UJEAS

UNIZIK JOURNAL OF ENGINEERING AND APPLIED SCIENCES

UNIZIK Journal of Engineering and Applied Sciences (2023), 23 - 30
Journal homepage: https://journals.unizik.edu.ng/index.php/ujeas

Morphological evolution and grain size distribution of as-cast and solution treated Cu-Zn-Al alloy

Francis Odikpo Edoziuno[1,2*], Cynthia Chinasa Nwaeju[1,3] and Eugene Ekedumogwu Nnuka[1]

[1]Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria.
[2]Department of Metallurgical Engineering Technology, Delta State Polytechnic, P.M.B. 1030 Ogwashi-Uku, Nigeria.
[3]Department of Mechanical Engineering, Nigeria Maritime University, Okerenkoko, Delta State, Nigeria.

Corresponding Author's Email: francisedoziuno@gmail.com; edoziuno.francis@mydspg.edu.ng

Abstract
The development of ternary Cu-20Zn-6Al shape memory alloys was carried out using an oil-fired crucible furnace for casting. The experimental alloy's chemical, morphological, and grain size distributions were studied in both the as-cast and solution-treated states. The alloy's microstructure was observed and examined using optical metallurgical microscope; it revealed that solution treatment greatly refines and homogenizes the grains. Single martensite phase could be seen in optical micrographs of the as-cast ternary Cu-20Zn-6Al alloy. The martensitic phases required for the shape memory effect are present in both the as-cast and quenched alloys. The as-cast Cu-20Zn-6Al SMA has a grain size distribution of 10 to 110 µm, whereas the solution-treated Cu-20Zn-6Al alloy has a grain size distribution of 60 to 150 µm. Thermal processing and the holding interval before quenching was adduced to have encouraged the observed rapid grain development. Because of the anticipated improvement in mechanical and shape memory qualities as a result of the significant purification and homogeneity of grains observed after solution treatment, the produced alloys may be used in structural vibration damping applications

Keywords: Shape memory alloy, Grain size, Solution treatment, Cu-Zn-Al alloys, Martensitic transformation, microstructure.

1. Introduction

A type of intelligent/advanced materials known as shape memory alloys (SMAs) restore their shape after being subjected to thermal or deformation forces (Alaneme et al., 2022; Christofidou et al., 2017; Dasgupta, 2014; Dasgupta et al., 2014; Stošić et al., 2017). Their importance as engineering materials cannot be overstated. Their two primary phases are high temperature austenite and low temperature martensite, and they can switch between them by being heated to a specific temperature or being stressed (Guerioune et al., 2008). Due to SMAs' ability to remember their shape during the austenite phase, even after deformation, their original shape can be restored. This phenomenon, often referred to as shape memory effect or martensitic transformation, alters the solid's atomic structure and microstructure. The ability of SMAs to display a variety of characteristics, including thermoelasticity, superelasticity, and damping capacity, makes them special.

Despite the fact that many alloys exhibit shape memory behaviour, Cu-based SMAs have been of particular interest to researchers for shape memory, structural, and damping applications because they are the least expensive, have better electrical and thermal conductivities, and are easily processed and welded shape memory alloys with exploitable shape memory properties (Alkan et al., 2018; Dar et al., 2016; Saha et al., 2018; Sampath et al., 2019).

For the development of inexpensive thermal actuators and sensors, intelligent/smart pipe joints, and couplings for marine and petroleum engineering applications, copper-based SMAs are recommended. (Yin et al., 2021). Cu–Zn–Al alloy is the most investigated copper-based SMAs, because it has a larger percentage of strain recovery than other Cu-based SMAs (Alaneme & Umar, 2018). Additionally, they can be produced and fabricated in a variety of ways, although these alloys are brittle because of their coarse grain structure and have weak mechanical characteristics including low fracture toughness and fatigue strength (Alaneme & Okotete, 2016; Yan et al., 2017). Due to their coarse grain microstructure, strong elastic anisotropy, concentration of secondary phases, and presence of impurities at the grain boundaries, Cu-Zn-Al alloys have low mechanical strength (Alaneme et al., 2019; Tian et al., 2019).

