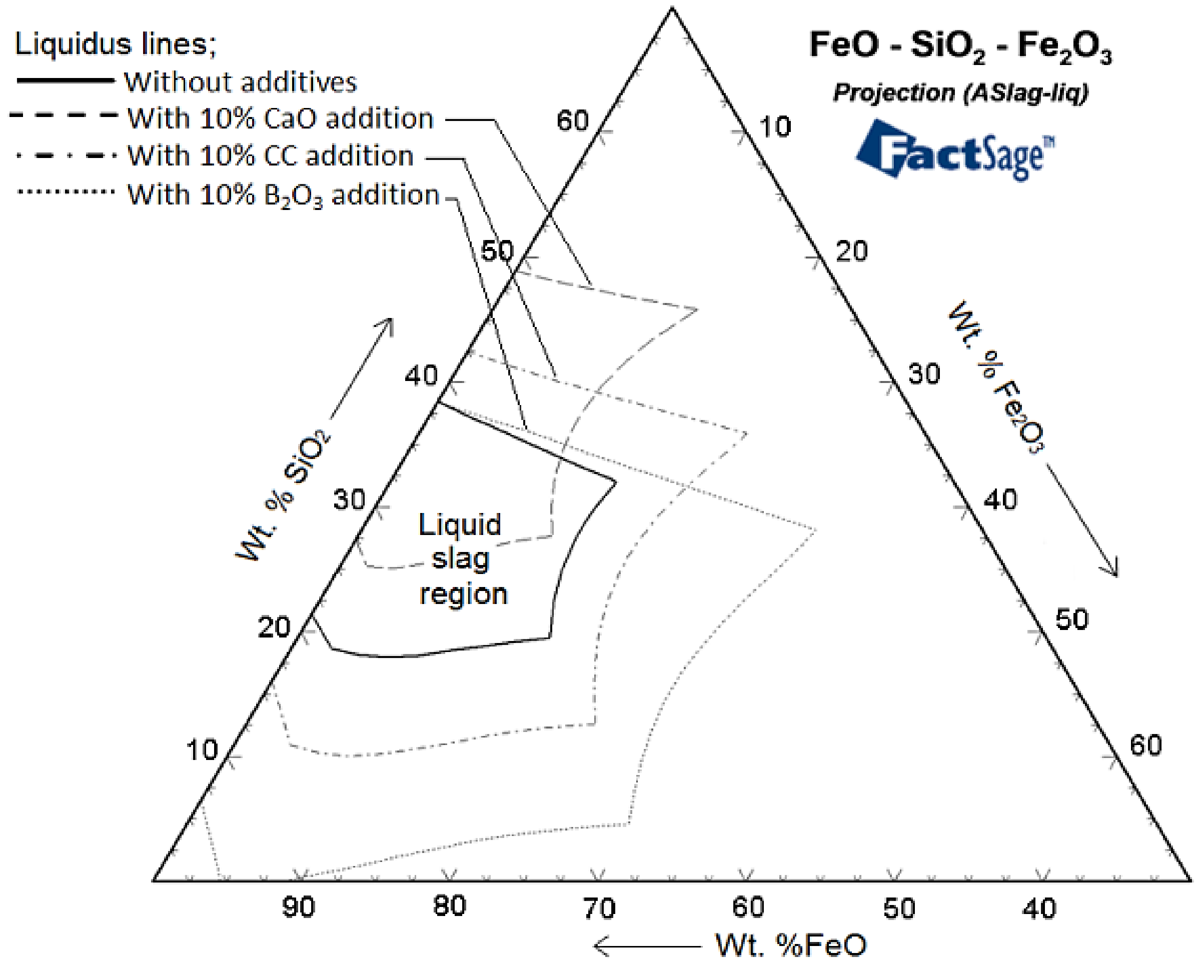


Experimental Parameters

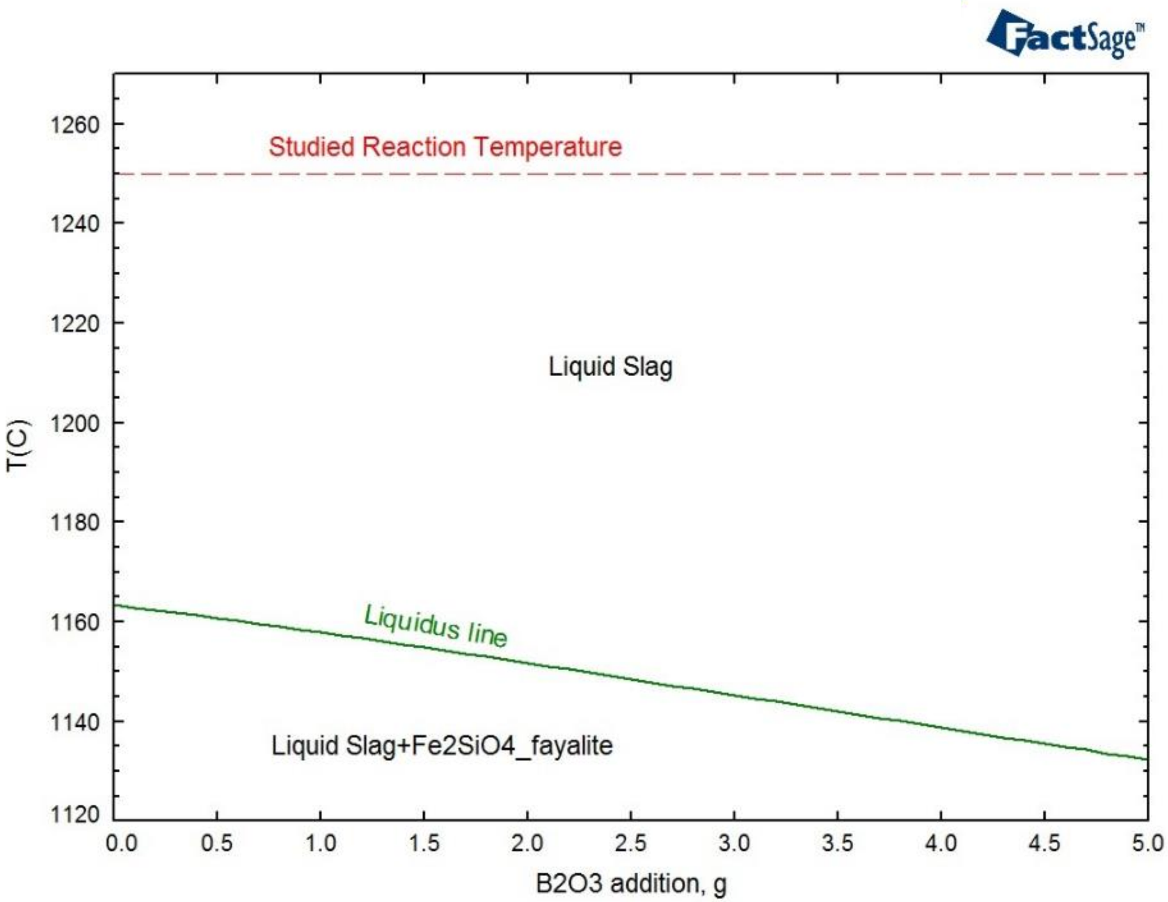
- **Additives** (calcined colemanite CC, CaO and B_2O_3) in various amounts (0%, 2%, 4%, 6% and 10%),
- **Time** (0.5, 1, 2 and 4 hours),
- **Temperature** (1200°C, 1250°C and 1300°C)
- **Atmosphere** (1 atm. nitrogen and low oxygen pressure atmosphere obtained by mixture of CO/CO_2 gases)



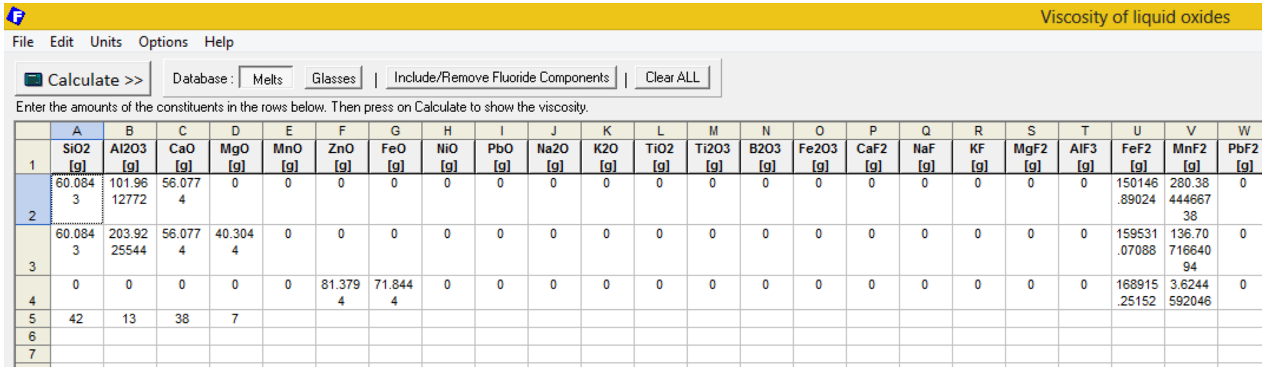
Change in liquid slag region with the addition of CC on phase diagram of FeO-Fe_2O_3-SiO_2 at 1250°C calculated by "Phase Diagram" module of FactSage



