Effect of Varying Nickel Addition on Shape Memory, Mechanical and Corrosion Behaviors of Copper-Aluminum-Niobium Alloys

S. M. Dar[1], Q. Nawaz[2], Z. Abbas[3]

[1]Materials Science and Engineering Department, Ghulam Ishaq Khan Institute of Engineering Sciences and Technology, Topi 23460, Khyber Pakhtunkhwa, Pakistan
[2]Materials Science and Engineering Department, University of Erlangen-Nuremberg, 91058 Erlangen Germany
[3]Metallurgy and Materials Engineering Department, University of Engineering and Technology, Taxila 47050, Pakistan
[2]qaisar.nawaz@ymail.com

Abstract-Shape memory alloys find their applications in automotive and aircraft structures as micro-actuators. In present study, shape memory and mechanical behaviors of Cu-Al-Nb shape memory alloys are investigated with varying Ni addition (0, 1, 2 and 3 w/w %) by bend and tension experiments. It is observed that Ni addition has resulted in gradual improvement of mechanical and shape memory properties. Microstructure observation and xrd analysis reveals that this improvement in properties is because of increased amount of monoclinic 18R type thermo-elastic martensite. Ni containing Cu-Al-Nb shape memory alloy has also shown better corrosion resistance.

Keywords-Shape Memory Alloy, Microstructure, Mechanical behavior, X-ray Diffraction, Corrosion

I. Introduction

Shape memory alloys (SMAs) have a variety of applications. These applications fall in two broad categories, namely, medical (implants) and non-medical [i, ii]. Recent interests are focused to improve the shape memory strain, thermal stability and creep resistance of these materials. SMAs when employed in engineering components in automotive and aerospace industries can improve their performance. The maximum operating temperature of binary Ni-Ti SMAs is limited to 100-120°C [iii, iv]. This has motivated scientists to develop shape memory alloys that are capable of sustaining working temperatures above 100°C to meet the future aircraft design and performance requirements [v]. Ni-Ti-(Pd/Pt) and Ni-Ti-(Hf/Zr) SMAs show some potential for such applications but these alloys also have some shortcomings [vi]: (1) difficult to process, (2) expensive due to constituent elements, also (3) abrupt decrease in the shape memory recovery when the operating temperature exceeds 300°C [vii, viii]. Compared with Ni-Ti-based SMAs, Cu-based SMAs, as the second family of SMAs, are low cost and easy to process. Cu-Al-Ni shape memory alloys have some disadvantages, namely microstructure instability and less ductility [vii, ix, x]. Cu-Al-Nb shape memory alloys, another class of Cu-based SMAs, have good thermal stability, ductility and high shape memory effect [xi]. Martensitic transformation temperature of these alloys is above 200°C which makes them appropriate candidate for actuation purposes [xii]. It is recently shown that the shape memory strain of these alloys shows dependency on annealing temperature and duration of time [xiii]. Different methods have been employed to manufacture Cu-Al-Nb SMAs, among which mechanical alloying is evaluated as a suitable method but no data has been reported about the mechanical properties or shape memory properties [xiv]. Effect of various alloying elements in Cu-Al-Nb system has also been studied along with grain refiners (like B and Ti) [xv]. No quantitative data has been presented about the shape memory recovery of these alloys.

Furthermore, effect of fourth element addition (e.g, Ni) in Cu-based SMAs is found to decrease the plasticity [xi]. However, very little quantitative information exists in literature about these alloys. This lack of key information demands more studies to be carried out to optimize the properties of Cu-based SMAs [xvi]. This work aims to study the effect of varying Ni content on the shape memory and mechanical behaviors of Cu-Al-Nb SMAs. Corrosion behavior of the prepared alloys is also studied.

II. Experimental

A. Alloy Preparation

Four compositions of Cu-Al-Nb SMAs were prepared from high purity element metals by electric arc-melting (locally manufactured arc furnace) in argon atmosphere. The alloy buttons were re-melted five times to achieve the desired composition. After processed, homogenization was carried out for 6 hrs at 950°C under shielding argon atmosphere in Carbolite Tube Furnace. Chemical composition of these alloys, given in Table 1, was determined by energy dispersive spectroscopy (EDS) analysis.

