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Prime Novelty Statement

The prime novelty of this research is the analysis of grain size *vs* inverse of the growth restriction factor for grain refined magnesium castings containing bismuth. A quantitative model, which was originally developed to predict the grain size of aluminium containing Al-Ti-B master alloy, has been successfully applied to study the potency of bismuth in pure magnesium.

The grain refinement potency of bismuth in magnesium

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Abstract

A quantitative model was applied to analyse the grain refinement potency of bismuth in magnesium. The formation of potent Mg-Bi-O intermetallic phases at 0.4wt.% Bi were attributed to a noteworthy reduction in the average grain size of α-Mg grains. The efficiency of the grain refiner was identified through the analysis of grain size *vs* inverse of the growth restriction factor *(Q)* plots, with a comparison of the Zr solute under similar experimental conditions. It was concluded that '*Q'* could be a suitable predictor of the relative grain size in the Mg-Bi system containing potent nucleant particles. The cooling rate analysis supported the efficiency of bismuth grain refinement in magnesium.

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1. Introduction

The potency of the nucleant particles along with the segregating power of solute is critical in determining the final grain size of the alloys [1, 2, 3, 4]. The potent nuclei activate nucleation at low undercooling while the solute provides the constitutional undercooling to activate the adjacent nuclei [5, 6, 7]. The solute could be present either at the columnar growth front competing with equiaxed solidification or from the particles which have already nucleated [8, 9]. For the spherical growth restricted by the

partitioning of a single solute, the crystal growth rate for a given undercooling is given by an inverse proportion to the parameter *Q*, defined by $mc_0(k-1)$, where *m* is the slope of the liquidus, c_0 is the solute concentration in a binary alloy and *k* is the partition coefficient [10]. The parameter *Q* is referred to as the growth restricting factor and is used as a measure of the effects of a solute on the grain refinement in the absence of solute interactions [3].

Earlier work [11] proposed an increase in yield strength and creep resistance of AZ91 alloy containing bismuth (Bi), which was attributed to the formation of Mg_3Bi_2 intermetallic phase. A similar research on AZ80 alloyed with 0.5wt% Bi is suggested to have an optimum composition of mechanical properties due to finely dispersed Mg_3Bi_2 phases [12] while the combined micro-alloying of calcium and bismuth in AM50 alloy also indicated a potential for increase in the hardness and yield strength of the alloy [13]. The focus of each of these research papers has been on the role of Bi solute in high Al (≥ 5 wt %) containing magnesium (Mg) alloys, while our recent study [14] has shown effective grain refinement even in commercial purity (CP) Mg and AZ31 direct-chill cast billets at significantly lower addition rates of Bi solute. Current research aims to understand the potency of this grain refinement effect of Bi through application of a quantitative model [3], which was originally developed to predict the grain size of aluminium castings inoculated with Al-Ti-B master alloy.

2. **Materials and Methods**

2.1.Model development and Grain refinement

The potency of Bi in magnesium was examined by making individual additions at 0.02, 0.04, 0.08, 0.1 and 0.4wt.% solute to a CP-Mg ingot (99.9% purity with 0.04%Al, 0.02%Mn, 0.013%Si, 0.002%Fe, 0.001%Cu, <0.01Ni and 1 ppm Be). A conventional furnace lined with a steel mould is used to melt around 350 g of Mg under a protective atmosphere of (N_2 + 0.5SF_6). When the temperature of the melts reaches 700 °C, the melt was held at this temperature for at least an hour before obtaining the reference sample or any addition of grain refiner in the form of Bi (size -100mesh, 99% purity metal basis from Sigma Aldrich) or Zr (Mg-33.3Zr master alloy supplied by Magnesium Elektron). Each of the solute elements was exposed to the Mg melt for 15 minutes at 700 °C. This time includes stirring (using a steel rod) for 30 seconds at about 5 minutes prior to pouring the melt in a 200 °C preheated steel mould. The steel mould is a cylindrical block of 95 mm diameter, incorporating a cylindrical cavity of 30 mm radius and 100 mm depth (actual length of sample). Each cast samples are sectioned vertically or transversally in half and exposed to solution heat treatment for 30 minutes at 413 °C in an air furnace to reveal the grain boundaries. These parameters are chosen to replicate the Zr solute addition results of Lee et al.'s study [15] in order to obtain a comparison with Bi solute effect in Mg. Samples were ground and polished using a standard procedure for optical microscopy. Polarised light microscopy was applied on samples etched with a mixture of 5 ml acetic acid, 10 ml distilled water, 100 ml ethanol and 6 gm picric acid. The linear intercept method was used to measure the grain size using a Zeiss Axioskop2 MAT optical microscope. The scanning electron microscope (SEM) using a Zeiss Supra 35VP FEG ~~microscope~~ and equipped with energy dispersive X-ray (EDX), Oxford Instruments Inca was applied to estimate the composition of the intermetallic phases in Mg-0.4Bi alloy.

