Development of Process Slags for Cu-Cr-Recycling Processes

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Abstract

In standard remelting processes of metallic copper scrap it is not necessary to add slag components. Mostly graphite is used to protect the melt against oxidation. If alloying elements have high affinity for oxygen like Mg, Zr or Cr the remelting takes place under vacuum or cover gas. Unfortunately, re-melting under such conditions is expensive and takes place typically in small scale batches. Therefore, depending on the mass flow of the alloy these processes are mostly not cost effective. In a current research programme IME investigates exemplary the recycling process of Cu-Cr-alloys, materials mostly used for welding electrodes, high temperature magnetic coils or recuperators. The Cr content of this material varies between 0.4 and 1.2 mass-%. Due to its ignoble character a huge amount of Cr becomes slagged while remelting in large open induction furnaces, despite of the use of common graphite protection layers. Besides that, the mixture of partially molten oxidic phases and graphite produces a highly viscous slag which has to be taken out of the furnace regularly by hand. The paper will present the results of thermochemical modelling performed for different slag systems appropriate for chromium containing copper melts. Subsequent equilibrium tests under inert gas atmosphere as well as kinetic experiments under defined atmospheres allow assessment of the slag’s oxygen permeability .The main objectives are to minimize the losses of the valuable metals and to create a fluid low viscous slag which can easily be tapped after melting from the metal surface without strong interaction to the furnace lining.

1 Introduction

From the world-wide copper production just 30 % of the metal is alloyed. The most important alloying elements are zinc, tin, nickel and Aluminium. Contrary to the solid solution hardening alloys like CuAg, CuCd or CuMg, which increase their strength by deformation at low temperatures, precipitation-hardening alloys possess high strengths with small loss of conductivity and high softening temperatures [1][2][3]. The requirements of high performance copper alloys are continuously rising, such as materials of high strength without loosing conductivity. Due to their characteristics CuCr alloys fulfil many of the requirements and such they are used for welding electrodes, engine commutators, high temperature solenoid coils, slip rings, pistons and Nozzles for plastic presses, points of oxygen lances, moulds for continuous casting plants and heat exchangers [4].

Figure 1: welding electrodes, moulds for continuous casting, nozzles for plastic presses

Already small quantities of chrome additions from 0.3 to 1.2 mass.-% increase the hardness of copper alloys. The tensile strength rises to a value of up to 500 N/mm^2 in opposition to copper with a tensile strength of just 350 N/mm^2. The conductivity of chromium containing copper alloys is $45\ m\cdot(\Omega\cdot mm^2)^{-1}$, which corresponds to about 80% of the conductivity of the pure copper [3].

2 Theoretical work

2.1 Binary system Cu-Cr

The ternary system Cu-Cr-Ni was firstly investigated by “Siedschlag” [5]. At this time he determined the binary phase diagram of Cu-Cr by using research results of “Hindrichs” from 1908 [5]. Those binary phase diagrams differ a lot to the nowadays used ones. These differences are due to an insufficient purity of 97% of the metals used by “Siedschlag” and a nitrogen atmosphere used by “Hindrichs”. Already small amounts of dissolved nitrogen and aluminium lower the melting temperature of chrome. In the last century the binary system Cu-Cr was therefore further investigated and the phase diagram of “Siedschlag” was improved up to today’s perception which is shown in Figure 2.

It can be concluded that the two elements do not mix besides an extreme small solid solution area which can hardly be seen in the figure. Also, no intermetallic phases are formed in this eutectic system. The eutectic point is located at a copper concentration of 98.36 atomic % and a temperature of 1075 °C. At room temperature chrome has a solubility of 0.01 atomic % in copper. Investigations of T. Mikuszewski ”changes of the chromium content in liquid copper during vacuum melting of a Cu-Cr-Ni-Si alloy” show that the maximum amount of chromium entering the melt decreases if more elements for the alloy were used [6]. Usually copper alloys have chrome contents up to two per cent. Therefore the detailed copper rich area of the binary system is shown in Figure 3.