Change in liquid slag region with the 10 wt% addition of CaO,B_2O_3,CC on phase diagram of FeO-Fe_2O_3-SiO_2 at 1250°C calculated by “Phase Diagram” module of FactSage



Change in liquid slag region with the addition of B_2O_3 in FeO-Fe_2O_3-SiO_2-CaO-Al_2O_3-ZnO at 1250°C calculated by “Equilib” module of FactSage



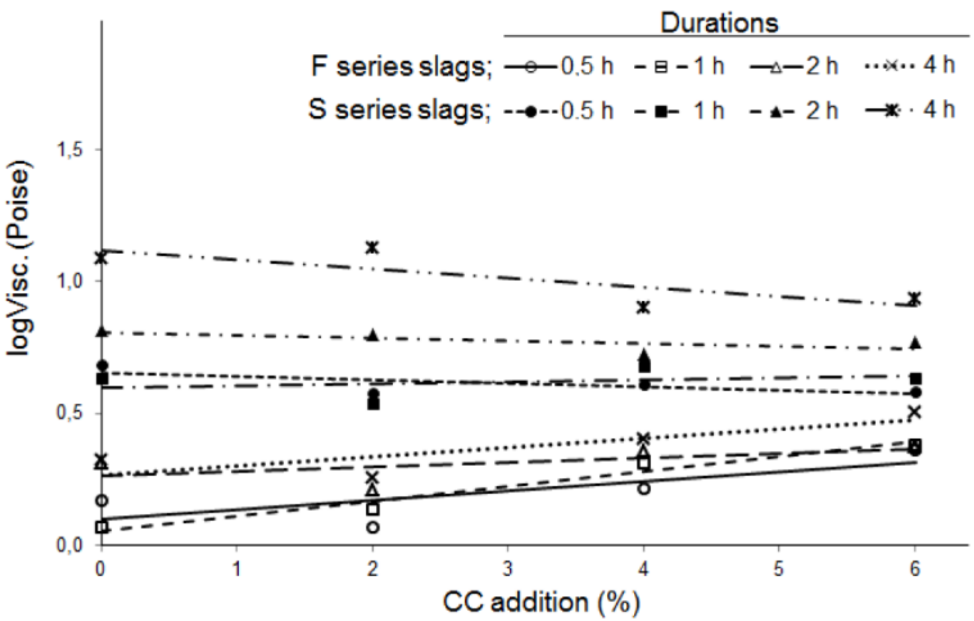
Viscosity of liquid oxides

File Edit Units Options Help

Calculate >> | Database : Melts | Glasses | Include/Remove Fluoride Components | Clear ALL

Enter the amounts of the constituents in the rows below. Then press on Calculate to show the viscosity.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W
1	SiO2 [g]	Al2O3 [g]	CaO [g]	MgO [g]	MnO [g]	ZnO [g]	FeO [g]	NiO [g]	PbO [g]	Na2O [g]	K2O [g]	TiO2 [g]	Ti2O3 [g]	B2O3 [g]	Fe2O3 [g]	CaF2 [g]	NaF [g]	KF [g]	MgF2 [g]	AlF3 [g]	FeF2 [g]	MnF2 [g]	PbF2 [g]
2	60.0843	101.9612772	56.0774	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	150146.89024	280.3844466738	0
3	60.0843	203.9225544	56.0774	40.3044	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	159531.07088	136.7071664094	0
4	0	0	0	0	0	81.3794	71.8444	0	0	0	0	0	0	0	0	0	0	0	0	0	168915.25152	3.6244592046	0
5	42	13	38	7																			
6																							
7																							



Variations of predicted viscosity of the resultant slags for F and S series with the addition of CC and reaction duration.

Case 2:

Self Propagating High Temperature Synthesis = Combustion Synthesis

In a SHS process, after ignition, the combustion front is formed and propagates throughout the reactant mixture yielding the desired product.

Movie clip: Institute of Structural Macrokinetics and Materials Science - Russian Academy of Sciences (ISMAN)

Self-propagating High-temperature synthesis (SHS) is the synthesis of compounds (or materials) in a wave of chemical reaction (combustion) that propagates over starting reactive mixture owing to layer-by-layer heat transfer.

http://shs2015.org/

SHS is known to yield the following classes of compounds:

- Advanced materials, biomaterials, magnetic and thermoelectric materials, refractory compounds, oxides, intermetallics, borides, nitrides, phosphides, hydrides, etc.
- Reduced elements (B, Ti, Mo, etc.)
- inorganic composites (ceramics, cermets, mineraloceramics, composite materials, etc.)
- organic compounds (piperazine malonate, quinhydrone, ferrozerone (o-carboxybenzoylferrozene), etc.)

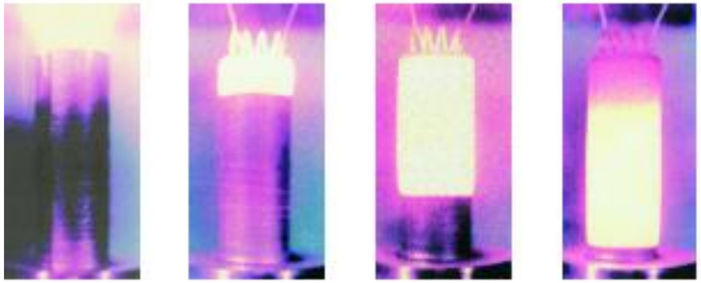


Photo of SHS process

Synthesis from the elements

- $Ti + C = TiC$
- $Ni + Al = NiAl$
- $3Si + 2N_2 = Si_3N_4$
- $Zr + H_2 = ZrH_2$

Redox reactions

- $B_2O_3 + 3Mg + N_2 = 2BN + 3MgO$
- $B_2O_3 + TiO_2 + 5Mg = TiB_2 + 5MgO$
- $MoO_3 + B_2O_3 + 4Al = MoB_2 + 2Al_2O_3$
- $3TiO_2 + C + 4Al = TiC + 2Al_2O_3$
- $2TiCl_4 + 8Na + N_2 = 2TiN + 8NaCl= YBa_2Cu_3O_{7-x}$ $Nb + Li_2O$

Oxidation of metals with complex oxides

- $3Cu + 2BaO_2 + 1/2Y_2O_3 + 0.5(1.5 - x)O_2 = YBa_2Cu_3O_{7-x}$
- $Nb + Li_2O_2 + 1/2Ni_2O_5 = 2LiNbO_3$
- $8Fe + SrO + 2Fe_2O_3 + 6O_2 = SrFe_{12}O_{19}$

Synthesis from compounds

- $PbO + WO_3 = PbWO_4$

Reaction of the elements with decomposition products

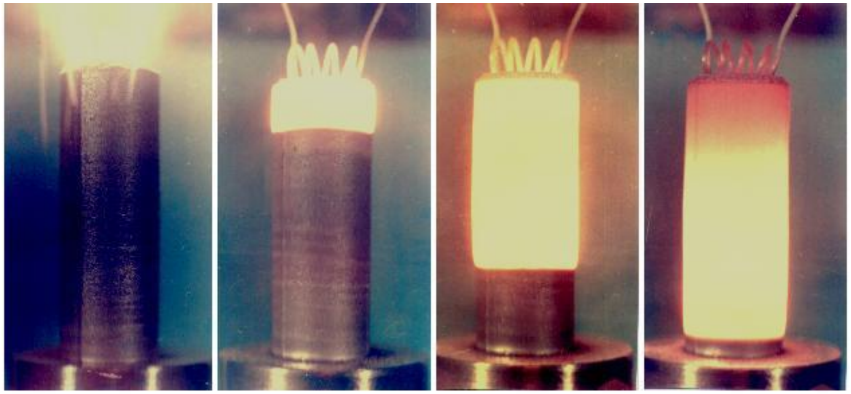
- $2TiH_2 + N_2 = 2TiN + 2H_2$
- $4Al + NaN_3 + NH_4Cl = 4AlN + NaCl + 2H_2$

Thermal decomposition

- $2BH_3N_2H_4 = 2BN + N_2 + 7H_2$

Typical parameters of SHS

- Burning velocity: 0.1–20 cm/s
- Combustion temp.: 2300–3800 K
- Heating rate: 103–106 K/s
- Duration for ignition: 0.2–1.2 s
- Ignition temp.: 800–1200 K



t=0s t=0.1s t=2.7s t=4.0s

The maximum temperature, Tad , which the reacted powders would reach if the reaction was strictly adiabatic was calculated from the general relationship

$$Q_V = \int_{T_i}^{T_{ad}} C_p \, dT + \Delta H_m$$

where Cp is the molar heat capacity of the product, Hm its heat of fusion and Ti the temperature at which the reaction is triggered.

