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Original Article

Anhydrous borax usage as a space holder for vacuum sintered porous magnesium: Microstructural and mechanical insights

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ABSTRACT

In this study, magnesium powder and anhydrous borax ($Na_2B_4O_7$) particulates sintered in a Hot Press (HP) machine by widely preferred space holder technique in three different weight ratios; to obtain the best ratio for a homogenous magnesium foam for specific usage in multi-disciplinary applications. Metallic foams are industrial products manufactured from porous metal materials. Although it is much lighter than other metal materials, it is gaining importance due to its high resistance, absorbing shocks, and vibrations, providing thermal insulation, gaining biodegradable implant solutions in orthopaedics, chemical filtration, and battery production, and many more for trying to increase its research to be used in practice. Anhydrous borax (ANB) used in thesis study was blended with commercial pure Mg powder at the rates of 20%, 40% and 60% by weight and sintered to produce metal foams. The ANB particle sizes used are T1 (250~400 µm), T2 (400~500 µm) and T3 (over 500 µm). Mg foam was prepared via a hydraulic pressure assisted HP sintering machine at various sintering temperatures 550˚C to 600˚C. The produced Mg foams evaluated in terms of density, porosity, and mechanical strength in general. Maximum achieved porosity ratio is 36.17%. Compression and three-point bending tests were performed to evaluate the usability of the samples as possible bone-fixing implants. The compressive stress measured for the max. porosity achieved is 32 to 44 MPa respectively. This study represents a novel implementation of ANB in metal foaming due to the lack of information on the use of ANB mineral in this specific space-holder metal foaming academic field. ANB is the richest B_2O_3 source relative to other natural borax minerals without H_2O molecules in it. So, this is believed to be a key advantage in foaming processes.

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INTRODUCTION

Magnesium, which is closely followed by the technology-leading countries in the world and whose sources are carefully monitored, has critical importance. Academic research shows that new production methods of porous magnesium and magnesium metals are being evaluated by researchers [1], and its use in the biomedical field and especially in implant manufacturing is becoming more common and increasing day by day [2]. It has been observed that magnesium implants have shown rapid growth since they were launched on the market in 2016 after CE certification was completed [3]. It attracts the attention of researchers' day by day, especially in medical applications, thanks to its ability to be more compatible and biodegradable in the body [4, 5]. This feature of the

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Table 1. ANB particle sizes and designations

Designation	Size of ANB particles	Producer	Brand name
T1	250~400 μm		
T2	400~500 μm	Eti Maden İşletmeleri Genel Müdürlüğü	Etibor 68®
T3	>500 μm		

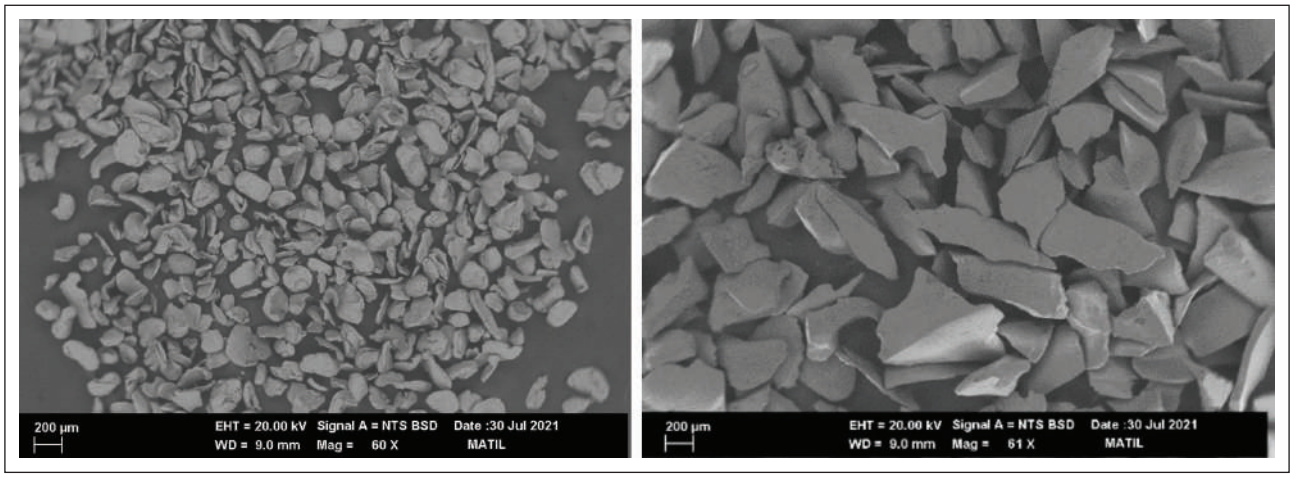

Figure 1. SEM Images of the starting powders: (1) Mg powder, (average 160 μm) (2) Anhydrous Borax spacer, (average 500 μm).