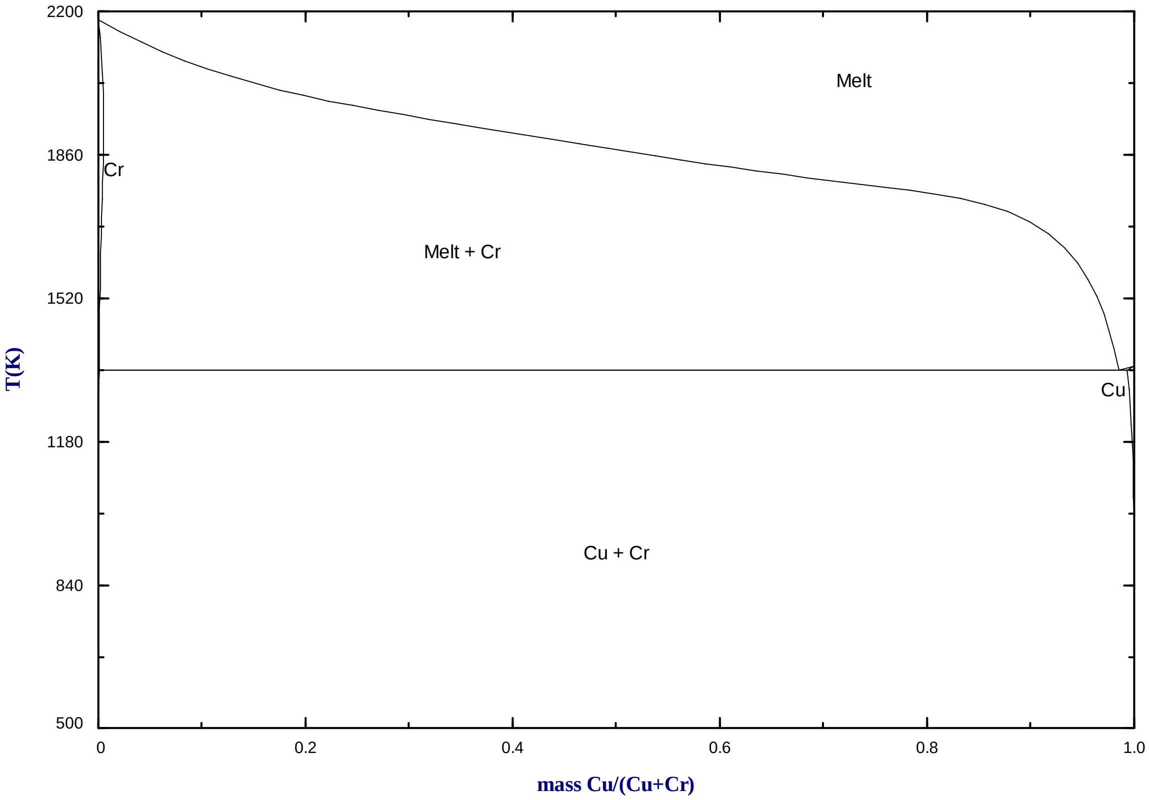

Figure 2: **phase diagram Cu – Cr [7]**

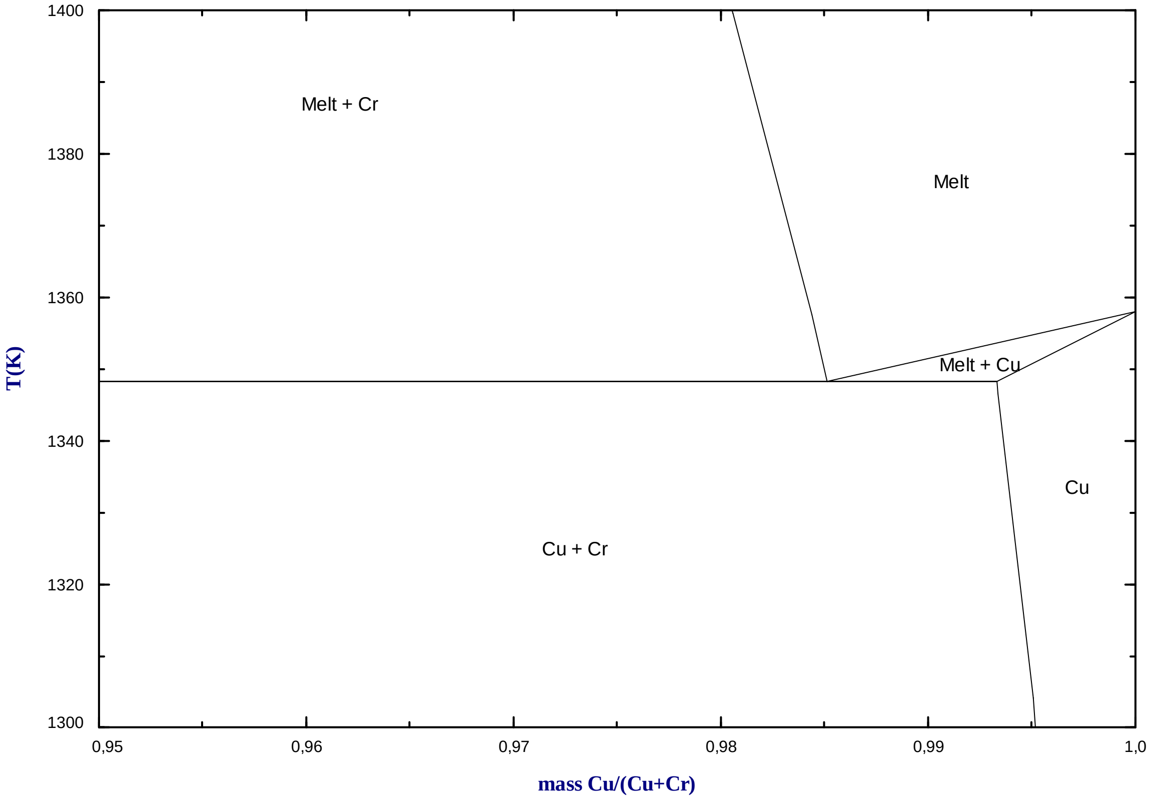

Figure 3: **copper rich area of phase diagram Cu – Cr [7]**

Figure 3 shows that at Cr-concentrations above 0.6 % a Cr-precipitation structure will be formed. Such precipitation hardening alloys increase strength and conductivity of the material compared to alloys with interstitial solved atoms.

2.2 Slag fundamentals

Besides metals slags represent the most important melting phase in metallurgical processes. Slags are used to separate the gangue of the ore from the metal phase. Here they absorb numerous impurities e.g. sulphur, phosphorus, arsenic, etc. They also protect the metal surface from the surrounding atmosphere and thus largely prevent gas absorption by the melt or cause heat insulation. Important properties of slags are viscosity, basicity, electrical and heat conductivity, density, melting point, metal activities, structure, surface energy, surface tension, gas solubility and permeability. In the table 1 only a few properties of slags in comparison to copper are listed.

