

Microstructure and Mechanical Behavior of CaCO₃-Doped Al–Al₂O₃ Composite Foams Produced by Powder Metallurgy

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Article Info Received: 25 Jan 2025 Accepted: 27 Feb 2025 Published: 31 Mar 2025 Research Article **Abstract** – In this study, closed-cell composite metal foam production was performed using the powder metallurgy method. Therefore, 7, 12, and 17 wt.% CaCO₃ as a foaming agent was added to the Al–Al₂O₃ powder mixture containing 5 wt.% Al₂O₃ after the grinding process. The CaCO₃-added Al–Al₂O₃ powder mixture was mixed wet and pulverized in a mortar after drying in an oven. Three separate powder mixtures were formed under a pressure of 40 MPa and sintered at 550 °C for 1 h and then at 1000 °C for 4 h. The samples' densities, mineralogical properties, microstructures, adsorption isotherms, and compressive strengths were investigated after sintering. The effects of different CaCO₃ ratios on the mechanical and microstructural properties of the composite metal foam were investigated under specific production conditions. The foam material produced from the mixture with 7 wt.% CaCO₃ added by weight had the highest compressive strength and a more homogeneous pore distribution.

Keywords - Ceramic, metal, composite, foam, powder metallurgy

1. Introduction

Closed-cell aluminum metal foams have a wide research area because of their mechanical strength and impact absorption capacity, such as high compression, bending strength, and damping. [1–4]. In particular, Al alloy closed-cell metal foams are used in automotive and aviation industries [5]. The inner surfaces cannot be reached in closed-cell metal foams because of the isolated pores. The powder metallurgy method is generally used to produce open-cell metal foams [6]. However, studies have also been using the powder metallurgy method to produce closed-cell metal foams [7–9]. Unlike the melting method, sintering with powder metallurgy can prevent the sudden melting of the metal alloy before the release of gas from the foamer. If gas release ends before the metal melts, the melted metal cannot be transferred. The powder metallurgy method has been observed to work even when the metal alloy is in a solid state. The powder metallurgy technique also reduces the gas release temperature of the foamer compared with the metal melting method [10, 11]. CaCO₃, as a foaming agent, is easily available, and its wettability of the Al melt is as good as that of the conventional foaming agent TiH₂ [12]. The metal alloy should not melt before CaCO₃ is wholly calcined. That is, homogeneity can be achieved before most of the gas is release [9]. Therefore, reinforcement can be made with a suitable additive material to increase the melting point of Al metal.

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One such reinforcement is Al₂O₃. Al₂O₃ also provides strength to the metal foams [13]. Lightness increases as the porosity increases in metal foams, but the mechanical properties decrease, and impact absorption properties are negatively affected [14]. However, it is possible to increase both the porosity and mechanical properties [15]. For this reason, reinforcing Al metal foam with Al₂O₃ ceramic and using powder metallurgy techniques can effectively preserve the mechanical strength without reducing the porosity. The biggest problem in metal foam production is the lack of control over process parameters [16]. The powder metallurgy method also allows control of these parameters [17]. In the production of metal foam by the melting method, it is difficult to control the pressure during cooling after mixing the foaming agent into a molten alloy. Thus, deformation often occurs in products. There is no handicap in the powder metallurgy method. In the powder metallurgy method, it is easy to control the pore size distribution and morphology by adding a foaming agent, which is one of the process parameters [18]. Particle sintering via powder metallurgy increases the expansion of the foam, resulting in a more homogeneous porosity and microstructure. [19].

In this study, we aimed to determine and compare the properties of materials with sufficient porosity and strength using different amounts of foaming agents in producing Al-based Al–Al₂O₃ metal composite foams. In the initial composition, where the amount of ceramic material remained constant, the specific changes in the metal/ceramic foam filter were measured as Al increased and the foaming agent decreased or vice versa. The effect of the increase or decrease in Al on the gas release during powder metallurgy can be understood as a result of the characterization tests.

