Thermodynamic criteria for the removal of impurities from end-of-life magnesium alloys by evaporation and flux treatment

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Abstract
In this paper, the possibility of removing impurities during magnesium recycling with pyrometallurgical techniques has been evaluated by using a thermodynamic analysis. For 25 different elements that are likely to be contained in industrial magnesium alloys, the equilibrium distribution ratios between the metal, slag and gas phases in the magnesium remelting process were calculated assuming binary systems of magnesium and an impurity element. It was found that calcium, gadolinium, lithium, ytterbium and yttrium can be removed from the remelted end-of-life (EoL) magnesium products by oxidization. Calcium, cerium, gadolinium, lanthanum, lithium, plutonium, sodium, strontium and yttrium can be removed by chlorination with a salt flux. However, the other elements contained in magnesium alloy scrap are scarcely removed and this may contribute toward future contamination problems. The third technological option for the recycling of EoL magnesium products is magnesium recovery by a distillation process. Based on thermodynamic considerations, it is predicted that high-purity magnesium can be recovered through distillation because of its high vapor pressure, yet there is a limit on recoverability that depends on the equilibrium vapor pressure of the alloying elements and the large energy consumption. Therefore, the sustainable recycling of EoL magnesium products should be an important consideration in the design of advanced magnesium alloys or the development of new refining processes.

Keywords: recycling of magnesium, thermodynamic analysis, impurity removal, distribution ratio, end-of-life products

1. Introduction

Metals such as iron and aluminum are more frequently used in the form of alloys rather than as pure metals in many industrial and infrastructure applications, with the exception of copper electric materials, aluminum foil and some metals used for special purposes. Magnesium has drawn much attention as a next-generation material for vehicles, because it is one of the lightest construction metals and the use of it will result in a remarkable improvement in fuel efficiency. Because of the high chemical reactivity of magnesium, alloying or coating is usually required for making practical magnesium products. Recently, extensive work on advanced magnesium alloys resulted in a significant improvement of their mechanical, physical and corrosion resistance properties. Bamberger and Dehm [1] have reviewed trends in the
development of new magnesium alloys. They have reported on the beneficial effects of adding aluminum, calcium, gadolinium, silicon, strontium, tin, zinc and rare-earth metals on the microstructure, mechanical properties and strengthening mechanism of magnesium [2, 3].

Figure 1 shows the chemical composition of various magnesium alloys as specified by the standards of the American Society for Testing and Materials (ASTM). For example, ASTM AZ91D is a typical industrial magnesium alloy. Its desired chemical and mechanical properties are obtained by alloying magnesium mainly with aluminum, manganese and zinc. However, many alloying elements can be very difficult to remove from end-of-life (EoL) magnesium products, including magnesium alloy scrap, because magnesium itself is a rather reactive metal. There are only a couple of papers on the recycling of post-consumer magnesium scrap based on an exergy analysis, mechanical testing of remelted alloy and refining of the specified scrap by salt flux [4–6]. Magnesium recycling has not been reported at the latest major international conferences on magnesium alloys [7, 8]. For the sustainable recycling of magnesium alloys, the equilibrium distribution ratios between the metal, slag and gas phases in the magnesium remelting process were investigated, and the limit on removability of impurities by the salt flux treatment was thermodynamically predicted. Because magnesium exhibits a relatively high vapor pressure, the possibility of recovering magnesium by distillation was evaluated.

2. Methodology

Nakajima et al [9–11] have discussed the recyclability of steel, copper, lead, zinc and aluminum products from secondary resources and the limitations on impurity removal in the pyrometallurgical process on the basis of chemical thermodynamics. The element radar charts shown in these studies provide useful information for understanding which minor elements are connected to which commodity metals and which metals can be economically recovered with present-day facilities. The recyclability or removability of elements in the magnesium remelting and distillation processes is analyzed in this paper by using the method established by the authors. Moreover, the refining capability of flux treatment...
and volatilization, which are general methods of removing impurities from the main metal product in the remelting process, is thermodynamically evaluated.

The driving force of a reaction can be determined by the corresponding value of the Gibbs free energy. Furthermore, if an element is distributed by a reaction with ambient oxygen into different phases such as the molten metal, slag and gas phases, the distribution of the element can be quantitatively evaluated by calculating the equilibrium constant from the change in Gibbs free energy and then converting it into its concentration in each phase. For such conditions, the following relationships were used to obtain the parameters controlling the distribution of elements among the metal, slag and gas phases.

