INDONESIAN MINING JOURNAL Vol. 18, No. 2, June 2015 : 82 - 91

PREPARATION OF METALLIC CERIUM BY METALLOTHERMIC REDUCTION USING CERIUM OXIDE AS RAW MATERIAL

PEMBUATAN LOGAM SERIUM DENGAN METODE METALOTERMIK MENGGUNAKAN SERIUM OKSIDA SEBAGAI BAHAN BAKU

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ABSTRACT

Cerium is one of the rare earth elements (REE) which many are found in rare earth minerals of monazite. Cerium is widely used for metal alloys in stainless steel, permanent magnets and automotive industries. In Indonesia, researchs for cerium extraction from such minerals of monazite to procure metallic cerium have not been intensively carried out, although cerium is potentially promising as raw material for alloying. The present research aims to study the conditions of cerium oxide (CeO_2) reduction process to yield metallic cerium (Ce). Cerium oxide reduction process was performed by a metallothermic method using a reductant of magnesium metallic powder and $CaCl_2$ as a flux. The parameters studied during the experiments were the quantity of the reductant, the composition of the flux and temperature of the process. The best result of the experimental process obtains the yield of metallic cerium about 50%, while the metal purity is 91% Ce. The process took place under conditions of that the oxide sample and reductant ratio were 1 : 1, the flux addition was 1%, with temperature of the process at 1200°C for 3 hours.

Keywords: monazite, REE, cerium, oxide cerium, metallothermic reduction.

SARI

Serium adalah salah satu unsur dari kelompok logam tanah jarang (REE) yang banyak ditemukan di dalam mineral tanah jarang seperti monasit. Logam serium banyak dimanfaatkan untuk paduan logam pada besi baja, magnet permanen dan industri otomotif. Penelitian untuk mengekstraksi serium hingga diperoleh logamnya secara intensif belum pernah dilakukan di Indonesia, walaupun potensi mineral mengandung serium cukup menjanjikan. Penelitian ini bertujuan untuk mempelajari kondisi proses reduksi serium oksida (CeO_2) menjadi logam serium (Ce). Proses reduksi serium oksida dilakukan dengan metode metallothermic menggunakan reduktor serbuk logam Mg dan penambahan fluks $CaCl_2$. Parameter-parameter yang dipelajari dalam percobaan ini adalah jumlah reduktor, komposisi fluks, dan suhu proses. Reduksi serium oksida menjadi logam serium diperoleh pada rendemen logam 50% dengan kemurnian 91% Ce. Proses berlangsung pada kondisi perbandingan REE oksida dan reduktor 1:1, penambahan fluks 1% dan suhu proses 1200°C selama 3 jam.

Kata kunci : monasit, REE, serium, serium oksida, reduksi metalotermik.

Received : 14 January 2015, first revision : 21 April 2015, second revision : 10 June 2015, accepted : June 2015

INTRODUCTION

Cerium is one of the rare earth elements (REE) that is considerably very rare and mostly associated with other metal elements in diminutive numbers. The REE is belonging to lanthanide group in the periodic system of elements that has 14 elements member, namely Ce-Pr-Nd-Pm-Sm-Eu-Gd-Tb-Dy-Ho-Tr-Tm-Yb-Lu. Other elements that are often associated in the same minerals are Sc-Y-La [Castor and Hedrick, 2010]. In Indonesia, the cerium is predominantly found in monazite sands which is especially associated with tin minerals, There are found potential areas of monazite deposits in Indonesia, some of them are: Bangka-Belitung, Karimata/Ketapang, Rirang-Tanah Merah [Atmawinata, 2011].

The utilization of Cerium is either in its metallic form or alloys. Cerium, which has characteristic of high affinity to sulphur and oxygen, is widely used in various aluminum and iron alloys. In steels for example, the presence of metallic cerium can assist in reducing the detriment of sulfides and oxides, which would increase the hardness of the stainless steel. The addition of about 3-4% of cerium to magnesium-zirconium alloys will help to obtain fine grain and size of complex shapes and to increase heat resistance of the alloys. Cerium metal is often added to aluminum to improve its resistance from corrosion. In addition, cerium alloys are mostly used for permanent magnets and carbon-arc lighting in film industry.

The whole REE process from the ore to metals up to its utilization can be seen in Figure 1. First, REEs are beneficiated and extracted from its minerals such as monazite to produce REE-oxides, the process can be carried out in two ways, i.e., an alkaline method (dissolving monazite concentrate in alkaline solution) or an acid method (dissolving monazite concentrate in acid solution). Secondly, its oxides mixture can be separated to produce its oxide, which can be conducted by solvent extraction method. Thirdly, its oxide is reducted and calcinated to produce its metal with metal purity up to 95%. The purity of the final product depends on its impurities of the previous product. Lastly the metal is melted with others metals to form alloys and ready for its special applications.