TABLE I
EXPERIMENTAL ALLOYS, CHEMICAL COMPOSITION MEASURED BY EDS

Alloy	Nominal composition, w/w%			
	Cu	Al	Nb	Ni
Alloy 1	85.9	11.6	2.5	-
Alloy 2	86.2	10.2	2.4	1.1
Alloy 3	84.0	11.8	2.2	1.9
Alloy 4	83.4	11.1	2.4	3.0

B. Hot rolling and Heat Treatment

Alloy buttons were rolled at 900°C into sheets by gradually reducing their thickness from 10mm to about 0.85-0.90mm. These sheets were further cut by diamond saw to prepare samples for bend test and tension test. Samples were solution treated at 850°C for 20 minutes in argon atmosphere and quenched into iced-salt water.

C. Microstructure Evaluation

For microstructure examination, samples were polished using Struers Polishing Machine and etched with a solution of 50ml NH_4OH, 50ml H_2O_2 (3wt%) and 50ml H_2O. Microstructure of samples was observed under an optical microscope (OLYMPUS B061). Grain size was measured by following an ASTM standard E112-10 using lineal intercept method. SEM micrographs were obtained using XL30 (Philips Japan) scanning electron microscope. For phase determination x-ray diffraction (XRD) experiment was carried out in the range of 2θ from 20° to 80° with PANalytical X'Pert PRO diffractometer. Ni filtered Cu-K_α radiations were used for this purpose.

D. Mechanical Properties Evaluation

Hardness experiment was performed using SEIKI DVK-2 (MATSUZAWA Japan) Vickers' hardness tester. Readings were obtained while setting following parameters: load of 1kgf, loading speed of 50µm/sec and dwell time of 10seconds. Samples for bend test had following dimensions: $40\times3\times0.9mm^3$. Annealing treatment, for shape recovery determination, was performed at 400°C for 20 minutes in argon atmosphere. Tension tests were carried out on a100kN universal testing machine (Instron-8501) at a strain rate of 5×10^{-5}/s. Tension test samples had the dimensions shown in Fig.1.

E. Shape Memory Evaluation

Shape memory effect was measured by pre-straining the samples followed by annealing. Pre-strain (ε) value of 3.5% was calculated by using the formula in Eqn. (1):

$$\varepsilon = \frac{t}{(t+2R)} \quad (1)$$

Where t is sample thickness, R is radius of curvature. Recovery (η), representative of shape memory behavior, was calculated by the formula [xii]:

$$\eta = \frac{\theta_s - \theta_t}{\theta_s} \times 100\% \quad (2)$$

Where θ_s is the spring back position, θ_t the heating position.

F. Corrosion resistance evaluation

Corrosion resistance of Alloy 1 (0 w/w% Ni) and Alloy 4 (3w/w% Ni) was investigated in a solution of 0.5M H_2SO_4 by Tafel scan. Corrosion current (I_{corr}) was determined from Tafel plot by Butler-Volmer equation fitting. Then corrosion rate was determined in mills per year (mpy).

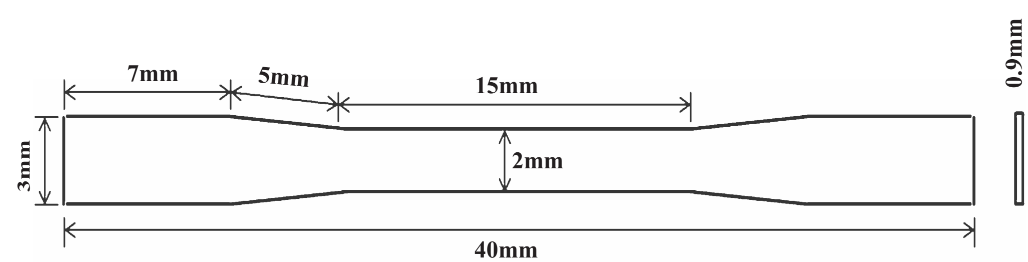

Fig.1. Dimensions of the samples for tensile testing

III. RESULTS AND DISCUSSION

A. Microstructure and Phases

X-ray diffraction (XRD) patterns of Alloys 1-4 are shown in Fig. 2, suggesting the presence of monoclinic 18R martensite (peaks at 2 of 40°~50°) in the studied alloys no matter how much amount of Ni is present. It is clear that in Alloy 1 few peaks are present between 40°~50°. In alloys with 1-3w/w% Ni addition more peaks of monoclinic 18R martensite appear in this range and further intensify. In Alloy 4 with maximum amount of Ni (i.e. 3w/w%), these peaks of monoclinic 18R martensite are intensified to a great extent. Optical micrographs of Alloys 1-4 in Fig. 3 indicate that Ni addition seems to have little influence on grain size (G). For Alloys 1-4, the grain size is in the range of 151μm-180μm. The presence of martensite can be seen in the optical images. The SEM images of Alloys 1 and 4 in Fig. 4 show twinned martensitic structure in the prepared alloys which is the characteristic of shape memory alloys.