The oxidation reaction of an alloying element M dissolved in liquid magnesium is expressed as

$$M + \frac{n}{2} O_2 = MO_n. \quad (1)$$

Throughout this paper, we assume that a monocationic oxide is formed in this reaction. For example, in the case of aluminum the product is AlO instead of the usual Al₂O₃ oxide. The dissociation of a stoichiometric oxide to a monocationic oxide is represented as

$$\text{M}_x \text{O}_y \text{(slag)} = x \text{MO}_y \text{(slag)}, \quad n = y/x. \quad (2)$$

The free energy change of this reaction is reasonably assumed to be zero [12–14]. Therefore, the free energy change for equation (1), \( \Delta G^o_T \), and its equilibrium constant \( K_1 \) can be evaluated from general thermodynamic references. \( K_1 \) is given by

$$K_1 = \exp \left( \frac{-\Delta G^o_T}{RT} \right) = \frac{a_{\text{MO}_n}}{a_{M} \left( P_{O_2}/p^\circ \right)^{n/2}} = \frac{\gamma_{\text{MO}_n} - \gamma_{M} \gamma_{O_2}}{\gamma_{M} \gamma_{\text{MO}_n} \left( P_{O_2}/p^\circ \right)^{n/2}}. \quad (3)$$

Here \( R \) is the gas constant \((\text{J/K mol})^{-1}\); \( T \) is the temperature \((\text{K}); a_M \) and \( a_{\text{MO}_n} \) are the activities of M and its oxide; \( p_{O_2} \) is the oxygen partial pressure \((\text{Pa}); p^\circ \) is a conversion factor \((101325 \text{ Pa atm}^{-1}); \gamma_M \) and \( \gamma_{\text{MO}_n} \) are the activity coefficients of M and its oxide, and \( x_M \) and \( x_{\text{MO}_n} \) are the mole fractions of M in liquid magnesium and of its oxide in the slag, respectively. From equation (3) the distribution ratio between the slag and metal, \( L_{\text{slag/metal}} \), can be expressed as

$$L_{\text{slag/metal}} = \frac{x_{\text{MO}_n}}{x_M} = \frac{K_1 \gamma_M \left( P_{O_2}/p^\circ \right)^{n/2}}{\gamma_{\text{MO}_n}}. \quad (4)$$

A larger \( L_{\text{slag/metal}} \) value corresponds to easier removal of M into the slag phase by oxidation. Hence, oxidation tendencies of impurity elements were theoretically considered.

The evaporation of an impurity element M from liquid magnesium is expressed as

$$M = M \left( g \right). \quad (5)$$

and the corresponding change in Gibbs free energy is

$$\Delta G^o_S = -RT \ln K_S. \quad (6)$$

\( K_S \) is the equilibrium constant, which can be expressed as

$$K_S = \left( \frac{p_M/p^\circ}{\gamma_M} \right)^{x_M} \left( \frac{p_{\text{MO}_n}}{p^\circ} \right)^{x_{\text{MO}_n}}. \quad (7)$$

Here, \( p_M \) and \( p_{\text{MO}_n} \) are the partial pressures of the element M in the bulk state and in the magnesium alloy, respectively. The distribution ratio of an element between the metal and gas phases is given by

$$L_{\text{gas/metal}} = \frac{p_M}{p_{\text{Mg}}} = \frac{\gamma_{\text{MO}_n} \gamma_M x_M}{\gamma_{M} \gamma_{\text{MO}_n} x_{\text{MO}_n} \left( P_{O_2}/p^\circ \right)^{n/2}}. \quad (8)$$

where \( p_{\text{Mg}} \) is the vapor pressure of magnesium in equilibrium with the molten magnesium alloy \((\text{Pa}). A larger gas/metal distribution ratio \( L_{\text{gas/metal}} \) corresponds to easier removal of M by evaporation.

