EFFECT OF FLUX COATING ON INTERFACIAL MICROSTRUCTURE IN BIMETALLIC Al7SiMg/Cu COMPOUND CASTINGS

*Aina Opsal Bakke[1], Yanjun Li[1], Jan-Ove Løland[2], Svein Jørgensen[2], and Jan Kvinge[2]

[1]Norwegian University of Science and Technology
Trondheim, Norway
(*Corresponding author: aina.o.bakke@ntnu.no)

[2]Benteler Automotive Farsund
Farsund, Norway

ABSTRACT

Compound casting is a very attractive approach to reduce the weight of components for some specific applications while keep both the functional and the mechanical property requirements. In this work, Al-7Si-Mg alloy /copper compound castings were produced through a low pressure die casting process. To reduce the oxide present in the interface, flux coating of the copper pipes was tested. The interface layer formed between the two alloys was investigated using Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Vickers Micro-hardness was also measured across the interface. Results showed that the flux coating prevented the formation of the metallic bond between copper and aluminum. Instead, high concentrations of potassium, magnesium and fluoride, coinciding with formation of $KMgF_3$ and MgF_2, were detected in the interface. In the castings without surface treatment, a continuous metallurgical bond was achieved. In the bond layer, various Al-Cu intermetallic phases have been detected. In addition, formation of primary silicon particles in the reaction layer was observed in all castings. The mechanism for the formation of the intermetallic phases and the strength of the interface layer have been discussed.

KEYWORDS

Aluminum alloys, Compound casting, Flux coating

INTRODUCTION

Recent development in the automotive industry has focused on producing lightweight components, which can reduce CO_2 emission and increase the efficiency. Often, one material alone is not able to meet the requirements for a specific use. The need for lightweight bimetallic components has therefore increased. Aluminum-copper bimetallic components can be used in wires and bus bars where conductivity is an important factor (Lee, Bang, & Jung, 2005). Compared to Al-Cu alloys, Al-Cu bimetallic components can reduce both weight and cost without reducing electrical and thermal conductivity (Sheng, Yang, Xi, Lai, & Ye, 2011). A challenge is, however, that aluminum and copper have high affinity to each other, especially at elevated temperatures. This causes formation of brittle intermetallic phases with high electric resistance (Liu, Wang, Sui, Wang, & Wenjiang, 2016). In addition, both metals are subjected to oxide formation on the surface. Copper is especially exposed to oxidation at elevated temperatures (Pinnel, Tompkins, & Heath, 1979), while a thermodynamically stable oxide layer will spontaneously form on the aluminum surface (Papis, Loeffler, & Uggowitzer, 2009). Oxides are known to be passive substrates, which will reduce wettability and will thus prevent the formation of metallic bonding between aluminum and copper (Papis, Hallstedt, Löffler, & Uggowitzer, 2008).

Several processes have been used to join aluminum and copper, such as friction stir welding (Abdollah-Zadeh, Saeid, & Sazgari, 2008) (Xue, Ni, Wang, Xiao, & Ma, 2011), cold roll bonding (Lee, et al., 2013), explosive welding (Honarpisheh, Asemabadi, & Sedighi, 2012) and diffusion bonding (Eslami & Taheri, 2011). Despite several of these processes creating sound bonding between aluminum and copper, they often require long process time and have specific geometrical requirements, making them less cost-effective for massive industrial production (Hajjari, et al., 2011).

Compound casting is a way of joining two metals, one in solid and one in liquid state. The solid material is pre-inserted in the mold with the liquid subsequently being poured around it. A diffusion layer will form between the two materials, creating a continuous metallurgical bonding. This process allows production of complex geometries, as well as the direct insertion of the solid material reducing a process step. This increases the process efficiency and lowers cost (Tayal, Singh, Kumar, & Garg, 2012). The study of Zare, Divandari and Arabi (2013) on Al/Cu compound casting showed that metallurgical bonding with formation of intermetallic phases could only form locally at the interface. A large fraction of the interface areas had gaps due to the oxide film forming on the aluminum melt. It was concluded that as the melt is poured, shear stress from the melt convection would be able to remove oxides in certain areas, which resulted in metal-metal contact and metallurgical bonding. To reduce oxides on the copper surface, Liu et al. used thermal spray coating of zinc on the copper pipes. This resulted in a continuous metallurgical bond at the interface. The intermetallic phases formed at the interface were determined as Al_4Cu_9 and Al_2Cu. 700°C was deemed preferable pouring temperature as lower temperatures caused segregation of zinc in the interface, while a higher temperature resulted in a thicker intermetallic layer (Liu, Wang, Sui, Wang, & Wenjiang, 2016).