magnesium implants reveals unnecessity of secondary surgical operations in some medical cases reported since 2014 [6–11]. It seems that there is a rapid growth in biomedical applications used in bone fixation surgeries of magnesium alloy implants. On the other hand, porous Mg implants are still in an evaluation period for further improvements. There are still many problems waiting to be solved in this field to predict suitable biodegradable porous implant materials [12]. Low corrosion resistance and mechanical strength are general problems mentioned in the literature. This study aims to manufacture a pure porous Mg foam using ANB as a spacer to withstand higher compression stresses. Additionally, the study aims to improve corrosion resistance by forming a thicker oxide layer on the cell surface using the oxygen-rich mineral ANB. Still, a common accepted fact is Mg is a biodegradable material and essential for many mechanisms in human bone metabolism [13]. Technic used in this study is also widely used by many researchers and many different materials and particulate sizes from 50 μm to 2200 μm's [14–18]. Commonly 250–600 μm cell sizes are mentioned in many of the research and it's also more suitable for manufacturing degradable metal foams via space holder technic [19]. In this study, we aimed to produce magnesium (Mg) foam incorporating ANB particles, as a novel approach that not previously explored in the literature. The objective was to investigate the interaction between ANB's unique properties in Mg melt to develop a new porous foam material. We evaluated ANB's performance during the sintering process for Mg foam production. Chemical stability of ANB at low sintering temperature of Mg powder blends were observed in this context.

MATERIALS AND SINTERING OF SAMPLES

The starting materials are pure Mg powder in the particle size range of 160 to 300 μm (purity is > %99.96). Powder used Mg has the CAS nr. of 7439-95-4 and supplied from "*Magnezyum ve Metal Tozları Endüstrisi Tic. A.Ş.*" (MME). As a space holder material anhydrous borax ($Na_2B_4O_7$) CAS number; 1330-43-4 is used. The brand name is known as Etibor-68® (ETI Mine Co.,) and supplied as its presented to market. ANB is mainly used in glass and ceramics industries to improve the quality and efficiency in production phases. The ANB used in the study classified into specific sizes designated in (Table 1). Powders were scaled on a precise electronic balance with different weight ratios (wt. %) of; 20%, 40%, and 60 % mixed in three different particulate sizes T1, T2 and T3. The microstructure of the used Mg powders and ANB spacers are shown in Figure 1. Powder mixtures milled with Ø5 mm zirconium balls in a proper laboratory sized mill. The rotational speed of the mill is set to 210~280 rpm during 0.5 h. of blending. Blends then sintered in graphite cylindrical moulds to get Ø19.7 x 4 mm samples with T1, T2 and T3 particulates. A vacuumed hot press chamber is used for sintering. The HP machine is a direct current, PLC (Programmable Logic Control) controlled sintering machine produced by DIEX Co. Compaction force applied during sintering was set to 46 MPa. (Fig. 2)

It's important to mention that using ANB particles as it is presented here found to be more cost-effective in domestic usage rather than precisely produced urea or carbamide spherical particles. The thermal sintering