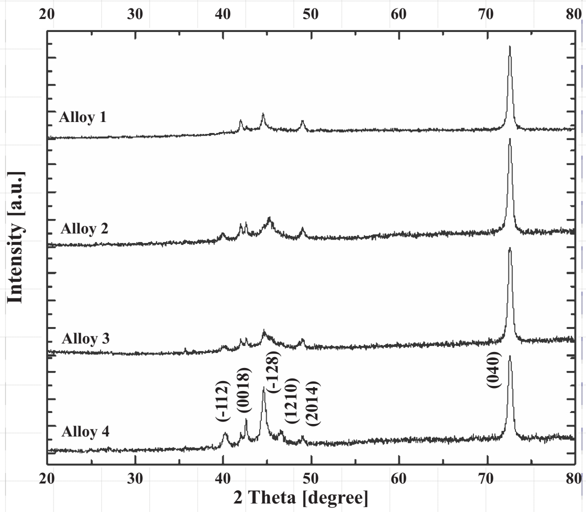

Fig. 2. X-ray diffraction patterns of Alloys 1-4

B. Shape Memory Behavior

Fig. 5 shows variation of shape memory recovery (SMR) in Cu-Al-Nb SMAs with Ni addition. For Alloy 1, the value of SMR for 3.5% pre-strain is 38.2% and it is considerably increased with Ni addition. However, when the amount of Ni is beyond 2w/w%, increase in SMR is slightly dropped. The maximum SMR is 91% for Alloy 4. This improvement in SMR is due to increase in critical stress and increased amount of monoclinic 18R martensite with Ni addition. This thermos-elastic martensite is responsible for shape memory effect [xiii-xiv].

When a shape memory alloy is deformed in solution treated condition stress-induced martensite is formed which demonstrates shape recovery upon annealing. Otsuka and Ren [xvii] has suggested that solid solution strengthening from alloying addition plays a very important role in improving the shape memory properties. In our study, addition of Ni in the Cu-Al-Nb SMAs has resulted in considerable improvement of shape memory recovery.

