

The effect of calcium on the type of intermetallic phases obtainable in the Al-Cu powder system and the microstructure

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Abstract

This study utilized aluminum, copper powder according to the stoichiometric ratio of Al₂Cu, and calcium powder in relation to the eutectic composition of Al-Ca at the ratio of 5.5 atomic percent. Two samples were prepared, one without calcium and another with calcium, and were analyzed to determine the impact of calcium on the formation of copper aluminide. Samples were subjected to thermal treatment at temperature of 400, 600, and 800°C. The obtained results indicated that disappearance of Al₂Cu phase at 800°C in calcium-free sample and existence of Al₂Cu phase in calcium sample indicating a possible role of calcium in stabilization of Al₂Cu phase. Furthermore, it was concluded that calcium influences phase formation. There was higher diffusion of aluminum in to copper resulting in formation of Al₄Cu₉ not only in the sample with calcium, but also in calcium-free sample. One more finding of the research is that calcium influences microstructure and its homogenization as well. In particular, it was found that calcium-containing sample has the least number of pores and was uniform in the structure.

Keywords: Copper, Aluminum, Calcium, Elemental powders, Microstructure.

Introduction

Aluminium-copper (Al-Cu) alloys have high strength-to-weight ratio, high toughness, and good aging properties. Their properties enable Al-Cu alloys to be used in many engineering works that require load-bearing [1-3]. Copper-aluminium alloys are used in electrical equipment too. Copper-aluminium alloys have properties, which include excellent corrosion resistance of copper and lightweight features of aluminium as well [4, 5]. This alloy has remarkable efficiency in building construction requiring certain features such as strength, corrosion resistance, and weldability [6]. In the Al-Cu system, various compounds can be produced. Among them, we can mention the compound Al₄Cu₉ (γ₂) with 62.5-69.0% copper and a cubic crystal structure. Also, Al₃Cu₄ (ξ₂) with 55.2-56.3% copper and a monoclinic crystal structure can be produced in this structure. AlCu (η₂) with 49.8-52.3% copper and a monoclinic crystal structure is another compound of this system. θ-Al₂Cu, which has a body-centered tetragonal (BCT) structure in the environment, is also among other compounds that can be produced [7, 8]. Research has shown that when mixtures of copper and aluminum powders are heated to high temperatures, they will experience an increase in volume. This increase in volume is proportional to the amount of aluminum present in the samples. This is explained by the diffusion of aluminum atoms into the copper, leaving a certain number of voids in place of the migrated aluminum [9, 10].

The θ phase (CuAl_2) melts at 591°C . In the stoichiometric ratio of CuAl_2 from elemental aluminum and copper powders, an endothermic peak at the melting temperature of the θ phase is observed in the DSC results. The next two visible peaks are attributed to pre-combustion reactions and the eutectic melting process. The heating rate can affect the number of peaks [11]. Dudina et al. [12] used Cu-10%Al and various methods such as spark plasma sintering (SPS), hot pressing (HP), and pressureless sintering, it has been shown that different phases and microstructures can be produced in this system. The major products included Al_2Cu , Cu_9Al_4 and $\text{Cu}(\text{Al})$, with the $-\text{Cu}_9\text{Al}_4-\gamma$ phase observed in both the Cu-14%Al, and Cu-35%Al molar ratios [13]. Various additives have been used in this powder system. For example, elements such as Ag [14, 15], and Ti [16] have also been used in Al-Cu compounds to improve properties. Calcium is one of the additives used in this system. Calcium is an element that can be used as a suitable substitute for rare earth metals in the composition of Al-Cu casting alloys and increase their fracture resistance properties. Calcium is environmentally friendly and forms a low melting point eutectic with aluminum [17, 18]. The presence of calcium can give better strength to Al-Cu alloys [19]. Calcium has also been able to create a more homogeneous and perfect structure in aluminum alloys [20]. Adding calcium to the aluminum matrix produces more compact interfacial reaction zones [21]. It has also been stated that calcium reduces the corrosion rate of aluminum alloys [22]. It has been reported that calcium can affect the mechanical properties of aluminum alloys in addition to the electrical properties [23]. In the aluminum-calcium system, three eutectic compositions with proportions of 5.5, 66.4, and 80.5 percent calcium are observed [24]. The number of phases that can be produced in the ternary Al-Cu-Ca system is reported to be very diverse compared to its binary system [25].

While an abundance of literature exists on the molten Al-Cu-Ca ternary system, the investigation of the powder system is quite new, particularly regarding how calcium impacts the development of phases and the microstructure during solid-state sintering. Most investigations into powder metallurgy up to now has focused exclusively on the binary mixing of Al and Cu and how they influence the stabilization of intermetallic phases as well as Kirkendall porosity. The innovation of the present research lies in three aspects: (1) the assessment of the influence of calcium on the type of intermetallic phases in Al-Cu powder system in the temperature range of 400 to 800°C ; (2) the exploration of the situation where Al-5.5%Ca eutectic alloy serves as a source of calcium leading to the observation of both the phase formation and the changes in the microstructure; and (3) the provision of quantitative information about the effect of calcium on Al_2Cu as stable intermetallic phase at high temperatures.

Experimental procedure

In this study, aluminum powders (99.5%, $<45\ \mu\text{m}$), copper (99%, $<20\ \mu\text{m}$), and calcium powders (99%, $<40\ \mu\text{m}$) were used. The desired composition was Al_2Cu . Based on the stoichiometry of this composition, the stoichiometric amounts of Al and Cu powders were mixed based on the molar percentages calculated in Table 1. Then, based on the copper-aluminum binary diagram and considering the amount of aluminum available, calcium was added to the second sample. The amount of Ca added was to create a eutectic composition with 5.5% calcium, and Table 1 also shows the calculation of the molar percentages of the elements related to this sample.

Table 1: Molar percentages used for samples containing and without calcium.

Sample	%Al	%Cu	%Ca
Calcium-free	66.67	33.33	.
Calcium-containing	64.18	32.08	3.74

To create a homogeneous mixture, the prepared powder mixture was first mixed for 10 minutes in a ball mill with a ball to powder ratio of 5:1 and at 200 rpm. Then, 2 grams of powder from each powder ratio was pressed into a cylindrical mold with a diameter of 1 cm under a pressure of 2 MPa to create proper contact between the powder particles. The obtained pressed samples were then heated for 5 hours at temperatures of 400, 600, and 800°C under an argon atmosphere in a tube furnace. XRD analysis (Bruker, D8) was used to determine the obtained phases, and SEM-EDX (KYKY, EM8000) was used to examine the microstructure of the samples.