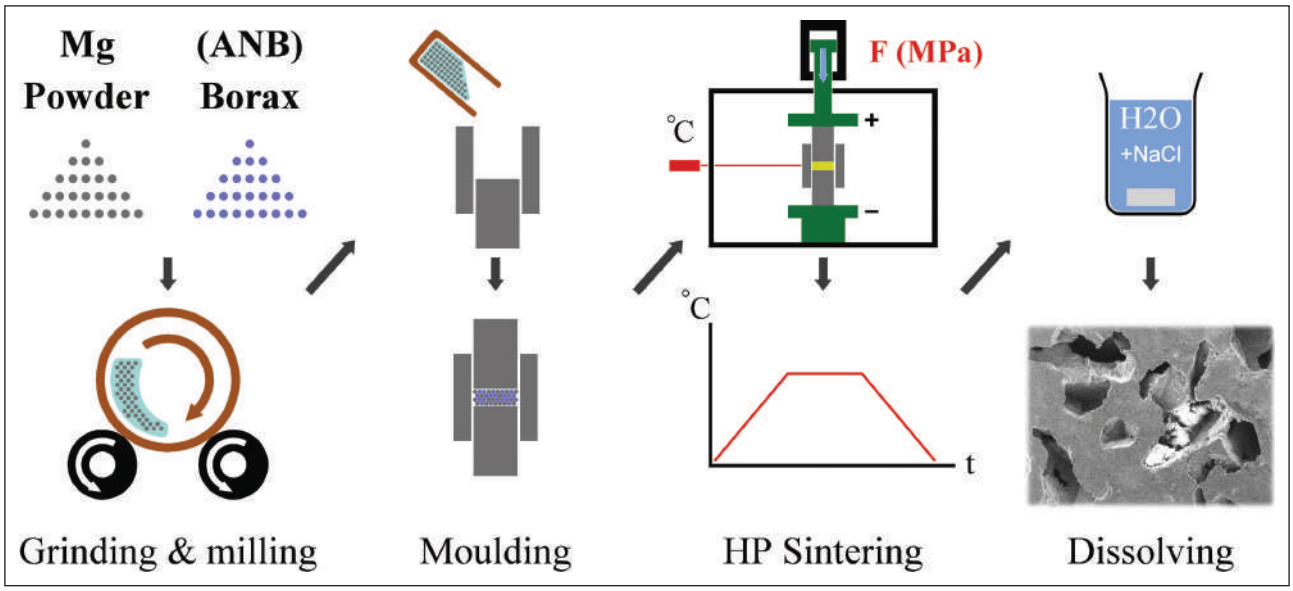

Figure 2. Schematic fabrication process of the porous Mg foam.

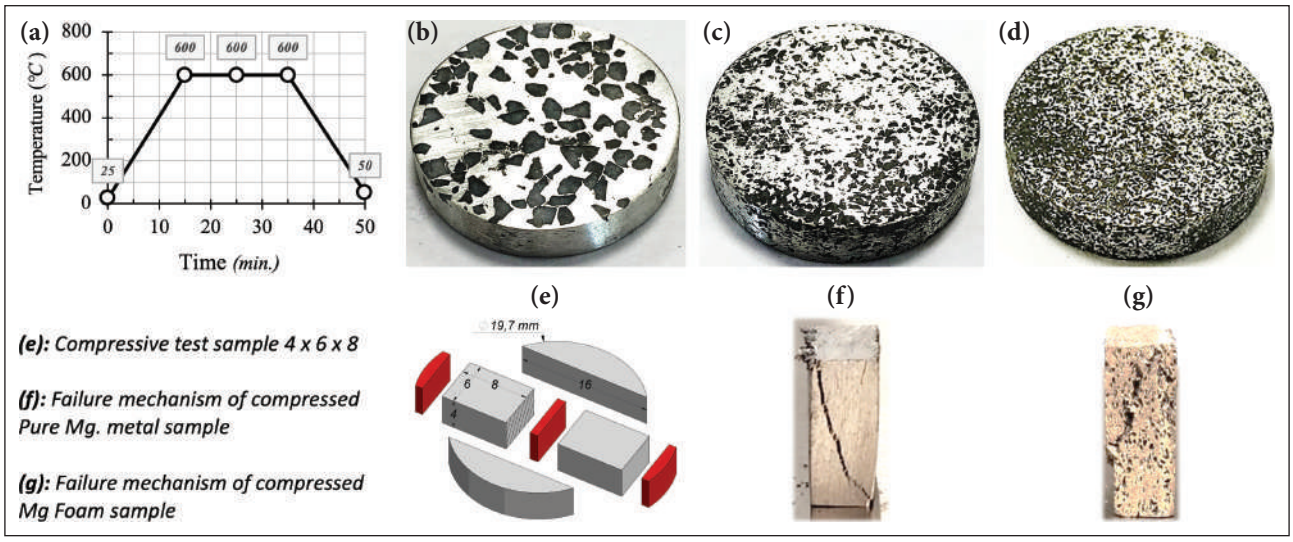

Figure 3. Sintering cycle of Mg & ANB samples with variable particulate sizes.