Note: The Tad calculation is easy when we assume the products are exactly same with the given formula.

Tungsten Boride

Properties

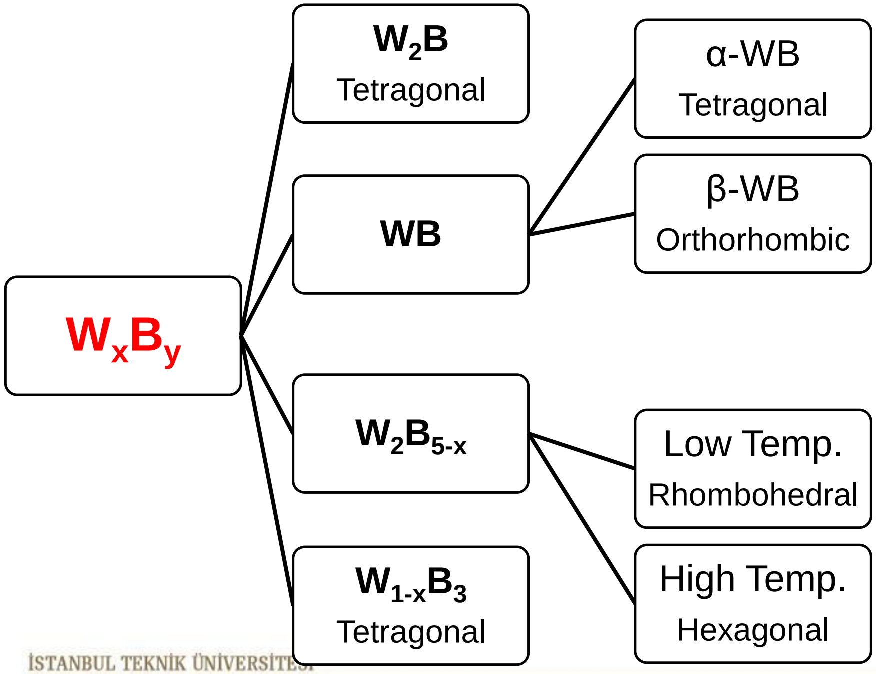
- High hardness values
- Chemical inertness
- Electronic conductivity
- Resistance to thermal shock.

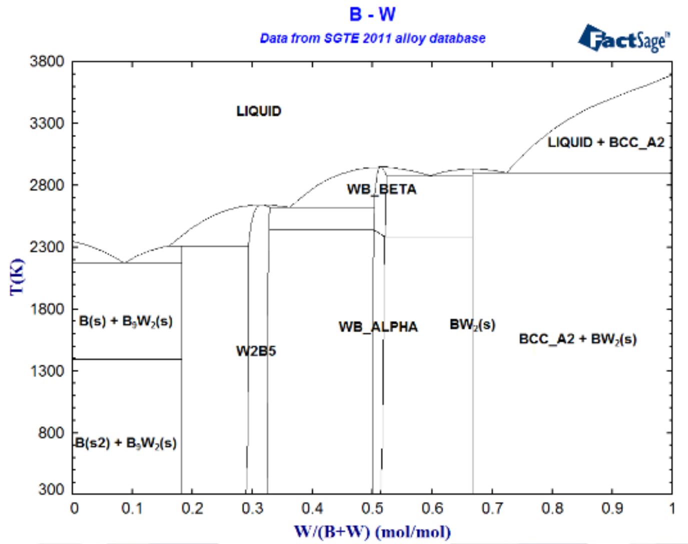
Applications

- Abrasive, corrosion resistant and electrode materials
- Crucibles and ingot molds for precision metallurgy
- Sputtering targets
- Sintering additives

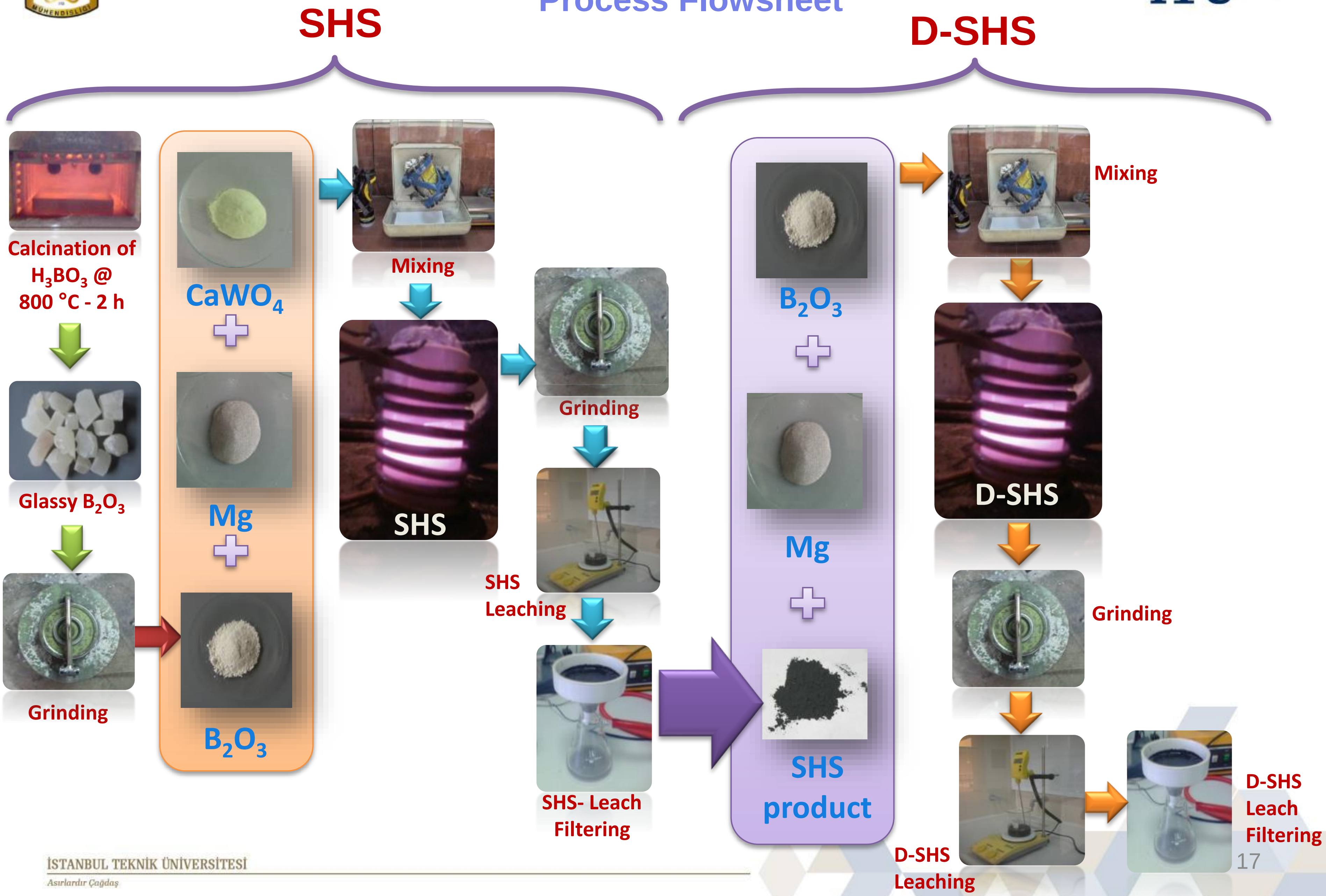
Synthesis Methods

- Solid state reaction
- Mechanical alloying
- Salt melt electrolysis
- Vapor deposition