A number of academics have studied many aspects in terms of how they affect the properties of SMAs, such as the micro-addition of new elements to the ternary SMAs, (Alaneme et al., 2019; Dasgupta, 2014), heat treatment and quenching methods (Dasgupta et al., 2014), thermomechanical treatment (Dar et al., 2016), surface improvement, modification, and various techniques for preparation. Several groundbreaking studies have shown that the quaternary addition of alloying elements as well as thermal treatments that purify grain boundaries, refine grains, and improve mechanical properties can improve some properties of Copper-based ternary SMAs such as superelasticity (ability to undergo large strains without plastic deformation or failure), shape memory effect, and the damping capacity (Lu et al., 2009). The goal of the current study is to design and develop a novel Cu-20Zn-6Al alloy and analyze how the solutionizing heat treatment affects the grain size and microstructure of the alloy.

2.0 Materials and Methods

The methodical approach used to carry out this study essentially entails alloy development via liquid metallurgy processing route using pure copper, zinc, and aluminum, solutionizing thermal treatment at 850°C and sample preparation from the as-cast and solutionized alloys for microstructural and grain size examinations.

2.1 Alloy Development

The Cu-Zn-Al alloys were developed by melting high purity copper, zinc, and aluminum (>99.97%) at a temperature of about 1200°C in an oil-fired crucible furnace. A mild steel 15mm diameter mold that had been preheated to 200–300°C was used for pouring and solidification of the molten alloy.

2.2 Solutionizing Heat Treatment

The as-cast alloys underwent a solution heat treatment at 850°C held for 10 minutes, followed by a direct quenching in water, to improve their chemical and microstructural homogeneity. These solutionizing parameters (temperature and time) were adopted because it was discovered that solution treating of Cu-Zn-Al SMAs for 10 minutes at 870°C produced a complete solution of the α-phase with an appropriate grain size, (Asanovic et al., 2004). Solution treatment, also known as solutionizing involves heating the alloy above the solvus temperature and soaking it there until a homogenous solid solution is generated. The second stage is quenching, which involves rapidly cooling the solid to create a metastable, supersaturated solid solution β-phase that contains excess copper. Rapid quenching prevents γ precipitates from forming because the atoms do not have enough time to disperse to possible nucleation sites. This metastable β-phase must be retained in copper-based SMAs in order to get a good, reliable shape memory effect, which necessitates a sufficiently quick cooling from the betatizing temperature in order to prevent the β-phase from disintegrating into the equilibrium phases (α and/or γ-phases) (Asanovic et al., 2000). Both the metastable β-phase and martensite in these alloys undergo temperature-dependent diffusional transformations to a more stable structure at high temperatures, resulting in a corresponding loss of shape memory.

2.3 Alloy composition Analysis

Using an energy dispersive x-ray spectroscopy (EDS) technique, the as-cast and heat-treated Cu-Zn-Al shape memory alloy samples' elemental chemical compositions were examined, identified and quantified.

2.4 Metallography and Grain Size Analysis

Using the optical microscopy (OM) technique, the microstructures of the generated alloys were characterized. Standard techniques were used to mechanically polish the specimens for optical rnetallography, and then they were etched in Nital etchant (ethyl alcohol + 2% HNO_3) for optical inspection under metallurgical bench microscope (Model: L2004). The optical micrographs were subjected to image analysis using the imageJ program in order to determine the volume proportion of the intermetallic phases and grain characteristics of the microstructures. The samples were examined longitudinally and transversally. To enhance observation, the camera-captured optical image was then processed by adjusting the contrast, and a pseudo-color representation was used to aid with interpretation. The perimeter, area, and diameter of each grain were calculated once the image contrast was optimized. The summarized procedures for the alloy's structural and image analysis are surface preparation (cutting, grinding, polishing, and etching), microscopic examination and image acquisition, image processing, quantitative image analysis (size, shapes, and distribution of grains), and result interpretation (Alo et al., 2018; Edoziuno et al., 2020).