Results and Discussion

As previously stated, the selected stoichiometric ratio was chosen based on the Al_2Cu composition. The calcium percentage was also chosen based on the aluminum-calcium binary diagram shown in Figure 1. At an atomic ratio of 5.5% calcium, a eutectic process is observed that lowers the melting temperature to 613°C . Since the most important step in the production of aluminides is the melting of aluminum [26-31], it was predicted that the effect of calcium on reducing the melting temperature of aluminum could also be effective in the production of aluminide compounds.

Figure 1: Aluminum-calcium binary diagram [32].

where the temperature was much higher (1000°C), the possibility of producing a molten phase was also provided, and eutectic phases with a dendritic structure appeared.

Alam and his colleagues [35] also produced Al_2Cu by the mechanical alloying method. They chose a powder ratio of 33.33 atomic percent Cu for their research. Using a ball mill for 25 hours and heating the samples at 1000 degrees, the production of the Cu_2Al phase was confirmed. Among the copper aluminide compounds that can be formed, Al_2Cu has been reported to have the most negative enthalpy. Therefore, it is stated that the system has a greater tendency to produce this phase compared to others [35].

Aluminum-copper compounds are also used in the strengthening process in the aluminum field. This result has been reported not only through solid dissolution strengthening, but also through the formation of stable and quasi-stable compounds such as Guinier-Preston (GP) zones, θ' (Al_2Cu), and θ (Al_2Cu) [36].

The crystal structure of these phases is given in Figure 2. The θ'' (Al_3Cu) structure is face-centered tetragonal, with a unit cell height approximately twice that of aluminum. θ' (Al_2Cu) has a body-centered tetragonal structure, with the same lattice unit length as the aluminum structure but with a larger C. θ (Al_2Cu) also has the same body-centered tetragonal structure, except that it has less symmetry than the θ' type [37].

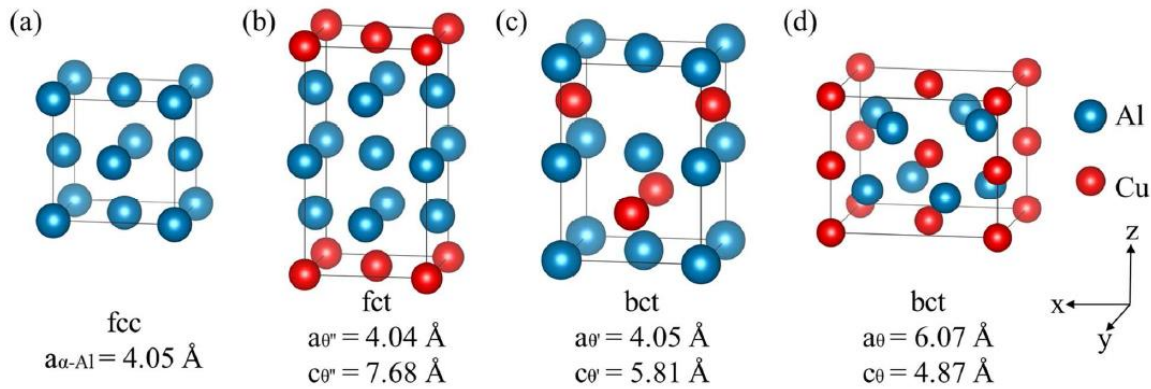


Figure 2: Crystal structures of different phases in the aluminum-rich part of the Al-Cu system. (a) $\alpha\text{-Al}$. (b) θ'' (Al_3Cu), (c) θ' (Al_2Cu), and (d) θ (Al_2Cu). Copper atoms are red and aluminum atoms are blue [37].

In the study by Liu et al., the formation energies of θ'' , θ' and θ were calculated by considering only the vibrational entropy [37]. The results of this study are shown in Figure 3.

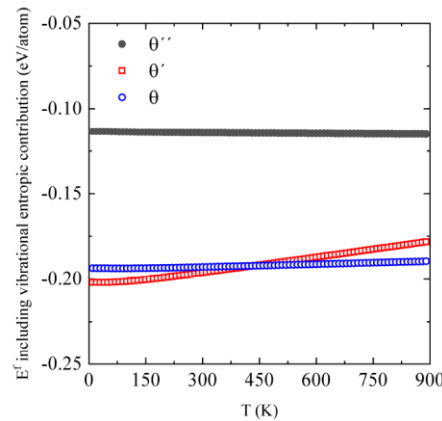


Figure 3. Formation energies θ'' , θ' and θ as a function of temperature, including the vibrational entropy contribution [37].

If the stability of the various copper aluminide phases is examined, it will be found that AlCu2 has the lowest formation energy (Figure 4).

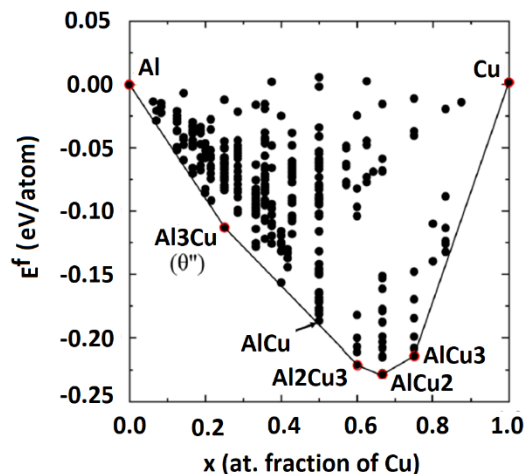


Figure 4. Formation energies of different phases in the Al-Cu system were calculated by DFT [37].

The enthalpy of formation as a function of copper concentration has also been investigated in more detail for Al₂Cu precipitates with different structures [38]. The effect of temperature on the free energy of formation of copper aluminide phases has also been calculated, and the results are shown in Figure 5. It seems that the results obtained in the study of Ouyang and his colleagues [38] are in contradiction with the results obtained in the study of Liu [37]. Because Ouyang introduced the ' θ ' phase as the phase with the minimum formation energy, while in the report of Liu, the θ phase was identified as the most stable phase after a temperature of 450 °C. Perhaps the reason for this can be found in the simplified hypothesis in the study of Liu, which only considered the contribution of vibrational entropy in determining the free energy of formation.