Process Flowsheet



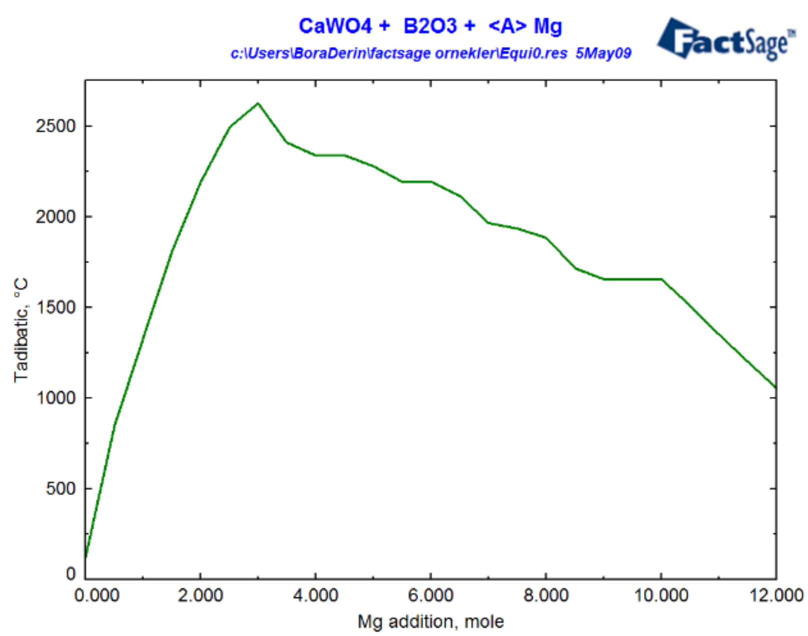
Theoretical Study

SHS PROCESS

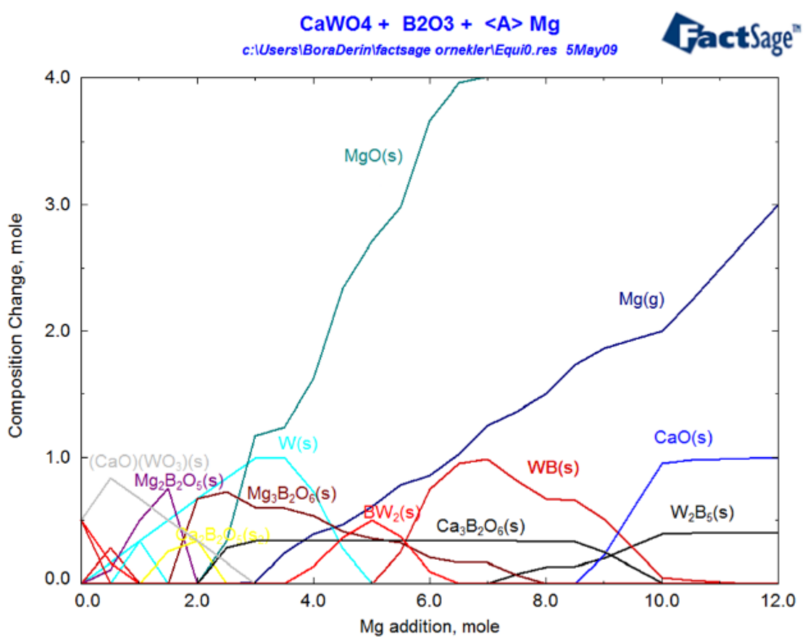
***FactSage* Software for Adiabatic Temperature and SHS products**

- **What is Adiabatic Temperature (T_{ad})?** → **T_{ad} > 1527 °C (1800 K)**
- **Which initial composition gives the best result** → **$CaWO_3 + x\ Mg + y\ B_2O_3$**

FactSage simulation for estimations of Adiabatic Temperature and SHS products
Effect of Mg addition



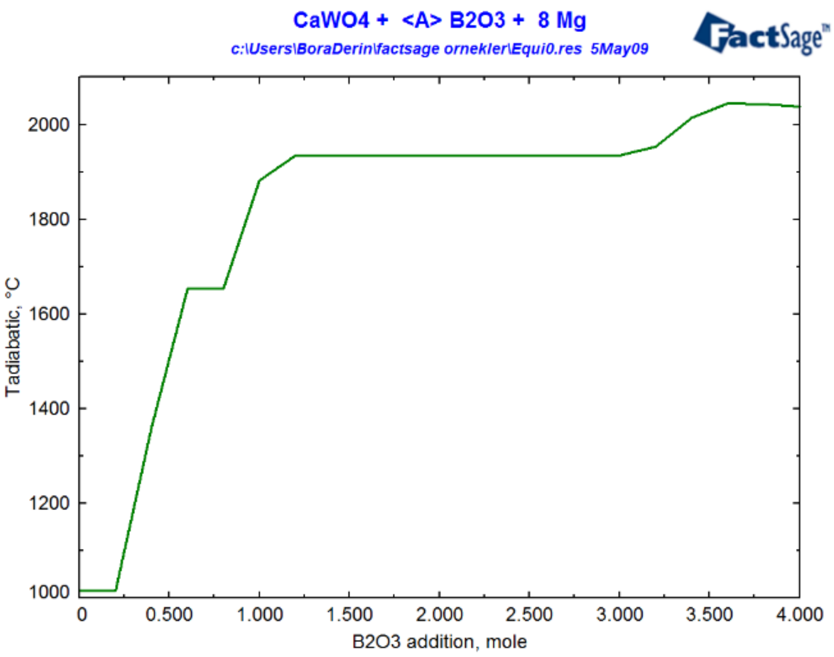
T_{ad} change with addition of Mg



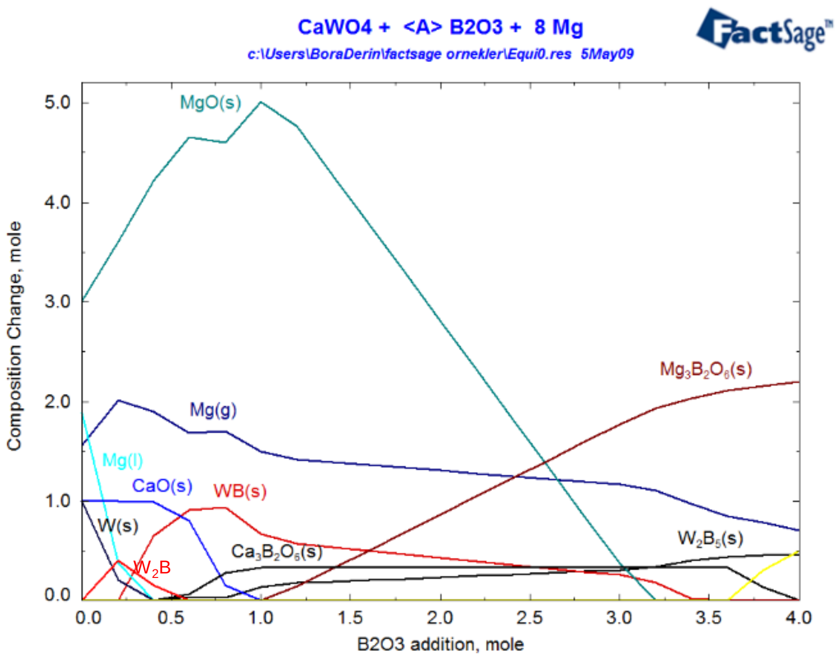
SHS products composition change with addition of Mg

Case 5

FactSage simulation for estimations of Adiabatic Temperature and SHS products Effect of B_2O_3 addition