3.0 Results and Discussion

3.1 Chemical Composition

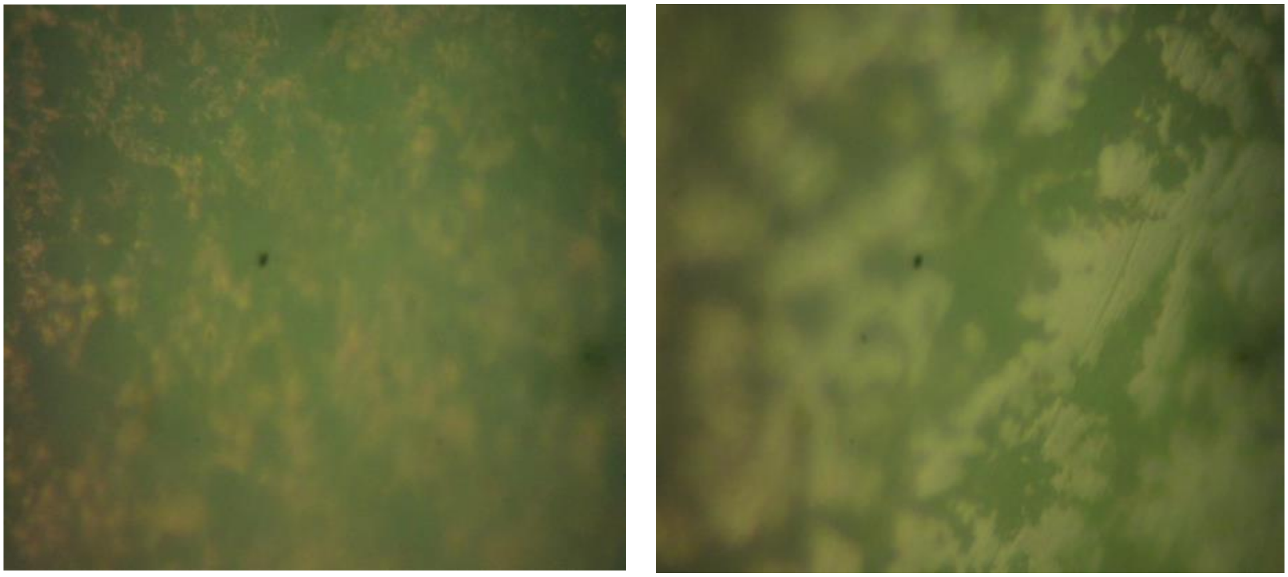
The bulk chemical composition of as-cast and solution-treated alloy samples were both determined (Table 1) using energy dispersive x-ray spectroscopy (EDS) analyses for metallic elements. To determine the variation in compositional measurements, the compositional analysis was performed twice. Taking into account the measurement error for the analysis technique of 1% of the absolute value, the measured elemental compositions reported for both as-cast and heat-treated samples were compatible with the specified composition of Cu-20-Zn-6Al. The significant burning and evaporation of zinc during the melting, pouring, and solutionizing procedures caused the observed decrease in zinc concentration (Dasgupta et al., 2014; Zhuo et al., 2020).

Table 1: Experimental chemical composition of the as-cast and solution-treated Cu-20Zn-6Al alloys.

Alloy	Cu (wt%)	Zn (wt%)	Al (wt%)
As-cast	72.92	19.18	5.55
Heat-treated	74.30	18.50	5.14