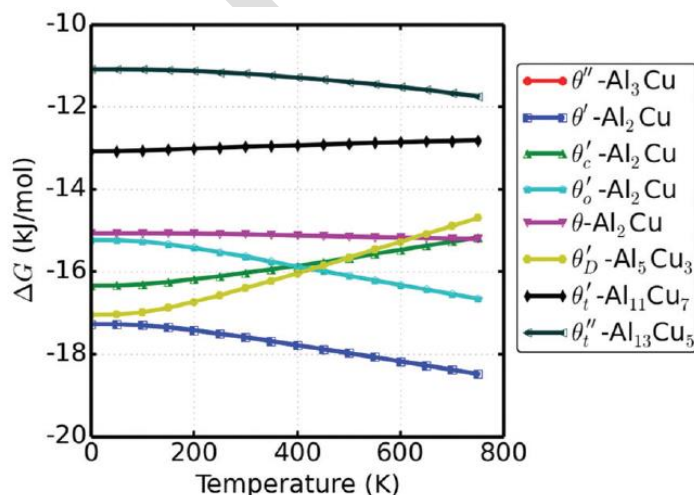


Figure 5. Effect of temperature on the formation energy (calculated free energy of formation of precipitates as a function of temperature) [38].

In the present study, XRD analysis was used to determine the produced compounds. First, the results obtained for the calcium-free sample that was heat treated at temperatures of 400, 600, and 800°C will be examined (Figure 6). It was observed that at 400°C, Al₂Cu, Al₄Cu₉ phases and residual aluminum and

copper are present in the products obtained from heat treatment at this temperature. This means that the reactions are not completed due to the low temperature. It is true that, according to the Gibbs free energy diagram, the formation of copper aluminide compounds of the Al_2Cu phase occupies the lowest free energy (Figure 5). However, due to the nature of powder metallurgy and the possibility of inhomogeneity and composition change in some areas of the sample, as well as due to the different penetration rates of copper in aluminum and aluminum in copper, the initial stoichiometry can change slightly in some powder areas. Therefore, it will be possible to produce other copper aluminide compounds. On the other hand, it has been reported that the kinetics of formation of some phases is faster than Al_2Cu [39, 40]. Therefore, the possibility of other phases in the products is not impossible. At a temperature of 600°C , the main phase seems to be Al_4Cu_9 , with Al_2Cu and AlCu also formed. It is likely that eutectic phases can also be formed at this temperature, which is slightly higher than the melting temperature of Al_2Cu . The melting temperature of Al_2Cu has been reported to be 548 to 550°C [41–43]. At a temperature of 800°C , the final phases observed in the final product included the phases Al_4Cu_9 and Al_2Cu_3 .

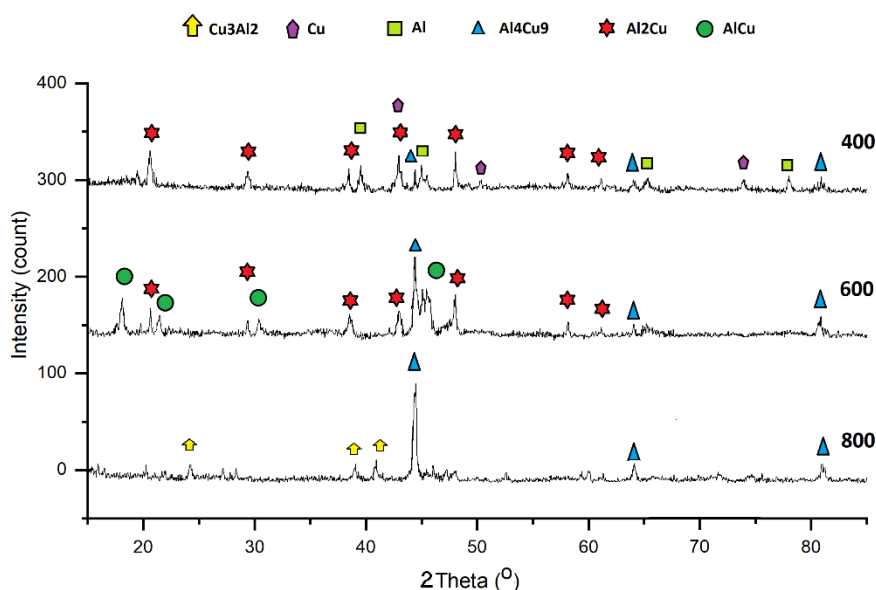


Figure 6: XRD analysis results of calcium-free samples heat-treated at 400 , 600 , and 800°C .

Figure 7 shows the XRD results of calcium-containing samples heat-treated at 400 , 600 , and 800°C . It can be seen that the ternary phases of Al, Cu and Ca were not formed at any temperature. This can be attributed to the low percentage of calcium in the sample.

At 400°C , the Al_2Cu , Al_4Ca phases are formed. However, the presence of residual aluminum and copper indicates that the process is not complete at this temperature. At 600°C , the same phases are formed as before, except that there is no trace of aluminum or copper. This temperature was sufficient to complete the reactions. With an increase in temperature to 800°C , the Al_2Cu phase is the dominant phase, with some Al_2Ca also appearing. It seems that the Al_4Ca phase that was formed at lower temperatures has completely converted to Al_2Ca .

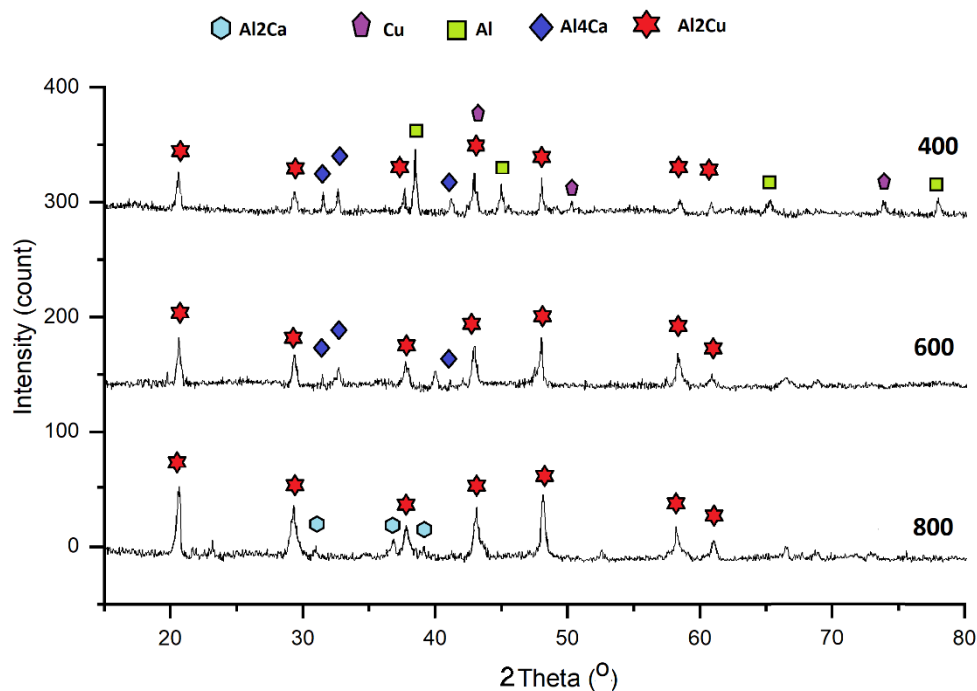


Figure 7: XRD results obtained from calcium-containing samples that were heat-treated at temperatures of 400, 600, and 800°C.