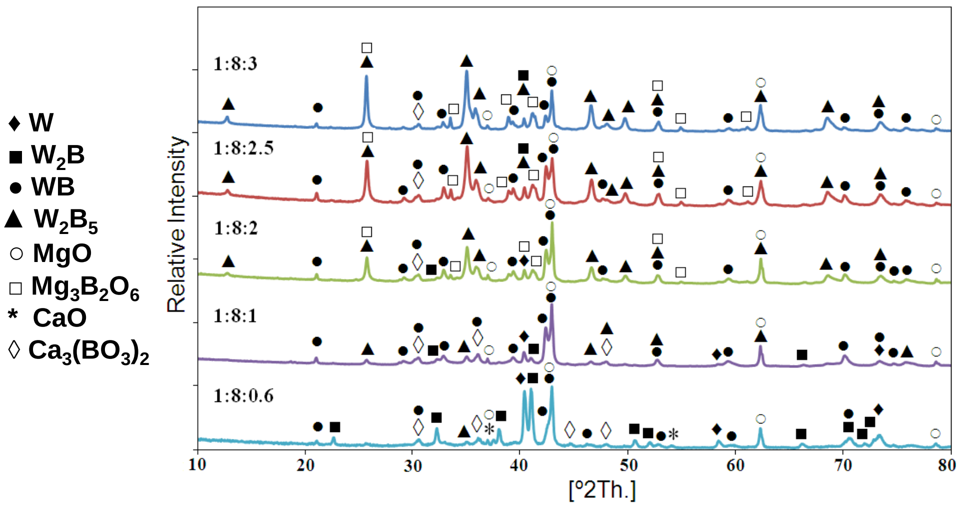
T_{ad} change with addition of B_2O_3



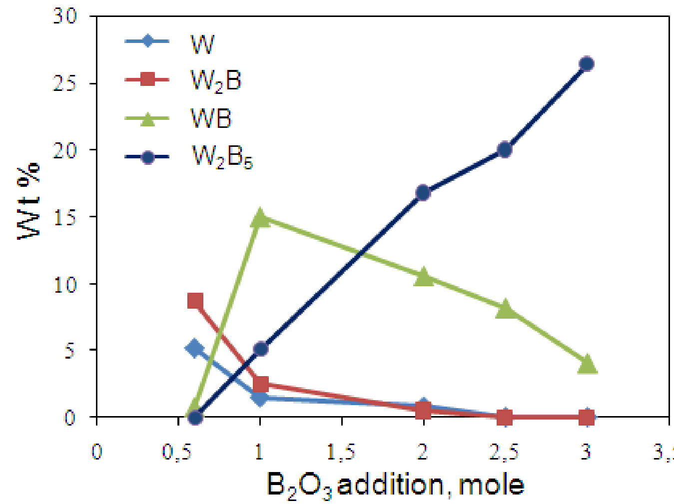
SHS products composition change with addition of B_2O_3

Experimental Results 1st Step- SHS PROCESS

$CaWO_4 + 8Mg + xB_2O_3$



XRD analysis of SHS products obtained by different stoic. B_2O_3 additions.



Change of W and tungsten boride compounds with addition of B_2O_3.

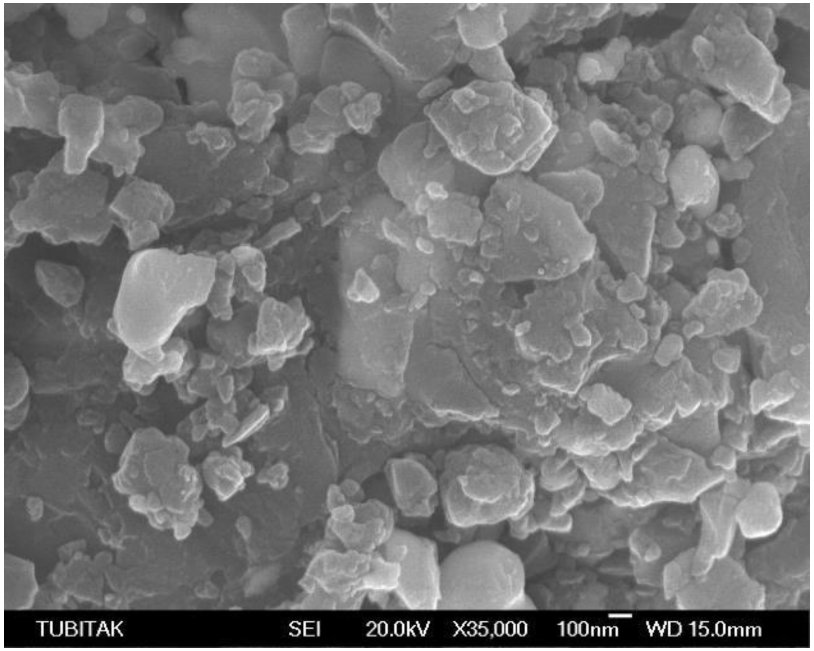
XRD/Rietvelt analysis of SHS products.

Exp. No	$CaWO_4$:Mg:B_2O_3 Molar ratio	Composition, wt. %							
		W	W_2B	WB	W_2B_5	MgO	$Mg_3B_2O_6$	CaO	$Ca_3(BO_3)_2$
1.4	1:8:0.6	5,2	8,70	0,8	-	68,1	-	3,8	13,4
1.9	1:8:1	1,5	2,5	15	5,1	62,6	-	-	13,3
1.6	1:8:2	0,8	0,5	10,6	16,8	43,1	16,6	-	11,6
1.10	1:8:2.5	-	-	8,2	20	34,5	28,6	-	8,8
1.32	1:8:3	-	-	4,1	26,4	34,6	27,8	-	7,1

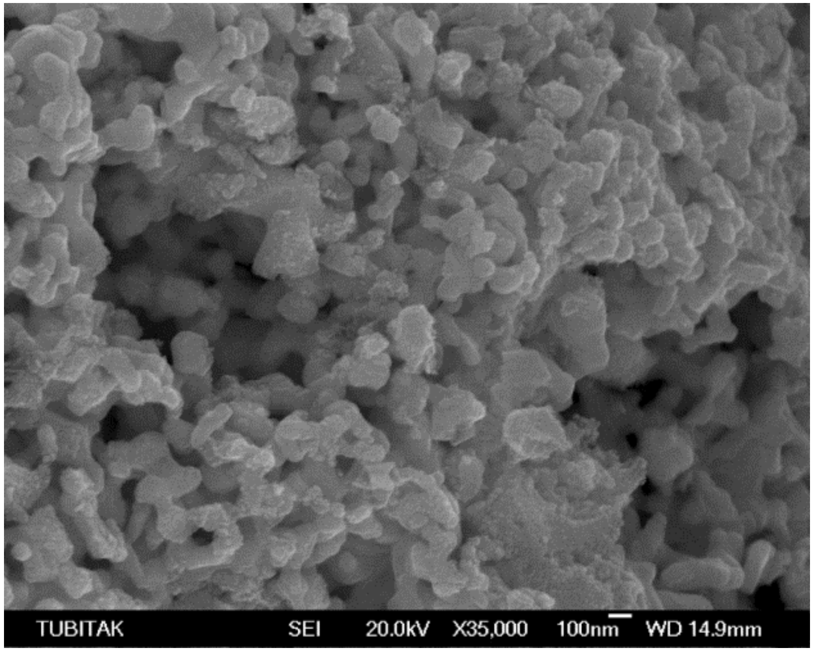
$a\mathrm{CaWO_4} + b\mathrm{B_2O_3} + c\mathrm{Mg} = x\mathrm{WB} + y\mathrm{MgO} + z\mathrm{CaO}$

FactSage™

$a\mathrm{CaWO_4} + b\mathrm{B_2O_3} + c\mathrm{Mg} = s\mathrm{W} + t\mathrm{W_2B} + u\mathrm{WB} + v\mathrm{W_2B_5} + w\mathrm{Mg_3B_2O_6} + x\mathrm{MgO} + y\mathrm{CaO} + z\mathrm{Ca_3(BO_3)_2}$



(a) unleached SHS product particle (SEM x35,000)



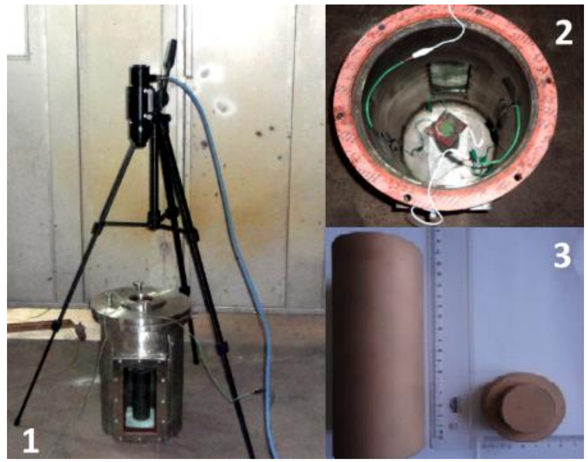
(b) leached SHS product particle (SEM x35,000)

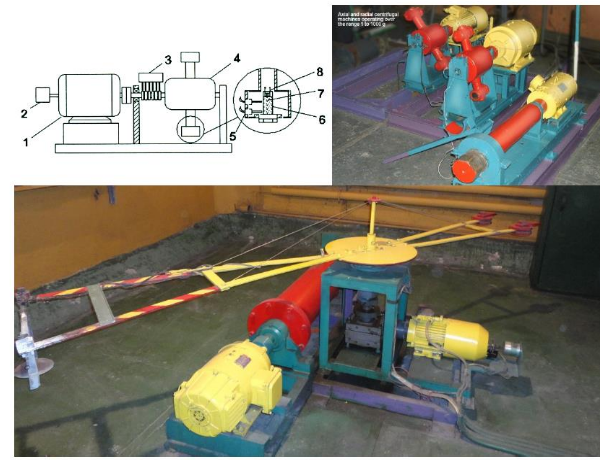
Case 3:

Multicomponant Alloy Systems for Wear/Corrosion Resistant Alloys and MMCs by SHS method

Co-V-Al
Ni-Co-Al
Ni-Cr-Al
Ni-Co-Mn-Al
Ni-Cr-B-Al
Co-Cr-Mo-Al
Fe-Co-V-Al

Mo-Ni-B-(Cr,Mn,Ta,V,Nb)
Mo-Co-B-(Cr,Mn,Ta,V,Nb)
Mo-Fe-B-(Cr,Mn,Ta,V,Nb)





These studies aims to establish a scientific and engineering background for high energy efficient, fast and low-cost production manufacturing technology of multi-component alloys by using Self-Propagating High Temperature Synthesis (SHS-metallurgy) method starting from relatively cheap materials (oxides).