The composition dependence of the activity coefficient \( \gamma \) for the element M in a Mg–M binary alloy can be conventionally expressed by a Redlich–Kister-type polynomial [15]:

$$RT \ln \gamma_M = 0\Omega_{\text{Mg}–M} x_M^2 + 1\Omega_{\text{Mg}–M} x_M (4x_M - 3) + 2\Omega_{\text{Mg}–M} x_M^2 (2x_M - 1)(6x_M - 5) + 3\Omega_{\text{Mg}–M} x_M^3 (2x_M - 1)^2(8x_M - 7). \quad (9)$$

The interaction parameters \( \Omega_{\text{Mg}–M} \) for 25 different elements in liquid magnesium were taken from the literature [16–37]. The standard Gibbs energies of oxide formation and the vapor pressures of pure elements can be found in thermodynamic tables [38–43] and are listed in tables 1 and 2. A typical industrial magnesium alloy is a multi-component system that contains at least four different elements as is shown in figure 1. The thermodynamic behavior of alloying elements during the recycling process has not been evaluated in the literature, and therefore the corresponding discussion in this paper is limited to Mg–M binary alloys as a first step. Note that the present approach can be extended to more complex alloys provided the activities of individual components are known.

| Table 1. References for the estimation of the activity coefficients in Mg–M binary alloys. |
|---------------------------------|-----------------|-----------------|-----------------|
| Element                         | Reference       | Element         | Reference       |
| Ag                              | [16]            | Na              | [28]            |
| Al                              | [17]            | Ni              | [21]            |
| Bi                              | [18]            | Pu              | [29]            |
| Ca                              | [19]            | Sb              | [30]            |
| Ce                              | [20]            | Si              | [31]            |
| Cu                              | [21]            | Sn              | [32]            |
| Fe                              | [22]            | Sr              | [33]            |
| Gd                              | [23]            | Tl              | [34]            |
| Ge                              | [24]            | Y               | [23]            |
| Hg                              | [25]            | Y               | [35]            |
| La                              | [26]            | Zn              | [36]            |
| Li                              | [17]            | Zr              | [37]            |
| Mn                              | [27]            |                 |                 |
Table 2. References for the vapor pressures of metals and the standard Gibbs energies of oxidation and chlorination reactions.