2.2.Cooling rate sensitivity analysis

Copper-shape wedge moulds 30 mm wide x 80 mm long x 130 mm height were used for the cooling curve analysis. The melt handling procedure was same as in section 2.1, except that 0.4 wt.% bismuth was left in the commercial purity magnesium melt for 20 min before casting in the wedge moulds. The standard grinding and polishing procedures were followed for observing the macrostructure of the as-cast Mg and the grain refined wedge shaped samples.

3. **Quantitative model**

The relationship between grain size and the combined effects of particles potency ΔT_n, and the solute content Bi on CP Mg alloy is calculated using the quantitative model (Equation 1) developed by Easton and StJohn [3, 16]. It is assumed that a negligible temperature gradient exists in the melt.

The solid fraction (f_{sn}) attained when the constitutional supercooling (ΔT_{cs}) reaches a critical value ΔT_n can be used as a measure of the relative grain size (RGS) and can be expressed as Equation (1) [3, 16]

$$RGS = f_{s,n} = 1 - \left(\frac{mC_0}{mC_0 - \Delta T_n}\right)^{1/(k-1)} \quad (1)$$

where $f_{s,n}$ is the amount of growth required to develop the undercooling (ΔT_n) necessary for nucleation to occur, m is the slope of the liquidus line, C_0 is the overall solute concentration and k is the solute partition coefficient. Equation (1) can be used to show the relationship between grain size and the combined effects of particle potency ΔT_n,

and solute content of the Mg-Bi alloy as shown in Figure 2. For small undercooling, a semi-empirical relationship between d and 1/Q was proposed [4, 7] and given as Equation (2)

$$d = \frac{1}{\sqrt[3]{\rho f}} + \frac{b' \Delta T_n}{Q} \quad (2)$$

where *d* is the grain size, ρ is the density of the nucleant particles, *f* is the fraction of these particles that are activated and *b* is a constant. This model has shown good agreement with the results obtained from aluminium alloy inoculation with TiB_2 and the phase-field microstructure prediction model for the grain size of magnesium alloys [17]. This equation model incorporates parameters from Gulliver-Scheil's equation, which assumes complete diffusion in liquid and therefore dismisses the development of constitutional supercooling [3]. Also, another limiting factor of this model is that it requires fitting factors to relate it to the actual grain size measurements. Despite these deficiencies, it is the first analytical model that has given a reasonable description of the grain refinement phenomena in aluminium alloys, magnesium alloys [4, 18] and Ti-based alloys [19]. This model forms the basis of evaluating the influence of nucleant potency and density in a melt for commercially available grain refiners or new grain refiner trials [20] and is applied in the current study to calculate the potency of the intermetallic phases formed in the Mg-0.4Bi alloy.

4. **Results and Discussions**

4.1.Model development and Grain refinement

The microstructures of the castings are shown in Figure 1. The average grain size of the reference Mg sample indicates a drop from 1200 µm (Figure 1a) to around 400 µm

at 0.4wt% Bi (Figure 1b). Under similar casting conditions, the average grain size of Mg inoculated with Zr solute resulted in an average grain size of 300 μm (Figure 1c).

Figure 1. Typical microstructures of (a) CP Mg, (b) Mg-0.4Bi and (c) Mg-0.4Zr

Figure 2 illustrates a decrease in the potency of the solute with increase in ΔT_n value. The particle potency seems to have a significant effect on the grain size for all Bi content. At lower Bi concentration, there is a dramatic effect on Mg grain size but very little effect at higher concentrations. Whilst the actual ΔT_n value of the Bi containing nucleant is not known, it can be seen that the trend in the average grain size with bismuth addition is similar to the trends in RGS and is pointing towards a lower value of ΔT_n. This is indicating a higher potency of Bi containing particles as noted by Easton & John [3].