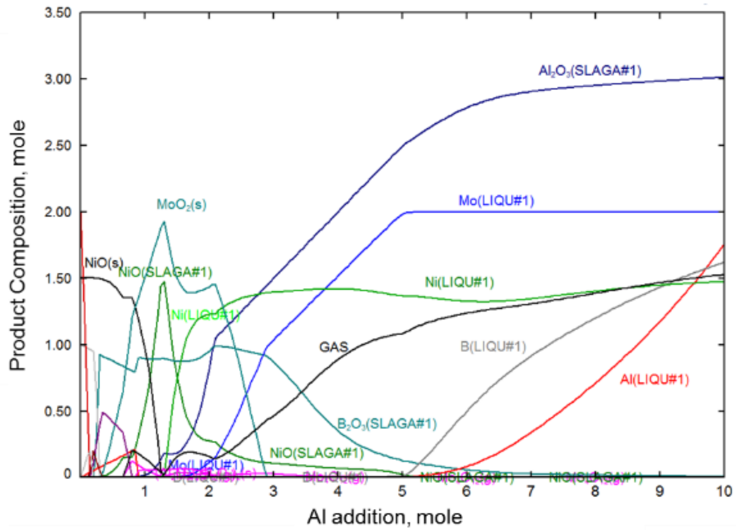
Experimetal Parameters:

Different composition and gravity values, heat sinkers, crucibles, additives etc.

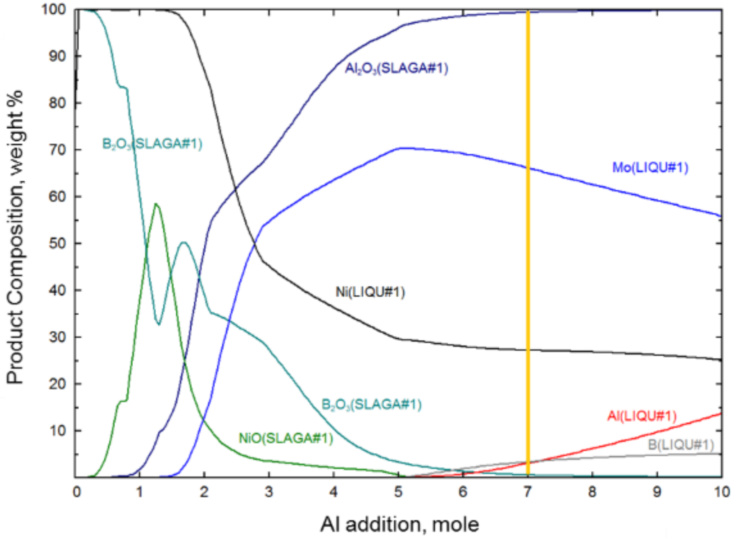
$x = 3$ 11 17 23 31

2 MoO3 + 1.5 NiO + B2O3 + <A> Al

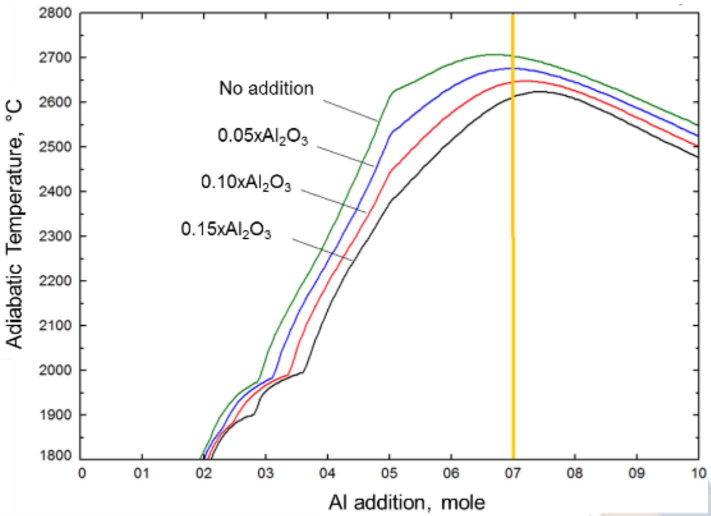
C:\FactSage\Equi0.res 05Apr15



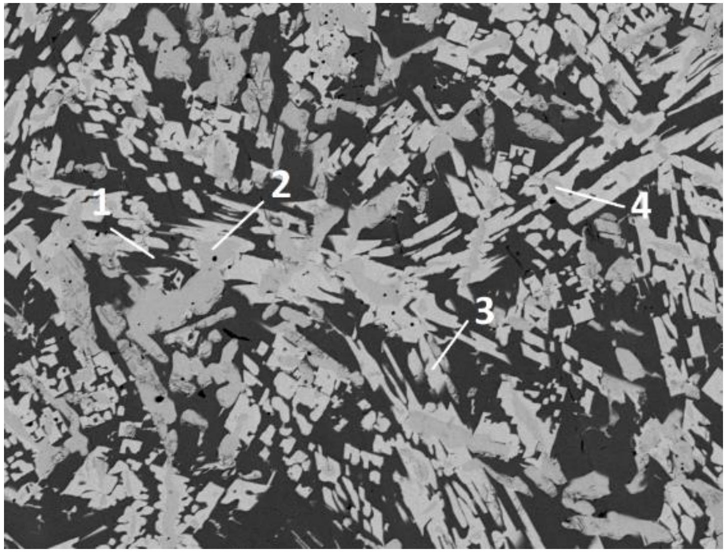
SHS products composition change with addition of Al, mole



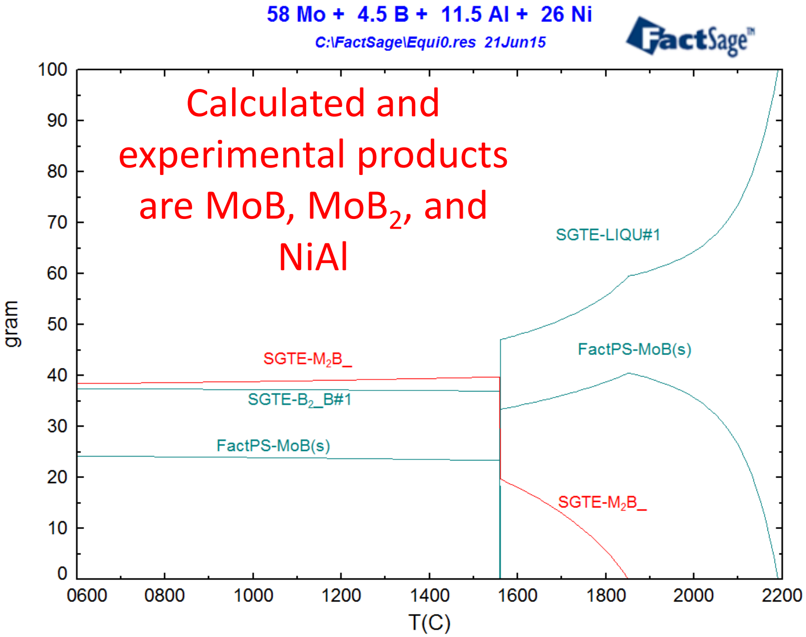
SHS products composition change with addition of Al, wt.%