2. Materials and Methods

The raw materials used in the study were commercially available Al powders ($\leq 100 \ \mu$ m), Al₂O₃ powders ($\leq 100 \ \mu$ m), and CaCO₃ powders ($\leq 500 \ \mu$ m). In this study, Al–Al₂O₃ metal foams were produced using the powder metallurgy method. CaCO₃ was used as a foaming agent. The initial compositions of the samples are listed in Table 1. Each sample was coded in a table according to its percentage ratio. AA7C, AA12C, and AA17C refer to Al–Al₂O₃ powder mixture with 7%, 12%, and 17% CaCO₃ by weight, respectively.

Sample code	Raw material (wt.%)		
	Aluminum	Alumina	Calcite
AA7C	88	5	7
AA12C	83	5	12
AA17C	78	5	17

Table 1. Compositions of samples for raw material preparation

Each raw material was weighed on an analytical balance (Shimadzu, Unibloc AUX 320, Kyoto, Japan) according to the composition values, and the samples were ground for homogeneous mixing (Restch RS 200, Haan, Germany). Then, the samples were mixed on a magnetic stirrer (IKA C-MAG HS7, Staufen, Germany), and after being dispersed in a mortar, they were dried at 100°C in a vacuum oven (Nüve EV 018, Ankara, Türkiye). Three separate powder mixtures (Nannenti Mignon S, Faenza, Italy) were pressed at 40 MPa, and two-stage sintering was performed to ensure a porous and durable material formation. In the first stage, sintering was performed for 1 h in air at 550 °C, and in the second stage, sintering was performed for 4 h in air at 1000 °C (Protherm PLF 110/8, Ankara, Türkiye) to obtain the disc-shaped semi-finished products.

Compressive tests were performed on a universal testing machine (Shimadzu AG-XD, Kyoto, Japan) at a 5 mm/min speed, according to ASTM E9-89a. The specimens had a diameter of 57 mm and a length of 7 mm. The pore volumes of the samples were measured using a Brunauer–Emmett–Teller surface area analyzer (Micromeritics Gemini VII, USA). Nitrogen adsorption measurements were performed for all the samples after degassing for 3 h at 300 °C. Mineralogical analyses of the samples were performed using X-ray diffraction

(XRD, PANalytical Empyrean). The phase quantities of the samples sintered at different temperatures were obtained using the PANalytical HighScore Plus software based on the Rietveld method. The samples were scanned using Cu K α radiation in the 2 θ range of 10–80°. Scanning electron microscopy (ZEISS Gemini SEM 500-71-08) was used to evaluate the porosity and morphological changes in the internal structure as a function of the sample composition. The density of each foam was determined based on Archimedes' principle according to the ASTM D 792 standard test method (Metler, Switzerland).

3. Results and Discussion

The maximum compressive strengths of the samples were better than those in the study conducted by Alizadeh and Aliabadi [20] with Al-Al₂O₃ composite metal foams. Similar results were obtained for the compressive strengths of Al metal foams using $CaCO_3$ as a foaming agent by Aboraia et al. [21]. As shown in the compressive stress-displacement diagram in Figure 1, the foam sample obtained from the raw material mixture containing 7 wt. % CaCO₃ had a lower strain rate at the same stress than the other two samples. The maximum stresses and percentage elongations of samples AA7C, AA12C and AA17C are 23.10 MPa (22.24%), 22.67 MPa (32.72%) and 23.12 MPa (29.55%), respectively. In addition, the AA7C sample had a higher stress for the same strain rate. When the $CaCO_3$ ratio increased, the compressive strength decreased at the same strain rate (AA12C), and when it was increased further (AA17C), it increased but remained below the compressive strength of AA7C. Although the strengths of the AA12C and AA17C samples were similar, that of AA7C was different. Therefore, it is beneficial for the CaCO₃ ratio not to exceed the limit of 7% by weight in terms of compressive strength. In addition, the CaCO₃ ratio is 7% by weight compared to the other samples means that the Al ratio is high, and not only the low porosity but also the high Al content is effective at high strength. Higher Al in the initial composition may provide strength, but it may also have caused a mechanism that will delay the completion of melting and provide gas release. In this case, the use of 7 wt. % foaming agent provided the best result in terms of compressive strength. Increasing the foaming agent ratio (> 7% by weight) increased the porosity ratio, causing the final structure to collapse into the cell walls under tension, causing deformation and losing strength [22].