Figure 2. Calculated variation of Mg grain size compared with experimental data of Mg-Bi alloy for a range of ΔT_n having an inverse relationship with the nucleant

The presence of intermetallic particles containing Bi were identified through the application of SEM-backscattered electron (BSE) analysis while the approximate prediction of the composition was enabled through EDS (Figure 3). The application of BSE facilitated the differentiation of the contrast between the particles rich in bismuth and the lighter atoms of silicon (Si), marked as A and B respectively in Figure 3a. The corresponding EDS shows the main difference between these particles, each measuring around 1.5 μm wide. The bright clusters of particle A are Bi rich Mg intermetallics and

are highly oxidised. The particle B is high in silicon and its bismuth content is negligible compared to that of particle A. The polishing procedure involving the use of standard colloidal silica suspension might have led to the extra silicon inclusion in this alloy. Also, it should be noted that at such high magnifications as in the case of particle A and B, the quantitative analysis based on EDS could be considered only as an approximate guide for the compositional analysis. Considering that the maximum solubility of Bi in Mg is 8.85 wt.% [21], Mg_3Bi_2 particles or any binary Mg-Bi type intermetallic phases are not anticipated to form as most of the Bi is expected to be dissolved in the α-Mg matrix during the melting process. Despite this, the occurrence of intermetallic phases Mg-Bi-O in our research proposes the potential contribution of heterogeneous nucleation in the grain refinement of Mg-0.4Bi alloy. This result is consistent with a previous work [22] where the Mg-5Si alloy shows the occurrence of hexagonal Mg_3Bi_2 phases only at 0.5wt% Bi and above addition levels. A combination of SEM-BSE with the RGS calculations (Figure 2) proposes Mg-Bi-O as the potential nucleation site.

Figure 3. (a) SEM BSE image for bismuth containing magnesium showing EDS of (b) particle A and (c) particle B (Inset is the higher magnification image showing particle A and B).

Recent work [23] has calculated the growth restriction factor of Bi as 1.55 which is very low compared to that for Zr at 30.24 for binary systems at C_0 =1.0wt%. So, according to the growth restriction theory, it is unlikely that Bi could contribute to the grain refinement of α-Mg through development of constitutionally undercooled zone.

Current study has shown the occurrence of the intermetallic phase containing Bi in the Mg-0.4Bi samples (Figure 3), which suggests that Bi has contributed to the grain refinement and it will therefore be required to assess whether the refinement occurs via solute or nucleant mechanisms. Equation 2 is one such model developed for aluminium and magnesium systems which takes into account the effect of nuclei on grain size in addition to the solute effect. After incorporating the values of ρ, f and b' in Equation 2, a simplified version can be given as

$$d = a + b/Q \quad (3)$$

where a represents the number of active nucleant particles and b is related to the potency of the particles. A steeper slope or in other words, a higher value of b corresponds to a lower potency of the nucleant particles; as more nuclei are introduced, the value of a reduces and it could theoretically become zero at infinite number of particles [4].

Equation (3) is used to plot the average grain size data from the current experimental work for Bi and Zr additions against the reciprocal of Q value (Figure 4). Casting conditions were similar to that followed by Lee et al. [15], which enabled the reproduction and comparison of their Mg-Zr alloys with the current study. However, it should be noted that the sample dimensions in this study were 30mmx100mm as opposed to 25mmx70mm considered in Lee et al.'s [15] work. The fact that the different data-sets in Figure 4 can be represented by linear fit lends support to the model [19]. In each case, an increase in solute content (or decrease in 1/Q value) leads to a reduced Mg grain size but the rate of reduction in grain size is widespread. The variation in gradient for both the solute lines suggests that the potency of nuclei, ΔT_n is

different in each alloy. Between Zr and Bi solute, Mg-Bi alloy has the lowest slope (Figure 4) value but this does not imply a better potency of Bi over Zr particles as observed in the micrographs (Figure 1). This is due to some of the Zr remaining as solid particles rather than solute resulting in an over estimation of the Q value [4]. The addition of Zr particles in Mg melt were all below the peritectic composition of 0.45 pct. Zr so all the particles should dissolve however, prior study [24, 25] has also reported the presence of 50 pct. undissolved Zr particles at longer holding times. A comparison of the two Mg-Zr alloys indicate that Lee et al. [15] achieved a smaller minimum average grain size despite a very low number of nucleating particles (lower *a* value). This means that higher number of nuclei were activated in Lee et al.'s work as opposed to current experimental conditions which led to coarser grain size with higher number of nucleating particles (higher *a* value). The similarity in the slopes of both the Mg-Zr lines in Figure 4 is indicating that the potency of the particles remained unchanged. So, the difference in the minimum average grain size for Mg-Zr alloys could be attributed to the potential slower cooling rates employed in this study.