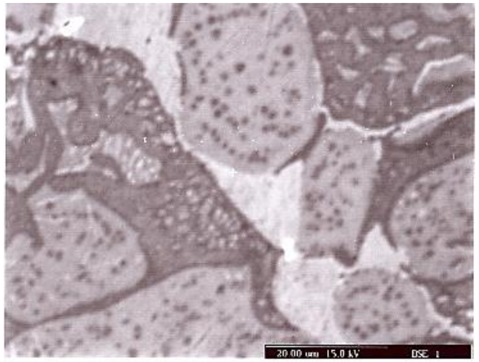
T_{ad} change with addition of Al_2O_3

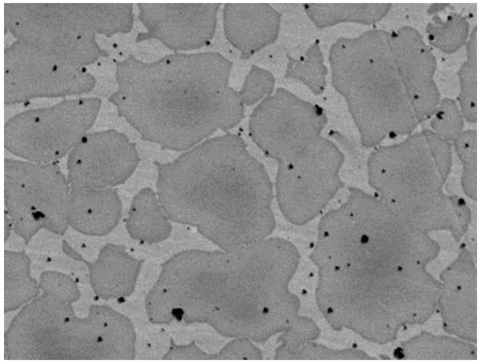


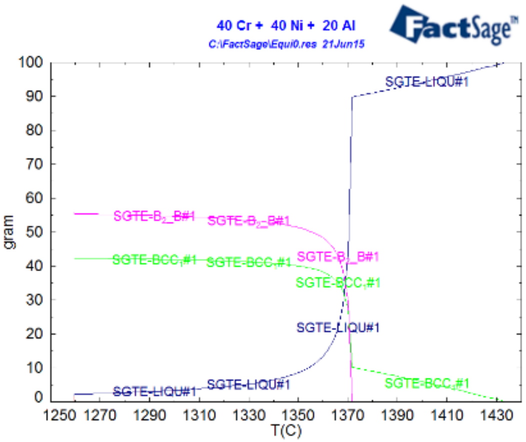
The SEM-BSE image of an SHS produced Mo-Ni-Al-B alloy (x500)



Equilibrium Cooling of an Mo-Ni-Al-B alloy







Types of precipitations or change of composition in dendrites & boundaries with Scheil Cooling

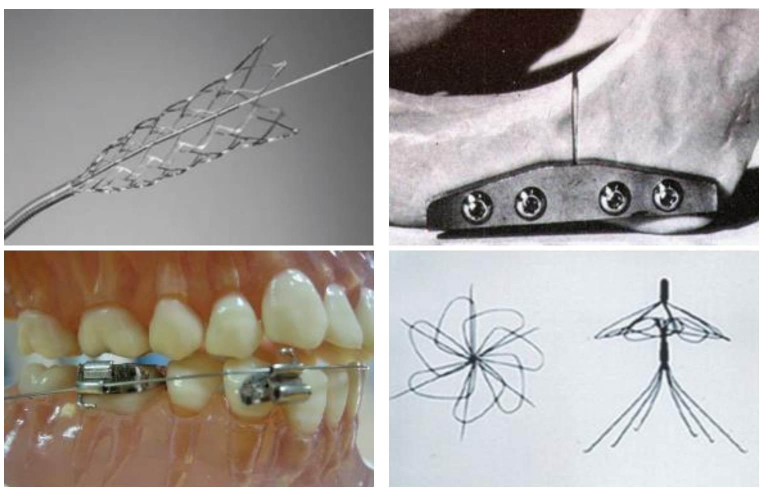
Case 4:

Self-Propagating High Temperature Synthesis (SHS) Based Production and Characterization of Ni-Ti-X (X=Cu, Fe, Nb) Shape Memory Alloys

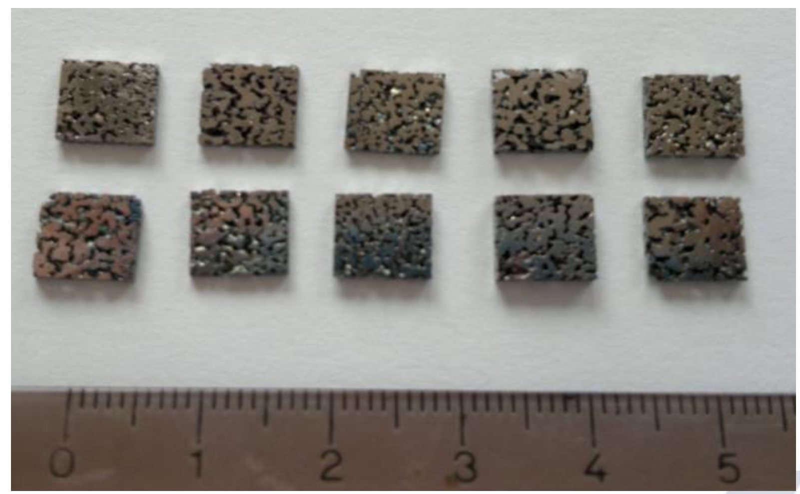
Consiglio Nazionale delle Ricerche

Shape memory alloys based on NiTi have found their main applications in manufacturing of new biomedical devices mainly in surgery tools, stents and orthopedics.

Porous NiTi can exhibit an engineering elastic modulus comparable to that of cortical bone (12-17 GPa). This condition, combined with proper pore size, allows good osteointegration.



SMA neurosurgical stent, plate, orthodontic wires, venous filter

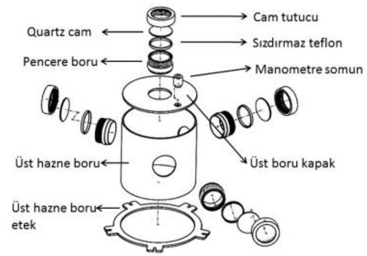


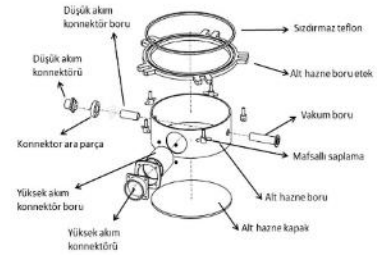
Representative porous SHS NiTi sample for biological tests

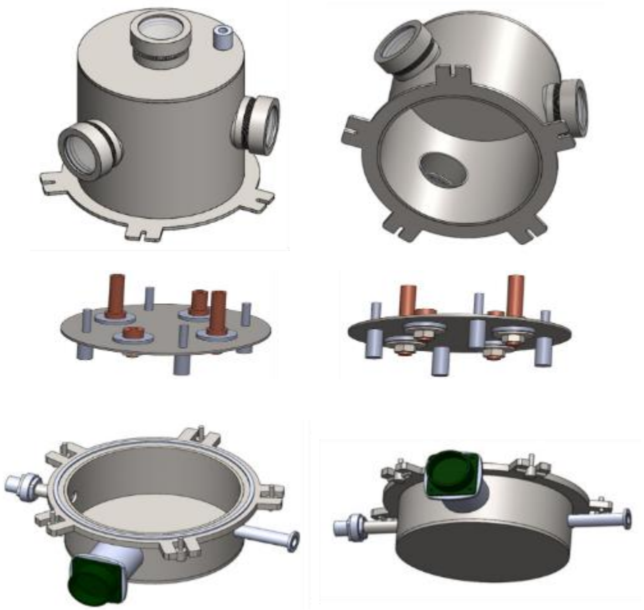
Image: L. Petrini and F. Migliavacca, Journal of Metallurgy Volume 2011, Article ID 501483

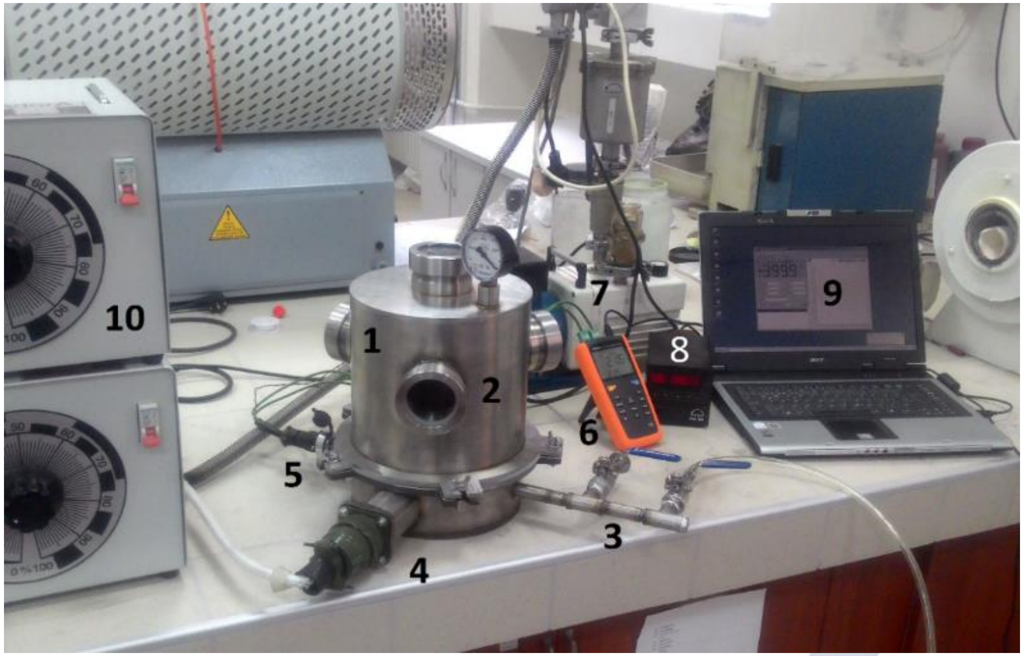
Image: Bassani *et al.* J Mater Sci: Mater Med (2014) 25:2277–2285

In the current project, open cells porous NiTi-X (X=Cu-Nb-Fe) will be produced by self propagating high temperature synthesis (SHS), which is a rapid, low cost and high efficiency production method.