Figure 1. Compressive stress-displacement curves of the samples

Figure 2 shows the nitrogen adsorption isotherms of the samples. According to the IUPAC classification, the adsorption isotherms are type III isotherms [23]. The system does not show significant macro and mesopore formation. At high relative pressure $(0.9 < P/P_0)$, there are distinct hysteresis loops in the samples (AA7C, AA17C) containing high and low CaCO₃. In the AA12C sample, sufficient adsorption could not occur at high pressures. The fact that the adsorption pressure occurs at high volumes, although not at a high rate, shows that adsorption occurs in macropores. It is known that foams containing macropores have sufficient mechanical strength [24]. Although macropores are low, the highest adsorption volume is in the AA7C sample with 28.56 cm^3g^{-1} as shown in the isotherm curves. This is also consistent with the compression test that resulted from the high Al and low CaCO₃ in the initial composition. Although they have similar adsorption volumes, AA17C sample has higher volume ratios (up to $12.28 \text{ cm}^3\text{g}^{-1}$) than AA7C sample at high pressures. Thus, it shows that the porosity of AA17C sample is high, although not much difference. This difference is consistent with the compressive strength in Figure 1. The lower porosity of AA7C sample causes it to be slightly more durable. In addition, although the porosity of AA7C sample is lower than AA17C sample, it is shown that there is not much difference between them in terms of isotherm curves. Thus, a durable Al-Al₂O₃ metal-based foam can be obtained without reducing the porosity too much. The fact that there is a less curved cycle in the isotherm curve of AA7C sample at high pressure $(0.9 < P/P_0)$ compared to AA17C sample indicates that the pore distribution of AA7C sample is homogeneous, and there are similar-sized pores.



Figure 2. Nitrogen adsorption isotherm curves of samples containing CaCO3 and Al in different ratios

The quantitative analysis results of the metal-ceramic foams prepared with different proportions of the foaming agent are shown in Table 2. In the AA7C sample, which is rich in Al compared to the other samples in the initial composition, Al is converted to corundum at a higher rate than in the different samples. This result also explains the reason for the highest compressive strength in the stress-strain curve shown in Figure 1. In addition, the AA7C sample had the lowest porosity according to the adsorption isotherms. The high level of corundum and low porosity compared with the other samples result from the high compressive strength. The presence of corundum indicates that the crystallization is complete, sufficient time is provided for gas release, and the sudden melting of Al in the initial composition eliminates the negativity. The high melting temperature of corundum delayed the complete melting of Al in the matrix, providing sufficient time for gas release. Thus, controllable conditions were provided for optimum metal/ceramic foam production.

Sample	Phase composition (wt.%)					
code	Corundum	Aluminum	Portlandite	Grossite	Calcite	
AA7C	50.4	41.9	2.2	4.7	0.8	
AA12C	42.0	56.7	-	1.2	0.1	
AA17C	42.4	50.9	1.1	5.2	0.4	

Table 2. Quantitative analysis of $Al-Al_2O_3$ foams prepared with different foaming ratios

As shown by the Al peak intensities in Figure 3, the Al ratio in the AA7C sample decreased compared to that in the AA12C and AA17C samples. More Al and less CaCO₃ in the initial composition resulted in a greater corundum transformation. The reactions that occurred due to the increase in the foaming agent ratio must have decreased the amount of corundum. In the Al–Al₂O₃/CaCO₃ system, Al is oxidized and transformed into corundum at high temperatures. As the temperature increased, Al was oxidized, and more corundum was formed. During this time, CaO formed by the decomposition of CaCO₃ reacts with Al₂O₃ in the system to form CaAl₂O₄ [25]. However, in our study, although the temperature was kept constant, more Al in the initial composition of the AA7C sample acted as a catalyst, allowing more corundum to emerge, as shown by the mineralogical analysis results. However, less CaCO₃ in the initial composition of the AA7C sample indicates that CaO reacts with less Al₂O₃ than the other samples, which is another factor explaining why corundum is more abundant in the AA7C sample. In other words, corundum formation can be provided with sufficient porosity to increase the mechanical strength without increasing temperature.