cycle required for manufacturing Mg & ANB samples is given in (Fig. 3a). Mg foams manufactured seen in (Fig. 3b) is 20% ANB additive with T3 particulate Mg foam. (Fig. 3c) is 40% ANB additive with T2 and (Fig. 3d) is 60% ANB with T1 particulate size. Samples shown here were cleaned and precisely scaled before and after dipping to 0.1 mol H_2O+NaOH solution for dissolving ANB to get half-open Mg foams. (Fig. 3b–d) shows the visual status of Ø19.7 x 4mm disc samples before dipping to H_2O+NaOH solution. (Fig. 3e) is a schematic explanation of how machining operation done to obtain 4 mm x 5 mm x 8 mm compression test samples manufactured from round Mg foam. (Fig. 3f) is the pure Mg sample and (Fig. 3g) is the Mg foam sample sintered and machined accordingly to compare mechanical properties of Mg foams produced. For the compression tests Shimadzu tensile testing machine (10kN) employed. The compression test was carried out at a speed of 0.5 mm/min.

RESULTS AND DISCUSSIONS

Porosity of Samples

Following dissolution process is done after sintering and cleaning process with P320, P600, P1000, and P2000 grinder mediums. There was 3 group of samples based on ANB ratio (20 %, 40 % and 60 wt.%) additionally 3 group for different (T1, T2 and T3) particle sizes. As a total number of 27 Mg foam sample is manufactured. A summary of achieved metal porosity levels in each of these group of foams (Fig. 4). Porosity is going up with the increasing of ANB ratio in magnesium matrix. Min. level of porosity achieved is 3.88% on 20% ANB addition, and in maximum level of porosity achieved is 36.17% on 60% ANB ratio. Porosity results obtained from three samples from each group were analysed according to Chauvenet's criterion, standard deviations were calculated and marked on the graphs. With the rising amount of ANB deviation of porosity level is rising. But it

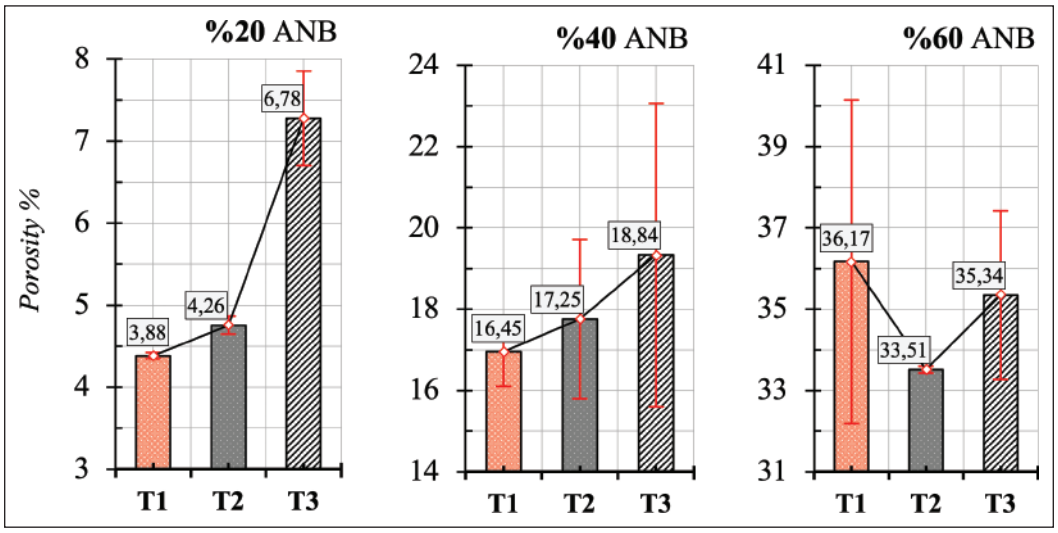

Figure 4. Manufactured Mg foams porosity values prior to pore sizes and ANB ratio.