Using HSC software, the stability of the phases that can be produced between aluminum and calcium was investigated (Figure 8). Based on the results obtained in Figure 8, it was determined that the Al_4Ca phase is formed first, and with increasing calcium content, the Al_2Ca phase will be stable. This is confirmed by comparing these results with the results obtained in Figure 7. Calcium also tends to form compounds with copper [44]. However, the lack of production of copper-calcium compounds indicates that in competition, aluminum has a greater tendency to form compounds with calcium than copper.

Previous studies have shown that calcium can affect the stability of the Al_2Cu phase and form ternary phases Al-Cu-Ca [45-47]. However, in the present study, these ternary compounds were not formed. Incidentally, the presence of calcium made Al_2Cu stable at all three temperatures of 400, 600, and 800°C, while in the calcium-free sample, Al_2Cu was not observed in the products at 800. This could be due to the presence of calcium and its positive effect on the formation and stabilization of Al_2Cu .

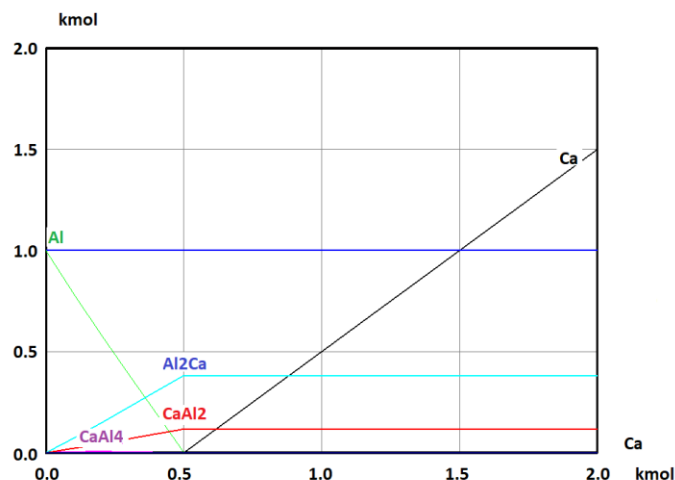
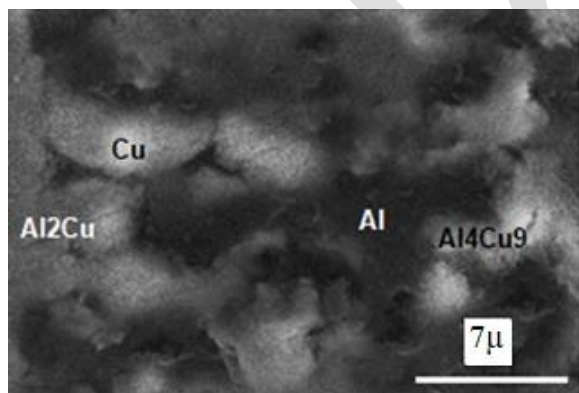
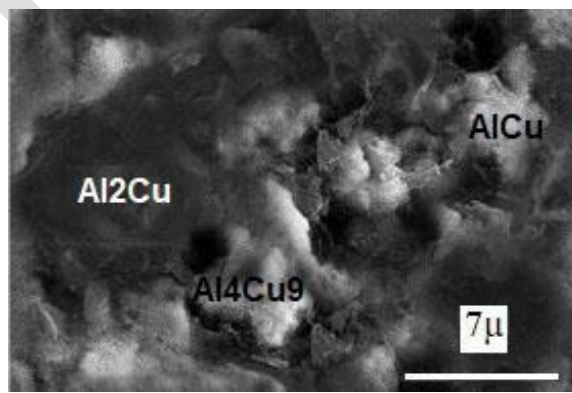


Figure 8: Study of intermetallic compounds that can be produced in the aluminum-calcium system obtained with the help of HSC software.

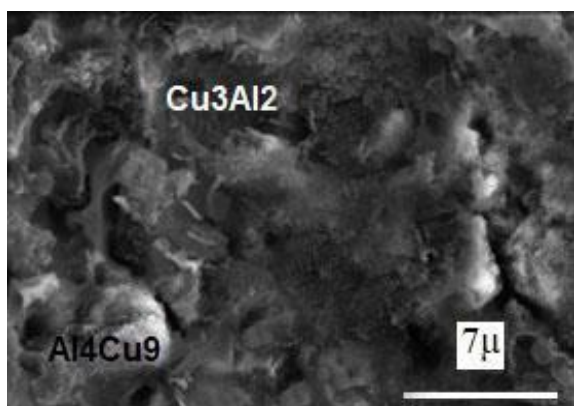
Next, the microstructure of the calcium-free sample that has been heat treated at temperatures of 400, 600, and 800 °C (Figure 9) is examined. As can be seen in this figure, the intermetallic phases Al_2Cu and Al_4Cu_9 are seen in the background. The remaining aluminum and copper are also visible in the structure. With the temperature to 600°C, the AlCu phase also forms in the structure, and there is no longer any trace of the remaining elemental phases. Upon reaching a temperature of 800 degrees, no trace of Al_2Cu is visible, but the Al_2Cu_3 phase has formed.



400



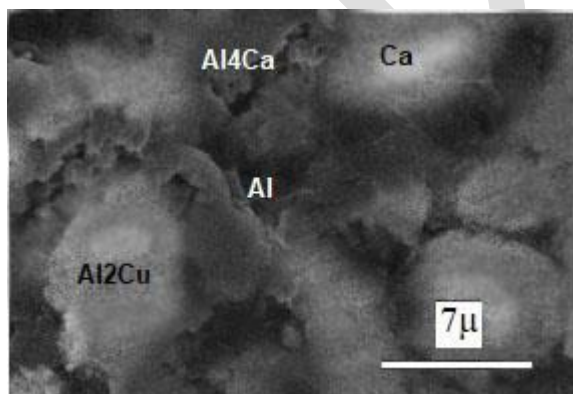
600



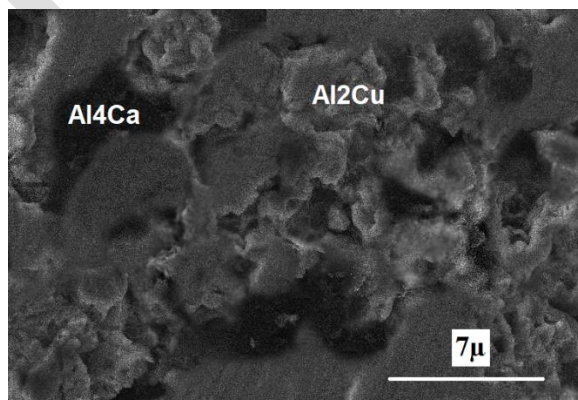
800

Figure 9: Microstructure of a calcium-free sample that has undergone heat treatment at temperatures of 400, 600, and 800°C.

