

METAL OXIDES REDUCTION IN VACUUM: SETUP DEVELOPMENT AND FIRST EXPERIMENTAL RESULTS

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Abstract

The paper describes a new setup for investigating the reduction of metal oxides in vacuum to avoid the extremely high reduction temperature required at atmospheric pressure. Vacuum environment allows decreasing the reaction temperature significantly. The first results obtained with carboreduction of alumina and thermal splitting of zinc oxide at temperatures 1500-1600°C and partial pressure of the emerging gases less than 10^{-4} bar demonstrate that forward reduction reaction can be successfully completed but the metal yield strongly depends on the reoxidation of reduced metal in the reverse reaction as a function of the temperature of the metal vapor deposition site. The test results demonstrate that depending on the deposit sites the metal content varied from 10% to 97.8% of pure zinc and from 0 up to 58.7% of pure aluminum.

1. Introduction

Endothermic carboreduction and thermal splitting of different metal oxides using concentrated solar energy are promising processes. However, the reduction temperature at atmospheric pressure of most of the metal oxides having strong metal-oxygen bond requires very high temperatures which imposes a constraint on available materials for constructing the reactors. One option to surmount this obstacle is to decrease the partial pressure of product gases by creating vacuum in the reactor (obviously part of the thermal energy is replaced by the pumping work [1]). Therefore it is essential to explore such operating conditions of the solar vacuum process that the electrical energy consumption in the vacuum pumping will be lower comparing to the consumption in the electrolytic industrial processes. Early experimental results confirming that pressure decreasing makes these reactions feasible at lower temperature, have been published 50-60 years ago [2, 3] and reconfirmed recently in connection with solar energy utilization [4, 5]. Additional experimental investigations are necessary before a solar reactor can be designed. Information about forward and reverse reaction rates, conversion as function of the pressure and temperature distribution in the reactor, especially for reactions with metals forming undesirable by-products, is essential [5].

2. Thermodynamics

According to the thermodynamic analyses using [6, 7] for different oxides of bi-, tri- and tetravalent metals, the minimal temperature required for full conversion in forward reaction can be substantially lowered by decreasing the partial pressure of the product gases from atmospheric pressure down to μ bar level. The examined reactions can be divided to three categories: 1) their reduction temperatures stay higher than 1800°C even at relatively high vacuum (thermolysis reactions of MgO, CaO, Al₂O₃, Fe₂O₃ and SnO₂ for example); 2) their reduction temperatures decrease in vacuum to temperature that is feasible for solar reactor (carboreduction reaction for alumina and magnesia, for example, as well as thermolysis reactions of ZnO and CdO); 3) their reduction temperatures are less than 1200-1300°C at atmospheric pressure when reactions can be successfully realized, and can be further decreased to 300-400°C under vacuum conditions (carboreduction of ZnO, CdO, Fe₂O₃, In₂O₃, GeO₂ and SnO₂). Priority is given to reactions of the second category, as presented in Fig.1. It must be noted here that under vacuum environment temperature decreases not only for the forward but also for reverse reactions that can lead to reoxidation of the reduced metals at

significantly lower quenching temperature as compared with atmospheric condition.

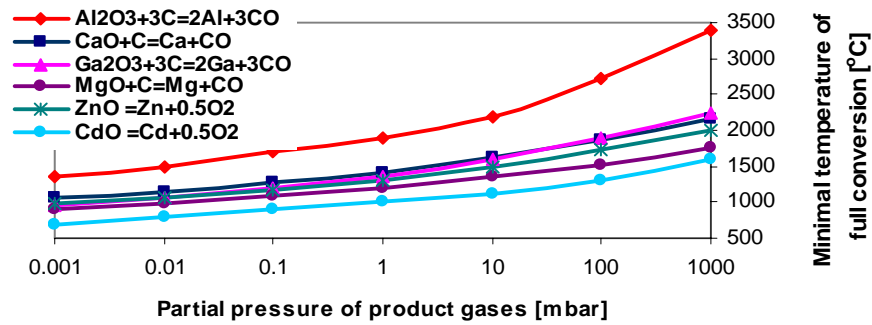


Fig.1 Minimal temperature of full conversion as function of partial pressure of product gases

When designing the experimental setup a few issues predicted by thermodynamics should be considered:

- 1) reliable working temperature can be guaranteed using high capacity dry vacuum pump for removing of the carrier and product gases which have to be analyzed at the exit (the pump must provide relatively high vacuum of less than 1 mbar absolute);
- 2) preheating of the reaction mixture must be done as fast as possible to avoid undesirable by-product formation, especially volatile in case of trivalent elements (induction heaters are more suitable for this purpose);
- 3) to study the amount of by-products produced in the reverse reaction after the metal vapors are deposited on the reactor walls with temperature gradient, as function of deposit site and its temperature.