This research focuses on the formation and characterization of the interface between an Al7SiMg alloy and copper. The possibility of reducing surface oxides was tested by applying a flux coating on the copper pipes prior to casting. The effect of the flux coating on bonding and formation of intermetallic phases was investigated.

MATERIALS AND METHOD

Bimetallic Al/Cu compound castings were produced by Benteler Automotive Farsund (now named Chassix Norway) through a low-pressure die casting process (named VCR/PRC) using commercially pure copper and A356 aluminum alloy. The chemical compositions of the experimental A356 alloy are presented in Table 1.

Table 1. Chemical composition of alloy A356

AA Alloy	Composition [wt%]								
	Si	Mg	Ti	Fe	Sr	Ga	Zn	Others	Al
A356.0	7.0	0.41	0.11	0.082	0.013	0.0089	0.0042	0.0029	Bal.

Copper pipes with 10 mm diameter and 0.8 mm wall thickness, thoroughly cleaned with ethanol were used for the compound casting. Flux coating was in addition applied to some of the cooper pipe inserts. NOCOLOK® Cs Flux, which is a mixture of $K_{1-3}AlF_{3-6}$ and $CsAlF_4$, was mixed with denatured alcohol to an alcohol/flux ratio of approximately 7.9. The mixture was then painted on the copper pipes using a small paint brush. The flux has a melting range of 558–566°C (GmbH). Both the flux coated and uncoated copper pipes were preheated to approximately 200°C before they were placed in a metal mold, as illustrated in Figure 1. Liquid A356 aluminum alloy was received from the smelter, Alcoa, at a temperature of 750°C. After degassing, the aluminium melt of 712–714°C was poured into the mold, resulting in compound cast Al/Cu components.
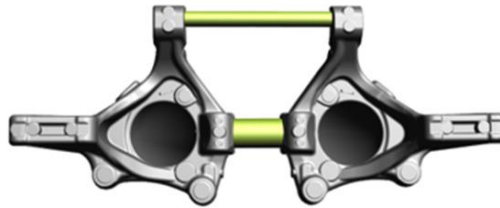

Figure 1. The Al/Cu compound castings. The copper pipe is in the yellow sections

Material Characterization

After casting, cross section samples with approximately 1cm thickness were cut from the casting for further inspection. Subsequently, the samples were ground up to 4000 grits using a Struers LaboPol-21 followed by polishing using 3 μm and 1 μm diamond suspension on a Struers Tegramin-20. The aluminum-copper interface and potential reaction zone was investigated using a Leica MEF4M optical microscope. Further characterization of the interface was done using a Zeiss Supra 55VP Field Emission Scanning Electron Microscope (FESEM). Working distance was set to 10 mm, while an acceleration voltage of 15 kV was used. To identify observed phases in the interface, Energy Dispersive X-ray Spectroscopy (EDS) was performed. Vickers micro-hardness was measured across the interface of each sample using a Leica VMHT MOT micro-hardness tester with 25 g force and 10 seconds holding time.

RESULTS AND DISCUSSION

Light Microscopy Observations

All castings had the same process parameters, except for the surface treatment. In the results four casting samples will be mentioned. The copper pipes in casting A and B were flux coated, while C and D had no surface treatment. In the interface of casting A and B, small cavities were observed, while no defects could be observed by visual examination in the interface of casting C and D. A closer inspection of the Al/Cu interface in casting A and B using an optical microscope is shown in Figure 2. In both castings, large gaps can be observed between the copper pipe and the cast aluminum. The gap has an average thickness of 8 µm for casting A and 18 µm for B. Interestingly, small droplet-like aluminium rich features can be observed frequently in the copper side of interface, as indicated by the arrows. This implies that aluminium melt has dissolved local areas of the copper pipe surface. The variation in color of the droplet-like areas suggests formation of intermetallic phases. Since copper has a melting point of 1085°C (Aylward & Findlay, 2002), which is much higher than the pouring temperature of the liquid A356, copper is not expected to melt during casting. However, some copper will dissolve into the aluminium melt, which leads to a high Cu concentration in the aluminum melt locally around the interface. This will cause the formation