Figure 3. X-ray diffraction (XRD) patterns of the samples

When the AA7C and AA12C samples were compared, increasing the amount of CaCO₃ foaming agent used from 7% to 12% by weight slightly increased the porosity. However, acceptable porosity and high strength required for a foam material were formed in the AA7C sample. However, the fact that Al was lower in the AA7C sample in the mineralogical analysis may create a disadvantage regarding material ductility. However, the difference between the Al contents of the two samples was not as high as the difference between the

strength values. Therefore, the AA7C sample could be evaluated on an industrial scale in terms of both the best strength and acceptable porosity rates.

Figure 4 shows the microstructure images of all the samples. When the SEM images of the AA7C and AA17C samples were examined, it was found that the pores were concentrated in certain regions in the AA17C sample. At the same time, they tended to show a more homogeneous distribution in the AA7C sample.



Figure 4. SEM images of Al–Al₂O₃ metal-ceramic samples using 7% (AA7C), 12% (AA12C) and 17% (AA17C) CaCO₃ by weight as foaming agent

The homogeneous distribution of pores can positively affect the strength of the AA7C sample. The quantitatively high corundum, partially fewer pores, and homogeneous pore distribution explain why the AA7C sample has a higher strength than the AA17C sample. When the microstructure of the AA12C sample

was examined, almost non-existent pores explained why the sample could not show adsorption in the isotherm curves. Although the initial composition of $CaCO_3$ in the AA12C sample has an intermediate rate compared with the other samples, it is understood that the $CaCO_3$ to CaO transformation is not complete. The incomplete gas evolution in the AA12C sample is explained by the high peak intensity of Al in the mineralogical analysis, as shown in Figure 3. This is because reactions that provide sufficient pores do not occur. However, Al was more abundant in the initial AA12C composition. SEM analyses indicated dark grey as the Al phase, light grey as the Al₂O₃ phase, and white as the CaCO₃ phase. The images show that the Al₂O₃ phase is denser in the AA7C sample, and the CaCO₃ phase is denser in the AA17C sample. The Al phase was the matrix phase in all samples.

Table 3 shows the experimental density results of $Al-Al_2O_3$ materials containing different weight ratios of foaming agent and Al. Although there is no obvious density difference between the three samples, the density of the AA7C sample is higher. This result is also consistent with the compressive strength. However, the density in the AA7C sample is not at a level that will have a negative effect on the porosity of the $Al-Al_2O_3$ material. It is not desired for the foams to have a very low density in terms of strength. In addition, the foams are expected to provide sufficient vitrification and crystallization during production, which is unsuitable for very low density. Therefore, although the AA7C sample is higher, all samples have acceptable densities for metal foams [15].

Table 3. Densities of samples at different initial compositions

Sample	Density (gr/cm ³)	
AA7C	2.71	
AA12C	2.65	
AA17C	2.63	

4. Conclusion

Using the powder metallurgy method, closed-pore metal-based foam production can be achieved with ceramic additives and sufficient foaming agents. The AA7C sample provides sufficient properties for the production of metal-based ceramic-added foams with a high corundum phase formed as a result of crystallization, a 23.10 MPa compressive strength with a small displacement of 1.5 mm, sufficient density, low macroporous content, high adsorption volume at high pressure, and homogeneous pore distribution, especially without the need for an increase in temperature. It was revealed that the closed pore structure of the foam does not create any obstacles in gas release without melting. In addition, the low CaCO₃ ratio in the Al–Al₂O₃ structures causes CaO to react with less Al₂O₃ and acts as a catalyst to convert more Al into Al₂O₃.

Author Contributions

This paper is derived from the first author's master's thesis supervised by the second author. The first author proposed the study and wrote the manuscript. The second author designed and performed the experiments. They all read and approved the final version of the paper.

Conflict of Interest

All the authors declare no conflict of interest.

Ethical Review and Approval

No approval from the Board of Ethics is required.

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