MOHAMMAD ZARAR RASHEED[1,2], SUN-WOO NAM[2], SANG-HOON LEE[2],
SANG-MIN PARK[2], JU-YOUNG CHO[2], TAEK-SOO KIM[1,2*]

PHASE EVOLUTION DURING EXTRACTION AND RECOVERY OF PURE Nd FROM MAGNET

Liquid Metal Extraction process using molten Mg was carried out to obtain Nd-Mg alloys from Nd based permanent magnets at 900°C for 24 h. with a magnet to magnesium mass ratio of 1:10. Nd was successfully extracted from magnet into Mg resulting in ~4 wt.% Nd-Mg alloy. Nd was recovered from the obtained Nd-Mg alloys based on the difference in their vapor pressures using vacuum distillation. Vacuum distillation experiments were carried out at 800°C under vacuum of 2.67 Pa at various times for the recovery of high purity Nd. Nd having a purity of more than 99% was recovered at distillation time of 120 min and above. The phase transformations of the Nd-Mg alloy during the process, from $Mg_{12}Nd$ to α-Nd, were confirmed as per the phase diagram at different distillation times. Pure Nd was recovered as a result of two step recycling process; Liquid Metal Extraction followed by Vacuum Distillation.

Keywords: Liquid Metal Extraction, Rare Earth Recycling, Vacuum Distillation, Phase Transformation

1. Introduction

Nd based rare earth (RE) permanent magnets are high-performance magnets which are used in many applications where compactness and high performance are required. Besides being key components of renewable energy technologies such as wind turbine, NdFeB magnets are used in Hybrid Electric Vehicles (HEV), electronic equipment like hard disk drives, CD-lens actuator, loudspeakers and LCD-screens etc. [1-3]. These applications have made them indispensable in the transition to a green and sustainable economy.

The biased distribution of RE reserves combined with the increasing demand create supply-demand risks and threat of price volatility. Moreover, conventional RE mining techniques cause significant environmental damages, and when 'value of nature' is taken into account RE recycling becomes a more feasible option than mining [4-6]. Therefore, recycling becomes of much importance, and the rising levels of REs present around the world in the form of end-of-life products need to be tapped on to reduce the dependency on mining. In fact, the amount of minor metals accumulated in a developed country is said to be comparable to that in any major, one-resource-rich country in the world [7].

Liquid Metal Extraction (LME) is an environmental friendly recycling process with the ability to extract clean materials with low carbon, nitrogen impurities and contamination of unwanted metallic from a wide variety of scrap feed materials i.e. from swarf to ingots. LME has been studied in detail in previous studies [8-11], in which Nd was selectively diffused into liquid Mg forming Mg-Nd alloys. However, further separation of Nd from Mg was not studied in detail. Therefore, this study covers a two-step recycling process of Nd from NdFeB magnets using LME followed by vacuum distillation (VD) where VD is of primary focus.

2. Experimental

Magnets having ~30 wt.%Nd-FeB were obtained from JAHWA electronics Co. Ltd. for LME experiment. Mg of 99% purity was procured from JC Korea. LME was carried out in a high frequency induction furnace at a temperature of 900°C for 24 h where the magnet to magnesium ratio was kept at 1:10 for optimizing extraction efficiency [11]. Vacuum was achieved inside the induction furnace up to a level of 2.67 Pa before high purity Ar gas was introduced in the chamber for providing inert environment. The Mg-Nd alloy was mechanically separated from the unreacted Fe-B system, and several pieces were cut from the Mg-Nd alloy by jaw cutter.

1   UNIVERSITY OF SCIENCE AND TECHNOLOGY, INDUSTRIAL TECHNOLOGY, DAEJEON, REPUBLIC OF KOREA
2   KOREA INSTITUTE FOR RARE METALS, KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY, INCHEON, REPUBLIC OF KOREA

*   Corresponding author:tskim@kitech.re.kr

In the second step, VD experiments were carried out on the cut samples at 800°C, vacuum condition of 2.67 Pa for times of 10 min to 6 h. The resultant samples, both from LME and VD experiments, were polished and characterized by techniques such as FE-SEM, XRD, XRF and ICP-OES.

