Aluminum and magnesium are metal elements with strong oxygen bonds and their oxides reduction demand high energy input in their production processes. Therefore, solar thermal carboreduction can be considered as a promising option when at least part of the necessary energy can be provided from concentrated solar radiation. A major difficulty is the high reaction temperature at atmospheric pressure that according to Le-Chatelier principle can be reduced in vacuum by decreasing the partial pressure of the product gases. This however, requires additional energy consumption for the pumping. Thermodynamic considerations associated with this process will be discussed along with experimental results obtained in a wide range of tests parameters.

The main features predicted by thermodynamics can be formulated as follow:

- Relatively high reaction temperature to achieve full alumina to aluminum reduction even at vacuum below 1 mbar compared to the temperatures required for carboreduction of magnesia [1] albeit it needs also high reaction temperature at atmospheric pressure (Fig1a).
- Complicated chemistry of alumina carboreduction because by-products such as oxycaribdes, carbides and volatile sub-oxide can be formed during the forward and/or reverse reactions [1, 2, and 3], whereas the chemistry of magnesia carboreduction is simple and demonstrates merely the presence of Mg and MgO.
- Significantly higher condensation temperature of the aluminum vapor comparing to magnesium which can promote oxidation and carbonization of the reduced aluminum in reverse reactions (Fig.1b).
- Higher volume of product gas released per unit weight of reduced Al compared to Mg (Fig.1c) that requires higher electrical energy consumption in pumping.

Tests were performed using experimental setup based on fast induction heating (IH) as described in details in [1]. The setup in addition to GC was complemented with Siemens infrared analyzer Ultramat 23. The CO composition in the outlet gases was recorded every 10 sec. Useful oxygen...
yield, that was estimated as ratio of O-atoms in CO originated from the oxides to the amount of O-atoms in the reacted oxides. This parameter is usually higher than the real aluminum yield because of carbide and oxy-carbide formation whereas it can be used for estimating of magnesium yield. Tests were stopped when CO content approaches zero. The amount of the residual products in the forward reaction was estimated by weighing the crucible before and after the tests. Content of metal, metal oxides and other by-products formation in the forward and reverse reactions (in alumina case) were determined by XR Diffraction quantitative analysis of the residual in crucible and deposits obtained at various sites of the reactor having different temperatures.

Stoichiometric reaction mixtures were prepared using wood charcoal as biomass source, alumina and magnesia powder of Sigma-Aldrih and 10 wt% sugar powder as binder. Mixture was pressed at 10 tons to pellets. After pressing the pellets were heated up to 165°C during 20 min. Tests were done at temperature range of 1400-1800°C and averaged CO partial pressure varied from about 0.01 to 4 mbar. The mass of the pellets loaded into a graphite crucible was 3-3.5 g and Ar carrier gas flow rate was changed from 0.1to11/min. It will be shown that in tests with averaged CO partial pressure less than 0.2 mbar the amount of residual by-products in the crucible (in alumina case) and amount of unreacted oxide (in magnesia case) is negligible at reaction temperature higher than 1650°C whereas in tests with averaged CO partial pressure of 3.5 mbar the loaded pellets vanished only at temperature higher than 1800°C. The useful oxygen yield (as a result of the forward and reverse reactions) calculated based on the CO amount in the outlet gases increases from 80% at reaction temperature of 1400°C to about 90% at reaction temperature of 1800°C in alumina case and from 75% to 85% in the magnesia case. Local amount of pure aluminum depends on the temperature at the deposit site and predominates in the outer layers of the deposit. It will be shown that depending on the reaction conditions pure aluminum can be observed as aluminum drops or from 60 to 90% content in a gray powder down to zero in a yellow-orange powder. These layers with low pure Al contain aluminum carbide and oxy-carbide which have been scraped off the hot sides where the temperatures are suitable for aluminum vapor condensation but also for substantial reverse reaction. Pure magnesium was obtained as continuous condensed layer in colder deposit sites and was almost 100wt% of all deposit at averaged CO partial pressure less than 0.2 mbar. Relative reaction rate was estimated as reaction time interval at half of the height of the CO peak during the total reaction time. It will be shown that reaction time estimated in such a way strongly decreases with the increase of the reaction temperature and not depending on the CO partial pressure. Reaction time in the magnesia case was lower than in the alumina case at lower temperature and approaching similar values as the reaction temperature increases.

To determine the correlation between the temperatures at different inner surfaces of the IH reactor with the intensity of the reverse reactions and to recalculate the measured temperatures by means of non contact temperature sensor to the actual reaction temperature, heat transfer modeling was applied. The same method was used to calculate the temperature distribution in a 10-15 kW solar reactor planned to operate with solar concentration at the level of 5000 suns. It will be shown that the main characteristics of this solar reactor is the high temperature (up to 2000°C) in the reaction zone and strong temperature gradient towards a water cooled space where the aluminum or magnesium vapors are deposited.

References: