

A Review on Influence of Alloying Elements on the Microstructure and Mechanical Properties of Cu-Al-Ni Shape Memory Alloys

Safaa N. Saud^a, E. Hamzah^{a*}, T. Abubakar^a, Raheleh Hosseinian. S^b

^aFaculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

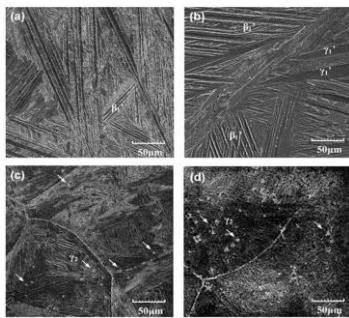
^bDepartment of Physics, Faculty of Science, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author: esah@fkm.utm.my

Article history

Received : 10 January 2013
Received in revised form :
25 July 2013
Accepted : 15 August 2013

Graphical abstract



Abstract

Cu–Al–Ni shape memory alloys (SMAs) have been developed for high temperatures engineering components such as sensor and actuators, due to their ability to work at temperatures near 200°C, rather than NiTi and Cu–Zn–Al alloys whose maximum working temperatures around 100°C. These alloys are widely used because they are much cheaper than NiTi/Cu–Zn–Al and do not require any complicated processing during their manufacturing as do for other shape memory alloys. In addition, these alloys have a small hysteresis and high transformation temperatures compared with other alloys. Despite all these advantages, these alloys have their limitations such as brittleness and low phase recovery strains and stress. The present review describes the role of alloying elements on the properties of Cu–Al–Ni shape memory alloys. It has been found that the additions of alloying elements have a significant effect on the formation, morphology, and structure of the obtained martensite, therefore, the properties of these alloys varied in accordance of these effects.

Keywords: Shape memory alloys; Cu–Al–Ni; martensitic transformation

© 2013 Penerbit UTM Press. All rights reserved.

1.0 INTRODUCTION

Shape Memory Alloys (SMAs) are smart materials that have the ability to return to their pre-deformed shape by heating above the transformation temperature. Below the transformation temperature, these alloys may have a low yield strength, which gives the ability to deform it to any new shape, but when it is heated above the transformation temperature, the crystal structure changed, which cause it to return to original shape. Due to the crystallographic reversible thermoelastic martensitic transformation, these alloys have a unique correlation of strain/stress and temperature. Shape memory alloys (SMA) undergo a reversible thermoelastic martensitic transformation (MT) between a high temperature phase γ , called austenite, and a low temperature phase, called martensite [1, 2], the martensite transformation is responsible for the specific thermomechanical properties of SMA such as superelasticity, shape memory and high damping [3]. The transformation temperatures for both phases are A_s (austenite start) and A_f (austenite finish), and M_s (martensite start) and M_f (martensite finish) during the heat treatment process. Recently, shape memory alloys (SMAs) have

been used as effective alloys for multi-purposes engineering components, such as actuator, sensing, medicine, robotics and space devices [4]. Although Ti–Ni [5] is the most widely used shape memory alloys for technological applications, Cu-based alloys have been used as an excellent alternative because they offer a wide range of transformation temperatures up to 200°C, a large superelastic effect, small thermal hysteresis and high damping coefficient. The main Cu-based alloys are Cu–Al–Ni and Cu–Zn–Al alloys [5]. Cu–Al–Ni SMAs have been used in a wide range of applications, especially when the high temperatures are required. This is attributed to their high thermal stability and high transformation temperatures. On the other hand, these alloys have some disadvantages like low reversible deformation and high brittleness, where their shape memory effects in one way and two ways are 4% and 1.5%, respectively. While, the reasons lie on the intergranular breakdown at low stress rate. The effects of alloying elements on Cu–Al–Ni SMA have been carried out by many researchers experimentally. However, there is no literature found to conclude on review the effect of all elements. This paper reviews the effect of different microalloying additives on the

microstructures and mechanical properties of Cu-Al-Ni shape memory alloys.