3. Results and discussion

An Mg-Nd alloy of 8.32 kg of was obtained as a result of the LME reaction. 20 pieces, each weighing ~10 g, were cut from the same region for homogeneity. The average Nd composition in the samples was 4 wt.% as per the XRF results. This paper does not cover the details of the LME process as they have been covered by other researchers. The SEM images and the EDS mapping results of the LME samples is given in Fig. 1. The corresponding XRD pattern is shown in Fig. 2.

Two distinct regions, black and grey, can be observed from the microstructure of the LME sample. The EDS analysis of the sample showed that the grey region was concentrated with Nd while the black phase was rich with Mg. The black phase was identified as Mg-rich phase whereas the grey phase was
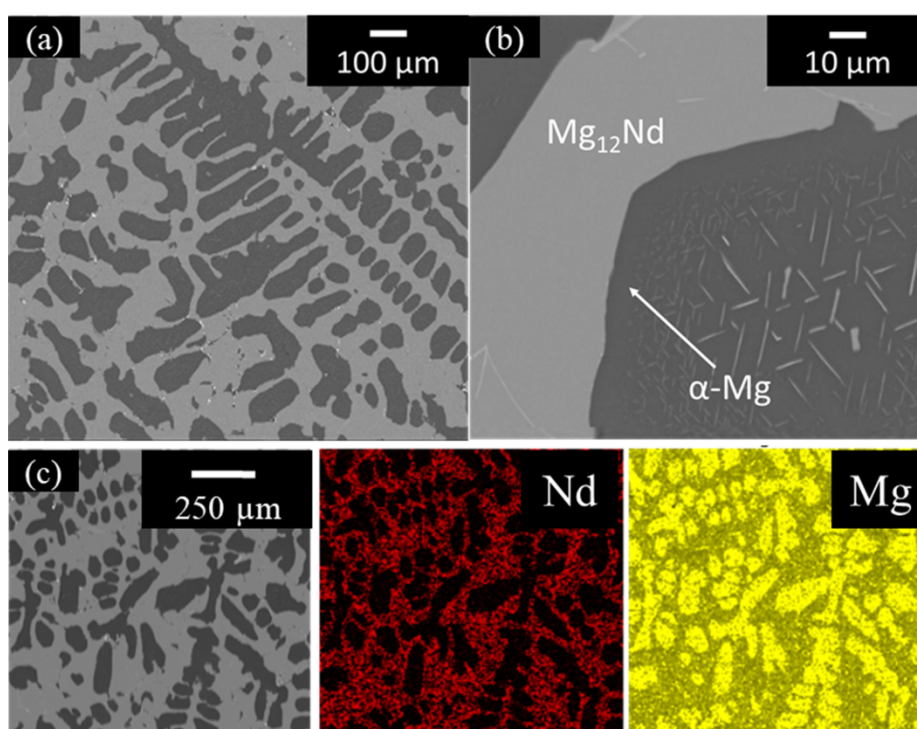

Fig. 1. (a) Microstructure of the Nd-Mg alloy obtained after the LME experiment, (b) magnified image of the $Mg_{12}Nd$-α-Mg region, and (c) EDS mapping of the microstructure identifying Mg and Nd rich zones
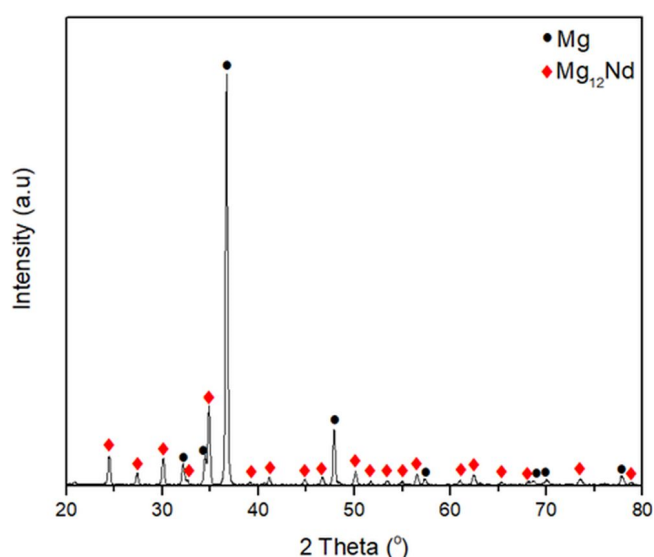