3.2 Metallographic Examinations

As shown in Figure 1a, the ternary Cu-20Zn-6Al alloy displays a sharp-edged, elongated grain structure of a single martensite phase. The martensite grain structures become more refined and dendritic with dendrite arms after solution treatment at 850°C (Figure 1b). As observed in the photomicrograph of the as-cast Cu-20Zn-6Al alloy, Cu-Zn-Al SMAs within the composition range taken into consideration in this work are frequently found to include sharp-edged directionally solidified grain features, (Alaneme & Umar, 2018). The black areas denote the fine β–phase (intermetallic compounds), and the light (bright) sections represent the α-phase matrix network of the microstructures (Haleem et al., 2021). The Cu-20Zn-6Al alloy features α (Fcc) + α two-phase area in its composition. Prior to quenching, single β-phase grains are known to be a necessary condition for the presence of pseudo elastic behavior in Cu-based SMAs. (Dasgupta et al., 2014). To obtain the desired single-phase material, α-phase must be removed from the microstructure (i.e., the microstructure should only include β-phase). The necessary (α + β) microstructure is achieved through quenching and homogenization in order to promote the evolution of a favorable texture during further processing. The structural characteristics described in earlier investigations and the microstructure results are in good accord. (Alaneme & Umar, 2018; Haleem et al., 2021). Both the as-cast and solution treated alloys have the ability to exhibit shape memory behavior, according to the obtained microstructure.



(a) (b)

Figure 1: Optical micrographs of Cu-20Zn-6Al; (a) as-cast, and (b) solution-treated samples.

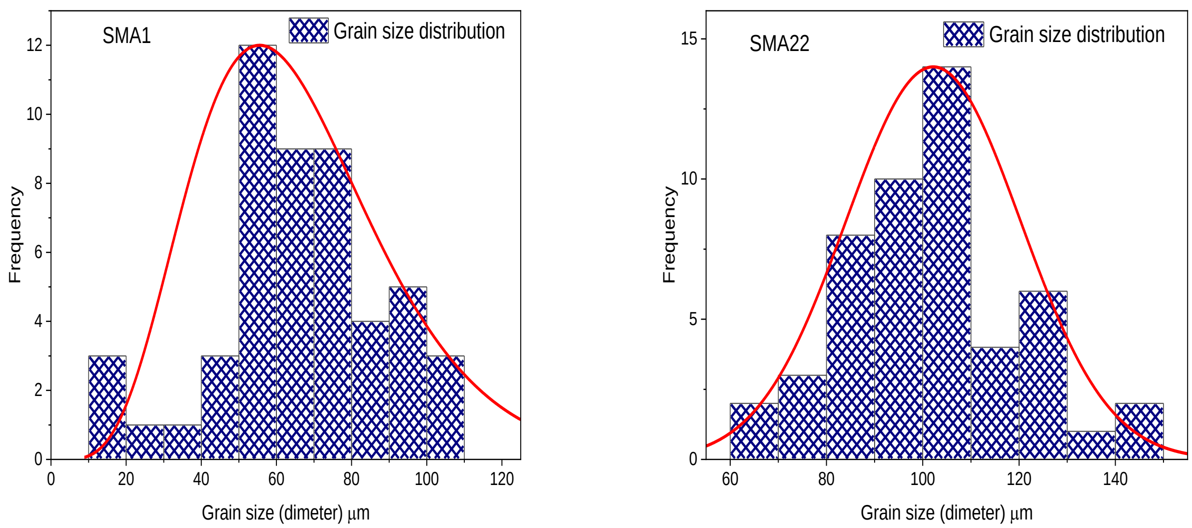
3.3 Grain Characteristics

The Cu-20Zn-6Al SMA's as-cast and solution-treated microstructural characteristics can be seen by image analysis utilizing the imageJ software. The grain size of the as-cast and solution-treated alloys varies significantly (Table 2). The table shows that the as-cast ternary alloy has smaller grains than the alloy that has been solution treated. Increased grain sizes are seen in the solution-treated sample, which was heated to 850°C before being quenched. Because the quenched sample had larger grains than the matching as-cast state, sudden quenching could not have stopped grain expansion. The development of grains has remained homogeneous in quenched samples as well. The martensitic phases required for shape memory behavior were expected to precipitate after quenching from high temperatures. The generated as-cast and solution-treated Cu-20Zn-6Al SMA's minimum, median, maximum, and average grain sizes are also shown in Table 2.

Table 2: Grain characteristics of as-cast and solution-treated Cu-20Zn-6Al alloy.