Table 1: Selected properties of slags versus copper [8],[9]

	unit	copper	slag
Density	g/cm^3	8,92	3 – 4
Viscosity	cP	1 – 3	150 – 1500
Electrical conductivity	$\Omega^{-1}cm^{-1}$	58	$0{,}5\cdot 10^{-4}$
Melting temperature	°C	1083	1100 – 1400
Thermal conductivity	W/mK	394	1-3
Surface tension	Kg/s^2	1,3	0,2-0,4

The oxygen permeability of slags is of special interest in the process of melting Cu-Cr-alloys. Due to the high oxygen affinity of chromium this value has to be as low as possible. This can be quickly explained by using simple correlations, as the oxidic slagging of metals generally takes place in accordance with the following reaction:

$$Me + \frac{n}{2}O_2 = MeO_n \qquad \textbf{or} \qquad Me + O^{2-}_{Slag} = MeO^{2-} \tag{1}$$

having the associated equilibrium constant as follows:

$$K = \frac{a_{MeO_n}}{a_{Me} \cdot p_{O_2}^{\frac{n}{2}}} \tag{2}$$

For the very common bi-valence type of the reaction according to equation 1

$$2Me + O_2 = 2MeO \tag{3}$$

and under ideal conditions the Me-phases exist as pure substances (condensed form) and the associated equilibrium constant simplifies to

$$K = \frac{1}{p_{O_2}} \qquad \textbf{with } \Delta G^0 = -RT\ln K = RT\ln p_{O_2} \tag{4}$$

The metal oxide contents (concentrations, activities) in slags are determined by the surrounding oxygen potential. Generally the accompanying metals in the copper as well as in the slag phase are in diluted form and activity coefficients have to be considered. Figure 4 assumes a pure Cr phase to make sure that if pure chromium (activity 1) will not react with selected elements it will neither react in a diluted form in copper(activity <1). Figure 4 gives a first impression of the stability ranges of selected (chromium relevant) metal oxides at rising temperatures and free Gibbs Energy of these impurities.