2.0 STRUCTURE-PROPERTY CORRELATION OF THE Cu-Al-Ni SHAPE MEMORY ALLOYS

Cu-Al-Ni SMAs are very sensitive to the effects of alloying elements, especially the phase transformation temperature-behavior, whereas these effects may cause some changes on the crystallographic properties and some other parameters of these alloys. Shape memory effects of the Cu-Al-Ni SMAs are promising smart and intelligent engineering materials. In addition, the low cost and ease to produce have attracted much attention comparing with other shape memory alloys, such as NiTi SMAs. The changes of domain and grain size in the term of microstructure effects as well as the changes of mechanical properties of Cu-Al-Ni SMAs on some transformation parameters (due to the effects of alloying elements additions) have studied by some of the scientists and researcher as have been discussed in this paper.

2.1 Effect of Alloying Elements on the Microstructure of Cu-Al-Ni SMAS

In Cu-Al-Ni shape memory alloys (SMA) the most determinant factor of the phase transformation behavior is the alloying elements. In commercial applications for this kind of alloys, the martensitic transformation behavior has a very strong dependence on alloying element contents especially, in order of design an alloy with the required characteristics. The main reason of the shape memory effect and other properties is the stability of the

disorder β -AlCu₄ phase with a cubic structure. So, during adding the alloying elements, the β stable phase evolves to another phases, that is dependent on the nature and effect of alloying element.

2.1.1 Effect of Aluminum and Nickel Elements on the Microstructure of Cu-Al-Ni SMAS

The characteristics of Cu-Al-Ni SMAs are mainly depended on the β phase of high temperature binary Cu-Al phase [8]. At low cooling rate, this phase decomposes to α and γ_2 at 565°C. But at high cooling rate, the martensitic transformation occurred. The transformation of β to ordered β_1 occur when the alloy contains at 11 wt.% of Al; the β_1 has a super lattice structure (DO₃) prior to martensitic transformation. With increase on Al content to 13 wt.%, the structure has changed to monoclinic 18 R and β'_1 as shown in Figure 1(a). When the Al content, have goes to 13.5 wt.% the structure transformed to orthorhombic 2H and γ'_1 as shown in Figure 1(b). The emergence of these phases mainly relies on the temperature and stress conditions. With a further increase the percentage of Al to 13.7-14%, the quantity and morphology of the precipitations led to increase as have been indicated by the arrows in Figure 1(c-d), where the microstructure become indistinct for both structure γ'_1 (2H) and β'_1 (18R) martensite, according to the relationship between the various phase transformation and varying alloy compositions [8]. The martensitic transformation temperatures are highly dependent on the contents of Al and Ni, where it can lie between -200 to 200 °C[8]. The temperature can be calculated from the following formula[9]:

$$M_s \text{ (}^\circ\text{C)} = 2020 - 45 \times (\text{wt.\% Ni}) - 134 \times (\text{wt.\% Al}) \quad (1)$$

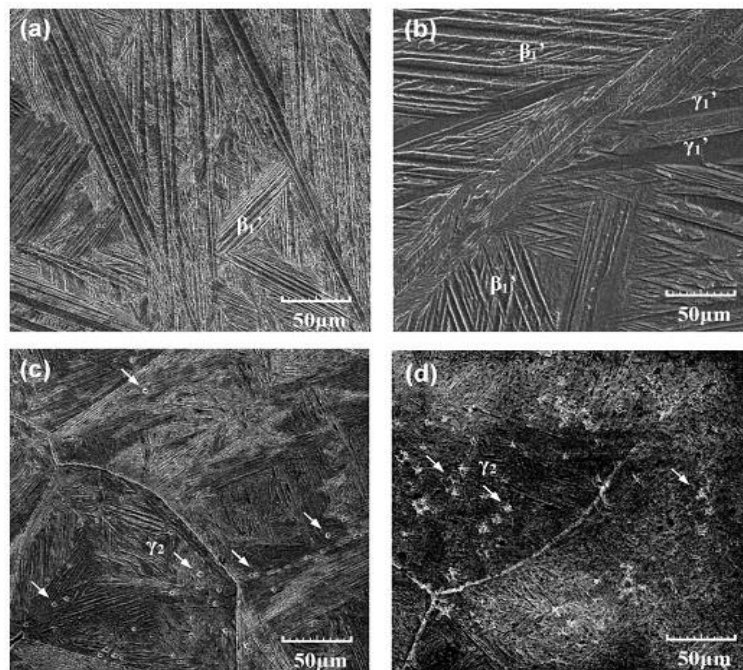


Figure 1 Electron micrographs of a) Cu-13 wt.% Al-4wt.% Ni, b) Cu-13.5wt.% Al-4wt.% Ni, c) Cu-13.7wt.% Al-4wt.% Ni, and d) Cu-14wt.% Al-4wt.% Ni. [8]

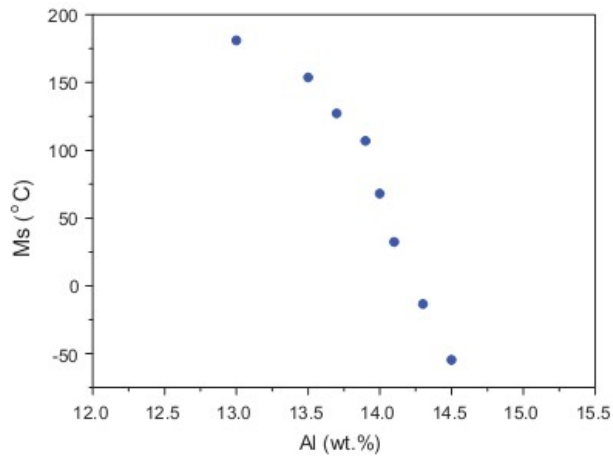


Figure 2 The M_s transformation temperature Vs Al content [8]

Chang [8] has found that with increase in the Al content more than 14 %, the M_s is around room temperature as shown in Figure 2. The addition of Ni to ternary alloys is to slow down the diffusivity of both Cu and Al atoms, which remain in the parent phase β_1 until the M_s temperature is reached.

2.1.2 Effect of Titanium, Zirconium and Manganese Elements on the Microstructure Cu-Al-Ni SMAs

Sugimoto, *et al.* [10] and Sure and Brown [11] have shown that the Ti and Zr addition to the Cu-Al-Ni SMAs have a significant effect in term of grain refinement and the restricted the grain growth rates. Meanwhile, these elements have uniformly distributed into the matrix and their most effectiveness have concentrated on the formation of the second phase. The martensite transformation temperature has behave according to the type of the alloying element, where it has decreased with increasing Ti amount and increased with increasing the Zr amount has been reported by Lee, *et al.* [12]. This is attributed to the dissolving percentage of Ti and Zr in the β -phase.

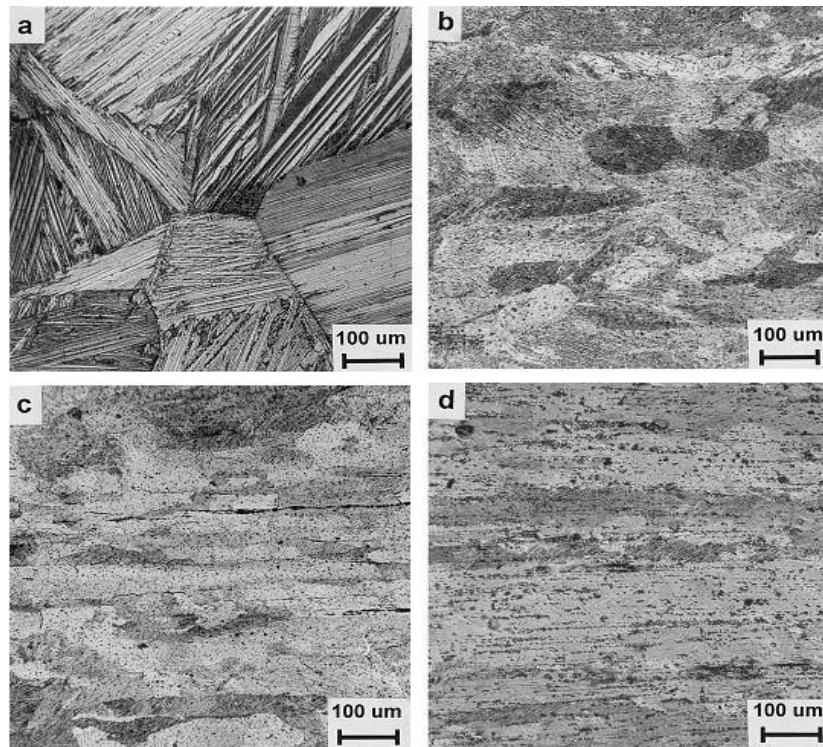


Figure 3 Optical micrographs of a) Cu-11.85wt.% Al- 3.2wt.% Ni- 3wt.% Mn, b) Cu-11.9wt.% Al- 5wt.% Ni- 2wt.% Mn-1wt.% Ti, c) Cu-11.4wt.% Al- 2.5wt.% Ni- 5wt.% Mn-0.4wt.% Ti, and d) Cu-11.8wt.% Al- 5wt.% Ni- 2wt.% Mn-1%wt.% Ti [13]

