7
Oxidation Behavior of the Feedstock

7.1 Introduction

An extremely high affinity of magnesium to oxygen, along with the highly developed surface area of magnesium alloy chips, used as a feedstock during injection molding, makes the system prone to oxidation. It is anticipated that alloy protection inside the machine barrel by an inert atmosphere of argon is essentially better than molten surface shielding by SF$_6$ gas during die casting. So far there is a lack of experimental verification, and existing data send a rather unclear message. First, the inertness of an argon atmosphere is sensitive to small amounts of entrapped air, and the growth rate of MgO on Al-based alloy at temperatures of 450 °C to 800 °C in a mixture of Ar+1%O$_2$ and Ar+5%O$_2$ equals 25% and 70%, respectively, of the oxidation rate in air [1]. Second, the final oxygen content in molded parts is still about one order of magnitude higher than that present in an initial feedstock [2]. A description of the alloy oxidation behavior is therefore of key importance for designing material feeding and Ar flow systems. It is also important for feedstock manufacturing in terms of morphology and its chemical modification against oxidation. In particular, it is helpful in verifying the necessity of beryllium additions routinely used in conventionally cast alloys.

The objective of this chapter is to identify factors controlling surface degradation of magnesium alloys at high temperatures, exposed to both reactive and inert atmospheres. Moreover, the techniques of molten metal protection during industrial processes are presented along with possible consequences of the protection perturbation.

7.2 Oxidation Kinetics

The progress of any oxidation reaction is most often controlled by a continuous monitoring of the weight change. Thermogravimetric measurements of AZ91D commercial alloy reveal the complex character of alloy weight changes versus time.
7.2.1 Initial Stage Reaction

The initial stage reactions typically cover the several first minutes after an alloy is exposed to high temperatures. A high affinity of magnesium to oxygen makes it difficult to preserve the oxide free metallic surfaces. A reaction with air at room temperature creates a thin passive film with an estimated thickness of 25 Å [3]. The film, preformed at room temperature, continues to grow first during heating up to the test conditions following kinetics represented by the thermogravimetric curves. As seen in Fig. 7.1a, the very initial stage of air exposure at temperatures in the range of 197°C to 487°C is characterized by rapid weight gain, similar for all samples. However, after a time interval of 2–4 min and a corresponding weight gain of 20–25 µg/cm², the further reaction kinetics depend on the temperature. While the alloys tested at 472°C and 487°C continued to increase their weight at a significantly lower rate, the alloy subjected to temperatures lower than 397°C experienced a weight reduction. In general, the lower the test temperature, the faster and larger weight loss is observed.

The maximum oxide thickness achieved during preheating, as converted from weight gain data, are equal to 640 Å and 840 Å for 197°C and 487°C, respectively. This calculation is based on the assumption that at this stage the oxide is uniform in thickness and the weight gain of 1 µg/cm² corresponds to a 28 Å thick MgO film with a density of 3.58 g/cm³. As pointed out in early studies by Pilling and Bedworth [4], due to the large difference in densities between the oxide and

![Graph](image_url)

**Fig. 7.1** Thermogravimetric measurements of weight change versus time for an as-cast AZ91D alloy in an air environment: a initial stage reaction at temperatures between 197°C and 487°C;