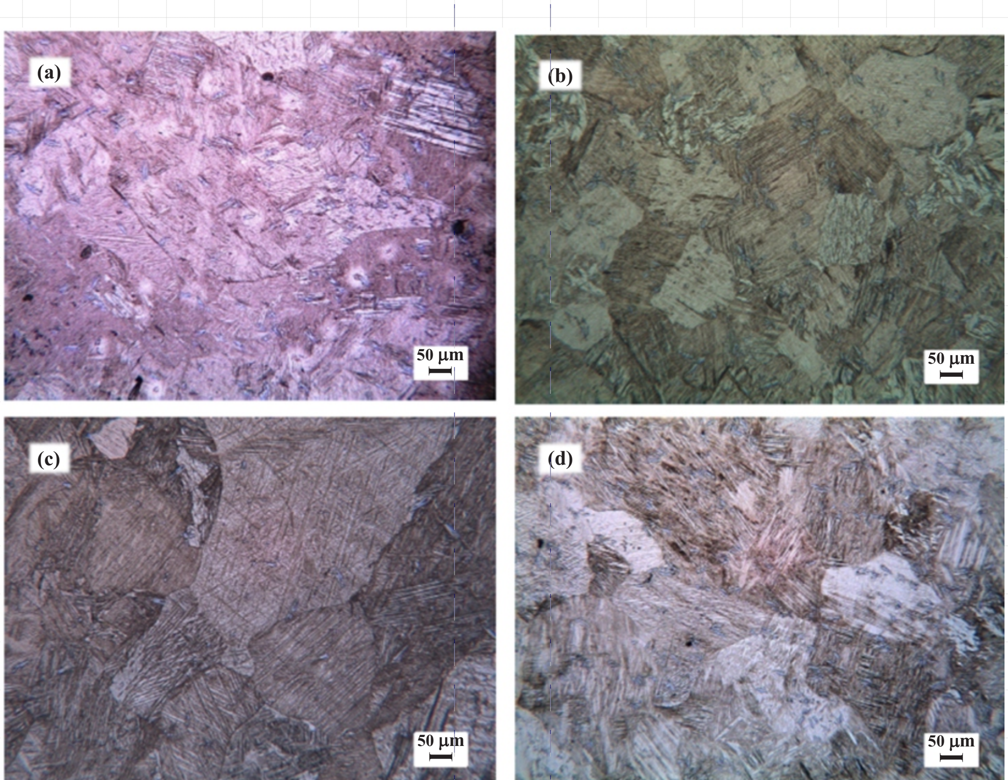

Fig. 3. Optical microscopy images showing martensitic structure, (a) Alloy1, (b) Alloy 2, (c) Alloy 3, (d) Alloy 4

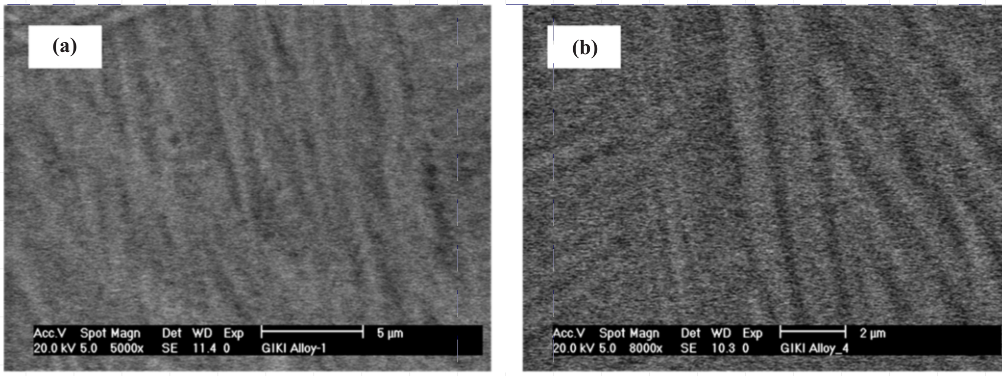

Fig. 4. Scanning electron microscopy images of the studied alloys showing twinned martensitic structure, Alloy 1 (a) and Alloy 4 (b)

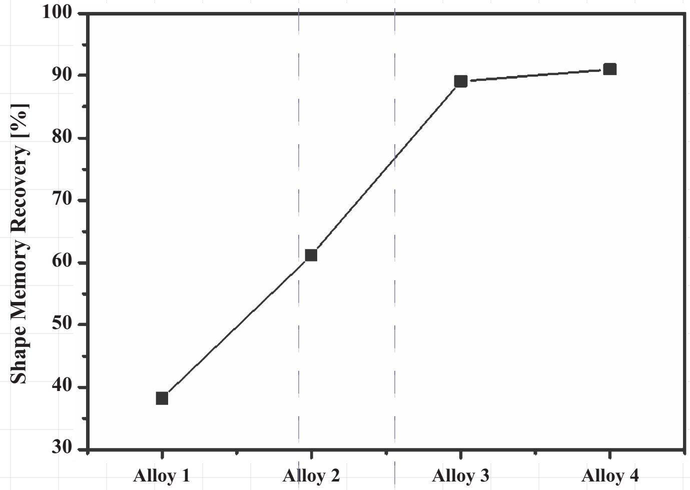

Fig. 5. Variation in shape memory recovery of Alloys 1-4, showing improvement in shape memory recovery with Ni addition

C. Mechanical Properties

Fig. 6 (a) shows engineering stress-strain plots for Alloys 1-4. It shows that yield strength of the prepared alloys is increased from 206MPa to 436MPa with Ni addition. Ultimate tensile strength (UTS) is also improved from 532MPa to 722MPa, while fracture elongation is decreased from 12.1% to 6.1%, as seen in Fig. 6 (b). For Alloy 1, UTS is 532MPa and fracture elongation is 12.1% quite close to the value of 12.7%reported in the literature [xii]. Maximum UTS of 722MPa is obtained in Alloy 4 while the fracture elongation drops down to 6.1%. The increase in strength is related with the solid solution strengthening from Ni addition. These results are in good agreement with the literature [xvii, xviii].