of a large fraction of Al-Cu intermetallic particles. In casting A and B, intermetallic phases can clearly be seen, but no continuous metallurgical bond has formed due to the gap. Nonetheless, the reaction layer suggests that the gap may have formed during solidification.
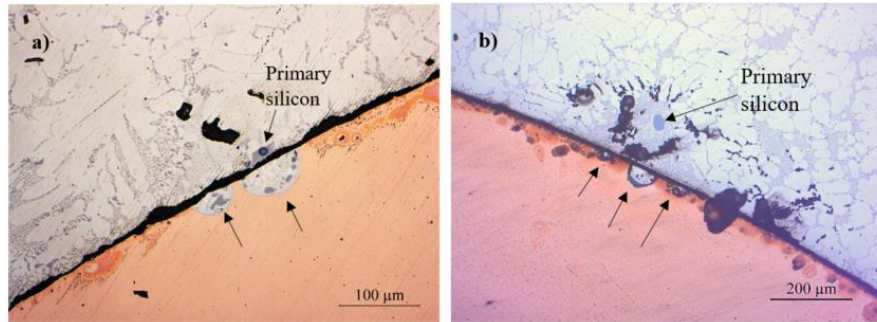

Figure 2. Optical micrographs of the Al/Cu interface in a) Casting A and b) Casting B, both with flux coating

Figure 3 shows optical micrographs of casting C and D. In both castings, local areas of continuous metallurgical bonding have formed. Despite the two castings having identical casting processes, bonding is significantly better in casting D, where the reaction area has relatively continuous thickness and only small gaps can be observed. Casting C shows reaction areas with distinct droplet shapes, with a gap of approximately 9 µm on both sides. This difference could be due to slight variations in the surface cleaning of the copper pipes prior to casting. However, based on the optical micrographs in Figure 2 and 3, it can be concluded that the flux coating has not improved bonding between A356 and copper. Instead, it appears that the flux has prevented the formation of a continuous metallic bonding layer.
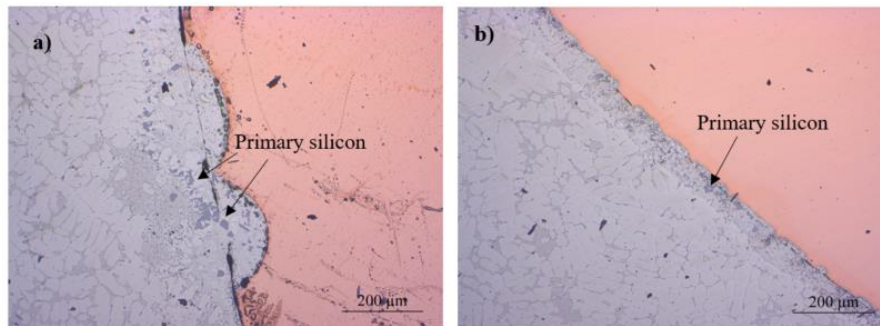

Figure 3. Optical micrograph of the Al/Cu interface in a) Casting C and b) Casting D, without surface treatment.

Microstructure Characterization

Figure 4a shows a backscattered electron (BSE) image of the droplet-like reaction area in casting A, while Table 2 presents the chemical compositions of the labelled features measured by EDS. For casting A, there is a continuous light grey layer between the droplet and copper (Area 1). This is determined to be Al_2Cu_3 phase. In connection to the Al_2Cu_3 layer is a thicker but less continuous intermetallic particle layer, which is determined as Al_2Cu phase (Area 2). These two layers compose the shell of the aluminum droplet. Inside the droplet, the irregular-shaped grey particles are concluded to be the eutectic Al_2Cu phase (Area 4). Primary Si particles can also be detected in the droplet (Area 3), although these dark particles are difficult to distinguish in the image due to poor contrast. Eutectic Al_2Cu and primary Si particles can also be detected in the aluminum side close to the interface. This shows that Cu has dissolved into the aluminum melt during casting. It can also be seen that the gap observed in the optical micrograph in Figure