Fig. 2. XRD pattern of the Nd-Mg alloy after LME reaction at 900°C for 24 h

identified as $Mg_{12}Nd$ phase by XRD. Mg was the dominant phase in all specimens. These results indicate that Nd successfully diffused from the magnet into liquid magnesium forming intermetallic phases.

The objective of this research was to recycle Nd from magnet while observe the phase evolution during the process. Most recent results agree that the Mg-Nd system consists of the liquid, the terminal solid solutions: hcp (Mg solid solution), bcc and dhcp (high and low temperature Nd solid solution, respectively) and the intermetallic compounds $Mg_{12}Nd$, $Mg_{41}Nd5$, Mg_3Nd, Mg_2Nd and MgNd [12-15]. The most cited phase diagram of the Nd-Mg alloy is the one calculated by S. Delifion et al. [12] which investigated the phase relationship between Nd-Mg and reported the sequence of transformation from low Nd to high Nd concentration in this order: $Mg_{12}Nd \rightarrow Nd_5Mg_{41} \rightarrow Mg_3Nd \rightarrow MgNd \rightarrow \alpha$-Nd.

VD was selected to separate Nd from Mg-Nd alloy based on the significant difference of the vapor pressure between Nd and Mg. Vapor pressure of Nd is extremely low compared to

Mg even at 1000°C i.e. approximately 0.1 Pa compared to Mg's vapor pressure of 73967.3 Pa 0.73 at the same temperature. This implies that liquid Mg has weak intermolecular forces and evaporates easily as compared to Nd [16]. The distillation temperature needs to be above the melting point and below the boiling point of the metal with higher vapor pressure (in this case Mg) so that it can melt and subsequently evaporate. It is not necessary for it to be much greater than the melting point of magnesium (650°C), therefore, a temperature of 800°C was set as temperature for VD experiments.

Although Mg evaporation did take place even on 5 min of distillation time, there was no change in the morphology as compared to that of the LME sample, and Mg remained the dominant phase. Mg evaporation increased from 5 min onwards but no change in the microstructure was observed till 20 min. The microstructure of the resultant samples after distillation times of 20 min, 40 min, 60 min, 90 min and 120 min, and 180 min are shown in Fig. 3.

