Thermochemical study of calciothermy of Scandium compounds

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Abstract

In this paper the results of thermochemical study on scandium production by calcium and calcium-zinc alloys as reduction agents are presented. Possible system components, reaction mechanisms, concentration ratios of charge components, as well choice of temperature ranges for those multi-component systems, are investigated by triangulation and tetraedration with help of software FactSage®.

The conditions for maximum ensured scandium (Sc) yield from Sc_2O_3 and ScF_3 compounds are listed to compare potentials of Sc production processes. Sc_2O_3 cannot be reduced directly by Calcium, but with Ca-Zn alloy. Minimum consumption of calcium and zinc as well maximum scandium content in product is reached by Ca-Zn alloy with 3 : 2 ratios. Next to pure calcium, it is possible to reduce ScF_3 also by Ca-Zn alloy where scandium content in product decreases with increase of zinc proportion in reducing alloy.

1 Introduction

Scandium became one of the important rare earth metals of today as its application in modern technologies increases, such as in PC memory, medical devices, but especially as alloying element for strengthening aluminium in aerospace industry [1 – 3]. Nevertheless its high price impedes even further utilization due to small concentration in ores and quite complex and costly production techniques.

Although first scandium (Sc) metal was extracted by electrolysis of $ScCl_3$ in a KCl-LiCl melt [4], it is abandoned due to many disadvantages. Currently, scandium is extracted from ScF_3 or $ScCl_3$ metallothermically by reduction with calcium [5] or magnesium [6] in an argon atmosphere. Because of the hygroscopic nature of chlorides, their high evaporation pressure and necessity for additional hydrometallurgical purification steps, reduction of $ScCl_3$ with Ca is avoided. Therefore, the focus of this paper is on Sc_2O_3 and ScF_3 as raw material for scandium production by metallothermy.

Usually, reduction is carried out in tantalum (Ta) or molybdenum (Mo) crucibles, sometimes in graphite crucibles with inner Mo sheet lining. After metal – slag separation, Sc is remelted in vacuum (ca 10^{-5} mm Hg) in order to remove volatile accompanying elements, especially calcium. Further purification from tantalum is done by sublimation. Intermediate alloy process is suggested to lower reduction temperature by addition of elements that form an alloy or compound with Sc, reducing the percentage of crucible material in Sc. An Mg-Sc alloy is desired when using Mg, whereas Zn is added to the charge when Ca is used, due to the fact that Ca does not form an alloy with Sc. For lowering the melting temperature of the slag, addition of LiF is proposed, specified by the following reduction reaction (eq. 1) [7]:

$$2\ ScF_3 + 3\ Ca + 8\ Zn + 12\ LiF = 2\ (Sc \cdot Zn) + 3\ (CaF_2 \cdot 4\ LiF) \qquad (1)$$

All known publications depict solely experimental results and all methods are based on empirical indications. Considerations concerning possible reduction mechanisms, explanations for the possible concentration ratios of charge components, as well as reasons for the choice of temperature ranges, are neglected.

In this study, all those aspects for reduction of Sc_2O_3 and ScF_3 by Ca are acknowledged. Thermodynamic properties of multicomponent systems are calculated and explained by triangulation and tetraedation. The conditions for maximum ensured Sc yield from expensive Sc compounds are listed to compare potentials of Sc production process.

2 Methodology of investigations

In order to conduct a thermodynamic calculation of a reaction correctly, it is necessary to know which compounds constitute the reactants and products of the reaction. Understanding possible multicomponent compounds of accompanying elements, reactions of these compounds with other components and the resulting reaction products is mandatory to estimate the effectiveness of the reactions within the system. Phase diagrams illustrate the mentioned relations graphically.

So called “Klärkreuze” method is suggested by W. Guertler to clarify which reactions occur in a ternary system and which products are formed [8]. This method divides the concentration triangle with quasi-binary lines forming secondary triangles. Thus, the ternary system disintegrates into a series of secondary subsystems from which every subsystem displays equilibrium conditions of basic substances (compounds) [9]. This partition of a ternary system into a series of secondary subsystems is called triangulation. Development of this “Klärkreuze” method for multicomponent systems are presented in [10 – 13], in which triangulation of the ternary systems were carried out at first. Based on that, partition of concentration tetrahedron of a quaternary system into a series of secondary quaternary systems is called tetraedration. The tetrahedron space of a quaternary system is divided in secondary tetrahedrons by quasi-binary planes (similar to triangulation, but with planes including tie lines). Every secondary tetrahedron represents equilibrium conditions of a system, whose components are basic substances. It allows conclusions about possible reactions, concentration ranges in which these reactions occur, and possible products forming in multicomponent systems. When investigating a metallurgical process, of which the exact state of its components are not well known, it is suggested to conduct triangulation and tetraedration of the corresponding systems first [13].