Figure 4. Relationship between average grain size d and inverse of Q for current research as well as Zr addition data from Lee et al. [15]

It can be seen from the Figure 4 that the Mg-Bi alloy has a very low value of slope *b* and a considerably high value of *a* demonstrating better potency of particles and a higher number of activated nuclei. Mg-Bi system has shown similarity with the Mg-Zr

system as each of these solute elements Bi and Zr when added below their solubility limits, resulted in formation of potent intermetallic particles in the Mg matrix.

4.2.Cooling rate sensitivity analysis

Pure magnesium sample and 0.4wt% bismuth containing magnesium sample is as seen in the Figure 5.

Figure 5. A copper wedge-shape mould for commercial purity magnesium (a) reference and (b) 0.4 wt.% bismuth

The narrow edge of the wedge mould has finer grain structure due to faster cooling rates while the broader edge of this mould has a slower cooling rate and much coarser grains for the pure magnesium sample. Most of the columnar grain area of the pure magnesium sample (Fig 5a) are seen to convert to equiaxed grains in the refined sample with the edges containing a narrower and much smaller columnar grains (Fig 5b). The grain refined magnesium sample suggested that bismuth is not sensitive to the cooling rates and therefore could act as an efficient grain refiner in magnesium.

5. **Conclusions**

These results are important as it recognizes the role of a new solute in the form of Bi that possesses an effective grain refinement potency in magnesium. A potential Mg-Bi grain refining system was identified through the calculation of relative grain size (RGS), which takes into account the potency of the nucleant and the rate of development of constituional undercooling of previously nucleated grains. The grain size trends were

obtained over a range of Mg-Bi compositions, with Mg-Bi-O intermetallics proposed to be the potent nucleating sites. The dominant effect of these potent particles was emphasised through the analysis of grain size '*d*' *vs* the growth restriction factor '*Q*' for the Mg-Bi alloy.

Acknowledgement

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Highlights:

- Bi dramatically refines grain size of α-Mg
- Refining mechanisms explained in terms of nuclei and growth restriction factor
- Grain refinement potency of Bi in magnesium is analysed
- Ternary Mg-Bi-O intermetallics identified