After 40 min of distillation time, a white region started to appear in the resultant Mg-Nd alloy which has been highlighted in Fig. 3(b). As can be seen in the figure, the white region increased with increasing distillation time until it became the dominant phase at distillation times of 120 min and above. The proportion of the dark region, which was preciously identifies as α-Mg phase, decreased with increasing time. Moreover, the dark region is replaced with light grey and grey region as time proceeds. EDS point ID analysis was carried out to identify the phases at different distillation times. The selected regions for EDS point ID after 20 min, 40 min, 60 min, 90 min, 120 min, and 180 min are shown in Fig. 3(j)-(l), respectively. The corresponding average values of the elements obtained by the analysis of the designated regions are shown in Table 1.
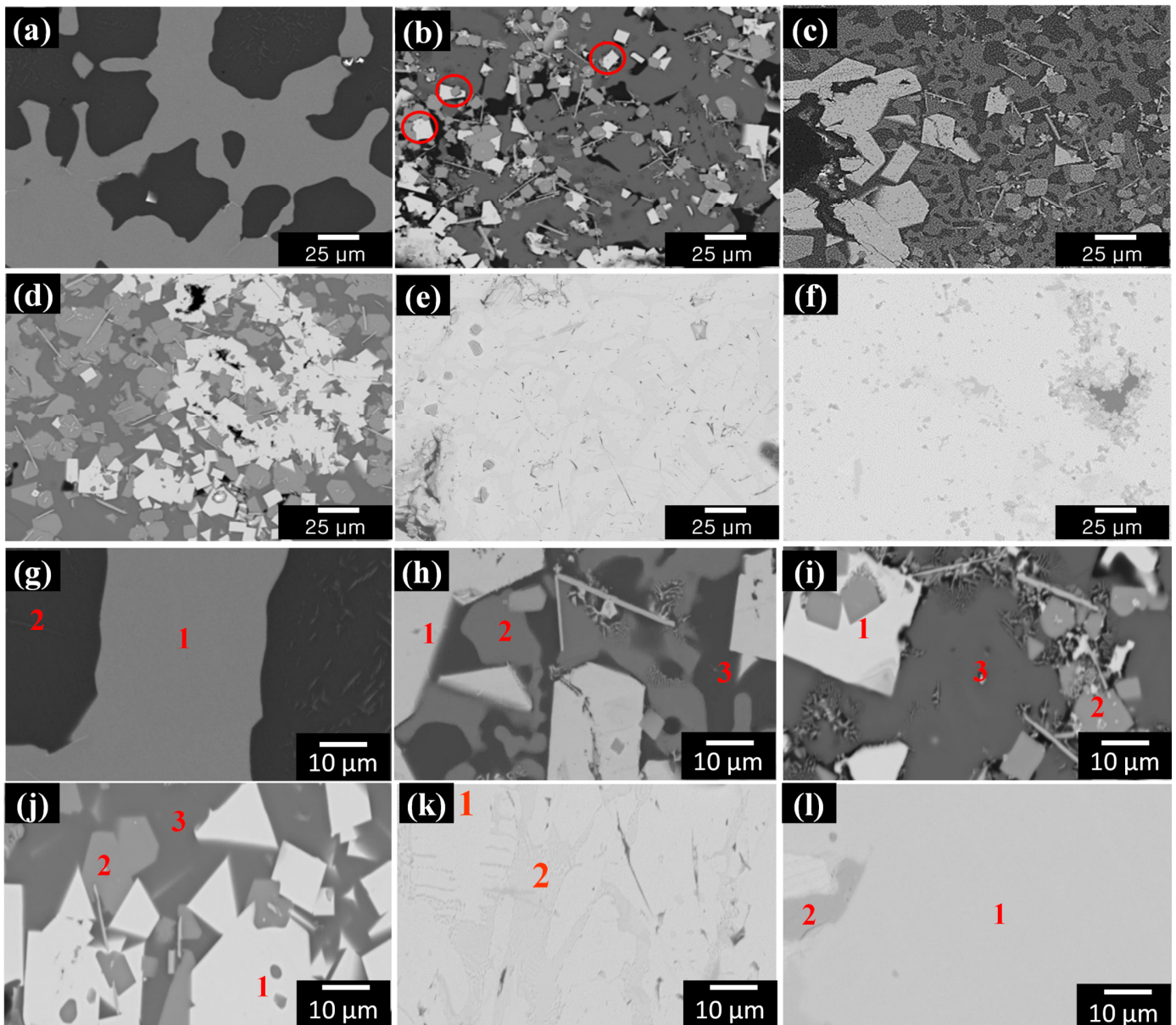

Fig. 3. SEM-BSE images of the resultant alloys after VD time of (a) 20 mins, (b) 40 mins, (c) 60 mins, (d) 90 mins, (e) 120 min, (f) 180 mins, and high magnification SEM-BSE images for EDS point-ID analysis at distillation time of (g) 20 min, (h) 40 min, (i) 60 min, (j) 90 min, (k) 120 min, (l) 180 min

Average values of the results of EDS point ID analysis at different distillation time of the selected regions shown in Fig. 3(g)-(l)