As a result, SEM obtained from the calcium-containing sample that was heat treated at temperatures of 400, 600, and 800°C (Figure 10) shows that at 400 degrees Celsius, Al_2Cu and Al_4Ca are formed. Of course, unreacted aluminum and copper are also observed in the products. With the temperature at 600°C, no trace of the remaining elemental phases is observed. Finally, upon reaching a temperature of 800 degrees, the Al_2Cu phase is the dominant phase, although Al_2Ca is also visible in the grain boundary regions. It seems that the formation of Al_2Ca at the Al_2Cu grain boundary has been able to prevent further copper penetration and the formation of copper-rich phases. Also, the homogeneity of the structure at a temperature of 800 degrees confirms that calcium has probably been able to minimize the effects of the Kirkendall phenomenon.



400



600

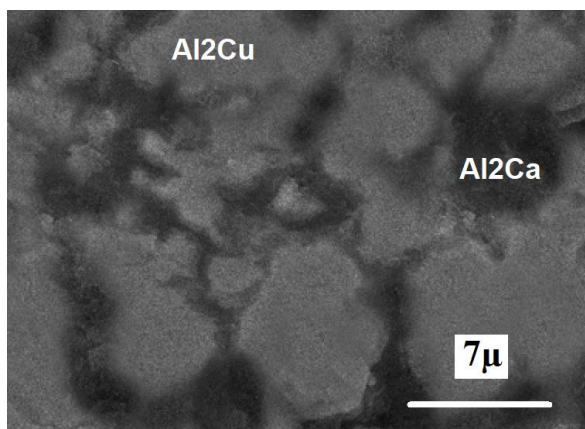


Figure 10: Microstructure of a calcium-containing sample that has undergone heat treatment at temperatures of 400, 600, and 800°C.

800

Now it is necessary to compare the results of the present study with previous studies: Wang et al.[4] used a temperature of 450°C for 30 minutes for the heat treatment of the aluminum-copper system. It was found that this time and temperature were not sufficient for the formation of Al and Cu intermetallic compounds. In comparison, in the present study, at a temperature of 400°C, the intermetallic phases Al_2Cu and Al_4Cu_9 were formed, which could be related to the long time of 5 hours used in the present study.

Rajasekhar et al.[48] evaluated percentages between 5% and 15% by weight of copper. They found that with 10% by weight of copper, good interfacial microstructure, microclusters, and relative density could be achieved. In contrast, Rashad et al.[49] found that the hardness and wear resistance of copper increased with increasing aluminum content. It seemed that the results of the present study were also in this direction. Because with the formation of a copper-rich phase (Al_4Cu_9) at a temperature of 600°C, considering that this phase has high hardness, it is expected that the hardness of the samples would have increased.

Ying et al.[13] have investigated the reaction of aluminum and copper in the solid state. For this purpose, mechanical alloying and subsequent heat treatment have been used. It has been found that for a powder ratio of Cu–14at.%Al, the $\theta\text{-CuAl}_2$ or $\gamma\text{-Cu}_9\text{Al}_4$ phase is formed first. While for a powder ratio of Cu–35at.%Al, the first phase was $\theta\text{-CuAl}_2$. In the present study, in addition to Al_2Cu , the Al_4Cu_9 phase has also been formed, which has become the dominant phase with an increase in temperature to 600°C.

Ren and his colleagues [50] have studied the liquid-solid reaction of copper and aluminum. They have shown that Al_2Cu and AlCu are the two main phases that can be produced in this system. With increasing temperature, the thickness of Al_2Cu increases and finally it transforms into AlCu phase. However, in the present study, the Al_2Cu phase is not observed at 800°C. The reason for this difference is probably that in Ren's study, a solid-liquid reaction was used, in which the mechanisms and diffusion rate are completely different from the solid state.

Zhao et al. [51] studied the reaction between copper and aluminum in the temperature range of 600 to 800°C. They reported that the intermetallic compound Cu_3Al_2 was formed with a larger thickness and Cu_3Al with a smaller thickness. They reported the formation of the phases in the following order: first, the Cu_9Al_4 phase was formed. Then CuAl and then Cu_3Al_2 , which finally converted to Cu_3Al . Ying et al.[13] also showed that the $\gamma_1\text{-Al}_4\text{Cu}_9$ phase was formed after 5.5 hours of milling. By increasing the milling time to 90 hours, the Al_2Cu phase could be produced. Of course, at low temperatures, more Al_2Cu was observed because it was stated that $\gamma_1\text{-Al}_4\text{Cu}_9$ is thermally unstable. Relatively speaking, the same sequence was observed in the formation of Al_4Cu_9 and its conversion to Al_2Cu_3 in the present study.

There is little research available on the ternary system Ca-Al-Cu. In one study by Akopyan et al. [25], high-aluminum compositions were used. In a study by Xingwen et al. [52], it was shown that in the range of 0.5 to 2.0 wt% Ca, Al_2Cu Al_8CaCu_4 phases were formed at 800 °C. AKOPYAN et al. [53] reported that $\text{Al}_8\text{CaCu}_4 + \text{Al}_2\text{Cu}$ phases were formed in the copper-rich region.

In the copper-rich and calcium-poor region, $\text{Al}_8\text{CaCu}_4 + \text{Al}_2\text{Cu}$ phases have been reported. It has been stated that the Al_8CaCu_4 phase is very hard and has a high coefficient of thermal expansion, and calcium can also replace and substitute for aluminum[53]. The reason why no ternary compound was formed in the present

study is that this can be attributed to the type of heat treatment, the local percentage of calcium, or the tendency of calcium to form a compound with aluminum compared to forming a ternary compound.

Research has also shown that as the sample is heated and the temperature rises to temperatures below the melting point of aluminum, copper, due to its smaller atoms, penetrates more into the aluminum particles than aluminum despite the melting point [54]. It is probably by this mechanism that the Al_2Cu phase is formed. Based on the results obtained from the research conducted by Junge and his colleagues [55], it has also been obtained that aluminum penetrates more into copper than copper into aluminum.

Therefore, with the penetration of aluminum into copper in the first step, a phase with a higher molar percentage of copper is formed. For this reason, at temperatures of 400 and 600°, we witness the formation of the Cu_9Al_4 phase. Of course, at the interface of this phase and aluminum, the possibility of producing the Al_2Cu phase is also provided. The formation of this phase is probably related to the low free energy of formation of this phase.