This paper presents first results for carbothermal reduction of aluminum oxide and thermal splitting of zinc oxide in vacuum. Their equilibrium diagrams at pressure of 10^{-4} bar, as an example, are presented in Fig. 2.

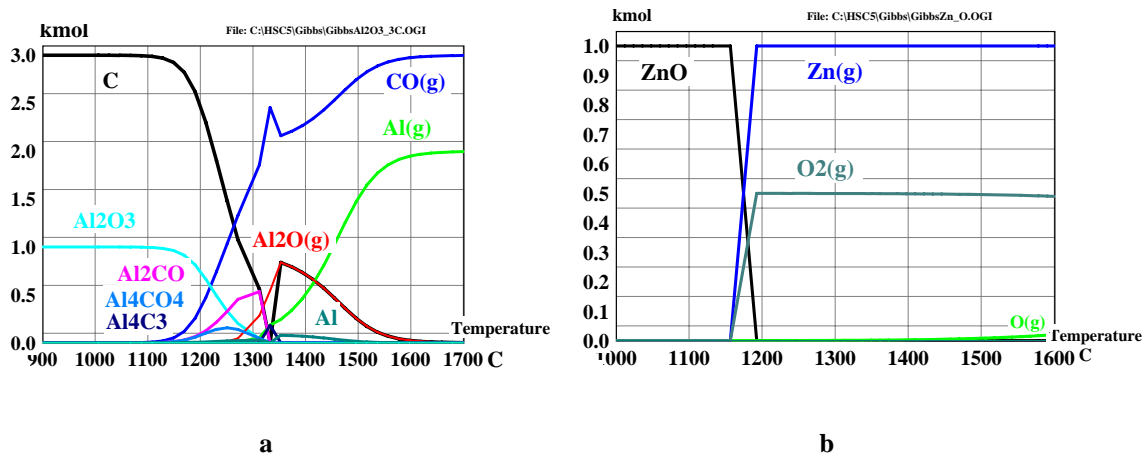


Fig.2 Equilibrium diagrams for alumina carbo-reduction (a) and zinc oxide thermal splitting (b) at pressure of 10^{-4} bar

It can be seen that the main challenge in alumina carbo-reduction is the by-products such as aluminum oxycarbides, carbide, volatile sub-oxide and carbon. They can be formed both in forward reaction if the temperature is not high enough and during the reverse reaction if the quenching temperature is too high. The temperature interval of the by-products formation is reduced from 600°C to 350°C with pressure decreasing from 10^{-3} to 10^{-6} bar respectively and also shifts to the lower temperatures. The chemistry of zinc oxide splitting is simple and the main problem is preventing reoxidation of the reduced zinc during the quenching. It is possible to assume that reaction temperature at the level of 1500°C can provide relatively high thermodynamic conversion in the forward reaction at product gases partial pressure less than 10^{-4} bar, and assure reliable exploitation of the solar reactor.

3. Experiment

3.1 Experimental setup

The scheme of the experimental setup is presented in Fig. 3.