There are two methods for REE oxides reduction to produce metals, i.e., electrolytic and metallothermic processes. The electrolytic process is carried out in two ways [Zhu, 2014], those are the REE-Cl_3 decomposition (REE-chloride) by dissolving it in alkaline molten salt or alkaline earth and decomposition of REE oxide by dissolving

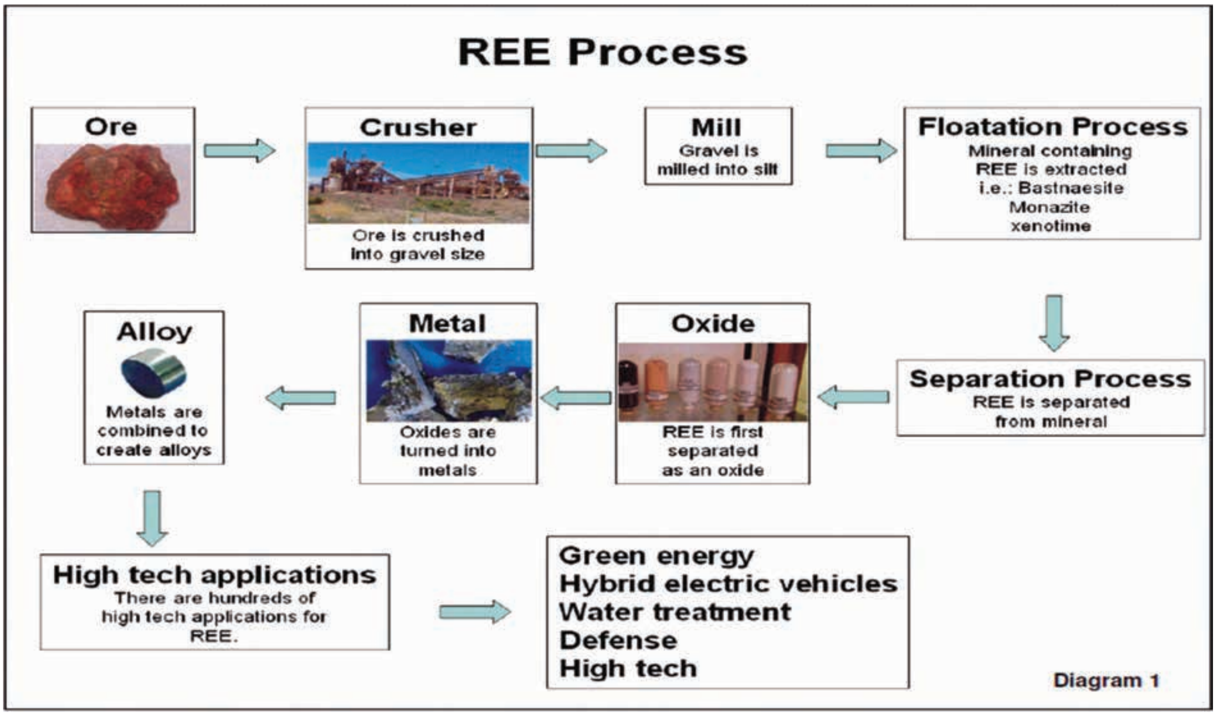


Figure 1. Production line of REE from the ore (Gupta and Krishnamurthy, 2005)

it into fluoride salt. Those methods have several disadvantages that are: the use of expensive and consumptive electrodes, the use of chloride or fluoride salts to prevent the unwanted formation of REE-OCl, which requires high temperature (>1000°C), in addition, the metal recovery is low (<40%), as well as REE-Cl_3 reduction process produces highly corrosive chlorine gas. On the other hand, the advantage of those processes can be carried out continuously, hence it could be easier to be implemented in industrial scale [Koltun and Tharumarajah, 2014]. Those processes are also more economical and easier to prepare metal products and alloys. Research on alloying by using one of the above methods was successfully to prepare REE-Ni_5 from mixture of Tb_4O_7 and NiO in molten $CaCl_2$ at temperature of 850°C [Qiushi et al, 2015]. Moreover, research on preparing cerium from cerium oxide using electrolytic method was conducted at high temperature with molten salts of alkaline chloride ($CaCl_2$-KCl) as the flux. In this case, metallic calcium was deposited on the cathode and its molten reacted with CeO_2 to form metallic cerium as well as cerium oxychloride [Claux et al, 2011].

Metallothermic process can be carried out in two ways, namely the reduction of REE- F_3 with calcium metal (calciothermic process) and REE-O_2 with calcium metal. This process has disadvantages, such as non-oxidizing process condition and high energy consumption. On the other hand, up to 90% of the metal recovery can be achieved (Weber and Reisman, 2012). While, a study of CeO_2 reduction using metallothermic method was conducted to prepare Al-4%Ce alloys. This product could replace Al-Si alloys that widely used at the automotive and aerospace industries. Another study in metal preparation process, such as CeO_2 powder was injected into molten Al-Mg alloys, which would generate metallic cerium during the injection process (Luna and Munis 2011). The current metallothermic developing process is called Ames Process, which has been developed in America. The Ames Process is purposed to prepare high purity REE through metallothermic reduction using alkaline earth metal [Riedemann, 2011].