Similar to the results obtained in this study, it has been observed that $\theta\text{-Al}_2\text{Cu}$ is formed first, and then $\gamma_2\text{-Al}_4\text{Cu}_9$ is formed [56] and finally AlCu can be formed. It has been stated that the activation energy of Al_2Cu formation is lower than the other $\text{AlCu} + \text{Al}_3\text{Cu}$ and Al_4Cu_9 layers [57].

Conclusion

In this study, the powder ratio of aluminum, copper, with a stoichiometric ratio of Al_2Cu , and calcium was investigated based on the eutectic composition of Al-Ca with an atomic ratio of 5.5. A sample containing calcium and a sample without it were prepared to evaluate the effect of calcium on the formation of copper aluminide. Temperatures of 400, 600, and 800°C were used for heat treatment.

It was observed that, considering the removal of Al_2Cu at 800°C in the calcium-free sample and the presence of the dominant Al_2Cu phase in the calcium-containing sample, calcium could probably have a stabilizing effect on the formation of the Al_2Cu phase. It was also found that calcium could change the sequence of phases. Due to the greater penetration of aluminum into copper, the Al_4Cu_9 phase was produced in both the calcium-containing and calcium-free samples.

Another result of this study was the effect of calcium on the microstructure and its homogenization. In the calcium-containing sample, the number of pores was minimized, and a uniform structure was achieved.

From a practical and engineering perspective, adding calcium can control phase stability and microstructure. In comparison to using rare earth metals, this is considered to be a more affordable option providing similar efficiency in terms of the performance of Al-Cu alloys. The alloy Al-5.5%Ca used in the research works properly owing to its melting point of 613 °C which helps to carry out the experiments without losses of calcium.

References

- [1] I. J. Polmear and M. J. Couper, "Design and development of an experimental wrought aluminum alloy for use at elevated temperatures," *Metallurgical Transactions A*, vol. 19, no. 4, pp. 1027-1035, 1988.
- [2] S. Mondol, S. Kashyap, S. Kumar, and K. Chattopadhyay, "Improvement of high temperature strength of 2219 alloy by Sc and Zr addition through a novel three-stage heat treatment route," *Materials Science and Engineering: A*, vol. 732, pp. 157-166, 2018/08/08/ 2018, doi: <https://doi.org/10.1016/j.msea.2018.07.003>.
- [3] L. Bourgeois, C. Dwyer, M. Weyland, and J. Nie, "Structure and energetics of the coherent interface between the θ' precipitate phase and aluminium in Al-Cu," *Acta Materials*, vol. 59, pp. 7043–7050, 2011.

- [4] Y. Wang *et al.*, "Effect of Cu–Al Ratio on Microstructure and Mechanical Properties of Cu–Al Alloys Prepared by Powder Metallurgy," vol. 14, no. 9, p. 978, 2024. [Online]. Available: <https://www.mdpi.com/2075-4701/14/9/978>.
- [5] J.-F. Nie, "Physical Metallurgy of Light Alloys," in *Physical Metallurgy (Fifth Edition)*, D. E. Laughlin and K. Hono Eds. Oxford: Elsevier, 2014, pp. 2009-2156.
- [6] M. Gurram, K. Adepu, R. R. Pinninti, and M. R. Gankidi, "Effect of copper and aluminium addition on mechanical properties and corrosion behaviour of AISI 430 ferritic stainless steel gas tungsten arc welds," *Journal of Materials Research and Technology*, vol. 2, no. 3, pp. 238-249, 2013/07/01/ 2013, doi: <https://doi.org/10.1016/j.jmrt.2013.02.009>.
- [7] T. Solchenbach, P. Plapper, M. Greger, J.-L. Biagi, J. Bour, and J. A. S. Bomfim, "Thermal and electrical aging of laser braze-welded aluminum–copper interconnects," *Translational Materials Research*, vol. 1, no. 1, 2014.
- [8] G. Liu, M. Gong, D. Xie, and J. Wang, "Structures and Mechanical Properties of Al–Al₂Cu Interfaces," *JOM*, vol. 71, no. 4, pp. 1200-1208, 2019/04/01 2019, doi: 10.1007/s11837-019-03333-x.
- [9] P. Dhayea, Z. Abdulwahid, and S. Omran, "The Effect of Heat Treatment for Alloys (Aluminum - Copper) on some Mechanical Properties," *Solid State Phenomena*, vol. 345, pp. 13-22, 07/28 2023, doi: 10.4028/p-p5DpGy.
- [10] A. V. Laptev, "Theory and technology of sintering, thermal and chemicothermal treatment," *Powder Metallurgy and Metal Ceramics*, vol. 46, no. 7, pp. 317-324, 2007/07/01 2007, doi: 10.1007/s11106-007-0051-3.
- [11] H. Sina, S. Iyengar, and S. Melin, *Ignition temperatures for Cu–Al and Ni–Al reactions in elemental powder mixtures using Differential Scanning Calorimetry*. 2012, pp. 940-951.
- [12] D. Dudina *et al.*, "Spark Plasma Sintering and Hot Pressing of Cu+Al Powder Mixtures and Pre-Deposited Cu/Al Layers," *Journal of Composites Science*, vol. 7, p. 466, 11/07 2023, doi: 10.3390/jcs7110466.
- [13] D. Y. Ying and D. L. Zhang, "Solid-state reactions between Cu and Al during mechanical alloying and heat treatment," *Journal of Alloys and Compounds*, vol. 311, no. 2, pp. 275-282, 2000/10/26/ 2000, doi: [https://doi.org/10.1016/S0925-8388\(00\)01094-X](https://doi.org/10.1016/S0925-8388(00)01094-X).
- [14] G. Abbas Gohar, T. Manzoor, and A. N. Shah, "Investigation of thermal and mechanical properties of Cu–Al alloys with silver addition prepared by powder metallurgy," *Journal of Alloys and Compounds*, vol. 735, pp. 802-812, 2018/02/25/ 2018, doi: <https://doi.org/10.1016/j.jallcom.2017.11.176>.
- [15] G. A. Gohar *et al.*, "Synthesis and investigate the properties of Cu–Al–Ni alloys with Ag addition using powder metallurgy technique," *Journal of Alloys and Compounds*, vol. 817, p. 153281, 2020/03/15/ 2020, doi: <https://doi.org/10.1016/j.jallcom.2019.153281>.
- [16] Z. Deng, H. Yin, C. Zhang, and W. Li, "Microstructure and mechanical properties of Cu–12 Al–6 Ni with Ti addition prepared by powder metallurgy," *Materials Science and Engineering: A*, vol. 803, p. 140472, 2021/01/28/ 2021, doi: <https://doi.org/10.1016/j.msea.2020.140472>.
- [17] T. K. Akopyan *et al.*, "Effect of high pressure torsion on the precipitation hardening in Al–Ca–La based eutectic alloy," *Materials Science and Engineering: A*, vol. 802, p. 140633, 2021/01/20/ 2021, doi: <https://doi.org/10.1016/j.msea.2020.140633>.
- [18] T. K. Akopyan, N. V. Letyagin, T. y. A. Sviridova, N. O. Korotkova, and A. S. Prosviryakov, "New Casting Alloys Based on the Al+Al₄(Ca,La) Eutectic," *JOM*, vol. 72, no. 11, pp. 3779-3786, 2020/11/01 2020, doi: 10.1007/s11837-020-04340-z.
- [19] W. Zhao, S. He, C. Zhang, Y. Li, Y. Zhang, and G. Dai, "Generation of a Strength Gradient in Al–Cu–Ca Alloy Foam via Graded Aging Treatment," vol. 12, no. 3, p. 423, 2022. [Online]. Available: <https://www.mdpi.com/2075-4701/12/3/423>.