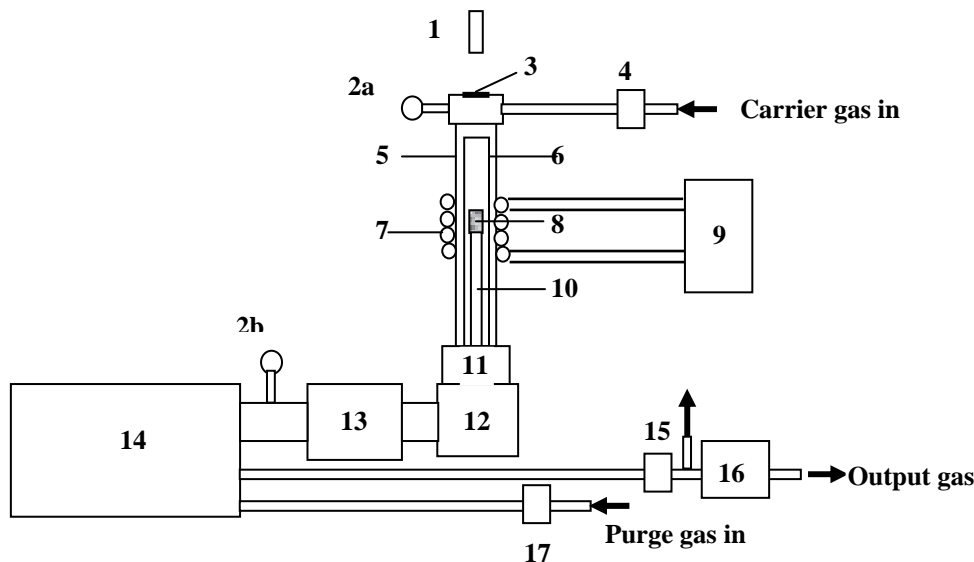


Fig.3 A scheme of the experimental setup: 1-pyrometer, 2a.b-vacuum gauges, 3-quartz window, 4, 15, 17-flow meters, 5-quartz tube, 6-alumina tube, 7-induction coil, 8-molybdenum or graphite susceptor, 9-induction heater, 10-molybdenum tube with zirconia support, 11- water cooled trap, 12- filter, 13- liquid nitrogen trap, 14-dry vacuum system, 16-gas chromatograph.

The experimental setup comprises 25 kW desktop Induction Heater SP-25A by MTI Corporation and dry vacuum system DRS1 by Alcatel. It is composed of ACP40 multi-stage Roots pump operating without internal lubricant and Roots blower RSV301B with bypass capable of 250 m³/h peak pumping speed with 1000 mbar maximal continuous inlet pressure and 0.003mbar ultimate pressure. The DRS1 is equipped with a filter and a liquid nitrogen trap (by Nor-Cal) at its entrance. The reactor is built of a quartz tube, 60 mm OD and 400 mm length, placed inside water-cooled induction coil. The ceramic tube with 48 mm OD is placed between quartz tube and susceptor for the quartz protection, energy saving and creating significant temperature gradient in the deposit sites. Vacuum is measured by two Convection Vacuum gauges Modules CVM-211 by Instrutech Inc. One is placed in the upper part of the reactor and the other at the entrance to the Pumping System. Temperature is measured by 2.2 μ m optical pyrometer SXSHTSF by Raytek through the quartz window in the upper vacuum flange of the reactor. Carrier gas entrance is also situated in the upper part of reactor to protect the quartz window and its flow rate is controlled by Tylan General Flow Controller FC260. Gaseous reaction products exhaust through the bottom vacuum flange fitted with a water-cooled trap. The outlet of the vacuum system is connected to flow meter FC360 and Tracor Gas Chromatograph. The reactor details and photos under test conditions are presented in Figs. 4 and 5.

The designs of the molybdenum (Mo) and graphite susceptors (crucibles) are different and presented in Fig 4. Although the temperature at site 2 near the Mo susceptor is higher than 1200°C (see in Fig.5, according to temperature color scale), it is adequate for the condensation of vapors of metals which have high boiling points, such as aluminum. The metal drops after the condensation can be further heated by the induction current which can promote the reverse reaction. The amount of aluminum in deposit site 1 was significantly higher than in deposit site 2 (see Fig.4) after tests with Mo crucible. The graphite susceptor was made from two crucibles to force the vapor down and condensate in a colder site 3 below the induction coil. The other

reason is the high emissivity of the graphite that makes the temperature in site 2 high enough to prevent vapor deposition. Temperature was measured inside the crucible in the tests with molybdenum susceptor (test type M) and on the top of the outer graphite crucible (test type G).