Figure 1

Click here to download high resolution image

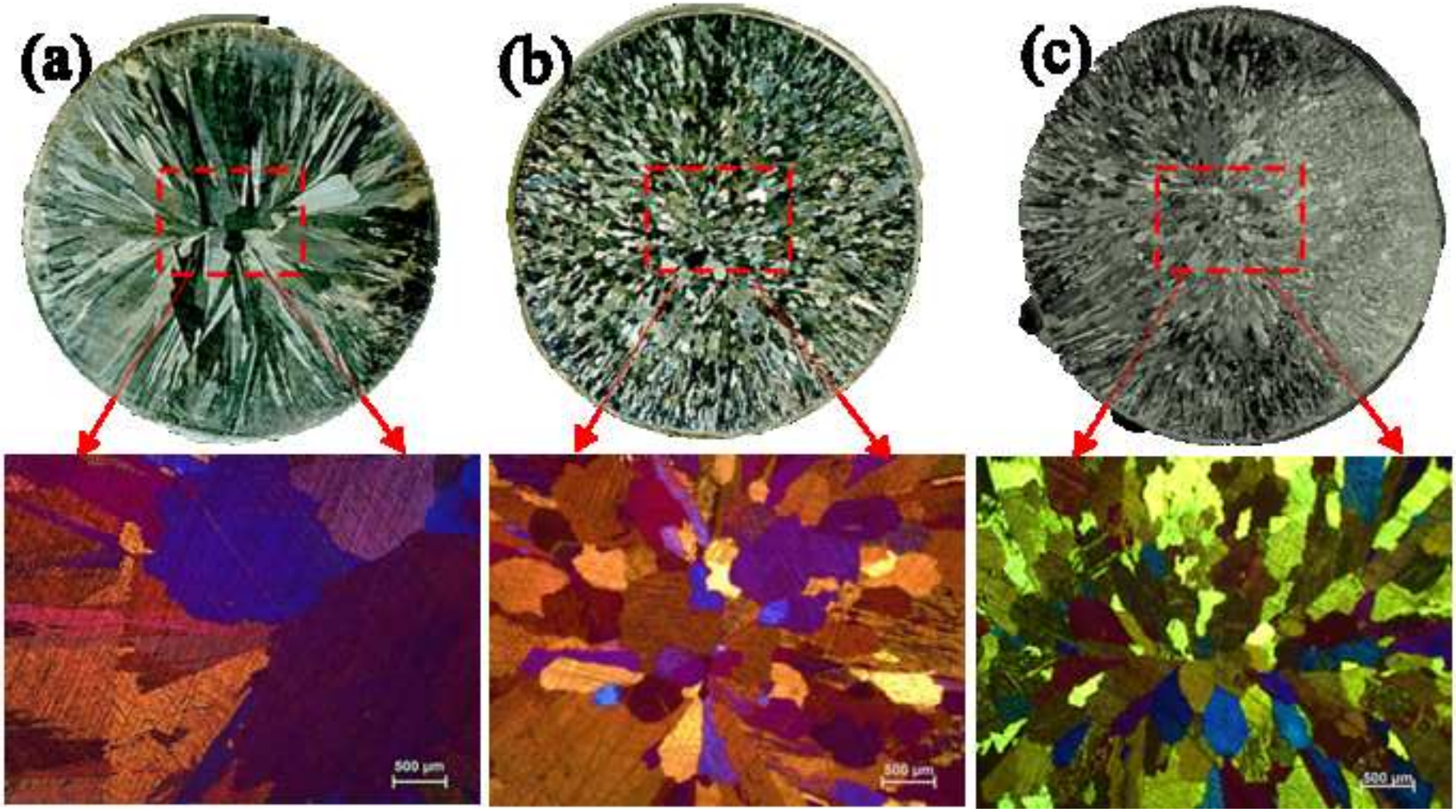