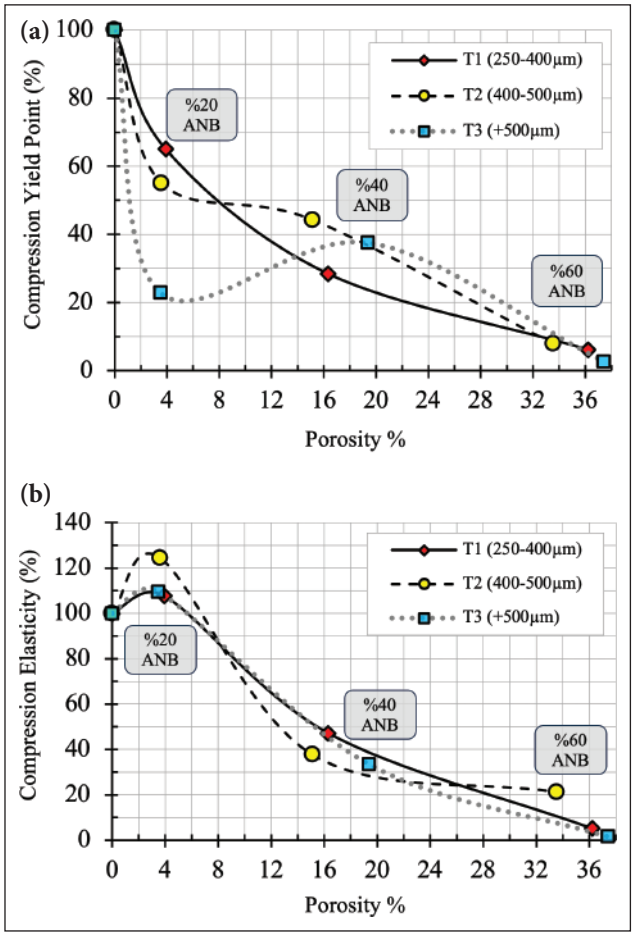

Figure 5. Rate of change in compressive strength with porosity and ANB wt.%.

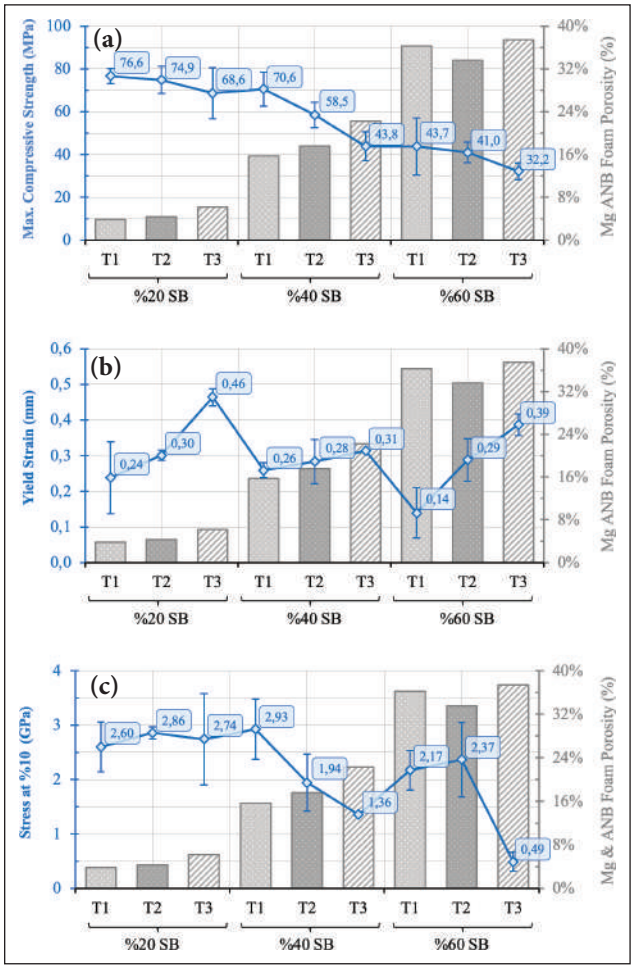

Figure 6. Rate of change in compression properties of Mg foams relative to porosity.

was observed that better stability seen in the porosity and compression properties of T2 particulate sized Mg foams. It is evident that ANB persists in the produced and dissolved samples. Given an average implant screw size and a potential Mg-ANB foam with 50% wt. ANB addition, it is strongly believed that the residual amount of ANB will not exceed toxic limits in the body, remaining below the recommended daily usage amounts. Moreover, it can dissolve in the body alongside the dissolving implant. Due to the regulations on many countries' boron element is essential like Mg for bone health in daily doses of 1 to 3 mg [20–23].

