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Influence of contamination on the thermal evaporation of a zinc melt

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ABSTRACT

In a thermal evaporation process, the melt will become enriched with elements of a lower vapor pressure than the evaporating species. Industrial coating facilities used in the steel industry are expected to run for days where the enrichment can become a serious problem because the accumulation of contaminants will influence the evaporation process. In this paper, two cases were investigated; a zinc melt contaminated with aluminum and a zinc melt contaminated with lead. These elements were chosen because they are present in significant amounts in commercially available zinc ingots, and at the tested temperature aluminum is completely soluble in zinc while lead and zinc form an emulsion. The results show that for a zinc melt at a constant temperature, the zinc evaporation rate is inversely proportional to the atomic percentage of aluminum. The influence that lead contamination has on the evaporation rate is much smaller and at 40 atomic percentage lead the evaporation rate is still more than 95% of its original value.

1. Introduction

The scope of physical vapor deposition as a coating technology is rapidly increasing since it is a highly versatile technique. It is therefore being adopted by manufacturers throughout the world to produce coatings with exceptional properties, that can be uniquely tailored to meet substrate material or end use requirements [1]. Such coatings cannot be produced by more conventional coating technologies. Also in the mild steel industry there is a growing interest into the exploitation of this technique, mainly in coating systems containing Mg and ZnMg (see [2–5]). This is due to the excellent corrosion properties of these kinds of coatings and thus the potential to reduce the coating weight. However, one of the major problems is that the campaigns in the steel industry usually run for several days and/or weeks. Hence, for a full scale vapor production facility to be able to compete with legacy systems it is essential to be able to operate for several days without interruption. It is therefore necessary to replenish the evaporated source material. There are different techniques available for this, however when a thermal evaporation process is used certain elements will not evaporate and they will accumulate in the melt. This is depicted in Fig. 1 where the contamination, in weight percentage, of a zinc melt of 10 l is given as a function of time, assuming an evaporation of 200 g/s and using the zinc composition given in Table 1. It is expected that this contamination will decrease the evaporation rate which for the evaporation of a single element is not an issue. It is straightforward to increase the melt temperature and as such, the evaporation rate. For an assumed evaporation rate decrease of 20%, the temperature of a zinc melt initially at 670 °C has to be increased by 15 °C. However, for the situation where a ZnMg coating is deposited from a single source, changing the temperature will also change the composition of the deposited film which is not desirable. In the literature [6] a solution is proposed where a ZnMg coating is deposited by evaporating Zn and Mg separately and mixing the vapors.

The two sources are placed outside of the vacuum chamber so that it is easier to replenish or to clean the melts. However, for evaporating ZnMg from a single source the composition of the melt is not the same as the composition of the deposited coating or the composition of the material that is used to feed the melt. This is a consequence of the difference in vapor pressure of Zn and Mg and therefore removing the melt and replacing it with the material that is fed in will result in a different coating composition and, is as such not straightforward. Therefore, it is important to study the influence of melt contamination in more detail. This report presents the effects of two different contaminants, lead and aluminum, on the thermal evaporation of a zinc melt, These two elements were chosen because they are present in commercially available Zn and Mg ingots. Furthermore, they present two different scenarios when added to zinc since the binary alloy Zn–Al is completely soluble and Zn–Pb forms an emulsion.

2. Theory

2.1. Vapor pressure of the elements and binary melts

Every material whether it is in a solid or a liquid state has a vapor pressure. The vapor pressure increases with temperature and reaches

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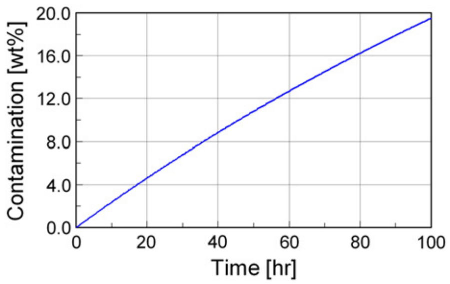

Fig. 1. Contamination of a droplet of 10 l.

a value of 1 atm at the normal boiling point. In a completely closed vessel kept at a constant temperature, the vapor pressure is the pressure at which the amount of atoms evaporating is equal to the amount condensing. The vapor pressures for most of the elements are known and are given for 5 elements in Fig. 2 [7].

The partial vapor pressures above a melt that is a binary mixture of two elements will depend on the properties of the mixture. For an ideal solution with thermodynamic properties analogous to those of a mixture of ideal gases, the vapor pressure of the solution is described by Raoult's law [8], which states that the vapor pressure is dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution. This is in equation form:

$$p = p_A x_A + p_B x_B + \ldots. \tag{1}$$

where x_i is the mole fraction and p_i is the vapor pressure of the pure component.