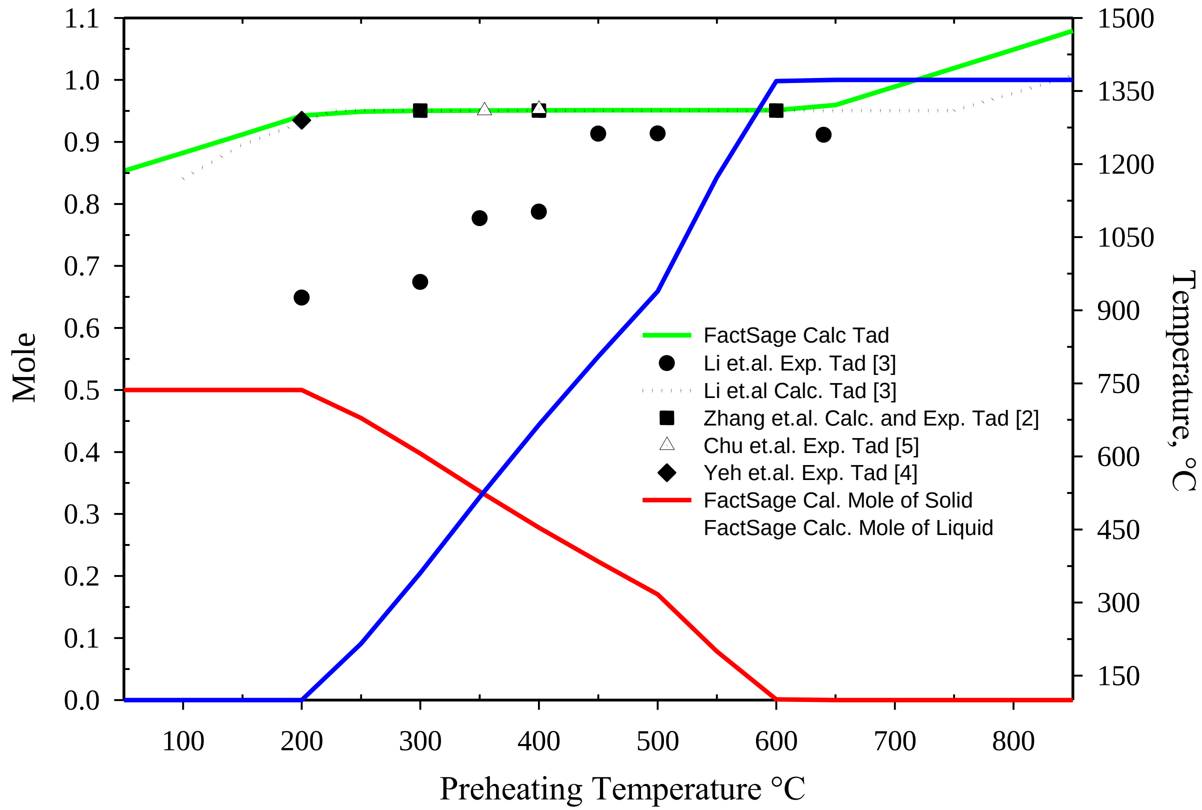








Morphological and thermomechanical properties of the ultimate products will be investigated via different characterization methods.



Adiabatic temperature and solid/liquid composition corresponding to preheating temperature for Ni-Ti mixture (50-50 at.%)

Case 5:

MODELLING AND SIMULATION

THERMOCHEMICAL COMPUTATIONS IN CARBOTHERMIC AND METALLOTHERMIC FERROALLOY PROCESSES

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Helsinki, Finland

In the case examples, **the interactions and effects of both oxygen and CaO on phosphorus and silicon removals during the second refining stage of the crude ferronickel**, **the optimum quantity of intermediate Fe-Si-Cr alloy needed to reduce molten rich slag in Perrin process**, **the effect of temperature on the carbothermic reduction of SiMn production**, and the ***effect of raw material on metallothermic production of FeMo*** were simulated and the results were tabulated and/or graphed.

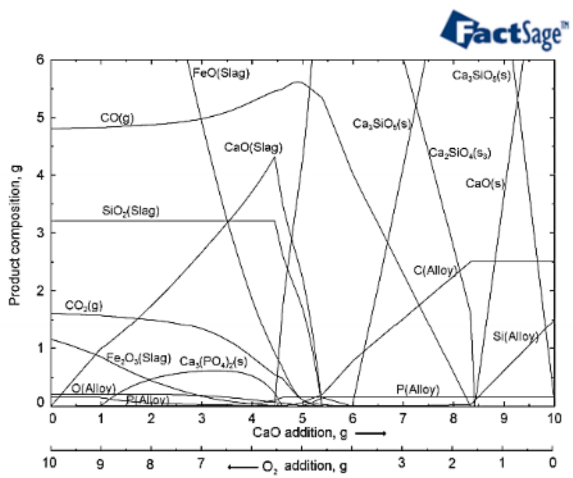

Figure 2: Simulation result of interactions and effects of both oxygen and CaO on phosphorus removal during the second refining stage of the crude ferronickel at 1600 °C and P_{tot}=1 atm.

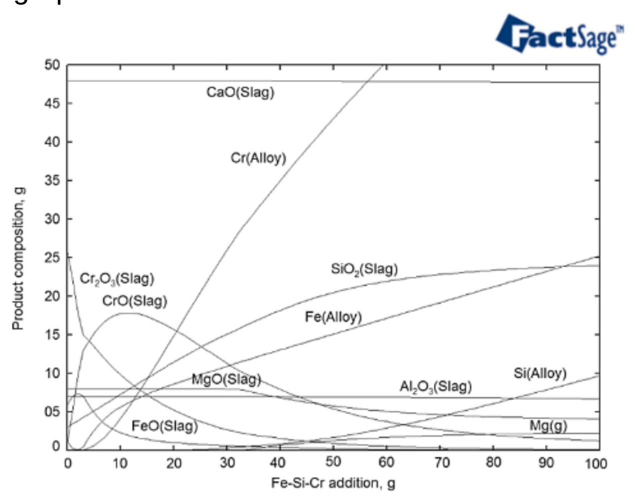

Figure 3: Simulation result of effect of intermediate Fe-Si-Cr alloy on perrin process for the production of LC ferrochromium

Table 1: The output substances of calculated LC FeCr alloy with 70% Cr

Alloy			Slag		
Comp.	wt, g	wt%	Comp.	Wt, g	wt%
Cr	27.26	70.00	CaO	48.00	52.01
Fe	11.21	28.79	SiO_2	15.48	16.78
Si	0.4088	1.050	CrO	10.79	11.69
Mg	0.0282	0.0723	MgO	7.953	8.619
C	0.0156	0.0401	Al_2O_3	6.979	7.563
O	0.0096	0.0246	Cr_2O_3	2.487	2.696
Al	0.01102	0.0283	FeO	0.5863	0.6354

Table 2: The amounts of input substances for the simulation of SiMn production.

Input, kg.	MnO_2	MnO	Mn	Fe	Fe_2O_3	Si	SiO_2	Al_2O_3	CaO	MgO	P	Fix C
Mn-ore	316				57		16	1	23	2	0.16	
HC-slag		546					308	156	181	82		
Metal in slag			174	33								7
Quartz					4		399	14	7	7		
Coke mixture					3		15	10	1		0.14	264
Dolomite								3	29	17		
Si-met.sculls				4		79	36	7	7			1
Total	316	546	174	37	64	79	774	191	248	108	0.30	272
Sum of mixture	2809	kg										

Case 6:

Graduate Course:

Computational Thermochemistry for Metallurgical Processes

FactSage is the workhorse of the course

Case 6:

New R&D department in Eregli Integrated Iron & Steel Company

Ereğli Iron and Steel Company (Erdemir) which is the largest flat steel manufacturer of Turkey, located in Kdz. Ereğli.

İsdemir, long and flat steel producer located in İskenderun,

Some New Research Studies with FactSage

- Nozzle clogging
- Refractory wear
- BOF simulations
- Recovering of valuable metals from flue dusts

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

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