| Element | $p^o$ at 973 K Pa | Reference | Equation | $dG^o$ at 973 K J | Reference |
|---------|------------------|-----------|----------|-----------------|-----------|
| Ag      | 2.96 x 10^-4     | [38]      | Ag(l) + 1/4O(g) = AgO_{0.5} | 49.6      | [39]       | Ag(l) + 1/2Cl(g) = AgCl | -82.0 |
| Al      | 4.19 x 10^-6     | [38]      | Al(l) + 3/4O(g) = AlO_{1.5} | -685.5    | [41]      | Al(l) + 3/2Cl(g) = AlCl_{3} | -511.0 |
| Bi      | 1.05 x 10^-2     | [38]      | Bi(l) + 3/4O(g) = BiO_{1.5} | -151.5    | [41]      | Bi(l) + 3/2Cl(g) = BiCl_{3} | -725.0 |
| Ca      | 1.79 x 10^4      | [38]      | Ca(l) + 1/2O(g) = CaO       | -534.6    | [41]      | Ca(l) + Cl(g) = CaCl_{2} | -646.2 |
| Ce      | 4.86 x 10^-11    | [38]      | Ce(l) + 3/4O(g) = CeO_{1.5} | -759.8    | [41]      | Ce(l) + 3/2Cl(g) = CeCl_{3} | -811.5 |
| Cu      | 3.82 x 10^-7     | [38]      | Cu(l) + 1/4O(g) = CuO_{0.5} | -51.9     | [41]      | Cu(l) + 1/2Cl(g) = CuCl | -1.7 |
| Fe      | 9.02 x 10^-10    | [38]      | Fe(l) + 1/2O(g) = FeO       | -214.8    | [39]      | Fe(l) + Cl(g) = FeCl_{2} | -227.5 |
| Gd      | 2.48 x 10^-10    | [38]      | Gd(l) + 3/4O(g) = GdO_{1.5} | -777.5    | [39]      | Gd(l) + 3/2Cl(g) = GdCl_{3} | -771.6 |
| Ge      | 9.47 x 10^-9     | [38]      | Ge(l) + O(g) = GeO         | -390.2    | [41]      | Ge(l) + Cl(g) = GeCl_{2} | -199.9 |
| Hg      | 5.10 x 10^0      | [40]      | Hg(l) + 1/2O(g) = HgO      | 13.3      | [39]      | Hg(l) + 1/2Cl(g) = HgCl | 11.7 |
| La      | 6.24 x 10^-12    | [38]      | La(l) + 3/4O(g) = LaO_{1.5} | -758.9    | [41]      | La(l) + 3/2Cl(g) = LaCl_{3} | -822.3 |
| Li      | 1.28 x 10^-2     | [38]      | Li(l) + 1/4O(g) = LiO_{0.5} | -235.3    | [41]      | Li(l) + 1/2Cl(g) = LiCl | -331.2 |
| Mn      | 1.33 x 10^-3     | [38]      | Mn(l) + 1/2O(g) = MnO      | -316.4    | [39]      | Mn(l) + Cl(g) = MnCl_{2} | -291.9 |
| Na      | 1.44 x 10^-6     | [38]      | Na(l) + 1/4O(g) = NaO_{0.5} | -141.4    | [41]      | Na(l) + 1/2O(g) = NaCl | -325.5 |
| Ni      | 5.39 x 10^-11    | [38]      | Ni(l) + 1/2O(g) = NiO      | -157.6    | [41]      | Ni(l) + 1/2Cl(g) = NiCl_{2} | -166.9 |
| Mg      | 8.75 x 10^-2     | [38]      | Mg(l) + 1/2O(g) = MgO      | -496.4    | [41]      | Mg(l) + Cl(g) = MgCl_{2} | -885.4 |
| P       | 1.04 x 10^-8     | [40]      | Pu(l) + 3/4O(g) = PuO_{1.5} | 42.8      | [39]      | Pu(l) + 3/2Cl(g) = PuCl_{3} | -788.0 |
| Sn      | 6.62 x 10^-2     | [40]      | Sn(l) + 3/4O(g) = SnO_{1.5} | -225.2    | [39]      | Sn(l) + 3/2Cl(g) = SnCl_{2} | -270.4 |
| Si      | 4.04 x 10^-11    | [40]      | Si(l) + O(g) = SiO_{2}     | -753.0    | [41]      | Si(l) + 2Cl(g) = SiCl_{4} | -556.1 |
| Sn      | 2.66 x 10^-6     | [38]      | Sn(l) + O(g) = SnO_{2}     | -381.2    | [41]      | Sn(l) + Cl(g) = SnCl_{2} | -210.6 |
| Sr      | 3.79 x 10^3      | [40]      | Sr(l) + 1/2O(g) = SrO      | -495.2    | [41]      | Sr(l) + Cl(g) = SrCl_{2} | -679.6 |
| Tl      | 1.00 x 10^1      | [38]      | Tl(l) + 1/2O(g) = TlO_{0.5} | -44.5     | [41]      | Tl(l) + 3/2Cl(g) = TlCl_{3} | -96.2 |
| Y       | 1.38 x 10^-1     | [38]      | Y(l) + 3/4O(g) =YO_{1.5}   | -816.4    | [39]      | Y(l) + 5/2Cl(g) = YCl_{3} | -780.9 |
| Yb      | 4.03 x 10^-10    | [38]      | Yb(l) + 3/4O(g) = YbO_{1.5} | -769.7    | [39]      | Yb(l) + 3/2Cl(g) = YbCl_{3} | -728.1 |
| Zn      | 8.15 x 10^-3     | [38]      | Zn(l) + 1/2O(g) = ZnO     | -251.2    | [41]      | Zn(l) + Cl(g) = ZnCl_{2} | -278.4 |
| Zr      | 5.10 x 10^-21    | [38]      | Zr(l) + 1/2O(g) = ZrO_{2} | -924.3    | [39]       | Zr(l) + 2Cl(g) = ZrCl_{4} | -770.2 |