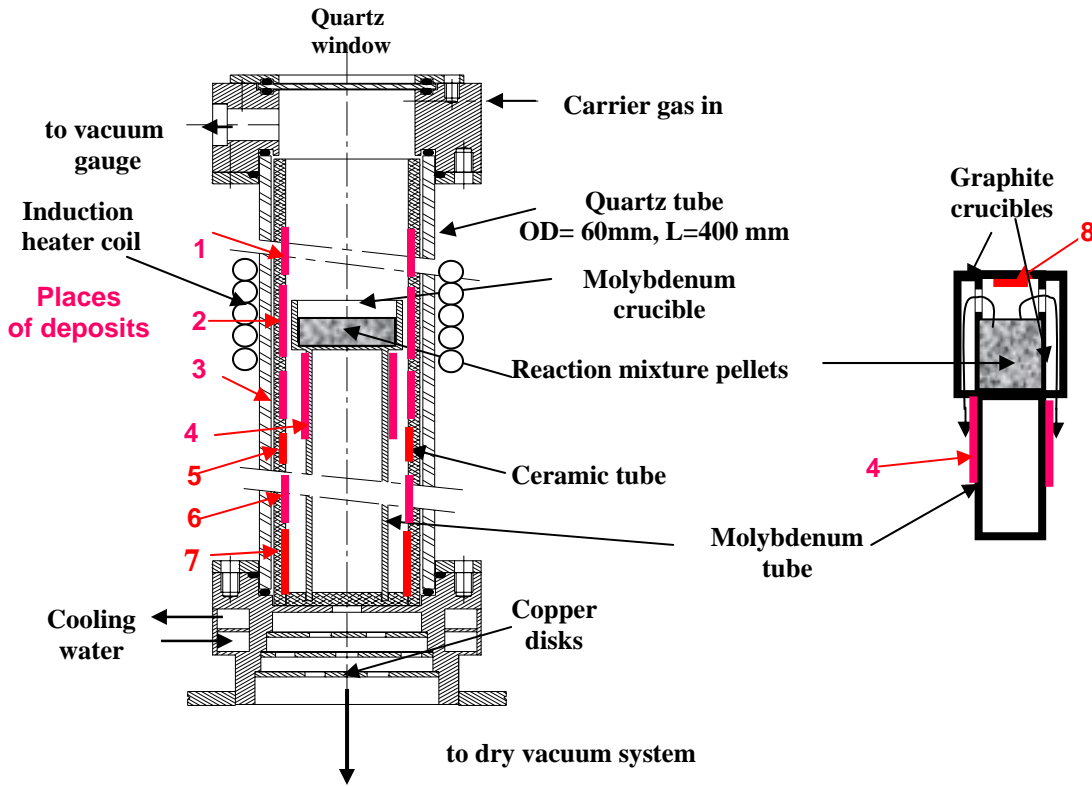


Fig.4 Reactors design

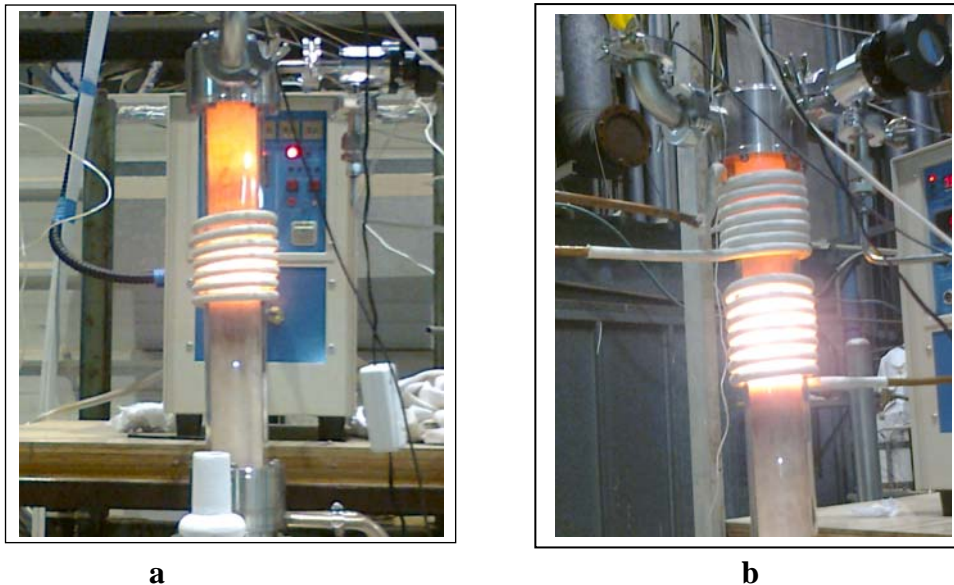


Fig.5 Reactor under test condition with molybdenum (a) and graphite susceptor (b) at 1500°C