2a is not as wide as initially believed. Instead, a discontinuous structure can be observed in most of the gap. From the analysis in area 5, high concentrations of potassium, magnesium and fluoride were detected in this area coinciding with formation of MgF_2. For casting B in Figure 4b, the EDS analysis shows that no Al-Cu intermetallic phases have formed, although the detection of copper in all areas indicates that a reaction has occurred. Detection of potassium, magnesium and fluoride (Area 2 and 3) suggests formation of $KMgF_3$ in the interface. The magnesium concentrations detected in the interfaces of casting A and B significantly exceeds the concentration in the A356 alloy.
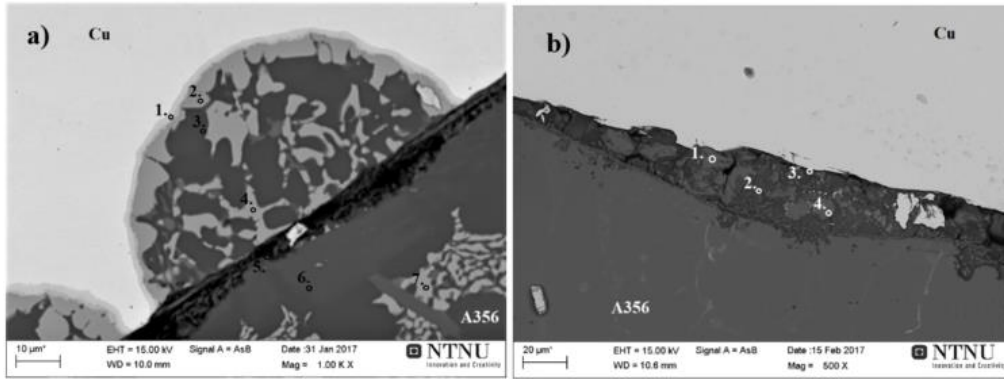

Figure 4. Micrographs of the reaction area formed in the Al/Cu interface in casting a) A and b) B

Table 2. Compositions and possible phases detected through the EDS analysis of the Al/Cu interface in casting A and B

Casting-Area	Composition [at%]							Possible phase
	Al	Cu	Si	Mg	K	F	O	
A-1	37.17	62.83	-	-	-	-	-	Al_2Cu_3
A-2	69.18	30.82	-	-	-	-	-	Al_2Cu
A-3	1.14	0.82	98.04	-	-	-	-	Primary Si
A-4	70.17	29.83	-	-	-	-	-	Al_2Cu
A-5	36.39	16.48	3.71	10.53	6.90	25.98	-	Flux residue + MgF_2
A-6	2.30	-	97.70	-	-	-	-	Primary Si
A-7	70.34	28.30	1.37	-	-	-	-	Al_2Cu
B-1	97.26	-	2.74	-	-	-	-	(Al)
B-2	27.44	0.70	2.98	2.69	3.70	20.01	42.49	$KMgF_3$+(Al)
B-3	17.09	7.18	-	-	11.61	9.22	54.91	Flux residue
B-4	64.29	1.37	22.15	-	-	-	-	(Al)+(Si)

K_xAlF_y fluxes are often used in brazing aluminum. Takemoto et al. reported that magnesium is highly reactive towards such fluxes and will therefore diffuse to the surface and create compounds with both potassium and fluoride (Takemoto, et al., 1997). MgF_2 and $KMgF_3$ both have higher melting points than the flux (Aylward & Findlay, 2002), which then would reduce its efficiency. This will decrease the wettability between aluminum and copper and prevent the removal of surface oxides, resulting in poor bonding. Garcia et al. however, reported that an addition of 2.0% Cs to the flux would prevent formation of detrimental magnesium compounds (Garcia, et al., 2001). Instead, cesium will form compounds with magnesium with lower melting points and will thus not interfere with the flux. NOCOLOK® Cs flux has a minimum of 1.5% cesium (GmbH, u.d.), which should be sufficient to prevent formation of magnesium compounds. However, as they are present in these interfaces, the flux will not be preferable to provide proper wetting between copper and aluminum A356.