In Indonesia, research to prepare metal from REE-oxide has not yet been done intensively, nevertheless, the research on REE extraction from monazite to acquire REE-oxide has been successfully carried out by BATAN (Indonesia National Atomic Energy Agency) and currently it is being developed to pilot plant scale. The present research purposes to study the conditions of cerium oxide reduction to procure metallic cerium. The expected result from this work is that the form of cerium metal phase in the molten reduction product would be governed by metallic cerium.

METHODOLOGY

Cerium oxide used as raw material in the present research was obtained from PSTA (Center for Science and Technology Accelerator) - BATAN that based on REE research cooperation agreement between the two institutions of Puslitbang *tek*MIRA (RDCMCT) and PSTA-BATAN. The samples prepared were in the form of cerium oxalate. Therefore, those samples were calcined in a muffle furnace at 900°C for 3 hours in order to bring out cerium oxide. A photo of produced cerium oxide is presented in Figure 2c, which shows that cerium oxalate color (Figure 2a) changed after calcining into cerium oxide.


(a) (b) (c)

Figure 2. Photos of (a) cerium oxalate samples; (b) Muffle furnace for calcination process; (c) cerium oxide as calcination product

Further, cerium oxide reduction process was carried out by metallothermic method using Mg metal powder as reductant and $CaCl_2$ as flux. The steps of cerium oxide reduction process can be seen in Figure 3. The equipment used for the process were a tube furnace, combustion boat, crucible and resistance furnace. In addition, it also required workplace safety toolkits such as masks and gloves. The parameters studied in this process were the variable quantities of reducing agents where the ratio of cerium oxide and reductant was tested as much as 1:1, 2:1 and 1:2 parts by weight, the flux composition was fixed about 1% by weight compared to the raw material, The temperature applied was 1000, 1200 and 1300°C with reaction time of 3 hours respectively. Materials and equipments used in this research can be seen in Figure 4.

In the reduction process, argon purges into the furnace to prevent the unwanted oxygen from air get in. After the reduction process finish, the metal phase was separated from the slag. Then, the metal and the slag were analyzed by ICP to determine the REE content and also were analyzed by XRD and SEM to further clarify the elements contained.

RESULTS AND DISCUSSION

In the cerium oxide reduction process, the metal that used as a reducing agent must be more reactive than cerium such as Ca, Al, Si, and Mg. During the experimental work, magnesium as reductant and $CaCl_2$ as flux were used. Due to the required reduction condition, argon must be purged. The overall reaction that occured in the process are:

$$CeO_2 + 2CaCl_2 + 2Mg \rightarrow Ce + 2CaO + 2MgCl_2$$

The sample of REE oxides used in this experiment contained mostly cerium oxides followed by neodymium, lanthanum, praseodymium, samarium and yttrium oxides (Table 1). A photo of the REEs oxides mixture can be seen in Figure 5.

The tested variables in this process were the ratio of CeO_2 to Mg powder, temperature, while the quantity of flux was fixed at 1% w/w. Prior to the tested variables, preliminary experiments were conducted to understand the characteristic of the process during chemical reaction is occurred.