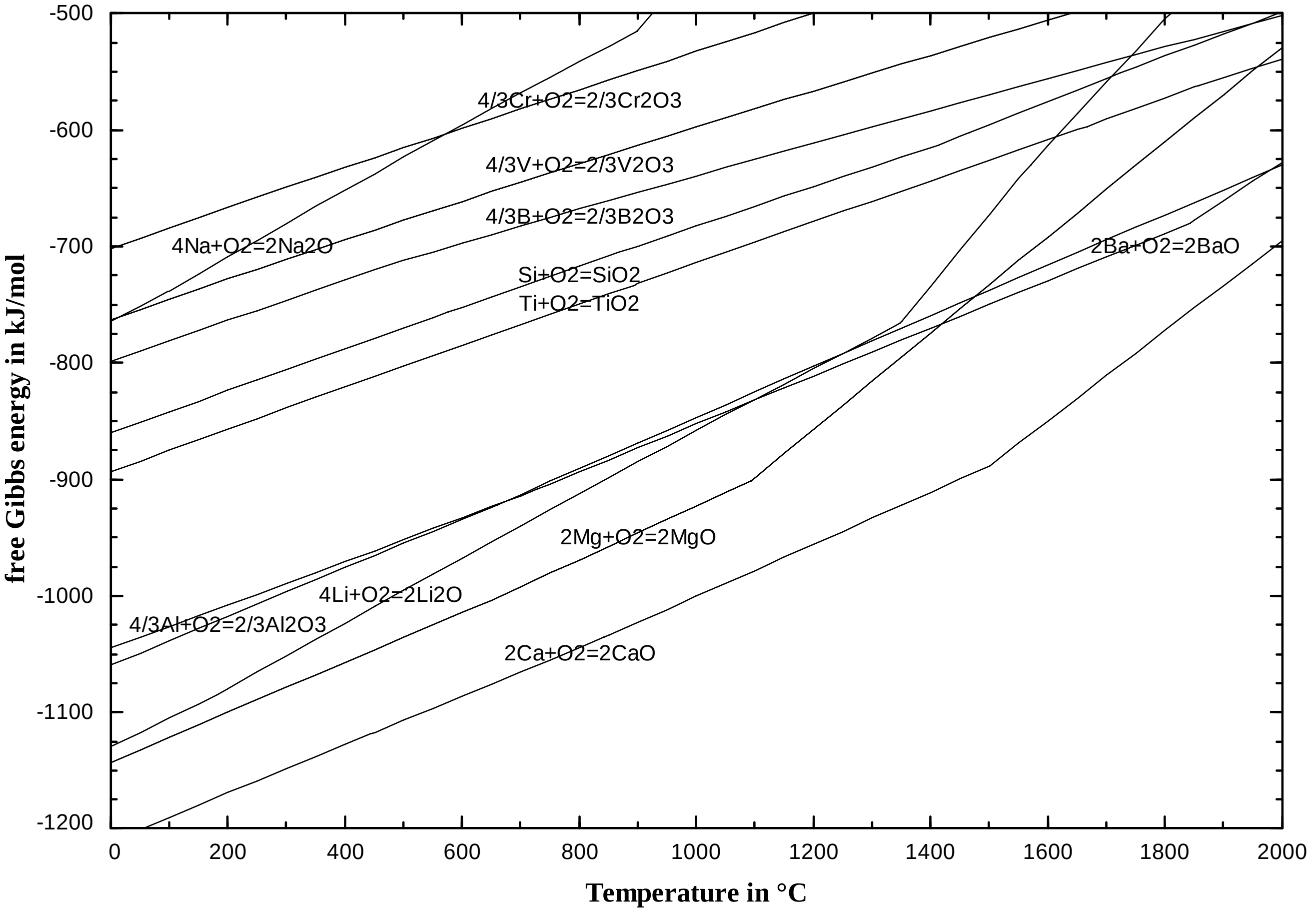

Figure 4: “Ellingham”–Diagram from -1200 to -500 kJ/mol of selected elements

Sodium is an exception because at a temperature of 550°C the free Gibbs Energy is higher than the one of Cr. The formation of chromiumoxid is easier than the one of sodium. But because of the fact that these calculations were made with pure substances as mentioned above, sodium could still be possible if Cr is diluted in copper.

In scrap melting the pick-up of oxygen into the slag should be prevented as best as possible to sustain reducing conditions. The transfer of oxygen from the atmosphere into the slag generally occurs in two ways, of cause depending on its partial pressure (Figure 5).

- oxygen physically dissolves in slag:

$$\{O_2\}_{gas} = [O_2]_{slag} \qquad \textbf{(5)}$$

- oxygen chemically dissolves in slag:

$$\{O_2\}_{gas} = 2\,O^{2-}_{slag} - 4\,e^- \quad \text{or} \quad \{O_2\}_{gas} + 4\,e^- = 2\,O^{2-}_{slag} \qquad \textbf{(6)}$$

Electrons (or cation vacancies) are generally available if transition metals are contained in the slag. The oxygen permeability of slags (described by transported moles O_2/cm·sec) is different for specific types of slags. The both types of oxygen solubility and the individual concentrations of electrons and/or cation vacancies lead to an extreme range of the oxygen permeability. For instance in the pure Al_2O_3-CaO-SiO_2 system the oxygen is physically dissolved and the permeability is directly proportional to P_{O2}. In all cases the oxygen absorption by the slag from the atmosphere is followed by an oxygen transition from the slag into the metal. If the metal is saturated with oxygen, an oxide is formed, depending on thermochemistry, according to figure 4 (slagging) [10],[11]).

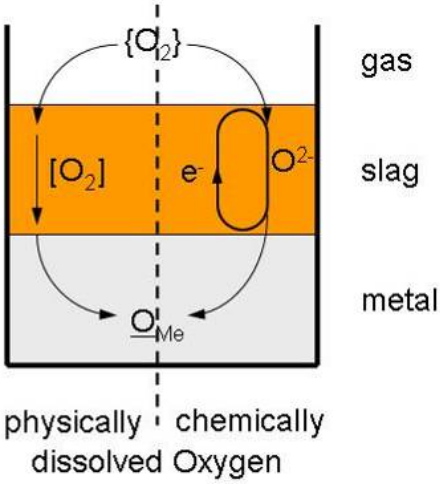

Figure 5: Transfer of oxygen from the atmosphere into the slag and forming of oxides

2.3 slag equilibrium calculations for Cu Cr

Regarding figure 4 most of the common slag former elements have free Gibbs energies below that of chromium and are potential candidates for the slag. Oxides of these elements should show only minor reaction tendencies with dissolved chromium. Also as long as these elements are present in the liquid copper the loss of chromium can be expected to be low (equilibrium state). As already mentioned Sodium is an exception as it becomes nobler above 550 °C and oxide formation of chromium is easier than those of sodium. But of course this is only valid for pure substances, the subsequent calculations will show whether this applies aswell to mixtures. Based on the findings above the following slag components might be technically applicable:

Cr2O3, Na2O, MnO, SiO2, TiO2, B2O3, BaO, ZrO2, Al2O3, Li2O, MgO and CaO.

The slags to be used need a melting point below the working temperature of the process. If possible the melting point should be even lower than the one of the copper alloy. This temperature is about 1079 °C calculated by Factsage®. Melting points of selected slag compounds are shown in table 2.

Table 2: Melting points of selected slag components

component	Melting point In K	component	Melting point In K
B_2O_3	723	BaO	2286
Na_2O	1405	Al_2O_3	2327
Li_2O	1843	Cr_2O_3	2708
SiO_2	1995	CaO	2845

Factsage® ternary phase diagrams calculations were done with “low” melting point oxides like Na_2O, B_2O_3, Li_2O and typical slag components like SiO_2, CaO, Al_2O_3 and MgO. The used Factsage® databases were BINS, Fact53, FScopp, FToxid, SGPS. For the calculations the following strategies were used:

- Firstly ternary phase diagrams are calculated for 1250 °C and liquid phase areas are described.
- Using fixed concentration sets calculations show, where slag and copper alloy reach equilibrium.
- The chromium and copper yields derived dependent on concentration gradients.
- Acceptable points of chromium and copper yields are taken out and the corresponding slag compositions are used in the practical trails.
- The calculations are validated experimentally and characteristics of the slag are determined.

A few of the ternary systems, for instance SiO_2– CaO– Al_2O_3 and SiO_2– CaO– MgO, are not suitable as no liquid phases exist at 1250 °C. Most of the potential slag systems consist of SiO_2 as structure component and many slag systems consist of B_2O_3 for lowering the melting point. As an example for the calculations the ternary system SiO_2 – B_2O_3 – Na_2O is discussed in detail. This system forms a large area of liquid phases (Figure 6) and therefore suits well to protect copper melts against atmosphere. To estimate the influence of individual components on the chromium yield, further calculations are performed at a constant content of each component (quasi binary diagrams)., one for a constant B_2O_3– content of 10 % and another for a constant SiO_2– content of 60 %. Both are marked in the ternary phase diagram with “I” respectively “II”.