Formation of primary silicon particles was also reported in the Al/Cu interface by Divandari and Golpayegani (Divandari & Golpayegani, 2009). They suggested that the formation of these particles was a

result of the increased cooling effect induced by copper. Based on density, copper has a much higher heat capacity than aluminum, which would increase the cooling rate of the A356 aluminum at the copper surface. This could cause an undercooling effect and thus create a nucleation site for primary silicon. Here, the formation of primary Si particles is also due to the different nucleation kinetics at the A356/Cu interface. Commercially pure copper often contains small amounts of phosphorous. Then, when copper dissolves in liquid A356, AlP particles will form. It has been reported that as little as 2 ppm under low undercooling is sufficient to form AlP, which can work as heterogeneous nucleation sites for silicon (Ho & Cantor, 1995). Therefore, primary Si particles can form above the Al-Si eutectic temperature. This would also explain why the primary silicon particles only formed in the interface region.

Figure 5 shows the interface in casting D, which was similar to that in casting C. There is a continuous Al-Al_2Cu eutectic layer with approximately 70 μm thickness. This differs from the observed gaps in casting A and B. However, a similar structure to that between the aluminum droplet and Cu matrix for can be seen for casting D. In addition to the irregular Al_2Cu eutectic particles, dark grey particles (Area 1 in Fig. 6) can be observed. This is believed to be the Q-phase, which is a quaternary phase with the chemical formula $Al_5Cu_2Mg_8Si_6$. The varying concentrations of Cu, Mg and Si compared to the formula are due to the size of the particle and that a large fraction of Al matrix was included in the measurement. Zheng et al. reported that a high Cu/Mg ratio would promote formation of Q-phase (Zheng, et al., 2015), while Samuel observed thick plates of $Al_5Cu_2Mg_8Si_6$ growing out of Al_2Cu during solution treatment of an Al-Si-Cu alloy with 0.45 wt% Mg (Samuel, 1998). As copper dissolves in the A356 melt around the interface, the Cu/Mg ratio can be very high in the present castings.
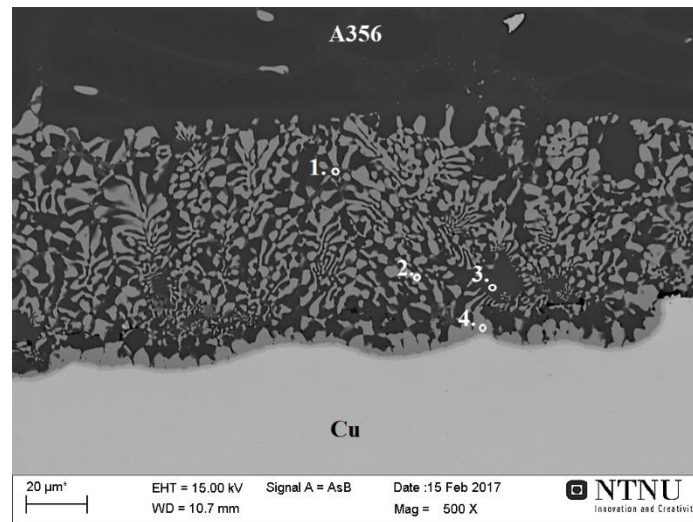

Figure 5. Micrograph of the reaction area formed in the Al/Cu interface in casting D

Table 3. Compositions and possible phases detected through the EDS analysis of the Al/Cu interface in casting D

Area	Composition [at%]					Possible phase
	Al	Cu	Si	Mg	O	
1	53.31	2.10	5.07	4.98	-	Q-phase
2	71.58	28.42	-	-	-	Al_2Cu
3	1.74	0.71	97.55	-	-	Primary Si
4	69.55	30.45	-	-	-	Al_2Cu

Figure 6 shows areas of the Al/Cu interface at the copper surface in casting C and D. As BSE was used, the contrast difference in the interface suggests formation of two intermetallic phases differing from Al_2Cu. This coincides with the findings of Tavassoli et al. (2016), who suggested that more copper-rich