Distillation time	Region	Nd (wt. %)	Mg (wt. %)	O (wt. %)	Probable Phases
20 mins.	1	30.52	68.8	0.69	$Mg_{12}Nd$
	2	1	98.8	0.2	α-Mg
40 mins.	1	96.96	0.64	2.4	α-Nd
	2	35.4	62.75	1.85	$Mg_{12}Nd$
	3	0.7	97.3	2.02	α-Mg
60 mins.	1	98.02	0.34	1.64	α-Nd
	2	53.22	45.23	1.56	$Mg_{41}Nd$
	3	28.38	70.25	1.38	$Mg_{12}Nd$
90 mins.	1	98.02	0.35	0.72	α-Nd
	2	79.91	19.12	0.97	MgNd
	3	67.15	32.29	0.56	Mg_3Nd
120 mins.	1	97.67	0	2.33	α-Nd
	2	96.02	3.12	0.86	α-Nd
180 mins.	1	99.99	0.01	0	α-Nd
	2	97.9	0.03	2.07	α-Nd

Phases were assigned to each region from the compositional analysis by point ID in accordance with the phase diagram. The white region which started to appear at 40 min was identified as Nd-rich phase with Nd concentration of more than 96%. The other two phases remained the same as that of the original alloy which were α-Mg and $Mg_{12}Nd$. After 60 min of distillation time the α-Mg phase could not be identified any longer as it was replaced by $Mg_{41}Nd_5$ phase. Of the intermetallic phases found in the Mg-Nd system, the $Mg_{41}Nd_5$ phase is the richest in Mg. Consequently, α-Mg transformed into $Mg_{41}Nd_5$ phase. The phases detected in the resultant alloy after 60 mins of evaporation time were α-Nd, $Mg_{41}Nd_5$, and $Mg_{12}Nd$ phase. This trend of transformation can be directly associated with the decrease in Mg content with increasing distillation time. Similarly, at 90 min, with further decrease in Mg content, $Mg_{41}Nd_5$ and $Mg_{12}Nd$ were replaced with phases of higher Nd concentrations which were MgNd and Mg_3Nd. However, Mg_2Nd Phase could not be detected as Mg_2Nd decomposes at 660°C into MgNd and Mg_3Nd as indicated by Delfino et al. [ref.]. Although at 120 min, the resultant alloy was mainly composed of α-Nd phase but two regions were still observed. Both regions were α-Nd but one region had traces of Mg in it (avg. Nd 96.02 wt.%, avg. Mg. 3.12 wt.%). At 180 min the regions identified in the sample had Mg concentration as low as 0.01 wt.% indicating the recovery of pure Nd. In order to confirm these findings, ICP-OES of the samples at six mentioned distillation times was carried to check the Nd recovery in wt.% with increasing distillation times. The results are shown in Fig. 4.

As expected, the Nd concentration increased with increasing distillation times, and the Mg concentration decreased. Between evaporation time of 20-40 min Nd was found to be in higher concentrations than Mg. Nd of more than 99 % purity was achieved for distillation times of 120 min and above.

The expected phenomena behind the phase transformation during the recovery process can be explained by the evaporation
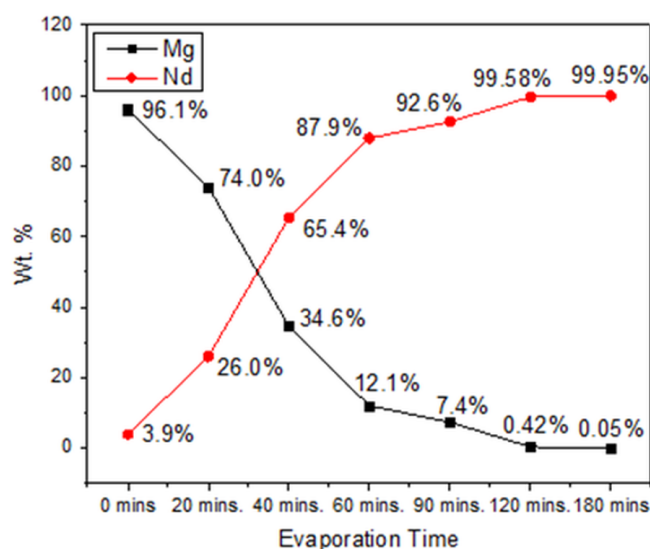