For triangulation of the ternary systems and for tetraedration of the quaternary systems, the quasi-binary sections and planes were determined by thermochemical calculations using FactSage 7.0. At first, all possible connection lines and planes between all elements and congruently melting components were calculated. Subsequently, all possible connection lines and planes between elements, congruently and incongruently melting compounds were calculated, depending on the formation temperature. This allowed determination of quasi-binary sections and planes.

3 Results

Because of the high oxygen affinity of scandium [14] direct reduction of Sc_2O_3 with calcium is not possible. In order to reduce Sc_2O_3, Sc has to constitute an alloy / compound with the reducing or additionally used metal. Addition of Zn was chosen to create Sc-Zn compounds, because Zn is easy to remove from the extracted alloy to produce Sc metal.

On the other hand, direct reduction of ScF_3 is possible, based on values of Gibbs energy of formation, where all products are in solid state. Since the enthalpy of formation of CaF_2 and ScF_3 do not significantly differ, the positive effect of Sc compound formation with Zn is investigated as well, as it is done for Sc_2O_3 reduction.

3.1 Triangulation of boundary systems and tetraedration of Sc-Ca-Zn-O and Sc-Ca-Zn-F systems

Boundary system triangulation as well as tetraedration of the quaternary systems gives information on reactants and reaction products of a possible Sc-compound reduction. In order to perform triangulation of a ternary system, the compounds formed within systems, Sc-O [15], Ca-Sc [16,17], Ca-O [18], Ca-Zn [15], Sc-Zn [19, 20], Ca-F [21], Sc-F [22, 23], Zn-F [24] are identified, as well as their melting behavior and melting points. Triangulation of boundary systems of Sc-Ca-Zn-O and Sc-Ca-Zn-F were conducted as described in methodology of investigations, where the tie lines $CaZn_5$–ZnSc and $CaZn_{11}$–ZnSc are considered quasi-binary based on topological laws, although it contradicts calculation in FactSage. As thermochemical data for Zn_2Sc is not reliable because of incorrect quasi-binary sections ($CaZn_2$–Zn_2Sc and $CaZn_5$–Zn_2Sc, doted lines in Figure 1 left), tetraedration was conducted at $T > 1300$ K, in order to neglect Zn_2Sc compound (quasi-binary section Zn_2Sc–Sc_2O_3). During tetraedration (Figure 2), incongruently melting compounds Ca_3Zn (667 K), Ca_5Zn_3 (687 K), CaZn (712 K), $CaZn_3$ (942 K) and $ScZn_{12}$ (748 K) were neglected, since they are non-existent in the investigated temperature range ($T > 1300$ K).