Mechanical Properties

Figure 5 shows the dependence of particulate size on compressive strength of Mg & ANB foams in comparison to pure magnesium sintered metallic sample. How compressive strength is decreased with the addition to Mg metal is seen in graphic (Fig. 5a). On the other hand, elasticity is approximately 20% rises with 20% ANB addition but with the rising porosity and ANB ratio it drops in (Fig. 5b).

On the other hand, additional compressive test applied perpendicular to sintering force direction from the cut samples (Fig. 2e) presented in (Fig. 6, 7). Presented mechanical properties ratios as bars in graphics are given referenced to pure Mg rigid metal sintered on the same process with Mg & ANB foams. Max. compression strength decreases with increasing porosity and ANB wt.% addition as shown in (Fig. 6a). The compressive stress measured for the max. porosity achieved is 32 to 44 MPa respectively parallel to previous academic studies [24]. Elongation properties change with porosity and particulate size shown in (Fig. 6b). Under compression stresses natural human bone exhibit a wide range of mechanical properties. The general range is accepted between is 0.1 to 20 GPa [25]. Mg & ANB metallic foam elasticity under compression drops 10% to 50% in average with the increasing particulate size (Fig. 6c). Due to the heterogeneity on the highest ANB addition the significant drop seen here at 60% ANB and T3 particulate size. With tolerable ANB ratio and cell size increase its clearly seen that Mg & ANB foams became more elastic from the results seen in (Fig. 6c). Figure 7 shows these mechanisms compared to pure Mg metal values with standard deviations on column bars. Which is max. compression strength of 90.22 MPa ±1.2 MPa, yield elongation of 0.61 mm ± 0.6 mm and elastic modulus of 2.75 GPa ± 0.25 GPa for the pure Mg metal reference samples.

ANB is a narrow form type of particulate has believed to be a negative effect unlike other spherical space holders used in previous studies. However, morphology of the open-cell, as evaluated via SEM, is quite similar to the pores observed in research. This form of particulate instead of spherical ones generally leads to deficient structural integrity when manufacturing an open-cell metal foam [26]. After evaluating the mechanical properties of Mg-ANB foams, no significant difference was observed compared to foams with spherical space holders.

Scanning Electron Microscopy

Scanning electron microscope (SEM) (Zeiss, Germany) equipped with energy dispersive X-ray spectrometer (EDS) was employed to observe porous structure details of the Mg foams (Fig. 8).

Figure 9 shows passivation mechanism starts and continues as shown in the scanning electron microscope (SEM) imaging results. Mg and ANB cross-section and exhibit a good contact surface. ANB particulate has a smooth oxidized surface in the beginning of the evaluation (Fig. 9a). A fallow up is made after a storage period of 21 months (Fig. 9b) harsh oxidation on the ANB particulate cross-section observed. After this period oxygen concentrations analysed on Mg matrix is 5 times raised. On the other hand, ANB matrix surfaces exhibit very low change on oxygen concentration, which is changed 58% to 64%, approximately 10% of change during this period.