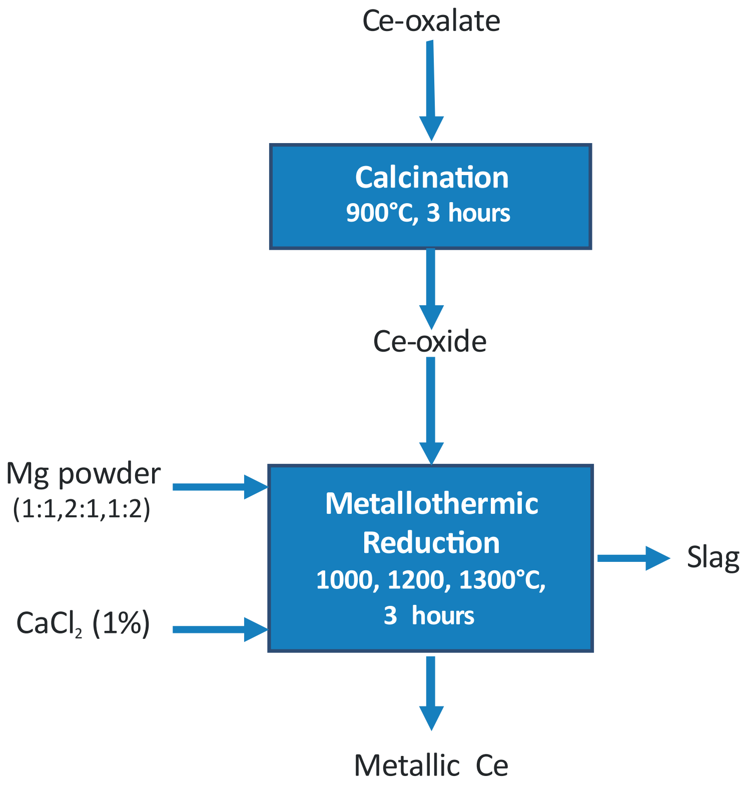


Figure 3. Steps of cerium oxide reduction process to produce metallic cerium

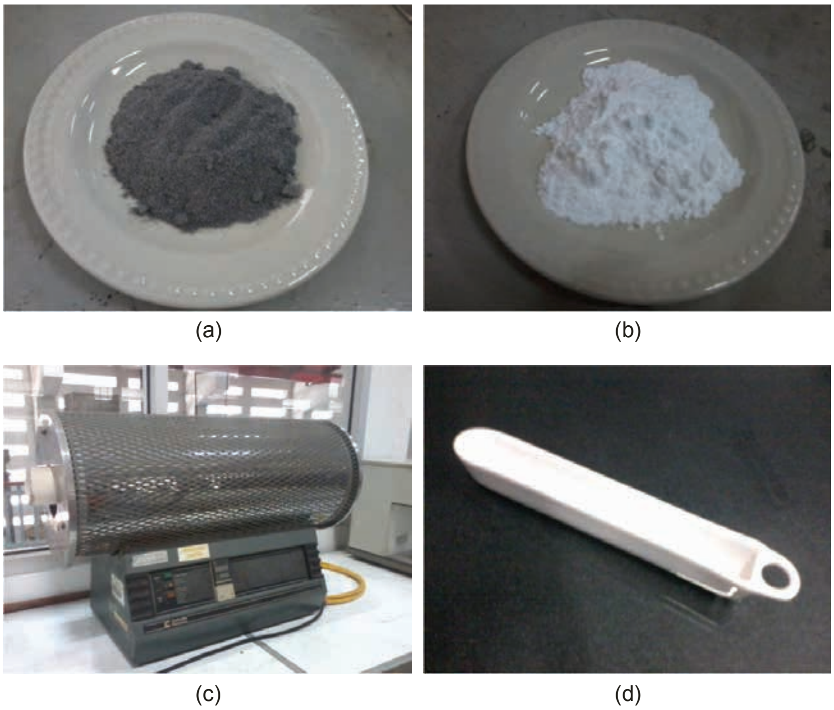


Figure 4. a) Metallic Mg powder; b) $CaCl_2$ powder; c) Tube furnace; d) Combustion boat

Table 1. REE oxides composition

No.	Oxide	Grade (%)	Element	Grade (%)
1.	CeO_2	97,580	Ce	79,440
2.	Nd_2O_3	0,622	Nd	0,530
3.	La_2O_3	0,510	La	0,435
4.	Pr_6O_{11}	0,209	Pr	0,173
5.	Sm_2O_3	0,113	Sm	0,097
6.	Y_2O_3	0,070	Y	0,060

Figure 5. A photo of cerium oxide sample as raw material for reduction experiment

Initial experiment was carried out at temperature 900°C, the ratio of CeO_2 and Mg were set in the stoichiometric calculation of CeO/Mg = 2/1 without and with flux addition. The experiments were conducted within the tube furnace. The initial experiment resulted that none of Ce metal was formed, however, two layers were likely formed i.e, CeO_2 and Mg alloyed powder, which had green color and brown of CeO_2. When they were analysed by SEM and XRD resulting undetected metallic cerium. While, green powder like-cerium is still associated with magnesium and it is binded or inclusion in the material (Figure 6). Whereas, the brown powder indicated cerium associated with magnesium is shown in Figure 7. The analysis results for these two products pointed that either metal or slag is still dominated by cerium oxide.

Preparation of metallic cerium might be effective to be conducted in a tantalum crucible type furnace for reduction smelting of cerium oxide under argon atmospheric condition compares to a tube furnace as was conducted by Spedding and McGinnis (1951) who had produced metallic of gadolinium.

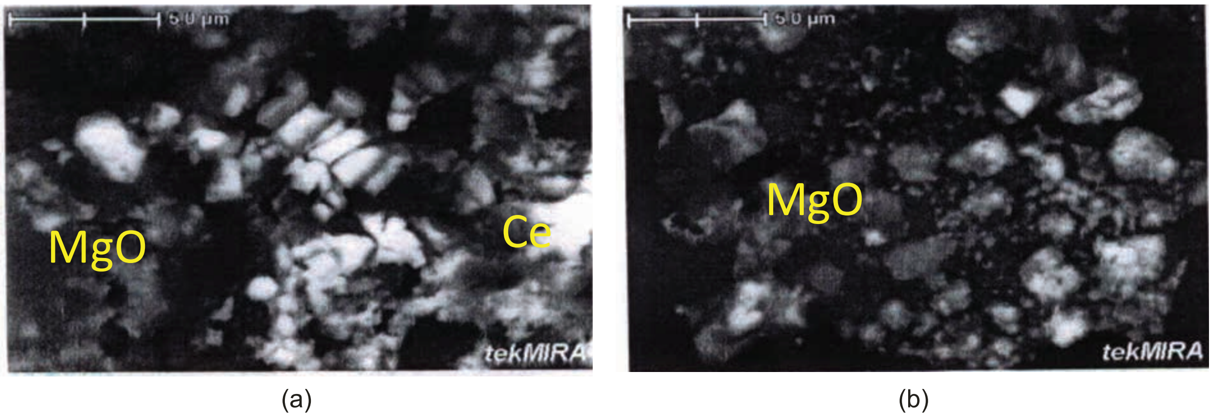


Figure 6. SEM X-Ray analysis of Mapping, a) melted with flux; b) melted without flux