phases form between Al_2Cu and Cu through solid-state phase transformation. It is, however, difficult to determine the two phases. In Casting C, as seen in Table 4, the intermetallic phase closest to the copper pipe is believed to be Al_4Cu_9, while the other intermetallic phase could be both AlCu and Al_2Cu_3. It is possible that both have formed in the interface due to the varying local concentration of available copper in the Al melt. In casting D, the intermetallic phase adjacent to the copper surface is likely to be Al_2Cu_3, while the second layer could be AlCu. These results show that more copper-rich phases formed in casting C, despite the casting parameters being identical. This could be due to locally higher temperature in the investigated area in casting C. Higher temperatures will allow more copper to be dissolved and thus increase diffusion. However, as in both cases the formation of intermetallic phases is continuous throughout the interface, the bonding strength compared to casting A and B has significantly increased.
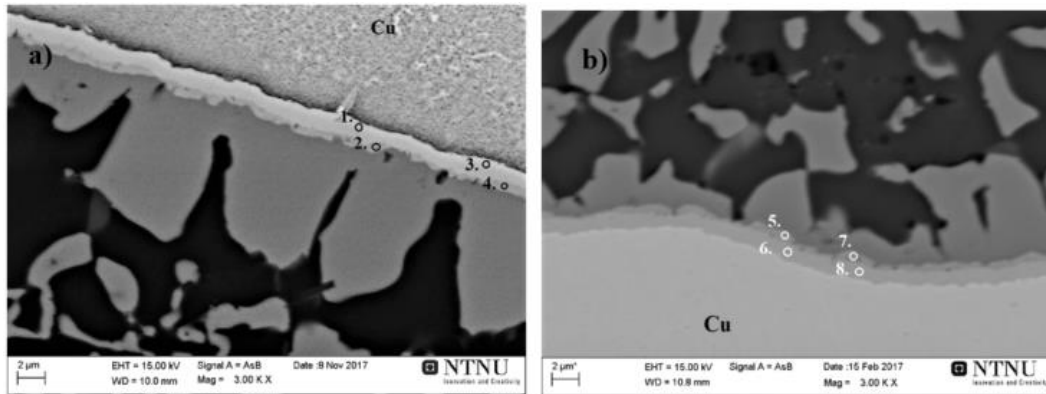

Figure 6. Micrographs of the Al/Cu interface at the copper surface of casting a) C and b) D

Table 4. Compositions and possible phases detected through the EDS analysis of the Al/Cu interface at the copper surface in casting C and D

Area	Composition [at%]				Possible phase
	Al	Cu	Si	O	
1	12.61	78.23	-	9.16	Al_4Cu_9
2	39.87	60.13	-	-	Al_2Cu_3
3	27.48	64.97	-	7.55	Al_4Cu_9
4	49.17	46.78	1.43	2.61	AlCu
5	54.43	45.57	-	-	AlCu
6	37.40	62.60	-	-	Al_2Cu_3
7	64.83	31.41	1.21	2.55	Al_2Cu
8	40.45	59.55	-	-	Al_2Cu_3