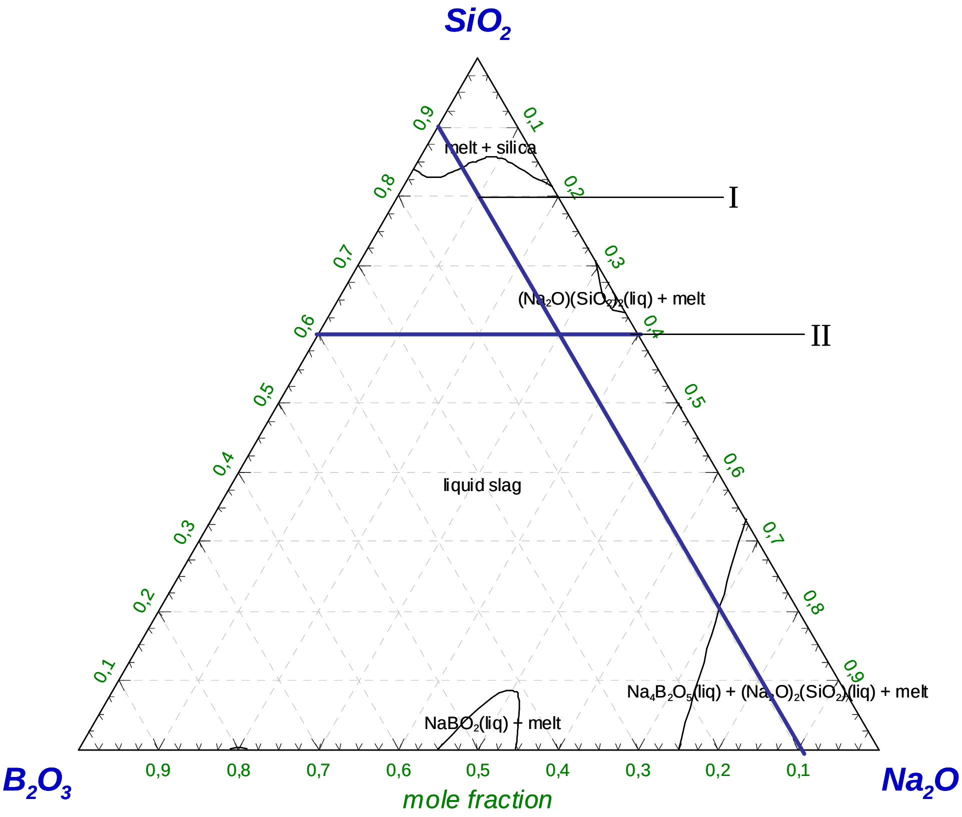

Figure 6: ternary phase diagram SiO_2– B_2O_3– Na_2O at 1250 °C

In Figure 7, the chromium yield in the copper phase of slag I (constant B_2O_3) and slag II (constant SiO_2) is plotted against the content of Na_2O.The calculations are made with the composition shown in Table 4 whereas the maximum amounts of alloying elements are used. In both cases, it can be recognized that with rising Na_2O-contents, the chromium yield increases as well. At a constant SiO_2 level of 60 %, this trend continues in the entire concentration area which ends at 40% Na_2O (see figure 6). The slag with the constant B_2O_3 content shows a sharp decrease of the chromium yield at a Na_2O concentration of 70% which is caused by entering another phase area (Figure 6).

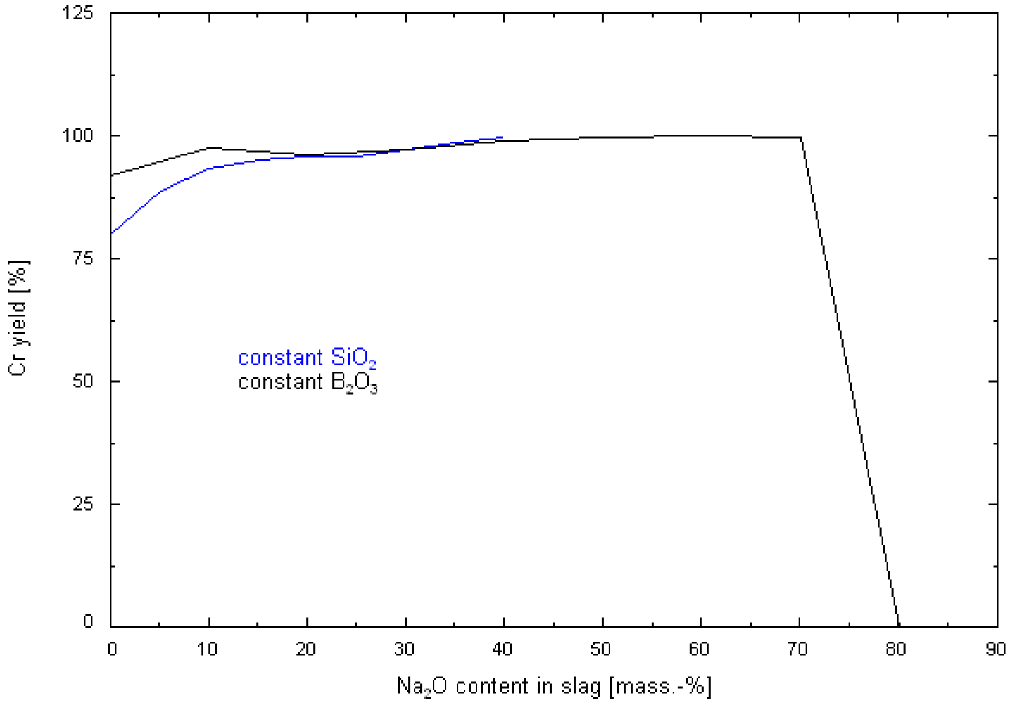

Figure 7: **Yield of chromium in copper after equilibrium with two slag-systems according to fig. 6 dependent on Na_2O–concentration**