3. Results

3.1. Element distribution tendency

The activity coefficient of MO$_3$ depends on the slag composition, but in the present analysis it is fixed at unity as a base case. The initial molar fraction of elements in the solvent metal is also fixed (at 0.01). The boundary between the metal and gas phases was assumed to satisfy the condition $\log(p_{M}/p_{Mg}) = 2$. In this boundary condition, the number of M atoms is 100 times as much as the number of magnesium atoms in the gas phase and thus appears to be adequate for preferential removal of Mg into the gas phase by evaporation. Figure 3 shows the distribution ratios of elements in the remelting process. The open circles represent the typical additive elements for industrial magnesium alloys. The elements with gray circles are those that must be removed to meet the ASTM standards. We have estimated the vapor pressures of AlO, Al$_2$O$_3$, Sb$_2$O$_3$, SiO and SnO$_2$ suboxide gases and found that they are negligibly low in this condition ($p_{AlO} = 2.31 \times 10^{-11}$, $p_{Al_2O_3} = 2.57 \times 10^{-14}$, $p_{Sb_2O_3} = 3.77 \times 10^{-138}$, $p_{SiO} = 4.91 \times 10^{-11}$ and $p_{SnO_2} = 1.05 \times 10^{-22}$ Pa) due to the relatively low temperature, very low activity of M and extremely low oxygen partial pressure. Therefore, we have ignored the coupling between oxidation and evaporation, such as suboxide evaporation. Our results indicate that calcium, gadolinium, lithium, ytterbium and yttrium can be
removed by oxidization (transferred to the slag). Removal of other elements, including aluminum, copper, iron, nickel and silicon, is difficult because these have a strong tendency to remain in the metal phase. These results agree with the experimental observation that most impurities remain in magnesium alloy scrap [45].

The concentration range of alloying elements varies widely depending on the alloy type (figure 1). The effect of a change in concentration on the distribution ratio of typical additive elements for industrial magnesium products, namely aluminum, manganese, zinc and zirconium, was investigated by varying $x_M$, and thus $\gamma_M$, in equations (3) and (7) considering their maximum and minimum concentrations specified in the ASTM standards. The effect of the composition range of these four common elements is represented in figure 3 by the bar on each point. The results indicate that no significant change in the distribution ratios, particularly $L_{\text{slag/metal}}$, can be expected within the composition range of the ASTM standards, and aluminum, manganese, zinc and zirconium are not removed.

3.2. Effect of thermodynamic parameters on the slag/metal distribution ratio

The possibility of removing impurities from remelted metal by evaporation or oxidation is thermodynamically governed by at least six parameters: the Gibbs free energy of the reaction $\Delta G^\circ$ (or the equilibrium constant), total pressure, activity coefficient (composition of the metal bath containing the impurity), temperature, oxygen partial pressure and activity coefficient of the oxidation product (slag composition). All these process parameters, except for $\Delta G^\circ$, should therefore be taken into account simultaneously.

Figure 4 shows the effect of temperature on the distribution ratio between the slag and metal phases. Considering the removability or controllability of elements at the industrial scale, a distribution ratio smaller than 0.001 is no longer meaningful. Therefore, elements that have $L_{\text{slag/metal}}$
greater than 0.001 (log $L_{\text{slag/metal}} > -3$) for the base case are selected here. Since the temperature dependence of $L_{\text{slag/metal}}$ is not notably large, a remarkable improvement in the distribution ratio cannot be expected even at high temperatures.

Figure 5 demonstrates the effect of oxygen partial pressure on the distribution ratio. The distribution ratio can be lowered if the partial pressure of oxygen can be increased significantly. Gadolinium and yttrium are removed or immobilized in the metal phase by controlling the oxygen partial pressure. The latter is governed by the following reaction, provided the thermodynamic oxidation reaction is taken into consideration:

$$\text{Mg} (l) + \frac{1}{2} \text{O}_2 (g) = \text{MgO} (s).$$ (10)

The highest equilibrium partial pressure of oxygen is evaluated as $p_{O_2} = 5.14 \times 10^{-49}$ Pa at 973 K with pure liquid magnesium and pure solid MgO. At a pressure higher than this value, metallic magnesium is no longer in a stable phase and significant oxidation loss of magnesium occurs. Therefore, oxygen partial pressure should be carefully controlled in the magnesium remelting process.

The activity coefficient of oxides in slag was assumed to be unity in the present study; if it is lowered to 0.1 by an appropriate selection of the slag composition, the distribution ratio becomes smaller by the same amount. Optimization of slag composition is hindered by two major factors: (i) the slag composition range that exhibits a homogeneous liquid phase is very narrow owing to the relatively low operating temperature of magnesium remelting and (ii) MgO generally has a low solubility in oxide slag. In conclusion, most of the alloying elements for magnesium are very difficult to remove by oxidation and evaporation refining except for some elements such as calcium and yttrium; this indicates that there may be a contamination problem in the recycling of EoL magnesium products. The development of new refining techniques or recycling routes is required in order to solve this problem.