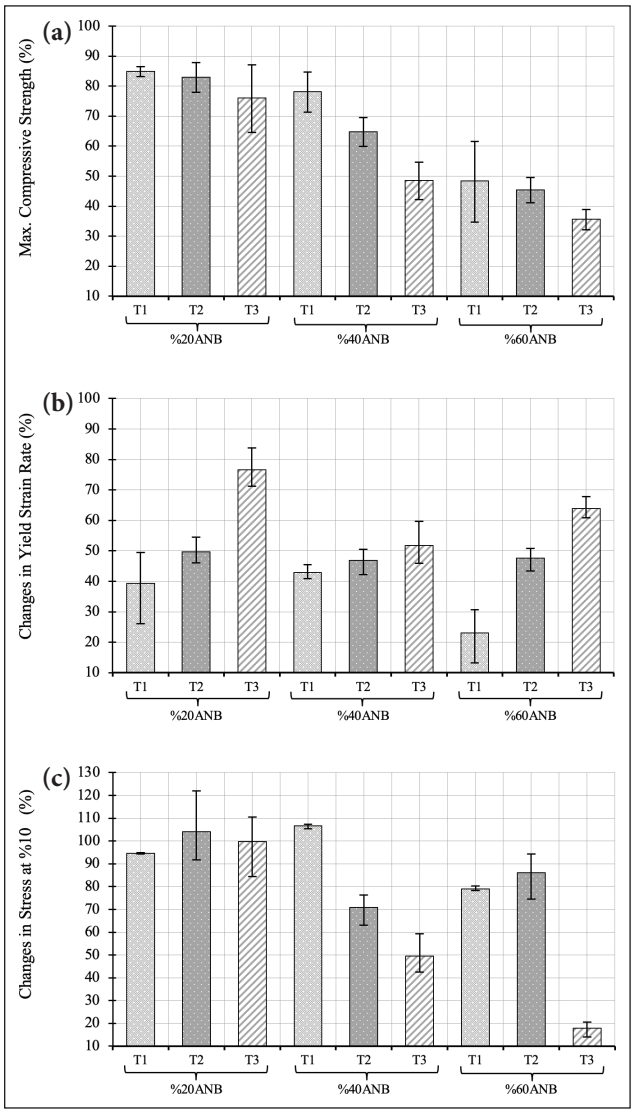

Figure 7. Rate of change in compression properties of Mg foams relative to pure Mg.

CONCLUSIONS

As a result of the study, Mg metal foam was successfully produced by using ANB particles as a space holder. After the evaluation of the data and information obtained from theoretical and experimental studies carried out in accordance with the stated objectives, the results, outcomes, comments, and suggestions of the study are listed below:

- Anhydrous borax was successfully used as a space holder which has not been subjected in the literature before.
- ANB is believed to establish a better MgO_2 layer on the cell wall, so in this case, it has a positive effect for controlling the corrosion rates for porous pure magnesium foams.
- ANB is an easily soluble material in water and could dissolve from the open pores of Mg matrix. The closed cells remain in the matrix is seemed to be covered with a good MgO_2 layer and have no reaction during sintering and very less corrosion dynamics even in 2 years of dry conditions storage.

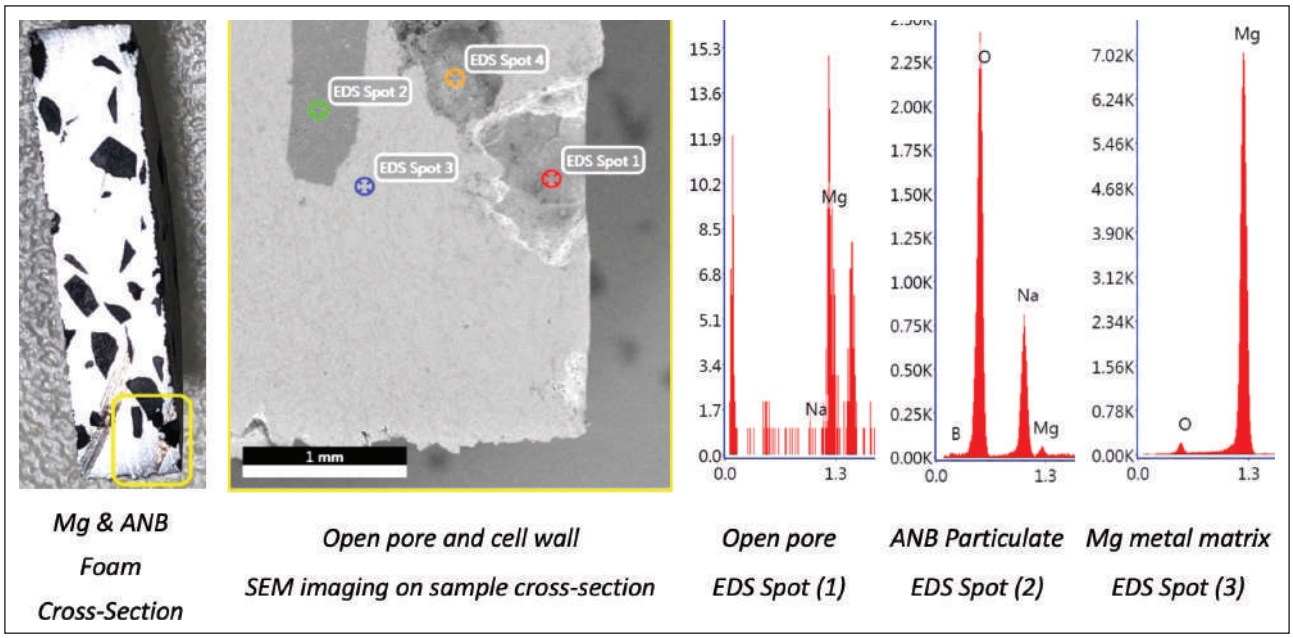

Figure 8. Section of porous Mg foam sample shows metal matrix and open cell.