Figure 2

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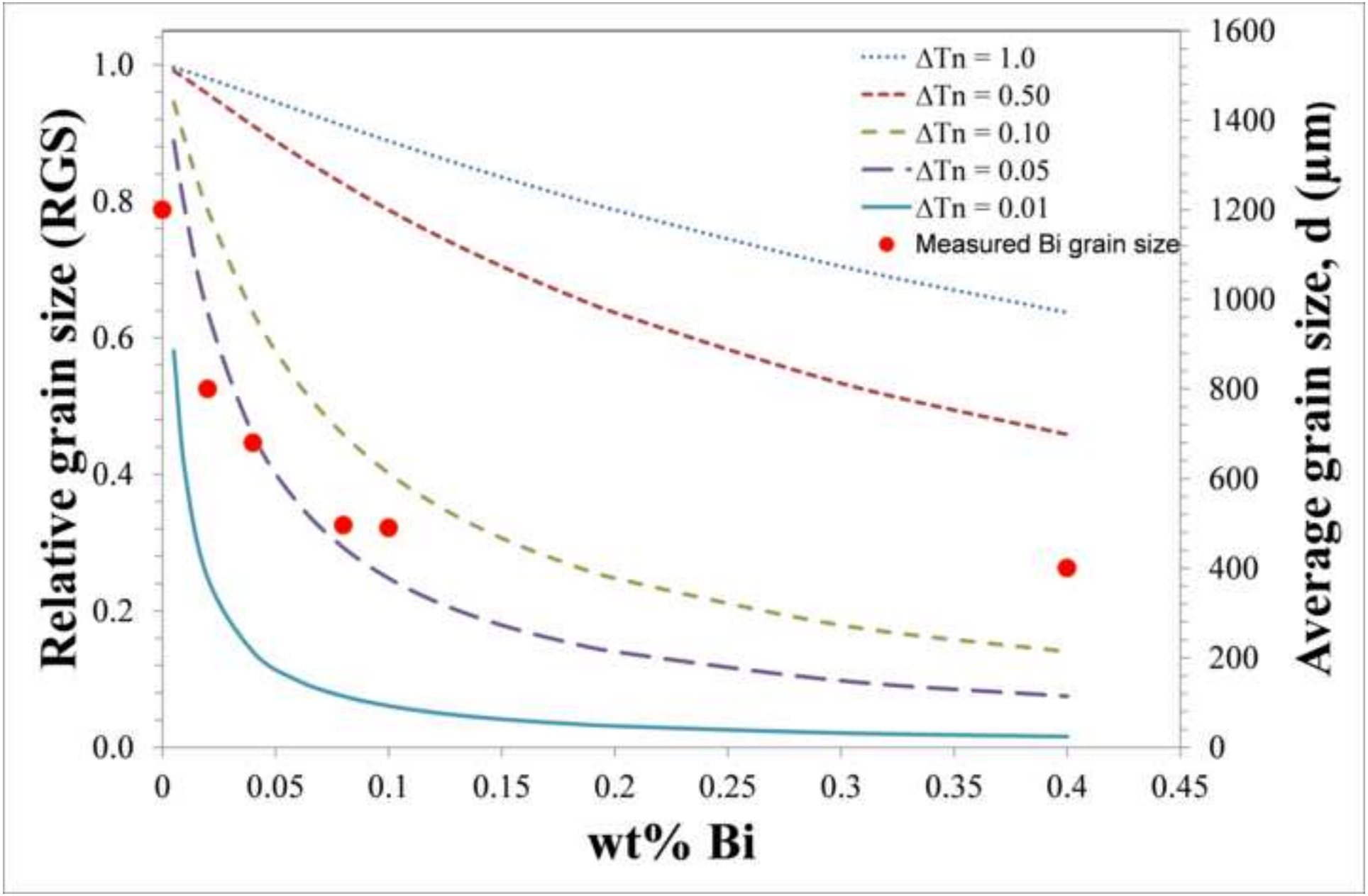