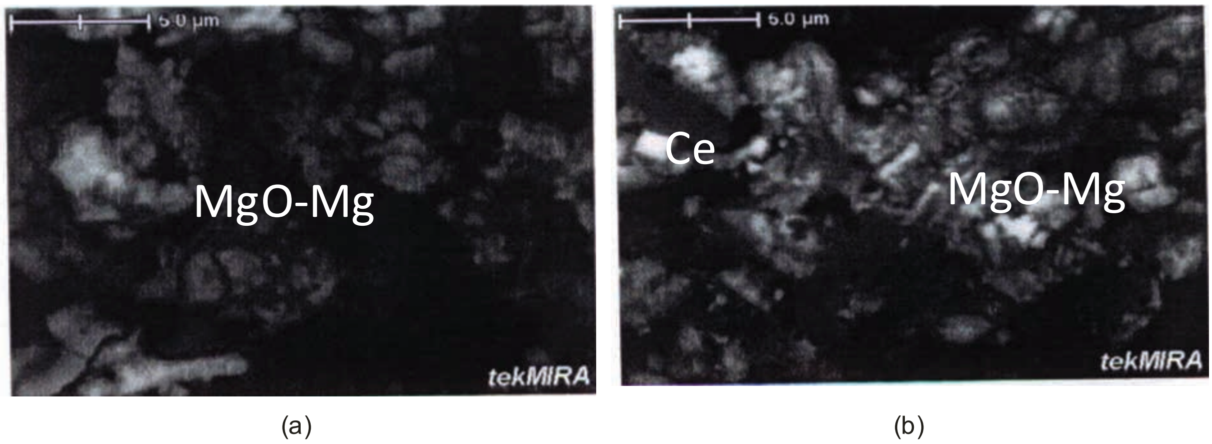
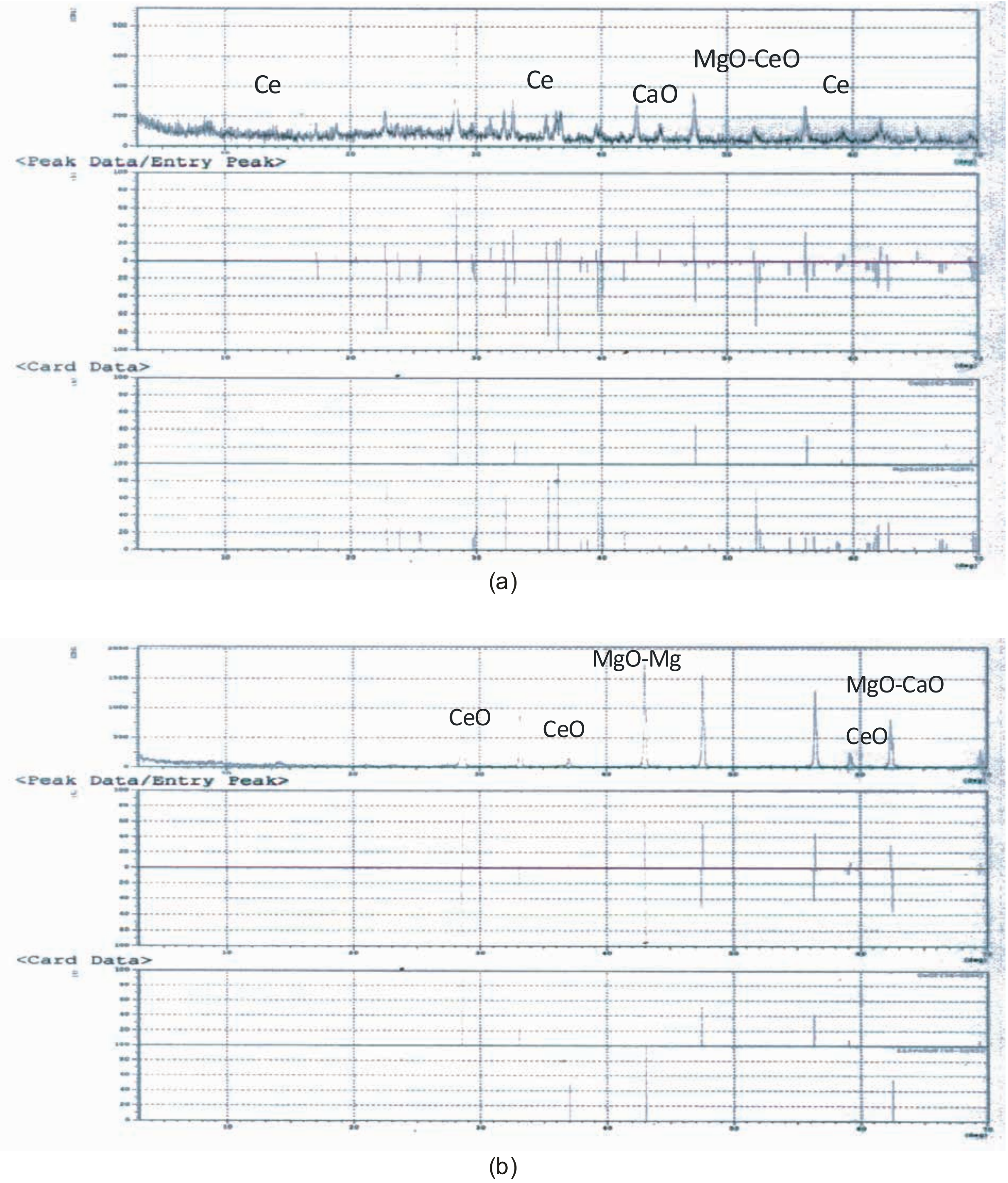