3.3. Thermodynamic consideration of salt flux treatment of liquid magnesium

Another technological option for the removal of alloying elements or magnesium extraction from EoL magnesium products is salt flux treatment of remelted magnesium scrap. In this case, the following chlorination reaction is considered instead of equations (1) and (4):

$$\text{M} + \frac{n}{2} \text{Cl}_2 = \text{MCl}_n.$$ (11)

In the same manner as in the derivation of $L_{\text{slag/metal}}$, the distribution ratio of the alloying elements between the salt flux and liquid magnesium, $L_{\text{salt/metal}}$, can be derived as

$$L_{\text{salt/metal}} = \frac{x_{\text{MCl}}}{x_{\text{M}}} = \frac{K_{117\text{M}}(p_{\text{Cl}_2}/p^*)^{n/2}}{y_{\text{MCl}}},$$ (12)

where $p_{\text{Cl}_2}$ is given by the following reaction:

$$\text{Mg} (l) + \text{Cl}_2 (g) = \text{MgCl}_2 (l).$$ (13)

The equilibrium constant of equation (13) is known [41], and $\alpha_{\text{Mg}}$ can be evaluated from $\Omega_{\text{Mg}}$. On the other hand, the activity of MgCl$_2$ can vary widely at about 973 K, because the basic system of salt flux NaCl–KCl has a wide homogeneous liquid range at this temperature and the solubility of MgCl$_2$ in this system is very large (the solubility limit is approximately $x_{\text{MgCl}_2} = 0.75$ [46]); meanwhile, the high MgCl$_2$ content in the flux means a notable chlorination loss of Mg. If the salt flux composition is selected as 0.53NaCl–0.27KCl–0.20MgCl$_2$ (flux A in figure 6), then the activity of MgCl$_2$ in this flux is 0.01 [47], which corresponds to $p_{\text{Cl}_2} = 6.1 \times 10^{-25}$ Pa. Under such conditions, the limit on removability of alloying elements by salt flux treatment was calculated thermodynamically. Little is known about the activity coefficients of chlorides in the liquid NaCl–KCl–MgCl$_2$ flux. However, the activity coefficients of aluminum, calcium, iron, lanthanum, lithium,
manganese, nickel, sodium, strontium and zinc chlorides in this molten salt can be evaluated by the quasi-chemical model [47–50]. Therefore, their distribution coefficients $L_{\text{salt/metal}}$ were calculated from the $\gamma_{\text{MCln}}$ values. For the other 15 elements, the activity coefficients were set to 0.3 (which is the average value for the former ten elements) as a first approximation for the calculation of $L_{\text{salt/metal}}$. The results are shown in figure 7 as closed circles in a plot of $L_{\text{salt/metal}}$ against $L_{\text{slag/metal}}$. Another flux composition, namely flux B ($0.33\text{NaCl}–0.17\text{KCl}–0.5\text{MgCl}_2$) in figure 6, was also examined for comparison, and the corresponding data were added as open circles to figure 7. This figure suggests that calcium, lanthanum, lithium, sodium and strontium can be removed by chlorination refining with flux A. The $L_{\text{salt/metal}}$ value is higher for flux B that adds cerium, gadolinium, plutonium and yttrium to the list of removable elements. This improvement is related to the higher activity of MgCl$_2$ in flux B and therefore higher $p_{\text{Cl}_2}$ value. However, other elements identified as ‘metals’ in figure 7 are still difficult to remove with either flux.

Wang et al [4] experimentally investigated the effect of salt flux treatment on the physical and mechanical properties of remelted magnesium–gadolinium–yttrium–zirconium alloy scrap. They used 45%MgCl$_2$–25%KCl–20%NaCl containing 0–10% of GdCl$_3$ and 10% of other chlorides (expressed in terms of mass percentages) as a flux at 1033 K, and reported the yield and loss of yttrium by salt flux treatment. Although their experimental conditions were somewhat different from those of the present study and there were some uncertain parts in their experiment, the distribution ratio of yttrium between liquid magnesium and salt flux could be estimated. Their flux was first approximated as NaCl–KCl–MgCl$_2$ (mass ratio 20 : 25 : 45, which is close to flux B), and the YCl$_3$ contents in the flux were estimated from the yttrium loss during the salt flux treatment and the added amount of flux. The mass balance calculation resulted in $L_{\text{salt/metal}} = 5.6$ ($\log L_{\text{salt/metal}} = 0.75$), in good agreement with the results of figure 7.