Sample	Std Dev.	Sum	Min	Median	Max	Count	Total Area	Average Size	%Area
As-cast	22.52576	3297.025	10.53	65.184	108.595	3238	74003.854	22.855	11.403
Solution-treated	18.14876	5108.942	68.877	101.538	145.671	2441	230307	94.349	11.995

Figures 3a&b show the grain size distribution of the Cu-20Zn-6Al alloys both as-cast and solution-treated. A solid line representing the log-normal function of the statistical scale fits the grain diameter distribution in Figures 3a and 3b well (Nwaeju et al., 2021; Soltani et al., 2021). This suggests that the grains found in the microstructures were primarily made up of smaller grains, with a few bigger grains filling in the gaps. The grain size frequency distribution profile diagrams clearly show the most common grain sizes for both the as-cast and heat-treated alloys. The as-cast Cu-20Zn-6Al SMA has a grain size distribution of 10 to 110 µm, whereas the solution-treated Cu-20Zn-6Al alloy has a grain size distribution of 60 to 150 µm. The heat processing and holding duration before quenching are responsible for the observed fast grain growth. (Alaneme et al., 2021; Dasgupta, 2014; Pang et al., 2019). Previous research has shown that when heat treated at high temperatures, the grains of ternary Cu-based SMAs without the inclusion of quaternary micro-additives grow quickly. (Agrawal & Kumar, 2018; Furlani et al., 2005; Xu, 2008; Xu et al., 2019).



(a) (b)

Figure 3: Grain size distribution of Cu-20Zn-6Al alloys: (a) as-cast (b) Solution treated.

4.0. Conclusion

The investigation's findings allow for the following deductions:

i. A hitherto unresearched polycrystalline copper-based SMA was developed, and the microstructure and grain size properties in both the as-cast and heat-treated states were examined.

ii. EDS elemental analysis showed the concentrations of the constituent elements in the as-cast and solutionized experimental alloys, with a decrease in the designed quantities of zinc due to quick evaporation of Zn at high temperature.

iii. A single martensite phase could be seen in the optical micrographs of the ternary Cu-20Zn-6Al alloy, however after solution treatment at 850°C, the martensite grain structures become more distinct and dendritic, with dendrite arms. The martensitic phases required for shape memory behavior are present in both the as-cast and the quenched alloys.

iv. The ternary Cu-20Zn-6Al alloy's grain size has grown noticeably quickly, according to the grain distribution, as a result of thermal treatment and holding time prior to quenching.

Acknowledgments

The management of Cutix Cables Plc Nnewi, Nigeria is gratefully acknowledged by the authors for providing the pure copper and aluminum wires utilized in this study.

References

Agrawal, A., & Kumar, R. 2018. Methods of fabricating Cu-Al-Ni shape memory alloys. *Journal of Alloys and Compounds*, *750*, 235–247. https://doi.org/10.1016/j.jallcom.2018.03.390

Alaneme, K. K., Anaele, J. U., Okotete, E. A., Kanayo, K., Uchenna, J., & Anita, E. 2021. Martensite aging phenomena in Cu-based alloys : Effects on structural transformation , mechanical and shape memory properties : A critical review. *Scientific African*, *12*, e00760. https://doi.org/10.1016/j.sciaf.2021.e00760

Alaneme, K. K., & Okotete, E. A. 2016. Reconciling viability and cost-effective shape memory alloy options – A review of copper and iron based shape memory metallic systems. *Engineering Science and Technology, an International Journal*. https://doi.org/10.1016/j.jestch.2016.05.010

Alaneme, K. K., Okotete, E. A., Oluwafemi, A., & Inyang, U. 2019. Assessment of the mechanical behaviour of thermally aged B and Fe modified CuZnAl shape memory alloys. *Revista De Metallurgia*, *55*(3), e151. https://doi.org/10.3989/revmetalm.151

Alaneme, K. K., Ubah, J. T., & Aikulola, E. O. 2022. On the material characteristics of Ni modified Cu32Zn10Sn shape memory alloys : Mechanical and damping behaviour in consideration. *Materials Today: Proceedings*, *xxxx*. https://doi.org/10.1016/j.matpr.2022.02.090