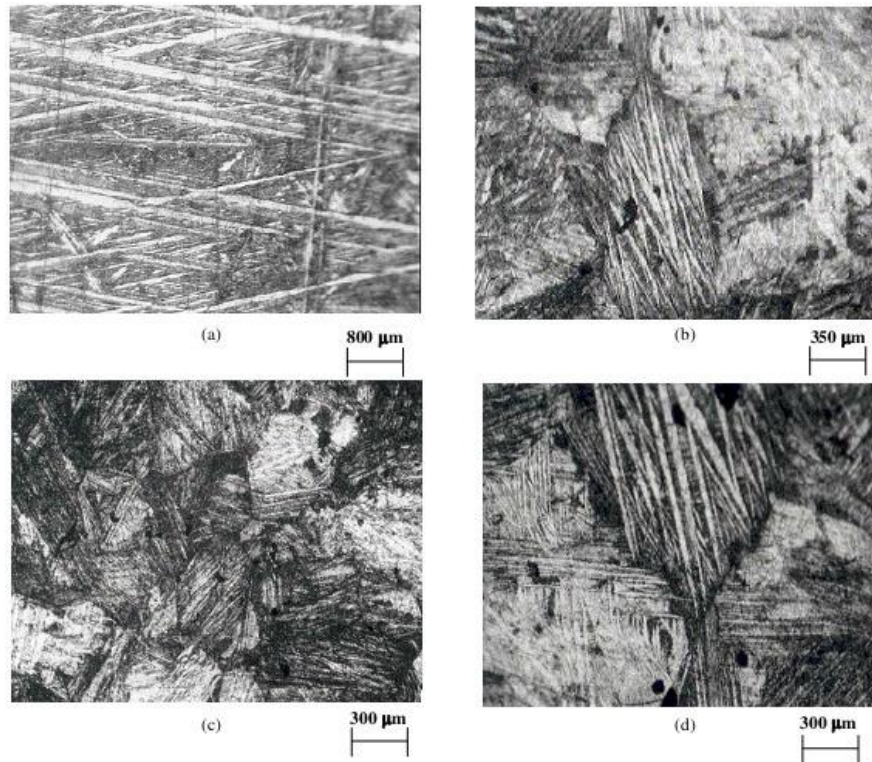


Figure 4 Optical micrographs of Cu–Al–Ni alloys: (a) Cu–Al–Ni; (b) Cu–Al–Ni–0.2Ti; (c) Cu–Al–Ni–0.4Mn; (d) Cu–Al–Ni–0.2Zr [16]

Other work has been done by J. Dutkiewicz, *et al.* [13], where they have agreed with that the addition of Ti to the Cu–Al–Ni causing a smaller and elongated grain size because the Ti addition is restricted the grain growth as shown in Figure 3 and disagreed with that Ti additions is decreased the M_s . Therefore, they have proved that the M_s temperature increases as grain size reduces, where the rapid drop of the transformation temperatures at the smallest grain size range. While, Sampath [16] has shown that there are two different morphologies are formed into the microstructure of Cu–13.3wt. % Al–4.3wt.%Ni SMA and these morphologies are γ_1 with a self accommodating structure and β_1 with a acicular structure. Also, found that with adding a minor addition of Ti, Mn, or Zr to the base alloy, a new precipitations/compounds have formed with Al element as shown in Figure 4. These precipitations are able to enhance the formation of martensite β_1 phase.