- [20] V. V. Doroshenko, A. A. Aksenov, K. A. Tsydenov, D. M. Strekalina, E. V. Yakushko, and L. E. Gorlov, "Study of the effect of calcium on structure, physicomechanical and technological properties of deformable alloy Al-3%Mg-0.8%Mn," *Metallurgist*, 2024/10/04 2024, doi: 10.1007/s11015-024-01774-7.
- [21] M. Nosko *et al.*, "Effect of Ca addition on interface formation in Al(Ca)/Al₂O₃ composites prepared by gas pressure assisted infiltration," *Materials & Design*, vol. 108, pp. 618-623, 2016/10/15/ 2016, doi: <https://doi.org/10.1016/j.matdes.2016.07.034>.
- [22] S. Haibo, W. Jianming, Z. Zhao, Z. Jianqing, and C. Chunan, "Inhibition Effect of Calcium as an Alloy Element of Aluminum and Its Cooperative Effect with Tartrate in an Alkaline Solution," vol. 61, no. 9, pp. 1420-1424, 2003-09-15 2003. [Online]. Available: https://sioc-journal.cn/Jwk_hxxb/EN/.
- [23] S. Kumari, R. Pillai, and C. Pai, "Role of calcium in aluminium based alloys and composites," *International Materials Reviews*, vol. 50, pp. 216-238, 08/01 2005, doi: 10.1179/174328005X14366.
- [24] O. Madelung, "Phase Equilibria, Crystallographic and Thermodynamic Data of Binary Alloys · Ac-Au – Au-Zr," *Landolt-Börnstein - Group IV Physical Chemistry*, vol. 5A, 1991.
- [25] T. K. Akopyan, N. A. Belov, N. V. Letyagin, S. O. Cherkasov, and X. D. Nguen, "Description of the New Eutectic Al-Ca-Cu System in the Aluminum Corner," vol. 13, no. 4, p. 802, 2023. [Online]. Available: <https://www.mdpi.com/2075-4701/13/4/802>.
- [26] R. Khoshhal and A. Vahid, "Effect of Silicon on the Synthesis of Iron Aluminides from Elemental Powders," *Silicon*, vol. 16, pp. 1-6, 11/14 2023, doi: 10.1007/s12633-023-02739-2.
- [27] R. Khoshhal and A. H. zadeh, "The Formation Mechanism of Iron Aluminide Phases in Fe-Al System with Different Raw Materials Ratio," (in en), *AUT Journal of Mechanical Engineering*, vol. 4, no. 3, pp. 407-414, 2020, doi: 10.22060/ajme.2019.16739.5831.
- [28] R. Khoshhal, H. Mirzaei-Ghasabe, and A. Hosseinzadeh, "The synthesis of a pure FeAl with a density greater than 95% of the theoretical density by optimizing the effective factors," *Amirkabir (Journal of Science and Technology)*, 02/14 2021, doi: 10.22060/AJME.2021.18021.5881.
- [29] R. Khoshhal and S. V. Alavi Nezhad Khalil Abad, "The use of copper as an accelerator for the formation of titanium aluminide intermetallic compounds," (in en), *AUT Journal of Mechanical Engineering*, vol. 7, no. 1, pp. 4-4, 2023, doi: 10.22060/ajme.2023.21934.6050.
- [30] H. Sina, J. Corneliusson, K. Turba, and S. Iyengar, "A study on the formation of iron aluminide (FeAl) from elemental powders," *Journal of Alloys and Compounds*, vol. 636, pp. 261-269, 2015/07/05/ 2015, doi: <https://doi.org/10.1016/j.jallcom.2015.02.132>.
- [31] S. Hossein, "Synthesis of Transition Metal Aluminides from Elemental Powder Mixtures," DOCTORAL DISSERTATION, Faculty of Engineering, Lund University, Sweden 2015.
- [32] H. Okamoto, "Al-Ca (Aluminum-Calcium)," *Journal of Phase Equilibria*, vol. 24, no. 6, pp. 580-580, 2003/12/01 2003, doi: 10.1361/105497103772084750.
- [33] Y. Xiao, H. Besharatloo, B. Gan, X. Maeder, R. Spolenak, and J. M. Wheeler, "Combinatorial investigation of Al-Cu intermetallics using small-scale mechanical testing," *Journal of Alloys and Compounds*, vol. 822, p. 153536, 2020/05/05/ 2020, doi: <https://doi.org/10.1016/j.jallcom.2019.153536>.
- [34] M. Aravind, P. Yu, M. Y. Yau, and D. H. L. Ng, "Formation of Al₂Cu and AlCu intermetallics in Al(Cu) alloy matrix composites by reaction sintering," *Materials Science and Engineering: A*, vol. 380, no. 1, pp. 384-393, 2004/08/25/ 2004, doi: <https://doi.org/10.1016/j.msea.2004.04.013>.
- [35] N. Syed, P. Shrivastava, D. Panda, B. Gunale, K. Susmitha, and P. Pola, "Synthesis of Al₂Cu Intermetallic Compound by Mechanical Alloying," *Materials Today Communications*, vol. 31, p. 103267, 02/01 2022, doi: 10.1016/j.mtcomm.2022.103267.