Figure 3
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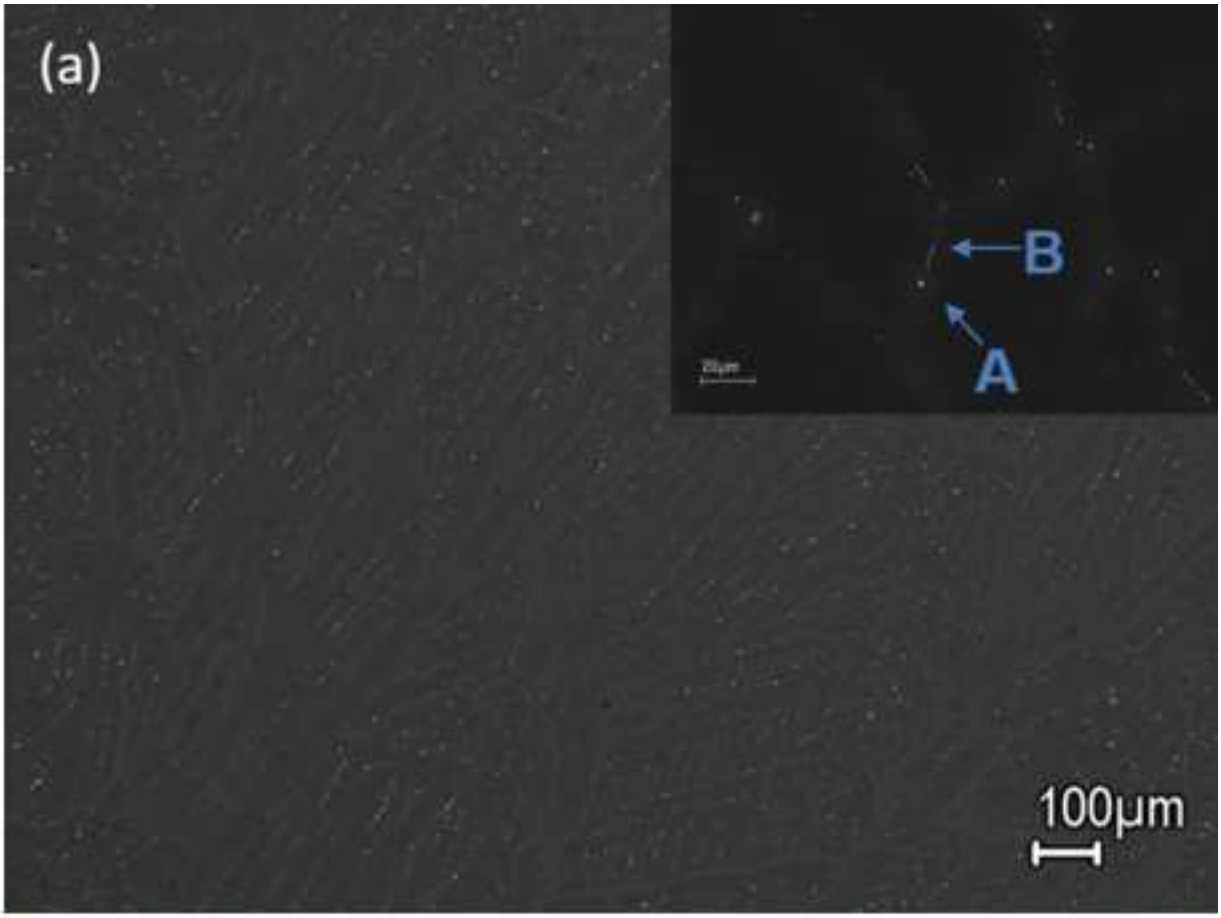
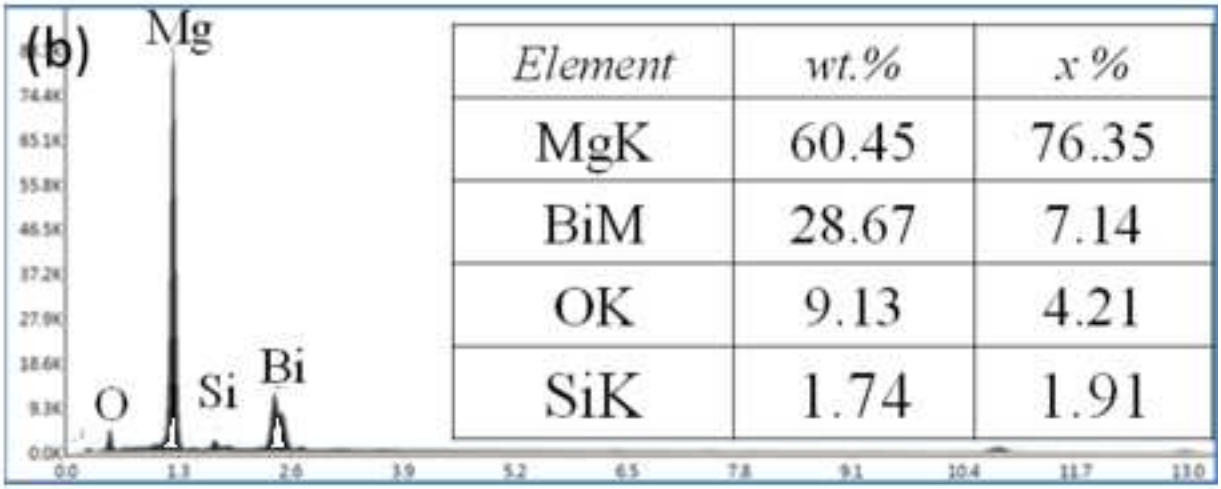
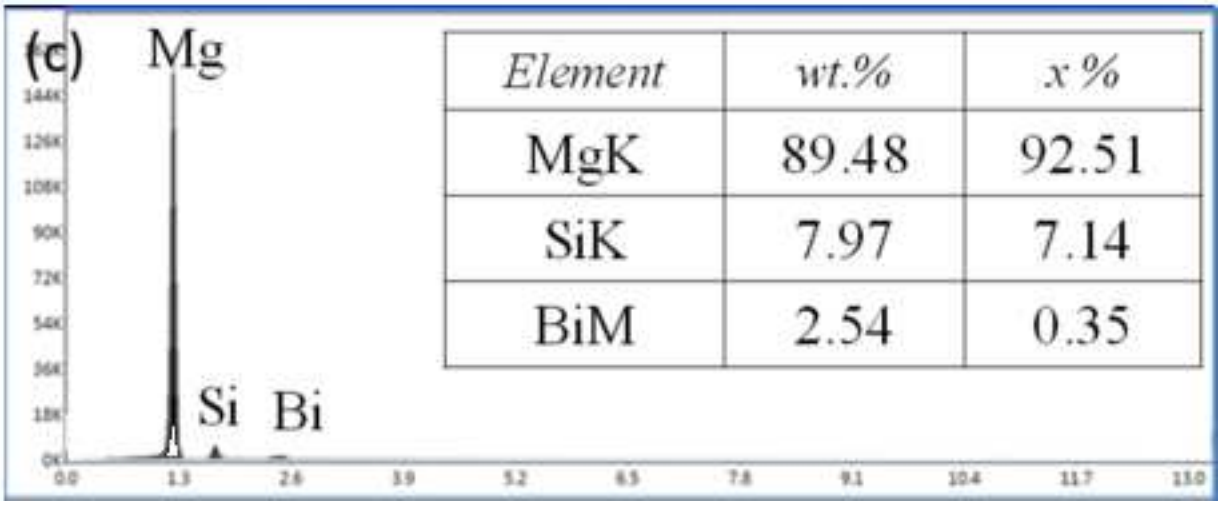