Figure7. SEM X-Ray analysis of Mapping, a)slag with flux; b) slag without flux

The next experiment done was to raise the melting temperature up to 1000°C in the same composition as previous experiment (based on the stoichiometry calculation). The experimental product was then analysed by XRD. Unfortunately, metallic cerium still has not been formed within this process condition. Even though, the metal and slag phases had been separated, but both separated phases still contain cerium oxide. In metal phase, however, magnesium silicate is formed. Figure 8 shows the XRD difractograms.

The next experiment was set in the weight ratio of CeO_2/Mg = 1/1 (w/w), then it was melted at temperature of 1200°C. The flux added was in the same condition as the previous experiment (1%, w/w). From the experiment results, it has been seen that the metal phase formation of metallic cerium is silver-gray color as shown in Figure 9.

SEM X-ray mapping analysis of the metal phase as seen in Figure 10 shows that the metallic cerium start forming, which is indicated by needle-like structure (the white color from the left to the right). However, it also appears the existance of Mg, Cl and Ca in the metal phase. The CeO appears in the form of chunk (at bottom right of the picture), which exhibit that not all CeO could be converted into metallic cerium during the reduction process. This phenomenon might be due to the presence of oxygen, where the argon does not yet purge well. In comparison with the reduction of rare earth oxide under helium injected atmospheric condition into the chamber of tantalum crucible could minimize the formation of REE-oxide as revealed by Spedding and McGinnis, 1951. The presence of oxigen (O_2) in the tube furnace would promote the formation of CeO.



(a)

(b)

Figure8. XRD Analysis a). metallic phase; b) slag phase

According to Figure 11, metallic cerium is also appeared in the slag phase (at the left side to the middle of the picture). In addition, metallic Mg is also showed in the form of chunk (at bottom right of the picture).

Having experience in obtaining metallic cerium from the previous experiments, furthermore, larger capacity experiments were carried out. As much as 100 g of CeO_2 sample was reduced using a resistance furnace. The parameters used for

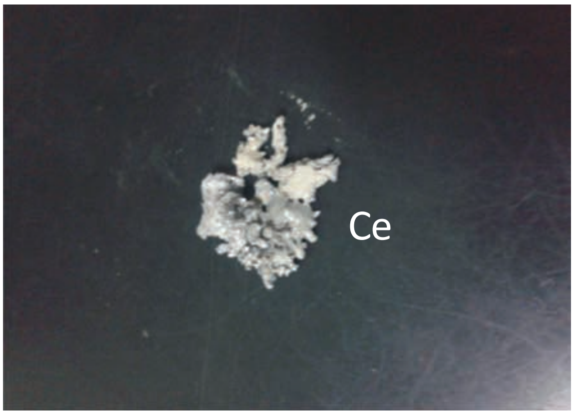


Figure 9. Metallic cerium

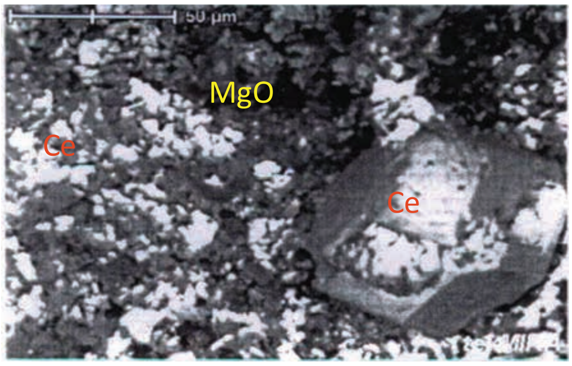


Figure 10. SEM X-ray mapping analysis of metal phase

the experiments were similar to the previous tests mainly the ratio of CeO_2 versus reductant as well as temperature process. The ratio of REE-oxides and reductant were 1:1, 1:2 and 2:1 (w/w). While, flux addition is kept constant as previous experiment within 1% (w/w), the temperature process was held at 1200°C and retained for 3 hours.