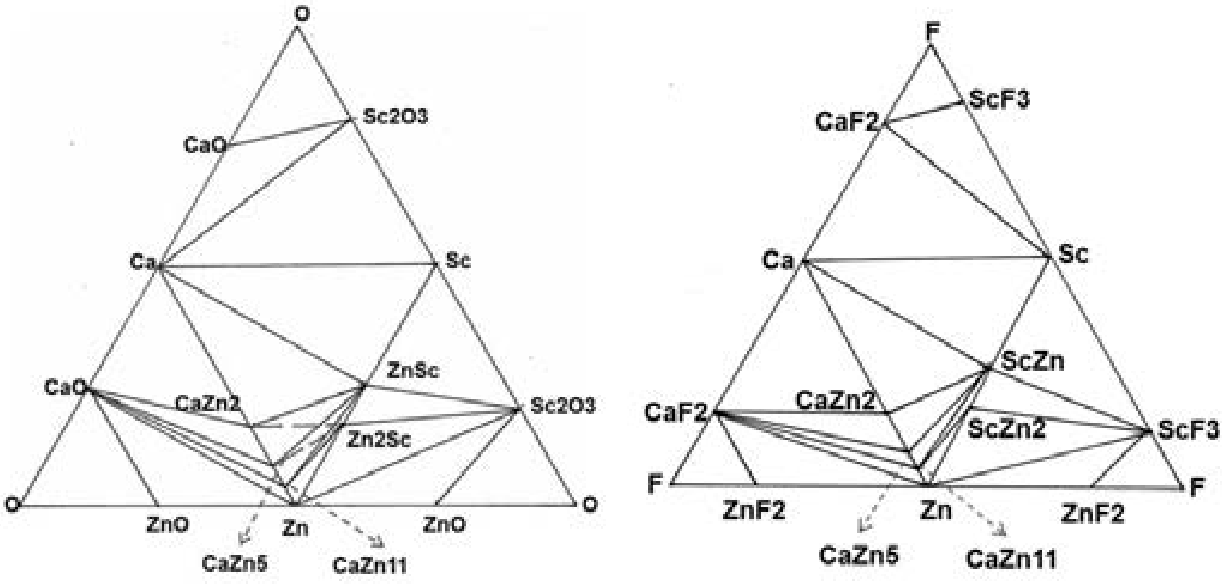

Figure 1: Boundary system triangulation of the quaternary Sc-Ca-Zn-O (left) and Sc-Ca-Zn-F system (right)

Figure 2 shows that the tie lines between Sc_2O_3/ScF_3 and the reducing agent (Ca-Zn alloy) cross several sub-systems as a function of the added amount of reducing agent. Thereby, every crossed sub-system depicts the final product that is formed at the corresponding addition of Ca-Zn alloy to Sc_2O_3 / ScF_3. The relevant sub-systems have mutual faces which are red and green colored in Figure 2. These mutual faces depict the end products of Sc_2O_3 and (*n*Ca + *mZn*) reaction depending on the (*n*Ca + *mZn*) amount and show their composition in case that the tie line Sc_2O_3/ScF_3–(*n*Ca+*m*Zn) passes through them.

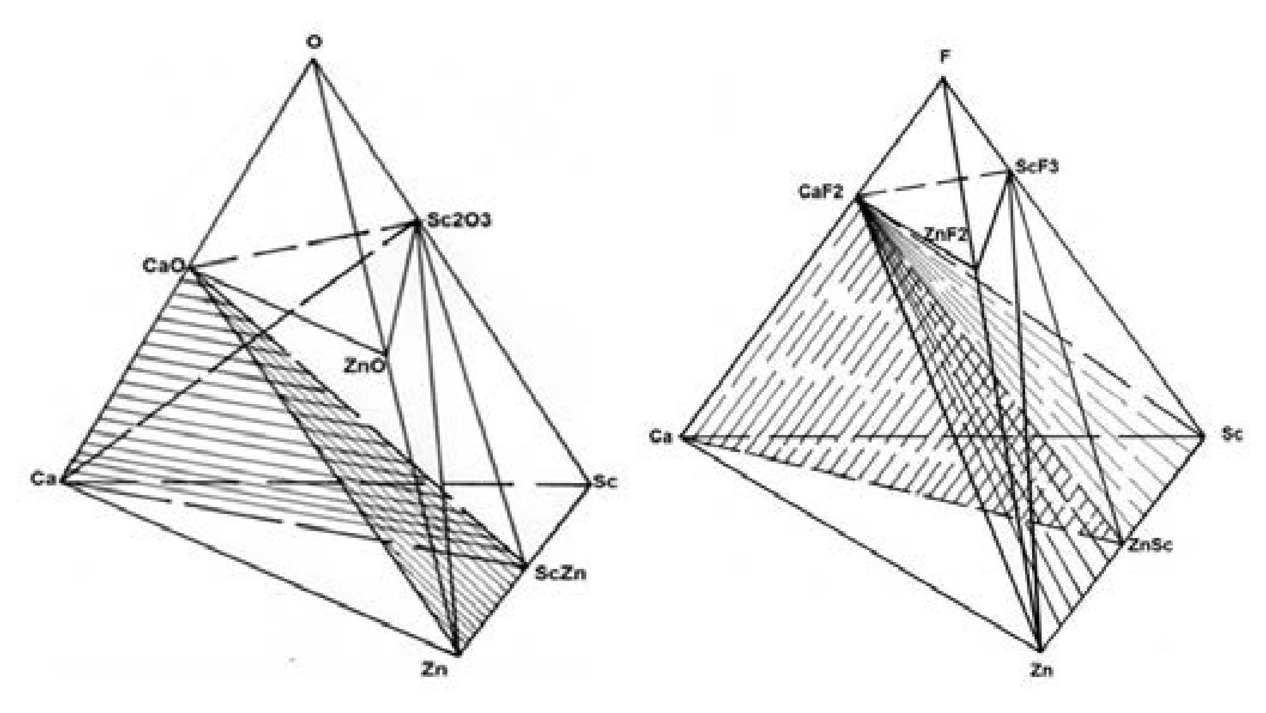

Figure 2: Tetraedration and sub-systems of the Sc-Ca-Zn-O (left) and Sc-Ca-Zn-F (right) system at T > 1300 K without consideration of $CaZn_2$, $CaZn_5$, $CaZn_{11}$; quasi-binary planes (red and green marked) as faces shared by two sub-systems

3.2 Equilibrium calculations

Using the “Equilib” module of thermochemical program “FactSage 7.0”, equilibrium products of the reactions Sc_2O_3/ScF_3 + Ca/Zn alloy were calculated, varying Ca/Zn compositions at 1300 K. The calculation procedure is shown here only on one example to keep the simplicity of the article’s structure, whereas all equilibrium calculation results are summarized in tabular form further in text.