3.2 The reactants

To avoid or reduce the blowing losses of the reactants when pumping to vacuum, pellets were prepared from the reactants powders using a press. In the case of the alumina the mole number of carbon was three times the

number of alumina moles. Beech charcoal from Chemviron, was used as the carbon resource from biomass and due to its high reactivity as a carbonaceous reagent [8, 9]. The density of the charcoal is significantly lower than the density of alumina powder with particle size 10 μm or larger. Therefore the preparation of the pellets requires the addition of organic bonding agent such as wheat flour, cellulose, starch or sugar which adds significant amounts of carbon, oxygen and hydrogen atoms. To avoid this it was decided to start with alumina nano-powder by Aldrich (544833-50G) with low density which enables preparing pellets without the need for the bonding agent.

ZnO pellets were prepared from ZnO powder by Merck (cat no 1.08849.1000).

3.3 Experimental procedure

Typical parameters that were measured during the test are presented in Fig. 6.

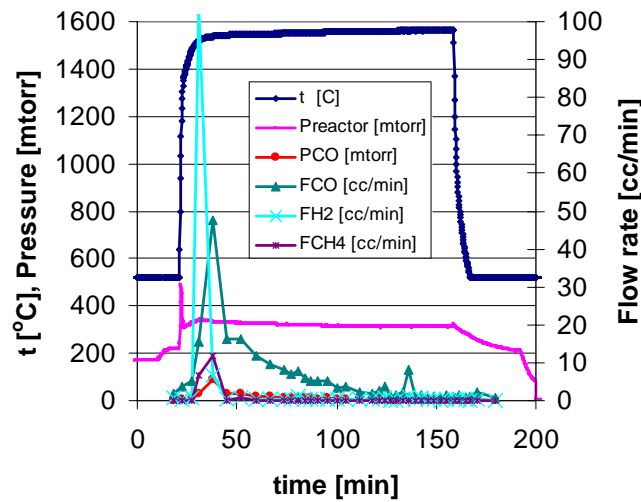


Fig. 6 Typical test parameters (molybdenum susceptor with 2.7 g pellets of alumina-charcoal mixture, as an example)

It can be seen that the heating rate was very high and the desirable temperature was achieved after a few minutes. The heating was stopped when the CO flow rate reached zero. The measured apparent temperature was corrected by calculation according to Planck distribution by Eq. (1) considering the quartz window attenuation factor that was experimentally determined as $k=0.91$. The effective emissivity of the cavity as created by the ceramic tube and the susceptor with the reaction mixture was estimated as $\epsilon \approx 0.9 \pm 0.05$. These assumptions were validated with a piece of steel placed in the crucible and measuring the temperature when the iron starts to evaporate out.

$$T_{real} = \frac{c_2}{\lambda \ln[k\epsilon(e^{c_2/\lambda T_{meas}} - 1) + 1]} \quad (1)$$

When each test was completed the deposits from different sites were scraped off separately, weighed and analyzed by XRD quantitative analysis (RIR method). Total conversion was estimated as ratio of CO or O₂ moles in the output gases related to their theoretical amount at full conversion calculated through oxygen atoms in the moles of alumina or zinc oxides that participated in the reaction and also as a sum of the pure metal gram-atoms in all deposit sites related to metal g-atoms in the reacted mixture. Total balance was estimated comparing the sum of oxygen g-atoms in the output gases and in the solid from all deposit sites with the amount of oxygen atoms in the reacted oxides. CO and O₂ average partial pressure as function of

time was calculated through total pressure measured by gauge 2a and the volume percent of CO or O₂. It can be assumed that the local partial pressure in the reaction zone might be higher.

3.3 Results and discussion

Parameters of tests with favorable results and estimation of total conversion are presented in Tables 1 and 2.

Oxide	Test type	Reaction t [°C]	Carrier gas flow rate [cc/min]	Maximal total pressure (gauge 2 ^a) [bar]	Maximal CO(O ₂) average partial pressure [bar]	Oxides under reaction* [mol/g]	Fix Carbon under reaction* [mol/g]
Al ₂ O ₃	<i>G</i>	1570	107	7.32*10 ⁻⁴	8.57*10 ⁻⁵	0.0148/1.508	0.0444/0.533
ZnO	<i>M</i>	1530	106	7.07*10 ⁻⁴	3.48*10 ⁻⁶	0.108/8.79	0

Table 1 Tests parameters

*Amount of oxides and carbon under reaction were calculated taking into account blowing losses that usually do not exceed 10% of loaded pellets mass.