Based on these calculations slag compositions were selected for trials (table 3). From the system mentioned above three compositions were chosen including the intersection point of the two lines in Figure 6. Table 3 is the source for the equilibrium experiments, in which the interaction between the slag and the copper alloy is investigated.

Table 3: **Slag compositions (in weight %) for experiments**

Slag No.	SiO_2	CaO	B_2O_3	Na_2O	Li_2O	Cr_2O_3	Al_2O_3	MgO
1	60		10	30				
2	80		10	10				
3	60		30	10				
4	70		25				5	
5	35		60				5	
6	35	40	25					
7	16	40	44					
8	50	45			5			
9	50	40			10			
10	40	40		20				
11	40	20		40				
12	20	40		40				
13		45	30			25		
14		20	30			50		
15		40	40			20		
16	60		35					5
17	13		34					53
18	18		24					58
19	73			15	12			
20	60			28	12			
21	60			35	5			

3 Experimental work

3.1 Equilibrium trials

Equilibrium experiments were done in a sealed induction furnace (Figure 8) under defined atmosphere and carried out to quantify the interaction between the slag and the copper alloy. Due to excellent stirring conditions the melt and slag reached equilibrium after a short time.

Figure 8: Induction furnace with controls (left) and construction inside furnace (right)

The received chromium yield of each slag system is shown in Figure 9. In general the SiO_2 based slag compositions have the best influence on chromium content of the alloy whereas CaO based slags have a worse impact. Li_2O always leads to positive results but it is one of the most expensive slag components. Nevertheless these slags are in principle suitable for the recycling process.

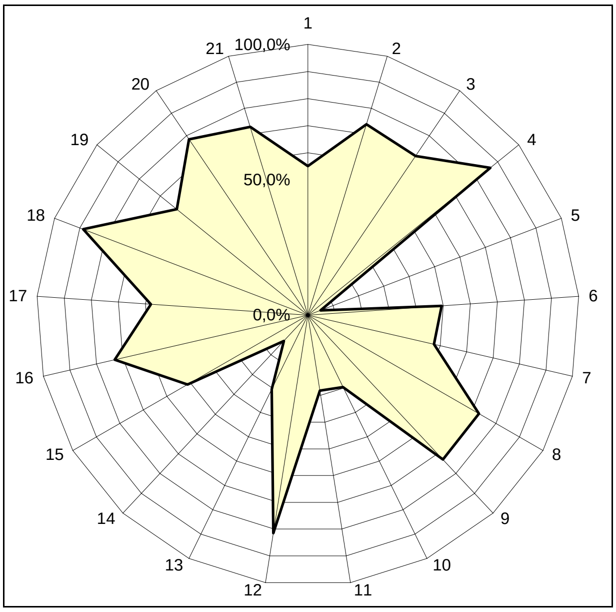

Figure 9: Chromium yield of equilibrium trials versus slag numbers, explained in table 3

Unfortunately the industrial copper alloy used for the experiments contained less Ti than originally planned and used for the Factsage®-calculations. The calculations were done with regard to the given data specifications (Table 4). An analysis of the delivered material using for the trials show a modified composition (Table 5). The alloy used for equilibrium trials has a 80% less titanium content.

Table 4: Composition of Cu-Cr-Alloy for calculations

Element	Cr	Ti	Si	Cu
Concentration (in mass-%)	0,15 – 0,40	0,01 – 0,40	0,02 – 0,07	rest

Table 5: Composition of Cu-Cr-Alloy for trials

Element	Cr	Ti	Si	Cu
Concentration (in mass-%)	0,283	0,067	0,024	rest

A comparison (figure 10) between the theoretical and the experimental results with regard to the Cr-yield reached high discrepancies as titanium acts as reducing element.