4. Discussion

4.1. Possibility of recovery of magnesium by distillation

Figures 3–5 and 7 demonstrate that most alloying elements are very difficult to remove from magnesium products or adjust to a desired concentration by either flux treatment or evaporation in the remelting process. On the other hand, magnesium has a particularly high vapor pressure at elevated temperatures. This feature may enable the recovery of pure magnesium by distillation unless the vapor of the alloying element in the EoL magnesium product obstructs the process. Thus, the distillation process was further investigated in this study.

As an example, let us consider the distillation of magnesium from Mg–Zn, Mg–Li and Mg–Mn alloys that have initially 1 mol% of the alloying element ($x_M^0 = 0.01$). Figure 8

Figure 6. Activity of MgCl$_2$ in the NaCl–KCl–MgCl$_2$ system at 973 K [34–37].

Figure 7. Distribution chart of elements between the gas, slag, and metal phases in a simulated magnesium melting process with $x_{\text{Mg}} = 0.01$ (mole fraction), $T = 973$ K, $p_{\text{O}_2} = 5.14 \times 10^{-49}$ Pa and $p_{\text{H}_2} = 866$ Pa.

Figure 8. The plot of mole fractions in the gas and liquid phases at 973 K.
shows the mole fractions in the gas and liquid phases at 973 K, where the y axis denotes $x_{Mg}$ defined as $p_{Mg}/(p_{Mg} + p_M)$. The solid lines are calculated from equation (6). The dotted line corresponds to $x_{Mg} = x_{Mg}^{eq}$; above this line, the mole fraction of magnesium against the alloying element in the gas phase is higher than that in the liquid phase and thus the distillation of magnesium is theoretically possible. Figure 8 demonstrates that the enrichment of magnesium does not occur in the Mg–Zn alloy due to the relatively high vapor pressure of zinc. However, it does occur in Mg–Li and Mg–Mn alloys because the vapor pressure for magnesium is much higher than that for lithium or manganese. It is theoretically possible to recover magnesium from magnesium alloy by distillation, provided the energy consumption and refining costs are not an issue.

4.2. Controllability of alloying elements in metal products

The distribution tendencies of elements in the remelting processes of steel, copper, lead, zinc and aluminum have been examined in previous studies [9, 10]. Since the thermodynamic criteria on impurity removal from EoL magnesium alloys by oxidation and evaporation have also been developed in this work, the removability of impurity elements for these metals and magnesium can be compared. The results are shown in figure 9 as an ‘element radar chart’. In the case of iron/steel recycling, it is difficult to remove incorporated tramp elements such as copper and tin [51]. Compared with other base metals, the removal of impurity elements for magnesium in the remelting process is considerably more difficult except for a very few elements such as yttrium. The possibility of recovering magnesium from EoL magnesium products by distillation has been demonstrated in this study. However, distillation has some problems such as high cost, large energy consumption and the limited availability of evacuation facilities. An important result of this study is that sustainable supply of magnesium requires a careful design of advanced magnesium alloys—to avoid contamination or accumulation of alloying elements—and development of refining processes for the EoL magnesium products.

5. Conclusions

The equilibrium distribution ratios between metal, oxide/chloride flux and gas phases in the magnesium remelting process were investigated by thermodynamic analysis for 25 elements that are likely to occur in industrial magnesium alloys. The following conclusions were drawn.

1. Calcium, gadolinium, lithium, ytterbium and yttrium can be removed by oxidization (transferred to slag) from
melted magnesium alloys. In contrast, the removal of other elements, including aluminum, copper, iron, nickel and silicon, is difficult and they remain in the metal phase.

2. The effects of temperature on the distribution ratio between the slag and metal phases are too small for removal. Gadolinium and yttrium are removed or immobilized in the metal phase by controlling the oxygen partial pressure.

3. Calcium, lanthanum, lithium, sodium and strontium can be removed by chlorination refining with a salt flux: 0.53 NaCl–0.27 KCl–0.20 MgCl$_2$ (flux A). Other elements are difficult to remove from magnesium by this salt flux treatment.

4. Pure magnesium can be recovered by distillation because of its high vapor pressure, but this produces a residue enriched in alloying elements.

5. Advanced magnesium alloys containing various elements have been developed in recent years. These elements may complicate magnesium recycling.

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