Oxide	Oxygen [g-atom] in oxide	Oxygen [g-atom] in output gases	Total Oxygen [g-atom] in deposits	Total Metal [g-atom]	Pure Metal [g-atom] in deposits	Conversion 3/2	Conversion 6/5	Balance (3+4)/2
1	2	3	4	5	6	7	8	9
Al ₂ O ₃	0.0444	0.0361	0.0032	0.0296	0.009	0.81	0.304	0.885
ZnO	0.108	0.0235	0.087	0.108	0.0533	0.217	0.494	1.023

Table 2 Total conversion estimation

It can be seen from Table 2 that within the accuracy of the measurement the balance is close to 1 in both cases, but for alumina reduction the total conversion estimated by the gas analysis is almost three times higher than the total conversion estimated from the XRD results. For ZnO splitting the results are opposite. This can be explained by conservative value of aluminum content, typical for powder with large metal drops [10], see Fig. 8 below (test type *G* with alumina) and accumulation of significant amount of oxygen in Zn₂Mo₃O₈ that forms on the ceramic tube wall near the molybdenum susceptor due to the formation of volatile molybdenum oxide MoO₃ (test type *M* with ZnO). The main purpose in the current work is to study aluminum and zinc reoxidation in the reverse reactions depending on temperature in the deposit site, estimated by its color (Fig 5). In the above tests no residue remained in the crucibles and it can be assumed that the forward reaction was fully completed and all products left the crucibles in gas phase. In the case of alumina carboreduction the aluminum vapor can be accompanied by small amount of Al₂O vapors that can be the cause of the presence of small amount of Al₂O₃ at the hot deposit site 4 (see Table 3 where the results of quantitative XRD analysis for different deposit sites are presented). This aluminum oxide could be formed together with liquid Al during deposition of aluminum sub-oxide gas. This is thermodynamically possible below 1100°C and at pressure of 10⁻⁴bar. Solid by-product formation in forward reaction is also absent at test temperatures higher than 1500°C. This is confirmed by the contents of the blowing losses and residue in crucible mixture when tests were stopped before full completion. In both samples only unreacted corundum was identified by XRD analysis. Carbides and oxy-carbides in addition to corundum were identified in the residue in the crucible only at lower test temperatures

It should be noted that both in alumina carboreduction and zinc oxide splitting tests in several deposit sites that are not exposed to direct emission from the hot susceptor and not located in colder zone at the lower part of the ceramic tube, the composition of the inner and outer layers was different. Usually the inner thinner layer contained less pure metal than the outer layer. Such phenomena can be explained by the lower partial pressure of reacted gases as reaction begins when temperature of the deposit site is high enough to support reverse reaction of the condensed or de-sublimated metal vapor. With the reaction course the partial pressure of product gases increases and the temperatures when the reverse reaction starts increase causing slower kinetic of reoxidation at the deposit site (see Figure 2). Also the inner layer can be considered as insulation between the outer layer and the hotter ceramic tube.

Reactants	Sample place	Sample mass [g]	Al	Al ₂ O ₃	Al ₄ C ₃	Al ₄ O ₄ C	C crystal.	Zn	ZnO	Zn ₂ Mo ₃ O ₈
			[weight %]							
Al ₂ O ₃ +3C	3a*	0.41	58.7	0	33.7	7.6	0	-	-	-
	3b	0.07	2.9	0	6.8	90.3	0	-	-	-
	4	0.1	0	19.2	55.6	25.2	0	-	-	-
	8	0.015	0	0	2	0	98	-	-	-
ZnO	1+3	6.63	-	-	-	-	-	9.6	38.6	51.9
	5	0.3	-	-	-	-	-	35.5	52.4	12.1
	6a+6b	1.15	-	-	-	-	-	84.5	15.5	-
	7	1.77	-	-	-	-	-	97.8	2.2	-

Table 3 Results of XRD quantitative analysis (RIR) for deposits from different places

* a – outer layer; b –inner layer

The powders with maximal contents of reduced metals are presented in Fig. 7 and their SEM images in Figs.8 and 9.