- [36] I. J. Polmear, *Light Alloys: Metallurgy of the Light Metals (Metallurgy and Material Science Series)*. Edward Arnold, 1989.
- [37] S. Liu, E. Martínez, and J. Llorca, "Prediction of the Al-rich part of the Al-Cu phase diagram using cluster expansion and statistical mechanics," *Acta Materialia*, vol. 195, pp. 317-326, 2020/08/15/ 2020, doi: <https://doi.org/10.1016/j.actamat.2020.05.018>.
- [38] Y. F. Ouyang, H. M. Chen, X. M. Tao, F. Gao, Q. Peng, and Y. Du, "A first-principles study of the structural, mechanical and electronic properties of precipitates of Al₂Cu in Al–Cu alloys," *Physical Chemistry Chemical Physics*, 10.1039/C7CP06757G vol. 20, no. 2, pp. 967-976, 2018, doi: 10.1039/C7CP06757G.
- [39] Y. Guo, G. Liu, H. Jin, Z. Shi, and G. Qiao, "Intermetallic phase formation in diffusion-bonded Cu/Al laminates," *Journal of Materials Science - J MATER SCI*, vol. 46, pp. 2467-2473, 04/01 2011, doi: 10.1007/s10853-010-5093-0.
- [40] A. O. Rodin and N. Goreslavets, "Formation of Intermetallic Compounds in Al-Cu System. Effect of Initial State.," *preprint*.
- [41] A. Lombardi, D. Sediako, C. Ravindran, and M. Barati, "Analysis of precipitation, dissolution and incipient melting of Al₂Cu in B206 Al alloy using in-situ neutron diffraction," *Journal of Alloys and Compounds*, vol. 784, pp. 1017-1025, 2019/05/05/ 2019, doi: <https://doi.org/10.1016/j.jallcom.2019.01.104>.
- [42] A. Lombardi, W. Mu, C. Ravindran, N. Dogan, and M. Barati, "Influence of Al₂Cu morphology on the incipient melting characteristics in B206 Al alloy," *Journal of Alloys and Compounds*, vol. 747, pp. 131-139, 2018/05/30/ 2018, doi: <https://doi.org/10.1016/j.jallcom.2018.02.329>.
- [43] T. Massalski, "The Al–Cu (Aluminum-Copper) system," *Bulletin of Alloy Phase Diagrams*, vol. 1, pp. 27-33, 09/01 1980, doi: 10.1007/BF02883281.
- [44] M. F. J. Boeije, E. K. Delczeg-Czirjak, N. H. van Dijk, O. Eriksson, and E. Brück, "On the phase stability of CaCu₅-type compounds," *Journal of Alloys and Compounds*, vol. 722, pp. 549-554, 2017/10/25/ 2017, doi: <https://doi.org/10.1016/j.jallcom.2017.06.134>.
- [45] N. Belov, T. Akopyan, K. Tsydenov, T. Sviridova, S. Cherkasov, and A. Kovalev, "Effect of Ca addition on structure, phase composition and hardness of Al–6 %Cu–2 %Mn sheet alloy," *Journal of Alloys and Compounds*, vol. 1009, p. 176955, 2024/12/25/ 2024, doi: <https://doi.org/10.1016/j.jallcom.2024.176955>.
- [46] T. Gopalakrishnan, S. R. Sankaranarayanan, and S. P. Babu, "Investigating the Effect of Calcium Addition on the Microstructural and Mechanical Properties of a Zn-Al-Cu-Mg Alloy via Squeeze Casting," *Metals*, vol. 15, no. 8, p. 922doi: 10.3390/met15080922.
- [47] W. Monnens *et al.*, "Substrate-dependent calcium plating on late-transition and p-block metals," *Royal Society of Chemistry*, vol. 2, pp. 700-708, 2026.
- [48] K. Rajasekhar, V. Suresh Babu, and M. J. Davidson, "Interfacial microstructure and properties of Al-Cu functionally graded materials fabricated by powder metallurgy method," *Materials Today: Proceedings*, vol. 46, pp. 9212-9216, 2021/01/01/ 2021, doi: <https://doi.org/10.1016/j.matpr.2020.01.401>.
- [49] M. Rashad, F. Pan, and M. Asif, "Room temperature mechanical properties of Mg–Cu–Al alloys synthesized using powder metallurgy method," *Materials Science and Engineering: A*, vol. 644, pp. 129-136, 2015/09/17/ 2015, doi: <https://doi.org/10.1016/j.msea.2015.07.061>.
- [50] Y. Ren, J. Chen, and B. Zhao, "Mechanism Behind Al/Cu Interface Reaction: The Kinetics and Diffusion of Cu in Forming Different Intermetallic Compounds," in *Light Metals 2021*, Cham, L. Perander, Ed., 2021// 2021: Springer International Publishing, pp. 100-104.
- [51] D. Zhao, W. Guo, Z. Shang, C. Xu, X. Gao, and X. Wang, "The growth behavior and kinetics of intermetallic compounds in Cu–Al interface at 600°C–800 °C," 2024. [Online]. Available:

https://ro.uow.edu.au/articles/journal_contribution/The_growth_behavior_and_kinetics_of_intermetallic_compounds_in_Cu_Al_interface_at_600_C_800_C/27818748.

- [52] W. Xingwen *et al.*, "Effect of Calcium Addition on the Aluminum Alloy A201 Foam," *Advanced Engineering Materials*, vol. 26, 04/09 2024, doi: 10.1002/adem.202302093.
- [53] T. K. AKOPYAN, T. A. SVIRIDOVA, N. A. BELOV, N. V. LETYAGIN, and A. V. KOROTITSKIY, "Intermetallic compounds in equilibrium with aluminum in Al-Ca-Cu ternary alloying system," *Transactions of Nonferrous Metals Society of China*, vol. 34, no. 5, 2024.
- [54] K. Liu, H. Yu, X. Li, and S. Wu, "Study on diffusion characteristics of Al-Cu systems and mechanical properties of intermetallics," *Journal of Alloys and Compounds*, vol. 874, p. 159831, 2021/09/05/2021, doi: <https://doi.org/10.1016/j.jallcom.2021.159831>.
- [55] J. Junge, S. Brechelt, H. Wiche, V. Wesling, and H. Schmidt, "Aluminium Diffusion in the Copper-Based Alloy CuCr1Zr as an Electrode for Resistance Spot Welding," in *Preprints*, ed: Preprints, 2025.
- [56] K. K. Wang, "The orientation relationships and interfaces of θ -Al₂Cu/Cu and γ 2-Al₄Cu₉/Cu and the formation sequence of θ -Al₂Cu and γ 2-Al₄Cu₉ at the Cu/Al interface. ," *Thin Solid Films* vol. 717, 2021, doi: <https://doi.org/10.1016/j.tsf.2020.138436>.
- [57] C.-Y. Chen and W.-S. Hwang, "Effect of Annealing on the Interfacial Structure of Aluminum-Copper Joints," *Materials Transactions - MATER TRANS*, vol. 48, pp. 1938-1947, 07/01 2007, doi: 10.2320/matertrans.MER2006371.