2.2 Effect of Alloying Elements on the Mechanical Properties

Cu–Al–Ni shape memory alloys (SMA) have been selected as high potential materials for high temperature applications. This is attributed to their high thermal stability at a temperature above 100°C [5,6]. On the other hand, these alloys have their limitations such as the high brittleness, because of the appearance of brittle phase γ_2 at grain boundaries, the enormous increase in grain size duplicated with a high elastic variation [1, 17,18]. Thus, their disadvantages have restricted the usage of these alloys for commercial applications [14, 19,20]. One of the ways to solve this problem is the grain refinement; By adding some of the alloying elements such as Ti, Mn, V, Nb, B and others or varying the compositions of Ni or Al, exhibited some improvement in mechanical properties of the conventionally Cu–Al–Ni SMAs [21–23]. The reason behind this improvement is attributed to the addition of alloying

elements, where these elements are restrict the grain growth and refine the grains. However, these alloying elements have a significant effect on the mechanical properties of Cu–Al–Ni SMAs due to the formation as a second phase structure in the microstructure [24].

2.2.1 Effect of Manganese and Boron Elements on the Mechanical Properties of Cu–Al–Ni SMAs

The addition of manganese and boron efficiently to refined the grain size however, the increasing of the boron concentration produced the highest strain hardening. Lee, *et al.* [12] have been found that the addition of boride particles helped to relieve the stress concentrations at the grain boundaries. While, Morris [25] found that with adding the boron to the Cu–Al–Ni SMAs, the ductility increased. This is also can attributed to the presence of boride particle. Another relevant point that, the boron addition can be effected on the fracture mode, whereas it has transferred from brittle failure to intergranular and transgranular failures. Another work for the same author [26], found that the values of yield stress, hardness and tensile strength have been increased with increasing the percentage of boron addition. It seems that the boride particles have restricted the interface movement, therefore the required stress to re-oriented the martensite phase is high. These particles have played a significant role by accommodating a new strain concentration generated by the coexistence of the new stress-induced martensite.

2.2.2 Effect of Beryllium Element on the Mechanical Properties of Cu–Al–Ni SMAs

Huaping Xu, *et al.* [27] found with adding the Be to the Cu–Al–Ni SMAs, the fatigue life has been increased, whereas the strain recovery has reached to 30 % higher than base alloy, that increasing in the recovery strain is almost equalized to the

recovery strain of the NiTi. Ming Zhu [24] found the bending performance, tensile strength, and elongation percentage of Cu-Al-Ni-Be are higher than Cu-Al-Ni alloy, where the maximum stress of this alloy could reached to 780 MPa with 18% of strain

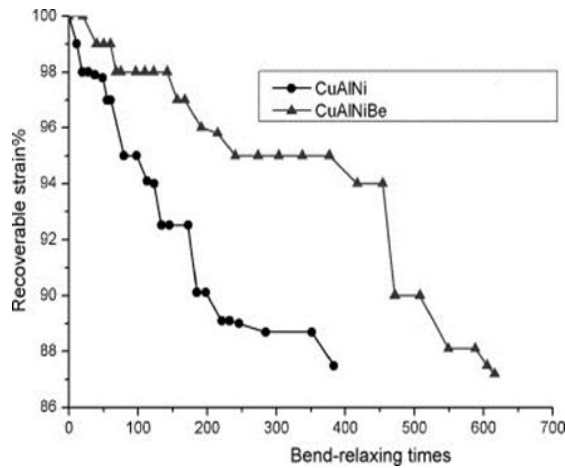


Figure 5 Recoverable strain vs. bend-relaxing times of CuAlNi and CuAlNiBe [24]

as shown in Figure 5 and Figure 6. This may imply that the mechanical property of Cu-based SMAs can be significantly improved by adding the alloying elements.

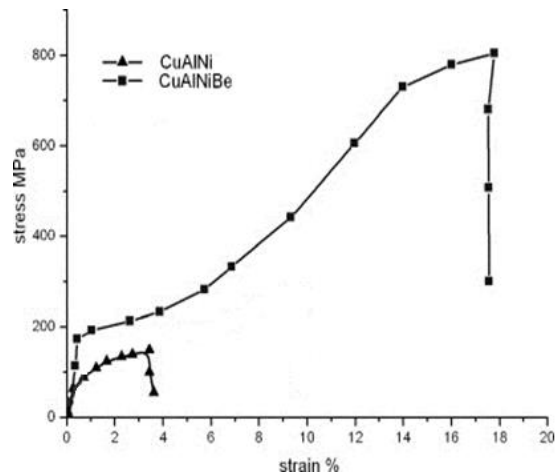


Figure 6. Stress–strain curves of SMA samples at room temperature (25°C) [24]