Micro-Hardness across the Al/Cu Interface

Vickers Hardness was measured across the Al/Cu interface. Figure 7 shows the areas where hardness was measured and the corresponding hardness profiles. In all castings, it can be seen that the hardness increases in the interface, although the indentation is too large to determine the hardness for each separate phase. In comparison to the copper pipe and cast A356 alloy, the hardness in the interface has approximately doubled. This is due to the solution hardening of Cu in Al and the hardening by the hard Al-Cu intermetallic phases. However, the Al-Cu compounds are known to be brittle, which will also cause cracks in the interface layer. In Figure 7c, one measurement differs greatly from the other indentations in the interface, with hardness exceeding 1000 HV. By comparing the graph and the optical micrograph, it can be seen that this measurement is made on a dark grey primary silicon particle. Silicon has a reported hardness of 13 GPa at room temperature (Vandeperre, et al., 2007), which is approximately 1326 HV. This is significantly higher than the measured hardness of aluminum of approximately 90 HV.
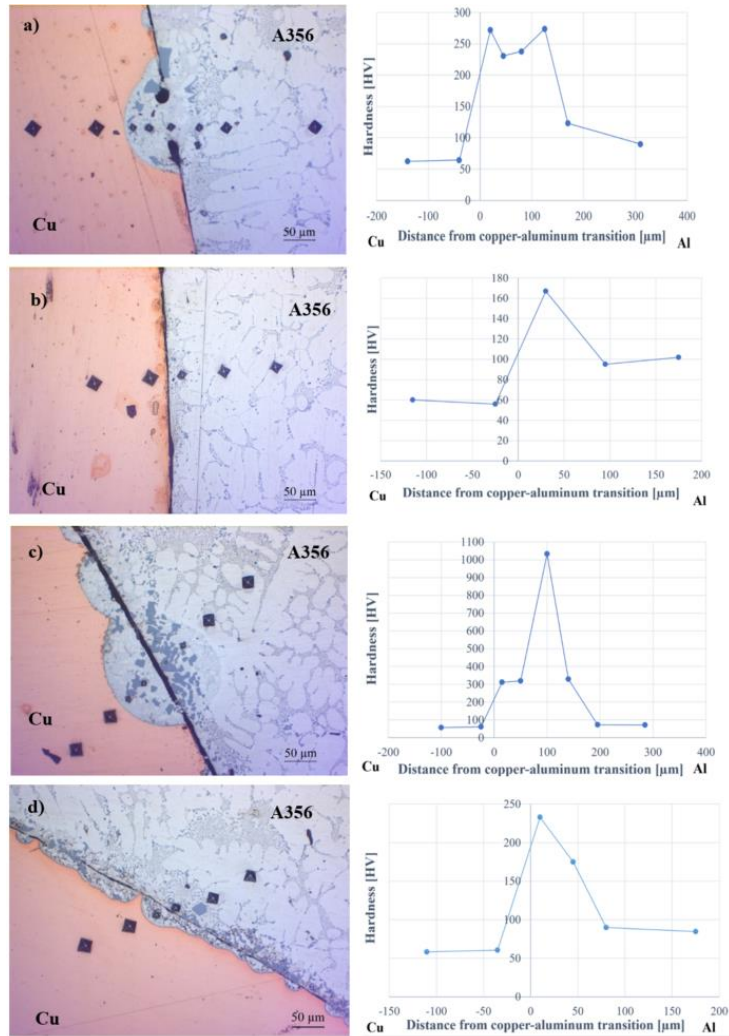
Figure 7. Vickers micro-hardness measured across the Cu/Al interface in Casting a) A, b) B, c) C and d) D

CONCLUSIONS

From this research, the following conclusions were made:

- Metallurgical bonding between Al7SiMg and Cu was achieved without surface treatment. Flux coating of the copper pipes caused formation of magnesium compounds with higher melting temperatures than the flux, thus preventing removal of surface oxides and decreasing wettability.

- Interface layer was observed in all casting samples. The interface layer mainly consisted of a eutectic Al_2Cu + (Al) structure in addition to a variation of binary Al-Cu compounds such as Al_2Cu, $AlCu$, Al_4Cu_9 and Al_2Cu_3.

- Primary silicon particles formed in the reaction area and in the cast aluminum adjacent to the copper pipe. These were believed to form due to dissolution of pre-existing phosphorous in the copper pipe into the aluminum melt and forming AlP, which act as nucleation sites for silicon.

- Micro-hardness measurements showed a significant increase in hardness around the interface layer, which is due to the solid solution strengthening effect of Cu in Al and the strengthening by hard Al-Cu intermetallic particles.

ACKNOWLEDGMENTS

REFERENCES

Abdollah-Zadeh, A., Saeid, T., & Sazgari, B. (2008). Microstructural and mechanical properties of friction stir welded aluminum/copper lap joints. *Journal of Alloys and Compounds, 460*(1–2), 535–538.

Aylward, G., & Findlay, T. (2002). *SI Chemical Data* (5. utg.). Milton: John Wiley & Sons Australia.

Divandari, M., & Golpayegani, A. R. (2009). Study of Al/Cu rich phases formed in A356 alloy by inserting Cu wire in pattern in LFC process. *Materials & Design, 30*(8), 3279–3285.

Eslami, P., & Taheri, A. K. (2011). An investigation on diffusion bonding of aluminum to copper using equal channel angular extrusion process. *Materials Letters, 65*(12), 1862–1864.

Garcia, J., Massoulier, C., & Faille, P. (2001). Brazeability of Aluminum Alloys Containing Magnesium by CAB Process Using Cesium Flux. *Society of Automotive Engineers*, 1–11.

GmbH, S. F. (u.d.). *Solvay - NOCOLOK Cs Flux Product Information.* Gathered 03 15, 2017 from https://www.solvay.com/en/binaries/NOCOLOK_Cs_Flux-product-information-179822.pdf

Hajjari, E., Divandari, M., Razavi, S. H., Emami, S. M., Homma, T., & Kamado, S. (2011). Dissimilar joining of Al/Mg light metals by compound casting process. *Journal of Materials Science, 46*(20), 6491–6499.