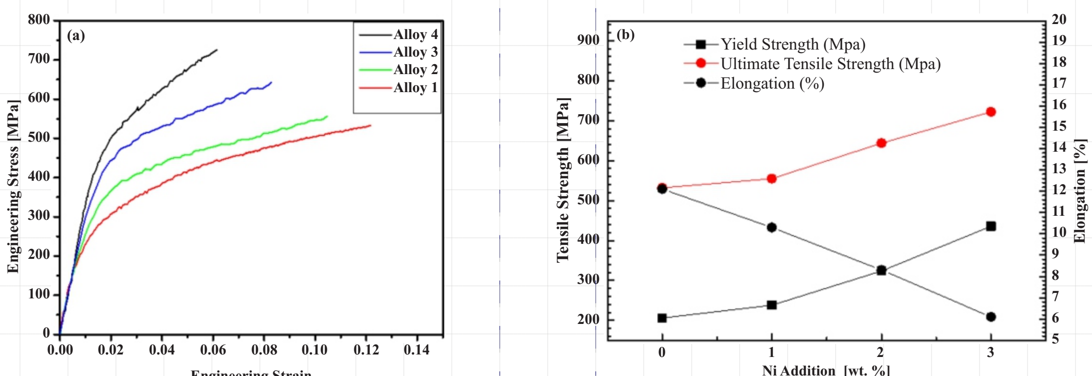

Fig. 6. Stress-strain curves of Alloys 1-4 (a), and variation in ultimate tensile strength and fracture elongation with Ni addition(b)

Hardness experiment results are shown in Fig. 7. Value of hardness for Alloy 1 is determined to be 207HV which is very close to reported value of 213HV in literature [xii]. With Ni addition, it is considerably increased and a maximum value of 238HV is reached for Alloy 4. It has been suggested in literature [xi] that addition of fourth element in shape memory alloys can result in strengthening of these alloys (in our case Ni).

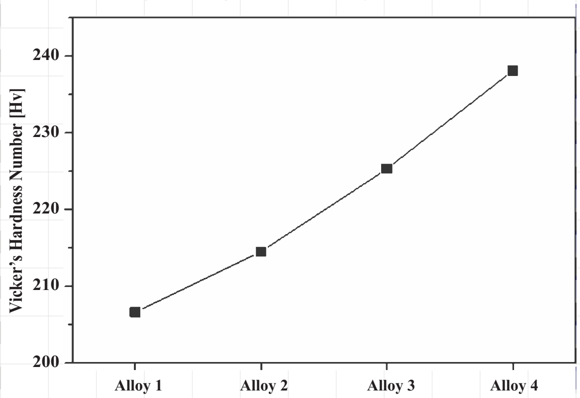

Fig. 7. Variation in Vicker's hardness number for Alloy 1-4, showing effect of Ni addition on hardness

D. Corrosion behavior

Two alloys Alloy 1 and Alloy 4 (with 0w/w%Ni and 3w/w%Ni) were selected to study the corrosion behavior. Corrosion experiments were performed in 0.5M H_2SO_4 solution by Tafel scan and the results are shown in Fig. 8. It is reported that Al content plays a key role in the corrosion protection of Cu-Al based alloys in 0.5M H_2SO_4 [xix]. In present investigation Al content was same in all the four alloys. For corrosion rate determination, first corrosion current (I_{corr}) was calculation by fitting Butler-Volmer equation on Tafel plot. It yielded values of 4.38mA and 2.45mA for Alloy 1 and Alloy 4, respectively. By using ASTM standard G102, the corrosion penetration rate (CPR) for Alloys 1 and 4 were determined to be 54.72×10^3mpy and 21.33×10^3mpy, respectively. These results are also summarized in Table II. So, Alloy 4 is more corrosion resistant than Alloy 1, namely, addition of Ni has enhanced the corrosion resistance.

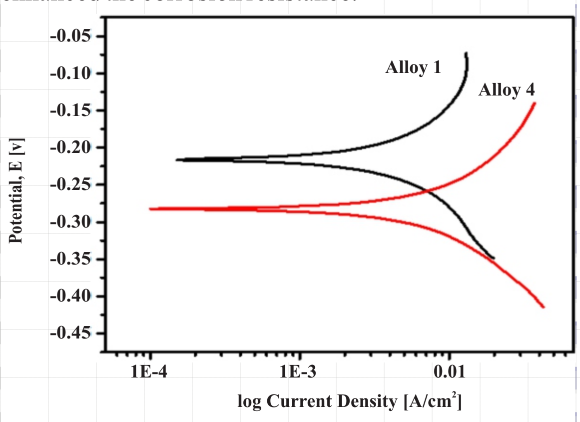

Fig. 8. Tafel scans of Alloy 1 and Alloy 4

TABLE II
CORROSION TESTING RESULTS OF ALLOY 1 AND ALLOY 4

	I_{corr} [mA]	E_{corr} [mV]	Corrosion Rate [mpy]
Alloy 1	4.380	-216.00	54.72×10^3
Alloy 4	2.450	-283.00	21.33×10^3

