Recovery of critical raw materials from production rejects of the special glass industry by means of gas phase reaction

Anna-Lisa Bachmann[1], Katerina Kunkel[1], Gert Homm[1], Katrin Bokelmann[1], Rudolf Stauber[1] and Anke Weidenkaff[1]

[1] Fraunhofer IWKS, IWKS , Brentanostraße 2a, 63755 Alzenau, Germany

anna-lisa.bachmann@iwks.fraunhofer.de

Abstract

Glasses from the optical specialty glass industry often contain considerable amounts of rare earth elements (REE) such as cerium and lanthanum, which are worth to be recycled. For this a new approach based on chemical gas phase transport was investigated.

After a mechanical pre-treatment of the production rejects, the main process – the gas phase reaction - offer the possibility to dissolve REE from the matrix selectively. The required gas can be recycled, and dissolution and precipitation reactions with environmentally harmful chemicals are unnecessary. First of all, theoretical calculations are used to estimate whether separation and recovery of the REE via solid/gas processes is possible and economically feasible. Then the process is tested experimentally in the laboratory and results are discussed.

Introduction

Rare earths are a critical elements that is often not recycled, as recycling involves a great deal of effort and often needs methods that are harmful to the environment. The recycling rate of end of life products is less than one percent, which is often related to the low concentrations of REE. In the case of production residues from the special glass industry, however, the rare earths are present in unusually high concentrations, so that environmentally friendly recycling offers great potential for savings.

In the underlying case of optical specialty glasses the REE are bound as oxides surrounded by silica matrix. To easily transfer them into the gas phase, they have to be reduced with a suitable reacting agent such as hydrogen. For many elements such as REE the sublimation temperature can be lowered by forming a gas complex, e.g. with chlorine. In some cases, the formation of highly volatile oxygen compounds may be considered. Numerous elements that form volatile halogen compounds are known and have already been investigated [Binnewies et al.].

Materials and methods

The tested lanthanum-containing borosilicate glass was examined for its composition at the beginning of the investigations using ICP-OES (optical emission spectrometry with inductively coupled plasma). The results of the analyses in Table 1 show that the strategic metals in oxidic form such as lanthanum (9.4 wt.%) and niobium (7.3 wt.%) are present in high concentrations in the glass sample. Additional measurements with X-ray fluorescence analysis show a content of 31 wt.% silicon oxide and 7.1 wt.% zirconium oxide.

Table 1: Composition of the examined optical glass.

Composition of the examined optical glass [wt.%]	
La_2O_3	9,4
B_2O_3	8,7
SiO_2	31
CaO	13,1
TiO_2	7,7
ZrO_2	7,1
Nb_2O_5	7,3
SrO	3,5
MgO	3,1
Na_2O	2,5
K_2O	4,2

Figure 1: Experimental setup for conducting the chlorination experiments

The laboratory setup used for the experiments at the Fraunhofer IWKS in Alzenau is shown in Figure 1. It consists of a two-zone furnace with integrated quartz glass tube. The cold zone (150°C) is used for the formation of gaseous aluminum chloride (AlCl3), the warm zone (temperature has been varied) is intended for the formation of rare earth molecules (lanthanoid chlorides or gas complexes XAlnCl3n+3).

Results and discussion

Figure 2 shows the percentage of metals remaining in the solid after the chlorination process. The in the glass present boron must be separated in a first step, as it lowers the melting point of the glass. To remove the boron, the glass was first treated at 500°C for 30 minutes. In a further step, a series of experiments was made to convert the target metal lanthanum from the glass powder into the gas phase by either direct sublimation of the chlorides or by gas complex formation on the material surface. For direct sublimation the lanthanum was chlorinated with chlorine gas, for gas complex formation $AlCl_3$ and Cl_2 were used in combination. For both variants, temperatures between 500 and 1000°C for 30 or 60 minutes were chosen. The results of the sublimation experiments (Figure 2 left) show that pure carbochlorination at 800°C does not lead to a significant transition of lanthanum into the gas phase. While niobium, titanium and zirconium already change into the gas phase at 800°C, temperatures of 1000°C and a treatment time of at least 60 minutes are required for the separation of rare earths such as lanthanum. In the case of gas complex formation (Figure 2 right), it can be seen that lanthanum is already partially converted into the gas phase at comparatively low temperatures of 500°C and a treatment time of 60 minutes. Best extraction rates with more than 90 % lanthanum reduction in the solid however can be achieved at a temperature of 1000°C, but at comparatively small treatment time of only 30 minutes.