Fig. 4. ICP-OES results of VD experiments showing the concentration of Nd and Mg (wt.%) against different distillation times

of Mg with increasing distillation times. At 800°C, the alloy changed into Mg-Nd liquid solution, and only Mg evaporates because of the high vapor pressure. When heating is turned off, the remaining magnesium re-reacts with Nd to form new phases. However, due to reduced amount of Mg, the phases formed have higher concentration of Nd hence we observe the phase transformation in accordance with the phase diagram. The reason why Nd-rich phase starts to appear after 40 min can be explained by the difference of density between Nd and Mg. Nd has a density of 7 g cm^{-3}, whereas, Mg has a density of 1.74 g cm^{-3}. This leads to the settling of Nd at the bottom of the crucible which results in some of the Nd not reacting with Mg hence Nd-rich phase is formed. Subsequently, at distillation times of 120 min and above, almost all Mg evaporates leaving behind only Nd.

4. Conclusion

A two-steps procedure was utilized to recycle Nd from NdFeB magnet. Nd was successfully extracted in liquid Mg during the first step using LME process resulting in a 4 wt.% Nd-Mg alloy. Mg selectively reacted with Nd to form Nd-Mg alloy leaving behind Fe-B. VD was carried out at different times to recover Nd from Nd-Mg alloy. The ICP-OES results confirmed that Nd of 99% purity was recovered at distillation times of 120 min and above. Mg of 99% purity was collected in some instances. Phase evolution was observed with the progress of VD. The initial sample (from LME) consisted of $Mg_{12}Nd$ and α-Mg phase. Nd-rich phase started to appear after 40 min. After 60 min no α-Mg phase was identified and the microstructure was predominantly composed of Mg-Nd phases. As Mg concentration further depleted, Mg-Nd phases were completely replaced by Nd-rich phases. The results indicate that VD is an efficient method for separation of Nd from Mg after LME. Therefore, it should be applied to other solvent metals as well e.g. Bi. Installation of a collection mechanism for Mg, and inclusion of Dy are two important future aspects for this study.

REFERENCES

[1] J.D. Widmer, R. Martin, M. Kimiabeigi, SM&T. **3**, 7-13 (2015).

[2] S. Kruse, K. Raulf, T. Pretz, B. Friedrich, J. Sustain. Metall. **3**, 168-178 (2017).

[3] N. Haque, A. Hughes, S. Lim, C. Vernon, Resources. **3** (4), 614-635 (2014).

[4] D. Schüler, M. Buchert, R. Liu, S. Dittrich, C. Merz, Study on Rare Earths and Their Recycling Final Report for the Greens/European Free Alliance Group in the European Parliament, Germany 2011.

[5] Saleem H. Ali, Resources **3**, 123-134 (2014).

[6] T.H. Okabe, Trans. Inst. Min. Metall. **126** (1-2), 22-32 (2016).

[7] K. Halada, J. Mater. Cycles Waste Manag. **20** (2), 49-58 (2009).

[8] T.H. Okabe, O. Takeda, Y. Fukuda, Y. Umetsu, Mater. Trans. **44** (4), 798-801 (2003).

[9] Y. Xu, L.S. Chumbley, F.C. Laabs, J. Mater. Res. **15** (11), 2296-2304 (2000).

[10] H.J. Chae, Y.D. Kim, B.S. Kim, J.G. Kim, T.S. Kim, J. Alloys Compd. **586** (s1), 143-149 (2014).

[11] T. Akahori, Y. Miyamoto, T. Saeki, M. Okamoto, T.H. Okabe, J. Alloys Compd. **703**, 337-343 (2017).

[12] S. Delfino, A. Saccone, R. Ferro, Metall. Trans. A. 21A, 2109-2114 (1990).

[13] A.A. Nayeb-Hashemi, J.B. Clark, Phase Diagrams of Binary Manganese Alloys, ASM International, Ohio (1988).

[14] [H. Okamoto, J. Phase Equilib. 12, 249 (1991).

[15] S. Gorssea, C.R. Hutchinsonb, B. Chevaliera, J.F. Nieb, J. Alloys Compd. **392**, 253-262 (2005).

[16] I. Barin, Thermochemical Data of Pure Substances, Germany (1989).