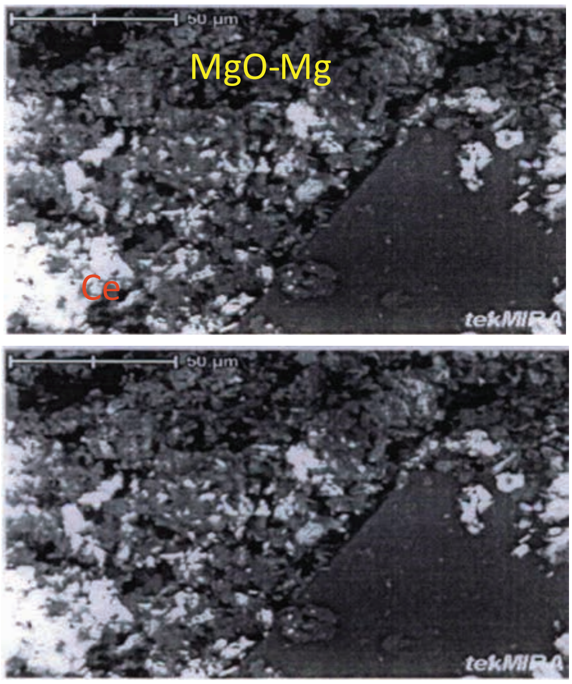


Figure 11. SEM X-ray mapping analysis ofslag phase

The experimental results for the different composition of quantities samples and reductant can be seen in Figure 12.

Figure 12 shows that ratio of the REE-oxide and reductant (1:2, w/w) is found as the best result to yield metallic cerium of 50% in the metal phase, while the rest elements contain others REEs such as La, Nd, Pr, Sm, which are detected in small quantities. This is due to the sample contains

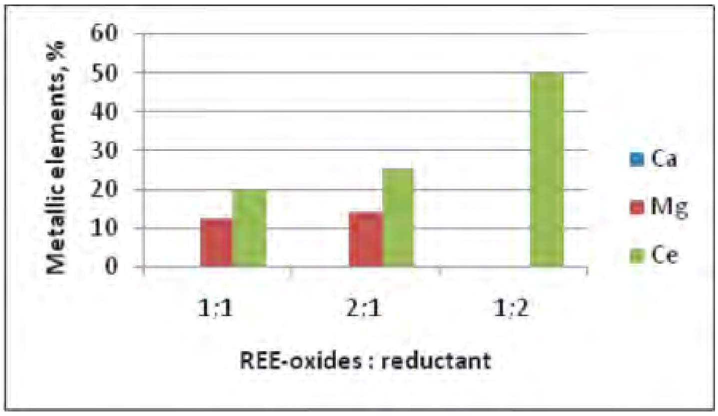


Figure 12. The influence of the ratio of REE-oxide:reductantto metal phase

those metals, indicated by slightly reddish color. While, the pure cerium oxide color itself is white. Fortunately, good clues of Mg and Ca are not presence in the metal phase. This is enlightenment that the reductant of Mg and the flux of $CaCl_2$ have completely reacted with the cerium oxides. This result was supported by SEM analysis as shown in Figure 13.

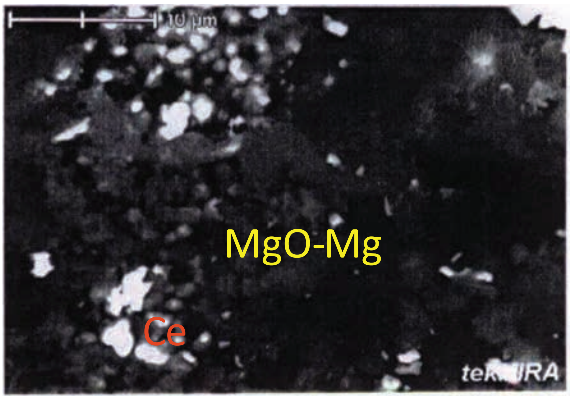


Figure 13. SEM analysis of metal phase of the ratio of REEs oxides: reductant = 1:2

Cerium metals is still detected and remained dominant in the slag phase, especially for the ratio of the sample and reductant = 1 : 1 (w/w). This phenomenon might be due to some metallic cerium from the metal phase are trapped into the slag. SEM analysis of the slag in the ratio of 1:1 is shown in Figure 14.

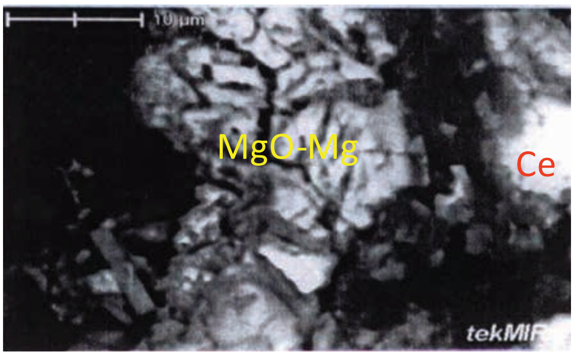


Figure 14. SEM analysis of slag phase for the ratio of sample : reductant = 1:1

The next experiments were carried out to study the temperature reduction effects. The samples were melted at 1000, 1200, and 1300°C. The experimental results of these temperatures effect can be seen in Figure 15.