Ho, C. R., & Cantor, B. (1995). Heterogeneous nucleation of solidification of Si in Al-Si and Al-Si-P alloys. *Acta Metallurgica et Materialia, 43*(8), 3231–3246.

Honarpisheh, M., Asemabadi, M., & Sedighi, M. (2012). Investigation of annealing treatment on the interfacial properties of explosive-welded Al/Cu/Al multilayer. *Materials and Design, 37*, 122–127.

Lee, K. S., Lee, S. E., Sung, H. K., Lee, D., Kim, J. S., Chang, Y. W., . . . Kwon, Y. N. (2013). Influence of reduction ratio on the interface microstructure and mechanical properties of roll-bonded Al/Cu sheets. *Materials Science & Engineering A, 583*, 177–181.

Lee, W.-B., Bang, K.-S., & Jung, S.-B. (2005). Effects of intermetallic compound on the electrical and mechanical properties of friction welded Cu/Al bimetallic joints during annealing. *Journal of Alloys and Compounds, 390*(1–2), 212–219.

Liu, T., Wang, Q., Sui, Y., Wang, Q., & Wenjiang, D. (2016). An investigation into interface formation and mechanical properties of aluminum-copper bimetal by squeeze casting. *Materials & Design, 89*, 1137–1146.

Papis, K. J., Hallstedt, B., Löffler, J. F., & Uggowitzer, P. J. (2008). Interface formation in aluminum-aluminum compound casting. *Acta Materialia, 56*(13), 3036–3043.

Papis, K. J., Loeffler, J. F., & Uggowitzer, P. J. (2009). Light metal compound casting. *Science in China Series E: Technological Sciences, 52*(1), 46–51.

Pinnel, M., Tompkins, H., & Heath, D. (1979). Oxidation of copper in controlled clean air and standard laboratory air at 50°C to 150°C. *Applications of Surface Science, 2*(4), 558−577.

Samuel, F. (1998). Incipient melting of Al5Mg8Si6Cu2 and Al2Cu intermetallics in unmodified and strontium-modified Al-Si-Cu-Mg (319) alloys during solution heat treatment. *Journal of Materials Science, 33*, 2283−2297.

Sheng, L. Y., Yang, F., Xi, T., Lai, C., & Ye, H. Q. (2011, September). Influence of heat treatment on interface of Cu/Al bimetal composite fabricated by cold rolling. *Composites: Part B, 42*(6), 1468−1473.

Takemoto, T., Matsunawa, A., & Shibutani, T. (1997). Chemical reaction of non-corrosive flux with magnesium containing aluminum alloys and the improvement of brazeability. *Welding International, 11*(11), 845−851.

Tavassoli, S., Abbasi, M., & Tahavvori, R. (2016). Controlling of IMCs layers formation sequence, bond strength and electrical resistance in Al-Cu bimetal compound casting process. *Materials & Design, 108*, 343−353.

Tayal, R. K., Singh, V., Kumar, S., & Garg, R. (2012). Compound Casting - A Literature Review. Faridabad: Proceedings of the National Conference on Trends and Advances in Mechanical Engineering.

Vandeperre, L. J., Giuliani, F., Lloyd, S. J., & Clegg, W. J. (2007). The hardness of silicon and germanium. *Acta Materialia, 55*(18), 6307−6315.

Xue, P., Ni, D. R., Wang, D., Xiao, B. L., & Ma, Z. Y. (2011). Effect of friction stir welding parameters on the microstructure and mechanical properties of the dissimilar Al-Cu joints. *Materials Science and Engineering A, 528*, 4683−4689.

Zare, G. R., Divandari, M., & Arabi, H. (2013). Investigation on interface of Al/Cu couples in compound casting. *Materials Science and Technology, 29*(2), 190−196.

Zheng, Y., Xiao, W., Ge, S., Zhao, W., Hanada, S., & Ma, C. (2015). Effects of Cu content and Cu/Mg ratio on the microstructure and mechanical propertie of Al-Si-Cu-Mg alloys. *Journal of Alloys and Compounds, 649*, 291−296.