2.2.2 Effect of Titanium, Manganese, Zirconium, Niobium, and Vanadium Elements on the Mechanical Properties of Cu-Al-Ni SMAs

The additions of Ti, Mn, and Zr to Cu-Al-Ni shape memory alloys have decreased the grain size reported as by V. Sampath [16], therefore the values of hardness increased. This is attributed to the formation of fine precipitates that restricted the grain growth by the pinning effect. Also, there are some other elements have shown a significant effect on the mechanical properties of Cu-Al-Ni SMAs during the addition such as Nb and V, the rupture strain has increased up to 14 % and 6 % respectively, which is much higher than the base alloy as it has been reported by Gomes, et al. [28].

3.0 CONCLUSIONS

Based on the review of several authors, it can concluded that:

- (1) Cu-Al-Ni SMAs are very sensitive to variations of Al and Ni contents; the structure of these alloys has completely changed due to this variation.
- (2) Adding the alloying elements can significantly effected on the microstructure in the term of grain refinements, whereas that effect can directly vary the whole properties of the Cu-Al-Ni SMAs.
- (3) The phase transformation behaviors – temperatures are completely dependent on type of the fourth or fifth addition element.
- (4) Ti and Zr additions have played the same role from the side of grain refinement, but Ti additions have decreased the transformation temperature that opposite to the Zr additions, which have increased, this is due to the dissolving percentage of these elements in the β -phase.

- (5) The improvements of yield stress, hardness, ductility, and tensile strength for the Cu-Al-Ni-B, is related to the restriction of boride particles for the interfaces movement, and then need a high stress to re-orient.
- (6) The adding of the Be to the of the Cu-Al-Ni SMAs has improved the recovery strain to be almost equalized to NiTi SMAs.
- (7) The rupture strain of the Cu-Al-Ni SMAs has increased to 14 % and 6 % during the adding of Nb and V elements respectively.

Acknowledgment

The author(s) would like to thank the Malaysian Ministry of Higher Education (MOHE) and Universiti Teknologi Malaysia for providing the financial support and facilities for this research, under Grant No. R.J130000.7824.4F150.

References

- [1] C. M. W. K. Otsuka. 1998. *Shape Memory Materials*. Cambridge University Press, Cambridge.
- [2] J. Van Humbeeck. 2001. Shape Memory Alloys: A Material and Technology. *Adv. Eng. Mate.* 3: 837–850.
- [3] K. Mehrabi, M. Bruncko, A. C. 2012. Kneissl: Microstructure, Mechanical and Functional Properties of NiTi Based Shape Memory Ribbons. *J. Alloys and Compounds*. 526: 45–52.
- [4] X. R. K Otsuka. 2005. Physical Metallurgy of Ti–Ni-based Shape Memory Alloys. *Progress in Materials Science*. 50: 511–678.
- [5] G. Lojen, I. Anžel, A. Kneissl, A. Krizman, E. Unterweger, B. Kosec, M. Bizjak. 2005. Microstructure of Rapidly Solidified Cu–Al–Ni Shape Memory Alloy Ribbons. *J. Mate Processing Tech.* 162–163: 220–229.
- [6] S. M. M. Fremond. 1996. *Shape Memory Alloys*. Springer-Verlag, Wien, New York.
- [7] M. H. W.a. R. J. B. D. E. Hodgson. 1991. *Shape Memory Alloys*. 10 ed. American Society for Metals, Cleverland, Ohio.