Alaneme, K. K., & Umar, S. 2018. Mechanical behaviour and damping properties of Ni modified Cu-Zn-Al shape memory alloys. *Journal of Science: Advanced Materials and Devices*, *3*(3), 371–379. https://doi.org/10.1016/j.jsamd.2018.05.002

Alkan, S., Wu, Y., Ojha, A., & Sehitoglu, H. 2018. Transformation stress of shape memory alloy CuZnAl : Non-Schmid behavior. *Acta Materialia*, *149*, 220–234. https://doi.org/10.1016/j.actamat.2018.02.011

Alo, F. I., Ajoge, E. O., Kunle, M. O., Isadare, D. A., Oyedele, A. A., & Emordi, N. 2018. Comparision of Imagej Analysis of Structure of Two Constructional Steel. *American Journal of Engineering and Applied Sciences*, *1*(1). https://doi.org/10.3844/ajeassp.2018.

Asanovic, V. D., Delijic, K. H., Leka, Z. B., & Bosnjak, B. T. 2004. The Effect of Heat Treatment on the Martensitic Transformation and Properties of Cu-Zn-Al Alloy. *Journal of the Mechanical Behavior of Materials*, *15*(4–5), 219–238.

Asanovic, V., Perovic, B., Markovic, Z., Kostov, A., Radulovlc, B., & Bosnjak, B. 2000. Precipitation Kinetic in Cu-Zn-AI Shape Memory Alloys. *Journal of Mining and Metallurgy*, *36*(3–4), 133–146.

Christofidou, K. A., Robinson, K. J., Mignanelli, P. M., Pickering, E. J., Jones, N. G., & Stone, H. J.n2017. The effect of heat treatment on precipitation in the Cu-Ni-Al alloy Hiduron® 130. *Materials Science and Engineering: A*, *692*, 192–198.

Dar, R. D., Yan, H., & Chen, Y. 2016. Grain boundary engineering of Co – Ni – Al , Cu – Zn – Al , and Cu – Al – Ni shape memory alloys by intergranular precipitation of a ductile solid solution phase. *Scripta Materialia*, *115*, 113–117. https://doi.org/10.1016/j.scriptamat.2016.01.014

Dasgupta, R. 2014. A look into Cu-based shape memory alloys : Present scenario and future prospects. *Journal of Materials Research*, *29*(16), 1681–1698. https://doi.org/10.1557/jmr.2014.189

Dasgupta, R., Jain, A. K., Kumar, P., Hussein, S., & Pandey, A. 2014. Effect of alloying constituents on the martensitic phase formation in some Cu-based SMAs. *Integrative Medicine Research*, *3*(3), 264–273. https://doi.org/10.1016/j.jmrt.2014.06.004

Edoziuno, F. O., Odoni, B. U., Alo, F. I., & Nwaeju, C. C. 2020. Dry Sliding Wear and Surface Morphological Examination of an Aluminium Matrix Composite Reinforced with Palm Kernel Shell. *Acta Metallurgica Slovaca*, *26*(2), 54–62. https://doi.org/10.36547/ams.26.2.537

Furlani, A. M., Stipcich, M., & Romero, R. 2005. Phase decomposition in a β Cu–Zn–Al–Ti–B shape memory alloy. *Materials Science & Engineering A*, *392*, 386–393. https://doi.org/10.1016/j.msea.2004.10.015

Guerioune, M., Amiour, Y., Bounour, W., Guellati, O., Benaldjia, A., Amara, A., Chakri, N. E., & Vrel, D. 2008. SHS of Shape Memory CuZnAl Alloys. *International Journal of Self-Propagating High-Temperature Synthesis*, *17*(1), 41–48. https://doi.org/10.3103/S1061386208010044

Haleem, A. H., Khulief, Z. T., & Kadhim, I. N. 2021. Modification of Corrosion and Mechanical Behaviour of Cu-Zn-Al Shape Memory Alloy. *Journal of Physics: Conference Series*, *1973*, 012049. https://doi.org/10.1088/1742-6596/1973/1/012049