In Fig. 3, this situation is depicted by pictures a, b and d. At a specific temperature two pure liquids have vapor pressures p_A and p_B. When these liquids are mixed in the same molar quantities, kept at the same initial temperature and indeed an ideal solution is formed, the total vapor pressure above the liquid is given by $1/2p_A + 1/2p_B$. For two elements that are immiscible it is somewhat more complicated and the situation that arises is determined by whether the liquid is stirred, picture e, or not, picture f. When it is not stirred, the lighter element will be on top and the vapor pressure is given by P_C. When it is stirred, the solution will be an emulsion and part of the free surface is occupied by liquid *A* and part by liquid *C*. This situation is simplified by the situation in picture g. There are two independent solutions, *A* and *C*. The vapor atoms of *A* do not dissolve in liquid *C* so this is seen as a part of the wall and the vapor atoms of *C* do not dissolve in *A* so this is also seen as a wall. The vapor pressure is now the sum of both pressures; $p_A + p_C$.

The two elements of Table 1 which represent the two scenarios depicted in Fig. 3 are aluminum, picture (b), and lead, (c), which are described in more detail below.

Scenario 1: when a zinc melt at 670 °C is contaminated with aluminum which is completely miscible, with a vapor pressure of pure zinc of 5000 Pa and that of aluminum $1 \cdot 10^{-6}$ Pa, it follows that the total vapor pressure will decrease linearly with the atomic concentration of aluminum.

Scenario 2: when a zinc melt is contaminated with lead which is almost immiscible with zinc an emulsion is formed. The vapor pressure of pure lead is 0.4 Pa at 670 °C so again much smaller than that of Zn. When they are stirred properly they will form an emulsion and without stirring, the Zn would be on top of the Pb. This can be seen in Fig. 4, which shows a cross section from such a melt after an experiment. The Pb is present in the bottom with Zn rich particles and the Zn is on top with Pb rich particles. To be able to determine the vapor pressures it is necessary to study the phase diagram of zinc and lead, shown in Fig. 5. At 670 °C 4 atomic percentage of lead is soluble in zinc, indicated by point *B*. Increasing the concentration of lead will result in the formation of a two phase emulsion; one zinc rich phase containing 4 atomic percent lead, and a lead rich phase with 23 atomic percent zinc. The fraction of each phase is given by the lever rule:

Table 1
Composition of commercially available zinc.

Element	Zn	Fe	Cu	Al	Pb	Cd	Sn	Others
Wt.%	99.98	0.003	0.002	0.002	0.003	0.003	0.001	0.006

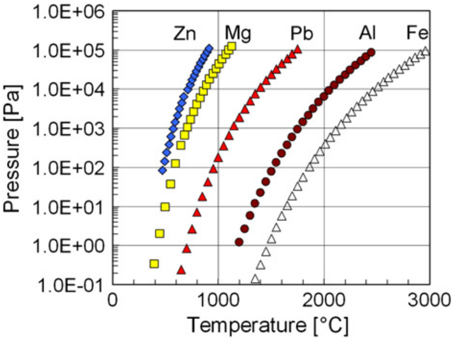

Fig. 2. Literature data of the vapor pressure of a selection of elements.

$$\begin{aligned} f_{\mathrm{Zn+4Pb}} &= \frac{C-A}{B-A} \\ f_{\mathrm{Zn+77Pb}} &= \frac{B-C}{B-A} \end{aligned} \tag{2}$$

where *A* and *B* are the points indicated in Fig. 5 and *C* is the composition of the melt.

With this equation it is now possible to calculate the vapor pressure for the cases in Fig. 3e–g as a function of the lead content and temperature.

Fig. 6 depicts the calculated vapor pressure above a zinc melt at 670 °C as a function of either the aluminum or the lead concentration, using Eq. (1) for aluminum and Eqs. (1) and (2) for lead. It is clear that the presence of one of these two contaminants on the vapor pressure above the mixture is enormously different and according to this prediction, the contamination with aluminum will be more detrimental than contamination with lead.

2.2. Evaporation rate

To be able to determine the evaporation rate, it is important to consider the set-up that is used in these experiments (see Fig. 7). A zinc droplet which is contained in an electrically non-conducting crucible is heated using an induction coil. The zinc droplet can be either fully or partly levitated, depending on the induction coil geometry. Due to the heating of the droplet, zinc vapor is produced and this vapor is guided through a heated vapor distribution box, called VDB hereafter, and sprayed homogenously onto a strip that is moving over the VDB.

With the Zn vapor pressure in Fig. 2, it is possible to calculate the evaporation rate at the droplet using the following formula [9,10]:

$$\dot{m} = f_c \cdot p_{sat} \cdot S \cdot \sqrt{\frac{M}{2\pi \cdot R \cdot T}} \tag{3}$$

where $\dot{m}$ is the mass rate in kg/s, f_c is the condensation coefficient, *S* is the evaporating surface area of the droplet in m^2, *R* is the universal gas constant in $\mathrm{J \cdot kmol^{-1} \cdot K^{-1}}$, p_{sat} is the vapor pressure in $\mathrm{N \cdot m^{-2}}$, *T* is the temperature in K and *M* is the molar weight in $\mathrm{kg \cdot kmol^{-1}}$.