Element	*wt.%*	*x %*
MgK	60.45	76.35
BiM	28.67	7.14
OK	9.13	4.21
SiK	1.74	1.91



Element	*wt.%*	*x %*
MgK	89.48	92.51
SiK	7.97	7.14
BiM	2.54	0.35

Figure 4

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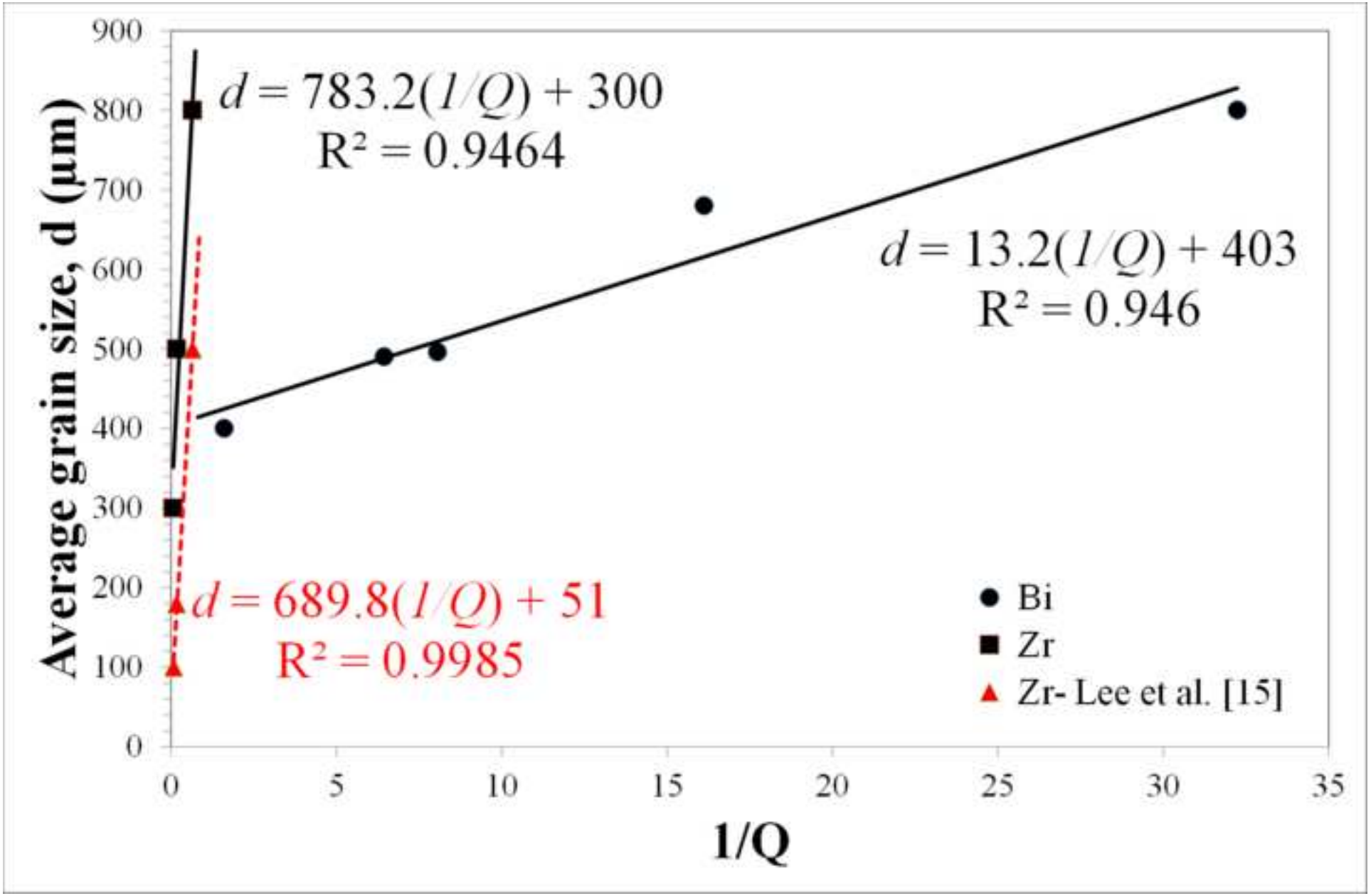

Figure 5

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