- [8] Y. Chen, X. Zhang, D. C. Dunand, C. A. Schuh. 2009. Shape Memory and Superelasticity in Polycrystalline Cu–Al–Ni Microwires. *Applied Physics Letters*. 95: 171906–171903.
- [9] A. C. Kneissl, E. Unterweger, G. Lojen, I. Anzel. 2005. Microstructure and Properties of Shape Memory Alloys. *Microscopy and Microanalysis*. 11: 1704–1705.
- [10] K. K. Sugimoto, H. Matsumoto, S. Komatsu, K. Akamatsu and T. Sugimoto. 1982. Grain-Refinement and the Related Phenomena in Quaternary Cu–Al–Ni–Ti Shape Memory Alloys. *Journal of Physics*. 43: C4–761.
- [11] L. C. Brown. G. N. Sure. 1984. The Mechanical Properties of Grain Refined β -Cu–Al–Ni strain- Memory Alloys. *Metall. Trans. A* 15: 1613–1621.
- [12] J. S. Lee and C. M. Wayman. 1986. Grain Refinement of a Cu–Al–Ni Shape Memory Alloy by Ti and Zr Additions. *Trans. Jpn. Inst. Met.* 27: 584–591.
- [13] J. Dutkiewicz, T. Czeppe, J. Morgiel. 1999. Effect of Titanium on Structure and Martensic Transformation in Rapidly Solidified Cu–Al–Ni–Mn–Ti Alloys. *Materials Science and Engineering. A* 273–275: 703–707.
- [14] K. Adachi, Y. Hamada, Y. Tagawa. 1987. Crystal Structure of the X-phase in Grain-refined Cu–Al–Ni–Ti Shape Memory Alloys. *Scripta Metallurgica*. 21: 453–458.
- [15] Ratchev, P., J. Van Humbeeck, L. Delaey. 1993. On the Formation of 2H Stacking Sequence in 18R Martensite Plates in a Precipitate Containing CuAlNiTiMn alloy. *Acta Metallurgica Et Materialia*. 41(8): 2441–2449.
- [16] V. Sampath. 2005. Studies on the Effect of Grain Refinement and Thermal Processing on Shape Memory Characteristics of Cu–Al–Ni alloys. *Smart Materials and Structures*. 14: S253.
- [17] K.O. S. Miyazaki, H. Sakamoto, K. Shimizu. 1981. Study of Fracture In Cu–Al–Ni Shape Memory Bicrystals. *Trans. Jpn. Inst. Met.* 22: 244–252.
- [18] P. C. C. S. W. Husain. 1987. Grain Boundary Embrittlement in Cu–Al–Ni β Phase Alloys. *J. Mater. Sci.* 22: 2351–2356.
- [19] J. S. Lee, C. M. Wayman. 1986. Grain Refinement of Cu–Zn–Al Shape Memory Alloys. *Metallography*. 19: 401–419.
- [20] Y. Gao, M. Zhu, J. K. L. Lai. 1998. Microstructure Characterization and Effect of Thermal Cycling and Ageing on Vanadium-doped Cu–Al–Ni–Mn high-temperature Shape Memory Alloy. *Journal of Materials Science*. 33: 3579–3584.
- [21] J. Kim, D. Roh, E. Lee, Y. Kim. 1990. Effects on Microstructure and Tensile Properties of a Zirconium Addition to a Cu–Al–Ni shape Memory Alloy. *Metallurgical and Materials Transactions. A* 21: 741–744.
- [22] K. Adachi, K. Shoji, Y. Hamada. 1989. Formation of (X) Phases and Origin of Grain Refinement Effect in Cu–Al–Ni Shape Memory Alloys Added with Titanium. *ISIJ International*. 29: 378–387.
- [23] S. K. Vajpai, R. K. Dube, S. Sangal. 2011. Microstructure and Properties of Cu–Al–Ni Shape Memory Alloy Strips Prepared Via Hot Densification Rolling of Argon Atomized Powder Preforms. *Materials Science and Engineering. A* 529: 378–387.
- [24] M. Zhu, X. Ye, C. Li, G. Song, Q. Zhai. 2009. Preparation of Single Crystal CuAlNiBe SMA and Its Performances. *Chem Inform.* 40.
- [25] M. A. Morris. 1991. Influence of Boron Additions On Ductility And Microstructure Of Shape Memory Cu–Al–Ni alloys. *Scripta Metallurgica*. 25: 2541–2546.
- [26] M. A. Morris. 1992. High Temperature Properties of Ductile Cu–Al–Ni Shape Memory Alloys with Boron Additions. *Acta Metal. Mater.* 40: 1573–1586.
- [27] Huaping Xu, Gaofeng Song, Xiemin Mao. 2011. Influence of Be and Ni to Cu–Al Alloy Shape Memory Performance. *Advanced Materials Research*. 197–198: 1258–1262.
- [28] R. M. Gomes, A. C. R. Veloso, V. T. L. Buono, S. J. G. Lima, and T. A. A. Melo. 2008. Pseudoelasticity of Cu– 13.8 Al–Ni alloys containing V and Nb. *Trans Tech Publications*. Switzerland.