Fig.7 Powders from place 3a with 59% of pure aluminum (a) and from place 7 with 98% of pure zinc (b)

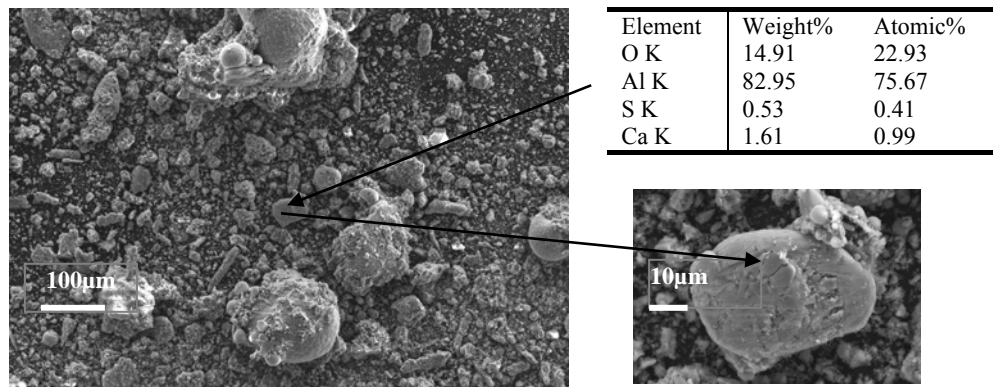


Fig.8 SEM image of deposit with reduced aluminum (place 3a) with EDS results

Shape of metal particle presented in Figs.8 and 9 show that aluminum vapor condensates and small drops coagulate to bigger particles whereas zinc vapors de-sublimate in cold sites of the ceramic tube.

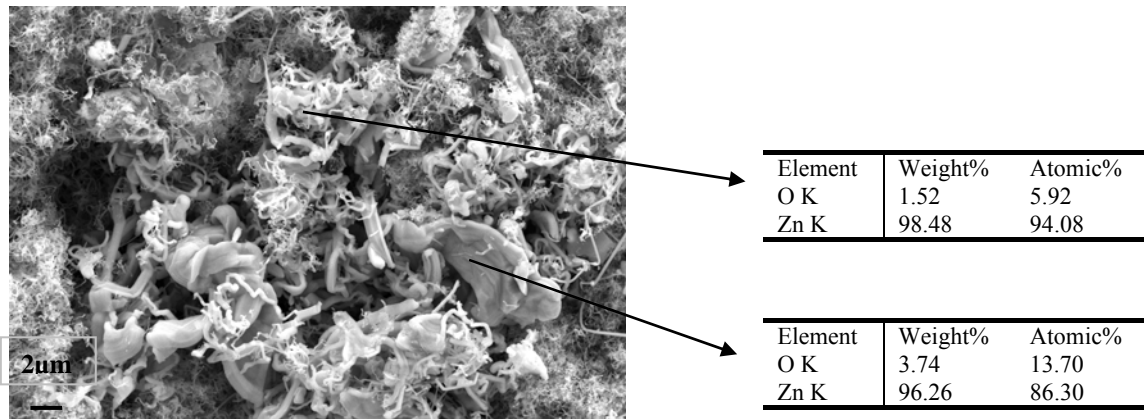


Fig. 9 SEM image of deposit with reduced zinc (place 7) with EDS results

4. Summary and conclusions

- New setup for metal oxides reduction in vacuum at temperatures up to 1800°C with pumping speed 250m³/h is described and first results of alumina carboreduction and zinc oxide thermal splitting are presented. Tests will be carried on in wider range of temperature and pressure.
- At temperature of 1500-1600°C and partial pressure of emerging gases less than 0.1 mbar, the forward reaction is fully completed and products of reaction in gas phase leave the crucibles which remained empty after the tests. Solid by-product formation in forward reaction is also absent.
- Round form of aluminum particles indicates that main mechanism of Al deposition is vapor condensation. Most aluminum vapor condensates on the surface of ceramic tube with highest temperature still suitable for condensation where the aluminum is subject of reverse reaction with by-product formation. The maximal aluminum yield is no more than about 60% according to XRD quantitative analysis.
- Specific shape of almost fully reduced zinc discovered on the coldest lower part of ceramic tube leads to the conclusion that the main mechanism of zinc vapor deposition is desublimation that happen in places with temperature suitable to avoid reoxidation.
- Solar reactor design has to guarantee drastic temperature drop at the interface between the reaction chamber and the quencher to ultimately avoid the reverse reaction.

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