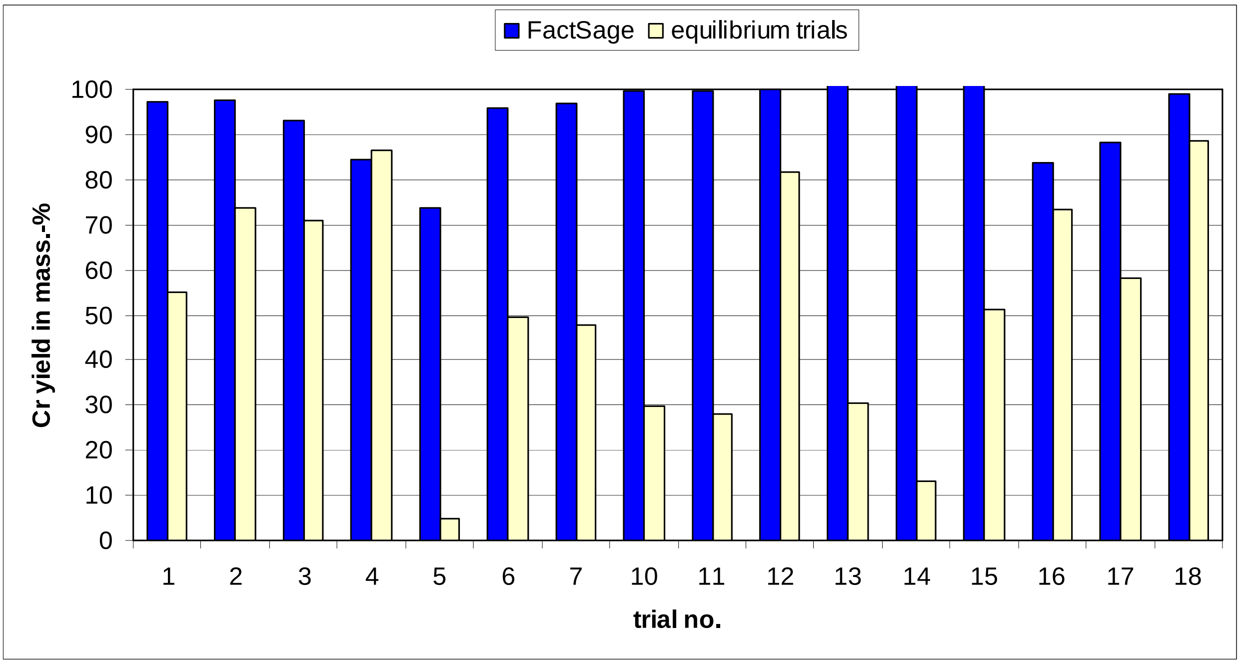

Figure 10: Experimental values for the Cr yield compared to calculation results for holding the CuCr-alloy in contact with selected slags according to table 3

The results of trials 8, 9, 19, 20 and 21 can not be presented because of a lack of data's within the thermo chemical calculation programme for Li_2O– Oxid

In figure 10 it can be seen that the forecasts of slags 2, 3, 4, 16, and 18 by calculations mostly fit with the results from equilibrium trials compare to slags 1, 5, 6, 7, 10, and 11 where forecasts do not fit with the results for Cr-yield.

The forecasts of slags 13, 14 and 15 differ up to 200 percent from the determined values. This is caused by the different amounts of titanium. Within the calculations a higher amount of titanium enables the reduction of chromiumoxid in the slag and lead to an alloy with high chromium content.

The quality of the calculations can b e directly related with the content of alkali oxides Na_2O and Li_2O. The higher the amount of alkali oxides the more differ the calculations from the results of trials. In trial 1 to 3 this influence is considerably obvious. The slag of trial 1 has 30% Na_2O content. The discrepancy between calculation and trial is 42,1%. The slag of trial 3 has a slag content of 10% and here the discrepancy is 22,2%.

The B_2O_3-content has no negative influence on the calculations. The discrepancy in trial 16 as well as 18 is around 10% and is independent from B_2O_3-content. Trial No. 17 can not be considered because while remelting the slag didn't melt completely.

3.2 kinetic trials

Trials were conducted to analyze quantitatively the interaction kinetics between the atmosphere and the system slag/metal. The slag acts as kinetic inhibition of metals oxidation. In these experiments the same slag systems were used as in equilibrium trials and the time-dependent slagging of alloying elements contained in the copper-alloy was measured. These tests were conducted in a resistant heated furnace (Figure 11). The procedures for melting tests are the following:

- Six alumina crucibles with a capacity of 150 ccm get filled with slag from six different slag compositions(~100g)
- The furnace is heated up up to work temperature of 1250°C
- After holding the work temperature for 15 minutes copper blocks are feeded (~80g). The solid cooper block is completely covered by liquid slag.
- The crucibles stay for one hour in the furnace
- After sixty minutes the crucibles are removed out of the furnace and cooled down in a sandbed

The interaction of the metal with the atmosphere is mainly determined by the oxygen transport through the slag. The measured slagging of copper as well as its alloying elements can be deduced to the amount of oxygen being transported during the experiment time. In conjunction with the slag height and surface, the oxygen permeability can be calculated.

Figure 11: resistant heated furnace for kinetic trials

The metal yield of Cu, Cr and Ti after kinetic trials is shown in Figure 12

The metal yields of Cu, Cr and Ti after one hour contact of the CuCr-alloy with slag compositions according to table 3 are summarized in Figure 12. The copper metal content is constantly around 100%, exceptions are experiments 8, 12 and 19 with losses of about 10-30% where the slag phase was not completely melted. Therefore the metal phase got into contact with the atmosphere and Cu met. got lost.