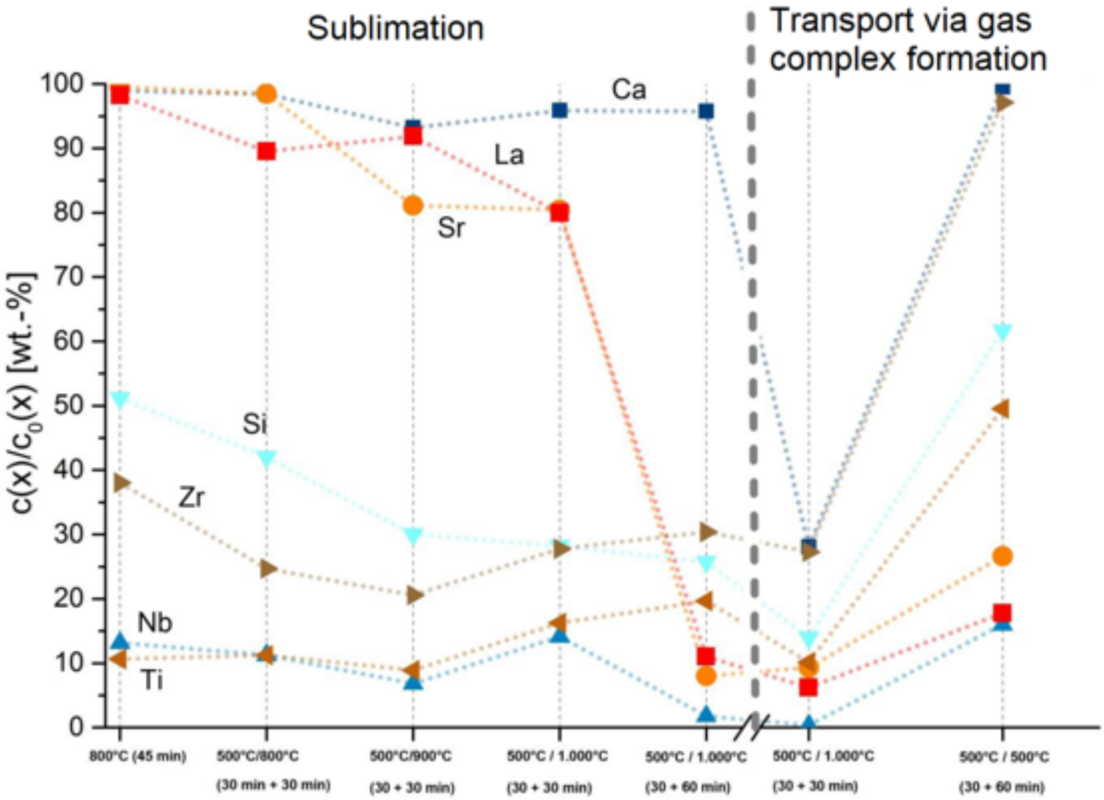

Figure 2: Investigation of the separation of metallic oxides by sublimation, carbochlorination and transport via gas complex formation (proportion of metals remaining in the solid).

Conclusion

In conclusion, it can be stated that the separation of strategic metals such as rare earths from production residues of the special glass industry is in principle possible using the gas phase reaction. It should be noted that the process must be run in two temperature gradients in order to remove the boron and avoid undesired melting of the glass material. First promising experiments show that in the case of forming a gas complex with chlorine ($LaCl_3$) an extraction rate of more than 90 % lanthanum can be achieved. This version also seems to show slight advantages over direct sublimation in terms of conversion efficiency and hence economy.

References

Binnewies, M.; Bokelmann, K.; Gellermann, C.; Gäth, S.; Stauber, R. (2015); Konzepte zur Wiedergewinnung strategischer Metalle über die Gasphase, Chem. Ing. Tech. Vol. 87, Nr. 11, 2015, S. 1486-1497.