3.2.1 Sc_2O_3 reduction by an alloy with composition corresponding to Ca_5Zn_3 in solid state

Sc_2O_3 reduction by Ca-Zn alloy with a mole ratio of 5 : 3 occurs in the sub-system Sc_2O_3-CaO-Ca-ScZn as can be seen in Figure 2 and Figure 3. For every extracted gram of Scandium, 1.487 g of Calcium and 1.455 g of Zinc are necessary.

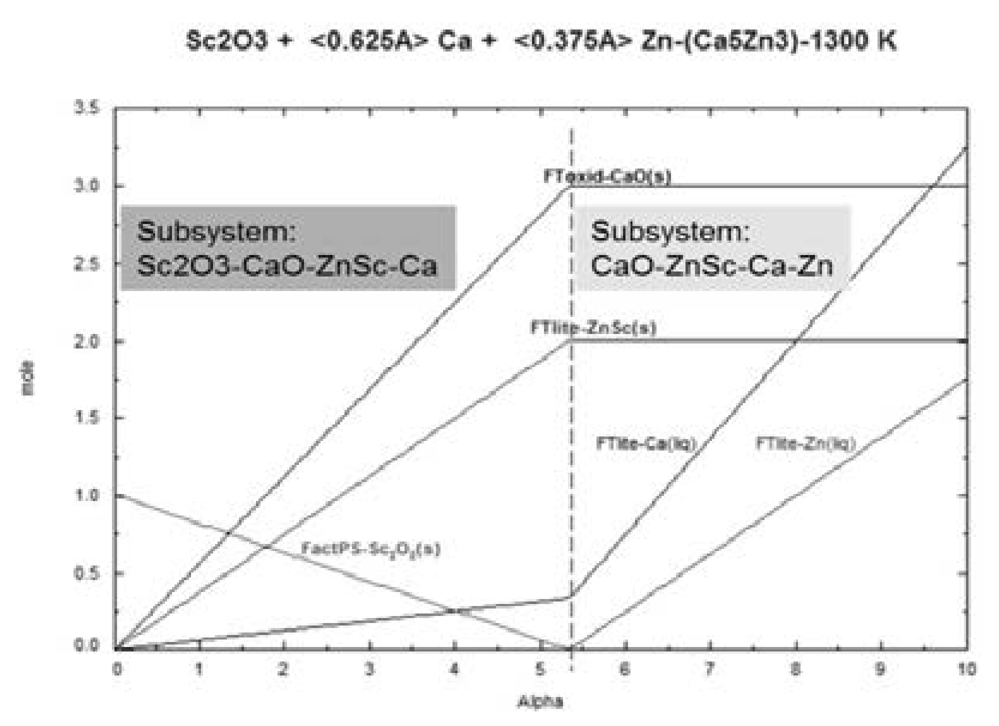

Figure 3: Sc_2O_3 reduction with 0.625 Ca + 0.375 Zn alloy (corresponding to Ca_5Zn_3 in solid state) as a function of the reducing agent addition at 1300 K (A = mol Ca_5Zn_3)

Since the complete Sc_2O_3 reduction occurs on CaO-Ca-Zn quasi-binary plane, the reaction can be expressed by eq. 2:

$$3\ Sc_2O_3 + 2\ Ca_5Zn_3 = 9\ CaO + 6\ ScZn + Ca \qquad (2)$$

Theoretical consumption of Ca and Zn for extraction of 1 g Sc according to reaction (2) amounts to 1.486 g Ca and 1.455 g Zn and is in exact accordance with “Equilib” module of “FactSage 7.0”. The Scandium content in reaction product reaches 37.74 wt.-%.

3.3 Summary of Sc_2O_3 and ScF_3 reduction by Calcium

By tetraedration of quaternary systems Sc-Ca-Zn-O and Sc-Ca-Zn-F, Sc_2O_3 and ScF_3 reaction mechanisms with Ca/Zn alloys were determined as a function of Ca/Zn alloy compositions. Required quantities of Ca and Zn for extracting 1 g Sc mentioned Sc-compounds as well as maximum Scandium content in the products were identified (Table 1).

Table 1: Required quantities of reducing agents for Sc_2O_3 and ScF_3 as a function of their composition and achievable Scandium content in the product

Reducing alloy	Ca consumption				Zn consumption				Sc in product [wt.-%]	
	[g/g] Sc		[g/g]	[g/g]	[g/g] Sc		[g/g]	[g/g]		
	Sc_2O_3	ScF_3	Sc_2O_3	ScF_3	Sc_2O_3	ScF_3	Sc_2O_3	ScF_3	Sc_2O_3	ScF_3
Ca	-	1.337	-	0.59	-	-	-	-	-	100
$Ca_{0,8}Zn_{0,2}$	3.565	1.337	2.324	0.59	1.455	0.524	0.949	0.231	21.35	63.68
Ca_3Zn	2.675	1.337	1.744	0.59	1.455	0.727	0.949	0.321	26.37	57.90
Ca_5Zn_3	1.487	1.337	0.970	0.59	1.455	1.363	0.949	0.6	37.74	42.32
$Ca_{0,6}Zn_{0,4}$	1.337	1.337	0.872	0.59	1.455	1.455	0.949	0.642	40.74	40.74
$Ca_{0,59}Zn_{0,41}$	1.337	1.337	0.872	0.59	1.520	1.526	0.992	0.673	39.61	33.66
CaZn	1.337	1.337	0.872	0.59	2.178	2.181	1.420	0.962	31.43	31.43
$CaZn_2$	1.337	1.337	0.872	0.59	4.356	4.362	2.840	1.924	18.64	18.65
$CaZn_5$	1.337	1.337	0.872	0.59	10.891	10.907	7.101	4.81	8.40	8.40

During reduction of Sc_2O_3 with Ca-Zn alloys, Sc_2O_3 is reduced by Ca resulting in the formation of CaO, where reduced Sc forms a compound with Zn (ScZn). Reducing alloy need to provide necessary quantities of Ca and also deliver sufficient amounts of Zn in order to bond with Sc in the form of ScZn. Up to a Ca : Zn ratio of 3:2, Ca consumption decreases from 2.675 g/g Sc to 1.337 g/g Sc and remains constant with further Ca : Zn ratio decrease. The situation with zinc is quite opposite. Zinc consumption remains constant with decreasing Ca : Zn ally ratio up to ratio of 3 : 2 and with decrease it increases. The Sc content in product increases from 26.37 wt.-% at Ca : Zn = 3 : 1 to 40.74 wt.-% at Ca : Zn = 3 : 2 and decreases with further reduction of the Ca : Zn ratio below 3 : 2 due to dilution with Zn.

During ScF_3 reduction with Ca, reduction is accompanied by the formation of CaF_2 and Sc. Using a Ca-Zn alloy, Ca reduces ScF_3 and the emerging Sc combines with Zn to a compound (ScZn). Calcium consumption remains constant with Ca : Zn ratio decrease, whereas zinc consumption increases below reducing alloy ratio of 3 : 2. Scandium is diluted in the product by zinc and its content inevitably decreases by increasing Zn consumption.

4 Conclusion

By tetradration of quaternary systems Sc-Ca-Zn-O and Sc-Ca-Zn-F the series of adequate reactions within the stated systems is determined and reduction mechanisms of Sc_2O_3 and ScF_3 with Ca/Zn alloys as a function of Ca/Zn compositions and their amounts is investigated. Consumptions of Ca and Zn for Sc_2O_3 and ScF_3 reduction are determined by established reactions and by calculations with module “Equilib” in thermochemical software “FactSage 7.0”. Minimum consumptions of Ca and Zn for extraction of 1 g Sc from Sc_2O_3 are accomplished at a Ca : Zn ratio 3 : 2 for the reduction alloy and here is maximum scandium content in end product reached. For reduction from ScF_3 calcium consumption remains same but zinc consumption increases with increase of its content in reducing alloy. Simultaneously, with increase of zinc content, scandium content in end product decreases. Thus, the reduction of Sc_2O_3 should be done with 0.6 Ca + 0.4 Zn reducing alloy and of ScF_3 with Ca or Ca-Zn reducing alloy with small Zn content.

The investigations are solely based on determination of Sc_2O_3 and ScF_3 reaction mechanisms by Ca/Zn reducing alloys. Problems concerning separation of Sc alloy and slag phases are not studied in this context.

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