Lu, X., Chen, F., Li, W., & Zheng, Y. 2009. Effect of Ce addition on the microstructure and damping properties of Cu – Al – Mn shape memory alloys. *Journal of Alloys and Compounds*, *480*, 608–611. https://doi.org/10.1016/j.jallcom.2009.01.134

Nwaeju, C. C., Edoziuno, F. O., Adediran, A. A., Tuaweri, T. J., & Kumar, M. S. 2021. Grain characteristics and mechanical properties of as-cast Cu-10 % Al alloy : Effects of alloying additions. *Results in Engineering*, *12*(September), 100295. https://doi.org/10.1016/j.rineng.2021.100295

Pang, G., Jin, M., Zuo, S., & Jin, X. 2019. Intermetallics Martensitic transformation and superelasticity in Au 7 Cu 5 Al 4 shape memory alloy microwires. *Intermetallics*, *112*, 106527. https://doi.org/10.1016/j.intermet.2019.106527

Saha, G., Ghosh, M., Antony, A., & Biswas, K. 2018. Ageing Behaviour of Sc-Doped Cu – Zn – Al Shape Memory Alloys. *Arabian Journal for Science and Engineering*. https://doi.org/10.1007/s13369-018-3621-4

Sampath, V., Gayathri, S. A. I. V., & Srinithi, R. 2019. Experimental and theoretical analyses of transformation temperatures of Cu-based shape memory alloys. *Bulletin of Materials Science*, *42*(229). https://doi.org/10.1007/s12034-019-1911-4

Soltani, H., Ngomesse, F., Reinhart, G., Benoudia, M. C., Zahzouh, M., & Nguyen-Thi, H. 2021. Impact of gravity on directional solidification of refined Al-20wt.%Cu alloy investigated by in situ X-radiography. *Journal of Alloys and Compounds*, *862*. https://doi.org/10.1016/j.jallcom.2020.158028

Stošić, Z., Manasijević, D., Balanović, L., Holjevac-Grgurić, T., Stamenković, U., Premović, M., Minić, D., Gorgievski, M., & Todorović, R. 2017. Effects of Composition and Thermal Treatment of Cu-Al-Zn Alloys with Low Content of Al on their Shape-memory Properties. *Materials Research*, *20*(5), 1425–1431.

Tian, J., Zhu, W., Wei, Q., Wen, S., Li, S., Song, B., & Shi, Y. 2019. Process optimization , microstructures and mechanical properties of a Cu-based shape memory alloy fabricated by selective laser melting. *Journal of Alloys and Compounds*, *785*, 754–764. https://doi.org/10.1016/j.jallcom.2019.01.153

Xu, J. W. 2008. Effects of Gd addition on microstructure and shape memory effect of Cu – Zn – Al alloy. *Journal of Alloys and Compounds*, *448*, 331–335. https://doi.org/10.1016/j.jallcom.2006.11.159

Xu, S., Kusama, T., Xu, X., Huang, H., Omori, T., Xie, J., & Kainuma, R. 2019. Large [001] single crystals via abnormal grain growth from columnar polycrystal. *Meterialia*, *6*, 100336. https://doi.org/10.1016/j.mtla.2019.100336

Yan, H., Marcoux, Y., & Chen, Y. 2017. Cyclic mechanical properties of copper-based shape memory alloys : The effect of strain accommodation at grain boundaries. *International Journal of Fatigue*, *105*, 1–6. https://doi.org/10.1016/j.ijfatigue.2017.08.011

Yin, M. yang, Li, Z., Xiao, Z., Pang, Y., Li, Y. ping, & Shen, Z. yan. 2021. Corrosion behavior of Cu−Al−Mn−Zn−Zr shape memory alloy in NaCl solution. *Transactions of Nonferrous Metals Society of China*, *31*(4), 1012–1022. https://doi.org/10.1016/S1003-6326(21)65557-7

Zhuo, L., Song, B., Li, R., Wei, Q., Yan, C., & Shi, Y. 2020. Effect of element evaporation on the microstructure and properties of CuZnAl shape memory alloys prepared by selective laser melting. *Optics and Laser Technology*, *127*, 106164. https://doi.org/10.1016/j.optlastec.2020.106164