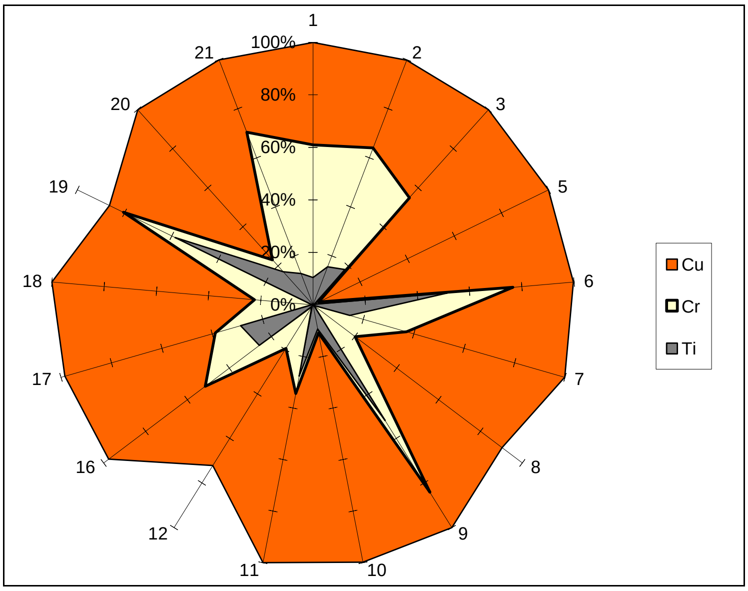

Figure 12: Metal yields of Cu, Cr and Ti after one our contact of the CuCr-alloy with slag compositions according to table 3

SiO_2-B_2O_3-Na_2O-slags (trials 1 to 3) are particularly well suited because they achieve with the various configurations the highest chromium yields of about 60%, very good chromium yields were also reached using SiO_2– Li_2O– Na_2O slags (trials 19 bis 21). The mixtures of SiO_2– CaO– Li_2O (tests 8 and 9), SiO_2– CaO– B_2O_3 (tests 6 and 7) and SiO_2– MgO– B_2O_3 slag systems (tests 16, 17 and 18) are acceptable for the process.

As a result of the equilibrium trials in comparison with the kinetic trials the idea was to achieve a reference value for the oxygen permeability of the slag. The higher amount of slag originated by kinetic investigations less slagging while equilibrium trials leads to an amount of slag which is caused by oxygen permeability. But comparing the slagging results of the equilibrium and kinetic trials it becomes obvious that the chromium and titanium yields of some kinetic trials is higher than those of the corresponding equilibrium experiments. The stirring due to induction melting used for equilibrium trials has an important influence. The exchange between melt and slag is as high as possible so that an equilibrium status of the two phases can be reached. But although the kinetic trials were done under air atmosphere and the oxygen transport through the slag including the interaction between metal and slag phase under static conditions could take place, the slagging was less. Thus the determination of the oxygen permeability, measured in $mol_{O2}/cm \cdot s$ is not possible. Instead of this the kinematic oxygen conductivity of the slag is calculated for those experiments, where slagging in the equilibrium trials was less. The kinematic oxygen conductivity J_k was calculated via:

$$n_{O2} = \frac{\left(\Delta m^0_{Cu} - m_{Cu}\right)\cdot 0{,}13 + \left(\Delta m^0_{Cr} - m_{Cr}\right)\cdot 0{,}46 + \left(\Delta m^0_{Ti} - m_{Ti}\right)\cdot 0{,}67}{2 \cdot M_O} \qquad \textbf{(7)}$$

n_{O2}: Oxygen; Δm^0_{Me}: slagging by equilibrium; m: slagging by kinetic; M_O: molar Mass of Oxygen

and:

$$J_K = \frac{n_{02} \cdot h}{A \cdot t} \qquad \textbf{(8)}$$

J_K: kinematic oxygen conductivity; n_{O2}: Oxygen; h: slag hight; A: slag surface t: time

The values of the kinematic oxygen conductivity for the slags are shown in the following Table 6. As an assumption due to observation while melting a conductivity $< 5 \cdot 10^{-7} mol_{O2}/cm \cdot s$ of the slag leads to good isolation of the molten metal against the atmosphere.

Table 6: **kinematic oxygen conductivity of used slags**

trial	2	3	5	7	8	10	12	16	17	18	20	21
koc*	0.25	0.28	0.06	0.15	8.07	0.33	22.7	1.44	1.31	0.58	0.69	0.16

*: kinematic oxygen conductivity of slags in $10^{-7} mol_{O2}/cm \cdot s$

4. Conclusion and Outlook

The idea was to develop a slag system which is suitable to remelt chromium containing copper under air atmosphere.

In a first theoretical step 21 slag systems were evaluated by theoretical equilibrium calculations with the Factsage® software. The choice for slag components was dependent on melting points, oxygen affinity towards chromium and the demand of no halogenides, zero sulphur, iron and manganese within the slag.

Afterwards these slags were investigated under real conditions in two different ways. First of all equilibrium trials in a vacuum induction furnace under inert gas atmosphere were done to confirm the results from calculations. In the second step the slagging caused by melting under air atmosphere is discovered.

By comparing the slagging of equilibrium trials with the slagging of kinetic trials a correlation can be determined which is called oxygen permeability. But because of the fact that the slagging of some equilibrium trials was higher than the one of kinetic trials, the kinematic oxygen conductivity was established and possesses an opportunity to evaluate the usage property of the slags.

The detected properties of slags of the experiments 1, 2, 3, 6, 9, 15, 19, 20 and 21 are identified as mostly positive and are therefore best suited for the remelting process. The slags of the experiments 2, 6 and 15 have a neutral rating.

The following slag systems are particularly suited for industrial remelting:

SiO_2-B_2O_3-Na_2O

SiO_2-CaO-B_2O_3

SiO_2-CaO-Li_2O

CaO-B_2O_3-Cr_2O_3

SiO_2-Na_2O-Li_2O

Following tasks will be the investigation of the viscosity not just from fresh slag but also from slag being contaminated by oxides and impurities.

Furthermore the influence and interdependency on refractory materials by metal and slag systems has to be investigated.

We like to thank “Wieland” for supporting the IME within this project.

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