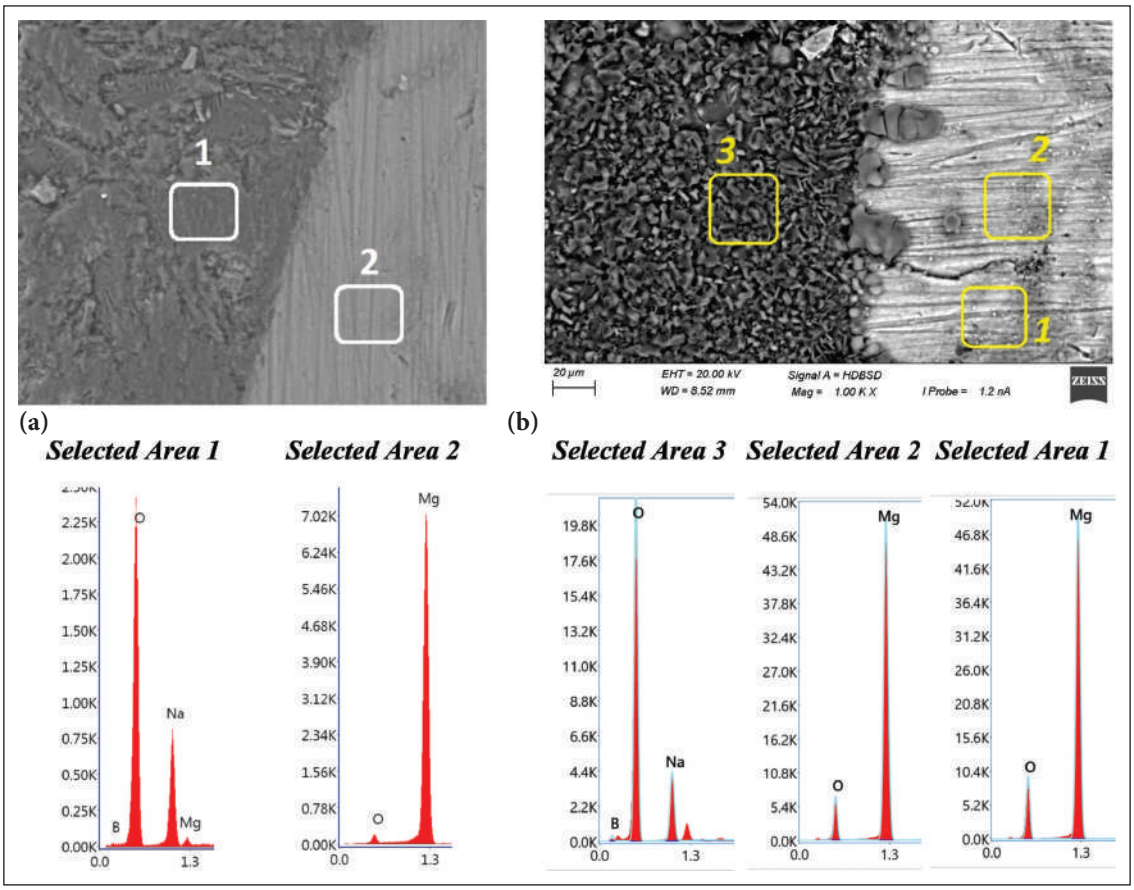

Figure 9. Cross section of Mg & ANB matrix particulate intersection on SEM.

- ANB could be a beneficial additive that has a significantly low chemical reaction with Mg during sintering. For half-closed Mg foam applications, it can be used and eventually dissolve in the implanted site with human body fluids. For this reason, it is thought that it will be useful in bone fixation cases of adult individuals who also suffer from osteoarthritis.
- To manufacture more porous Mg & ANB foams its recommended to do research for making ANB particulates in spherical form.

Data Availability Statement

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

Conflict of Interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Use of AI for Writing Assistance

Not declared.

Ethics

There are no ethical issues with the publication of this manuscript.

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