Figure 15 shows that the temperature of 1200°C is the best performance to produce metallic Ce with yield up to 50%, while Ca and Mg metals are undetected within the metal phase. When the temperature was increased up to 1300°C, the yield of metallic Ce declines down to 25%. Therefore, it is clearly found that the highest yield of metallic cerium is 50% with metal purity about 91% Ce. Comparing to similar work by Luna and Munis (2011), who found that the best temperature of the reduction process was ranging in between 800-900°C by using alloy of Al-Mg as reductant. So, it may be considered that flux of $CaCl_2$ is not

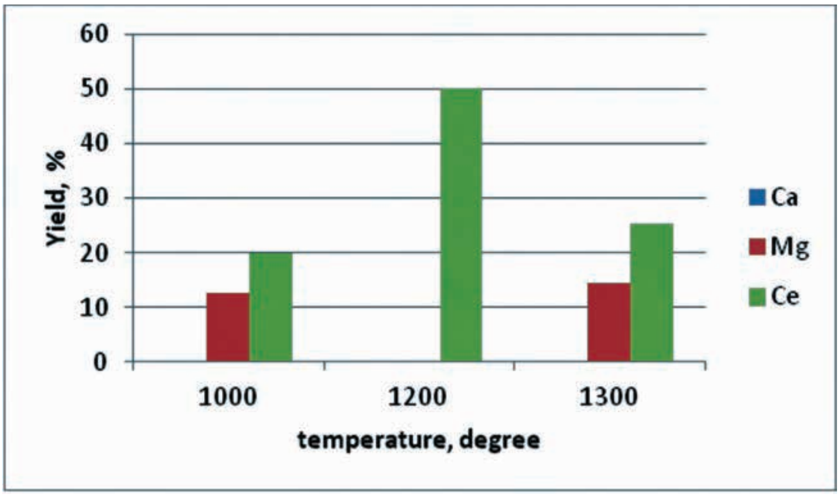


Figure 15. The influence of temperature to metal content for metallic phase

effective yet to reduce the temperature during the reduction-smelting process. It is suggested to try other reductant and flux in the next experimentation.

CONCLUSION

Cerium oxide reduction to produce metallic cerium can be conducted by metallothermic method using Mg as reductant and $CaCl_2$ as flux at temperatures > 1000°C. The best result is attained that the yield of metallic cerium is 50% with metal purity 91% Ce. The Mg and Ca metals were undetectable, within the condition of the ratio of REEs sample with reductant = 1 : 2 (w/w), temperature 1200°C. To increase Ce metal content, it might be suggested to execute some more experiments by reducing the oxide in vacuum condition as well as to select other reductant and flux.

ACKNOWLEDGEMENT

The author wishes to thank profusely to the PSTA-BATAN on research cooperation, especially for the cerium oxide as sample supply that were used for preparing the metallic cerium at *tek*MIRA Laboratory. The author also thanks to the MEMR for the funds provided for this research as well as my colleagues who have assisted in this research.

REFERENCES

Atmawinata, A., 2011. *Pengembangan industri REE di indonesia*. Kementerian Perindustrian, Jakarta.

Castor, S., and Hedrick, J., 2010. *Rare earth element*. www.fieldexexploration.com, Cited on April 9, 2011, at 14:00 pm.

Claux, B., Serp, J. and Foulesier, J., 2011. Electrochemical reduction of cerium oxide into metal, *Electrochimica Acta, Vol. 56, Issue 7*, pp 2771-2780.

Gupta, C.K. and Krishnamurthy, N., 2005. *Extractive metallurgy of rare earth*, CRC press, Boca Raton, London, New York, Washington D.C.

Koltun, P., and Tharumarajah, A., 2014. Life cycle impact of rare earth elements, ISRN (International Scholarly Research Notices) *Metallurgy*, Volume 2014, Article ID 907536, pp 654-661.

Luna Flones, and Munis Torres, 2011. Cerium extraction by metallotermic reduction using cerium oxide powder injection, *Journal of Rare Earths, Vol. 29*, Issue 1, pp. 74-76.

Qiushi, S., Qian, X., Shuang, Li., Yang, Q., Zhiqiang, N., and Kai, Yu., 2015. Direct Electrolytic Preparation of $RENi_5$-xAlx (RE=La, Ce, Pr, and Nd) from rare earth oxides in molten $CaCl_2$-NaCl, *International Journal of Electronical Science*, Volume 10, pp 175-184.

Riedemann, T., 2011. *High purity rare earth metals in separation*, US Department of Energy Specialized Research Center.

Spedding F. H. and McGinnis W.J., 1951, *Preparation of rare earth metals*, Ames Laboratory, United States Atomic Energy Commission.

Weber, R. and Reisman, D., 2012. *REE: A review of production, processing, recycling and associated environmental Issues*, U.S. Environmental Protection Agency.

Zhu, H., 2014. Rare earth metal production by molten salt electrolysis. *Encyclopedia of Applied Electrochemistry*. Springer New York.