IV. CONCLUSIONS

Ni addition in Cu-Al-Nb shape memory alloys results in considerable increase in yield strength and ultimate tensile strength. Due to increased yield strength more stress-induced martensite is formed during plastic deformation and demonstrates improved shape memory recovery upon annealing. At the same time, Ni addition improves the corrosion resistance of Cu-Al-Nb shape memory alloys.

REFERENCES

[i] M. H. Elahinia, M. Hashemi, M. Tabesh and S. B. Bhaduri, Manufacturing and processing of NiTi implants: A review, *Progress in Materials Science*, 2012, 57(5), p 911-946

[ii] R. Mahlangu, M. J. Phasha, H. R. Chauke and P. E. Ngoepe, Structural, elastic and electronic properties of equiatomic PtTi as potential high-temperature shape memory alloy, *Intermetallics*, 2013, 33(0), p 27-32

[iii] K. V. Ramaiah, C. N. Saikrishna, Gouthama and S. K. Bhaumik, Microstructure and transformation behaviour of $Ni_{75-X}Ti_XPd_{25}$ high temperature shape memory alloys, *Journal of Alloys and Compounds*, 2013, 554(0), p 319-326

[iv] F. Yang, L. Kovarik, P. J. Phillips, R. D. Noebe and M. J. Mills, Characterizations of precipitate phases in a Ti–Ni–Pd alloy, *Scripta Materialia*, 2012, 67(2), p 145-148

[v] R. D. Joslin, R. H. Thomas and M. M. Choudhari, Synergism of flow and noise control technologies, *Progress in Aerospace Sciences*, 2005, 41(5), p 363-417

[vi] S. Shirnizu, Ya Xu, E. Okunishi, S. Tanaka, K. Otsuka and K. Mitose, Improvement of shape memory characteristics by precipitation-hardening of Ti Pd Ni alloys, *Materials letters*, 1998, 34(1), p 23-29

[vii] J. Ma, I. Karaman and R. D. Noebe, High temperature shape memory alloys, *International Materials Review*, 2010, 55(5), p 257-315

[viii] J. V. Humbeeck, Shape memory alloys with high transformation temperatures, *Materials Research Bulletin*, 2012, 47(10),

p 2966-2968

[ix] U. Sarı, T. Kırındı, Effects of deformation on microstructure and mechanical properties of a Cu–Al–Ni shape memory alloy, *Materials Characterization*, 2008, 59(7), p 920-929

[x] S. N. Balo and N. Sel, Effects of thermal aging on transformation temperatures and some physical parameters of Cu–13.5 wt.%Al–4wt.%Ni shape memory alloy, *Thermochimica Acta*, 2012, 536(0), p 1-5

[xi] J. Lelatko and H. Morawiec, The effect of Ni, Co and Cr on the primary particle structure in Cu–Al–Nb–X shape memory alloys, *Materials Chemistry and Physics*, 2003, 81(2–3), p 472-475

[xii] J. Lelatko, N. Morawiec, Y. N. Koval and V.I. Kolomyttsev, Structure and properties of high-temperature alloys with the effect of shape memory in the system Cu−Al−Nb, Metal Science & Heat Treatment, 1999, 41(8), 351-353

[xiii] C. Liu and H. W. Mu, Martensitic transformation and shape memory recovery property of Cu72Al26.5Nb1.5 high temperature shape memory alloy, *Journal of Alloys and Compounds*, 2010, 508(2), p 329-322

[xiv] M. d. C. A. d. Silva and S. J. G. d. Lima, Evaluation of mechanical alloying to obtain Cu-Al-Nb shape memory alloy, *Materials Research*, 2005, 8(2), p 169-172

[xv] C. J. de Araújo, A. A. C. Gomes, J. A. Silva, A. J. T. Cavalcanti, R. P. B. Reis and C. H. Gonzalez, Fabrication of shape memory alloys using the plasma skull push–pull process, *Journal of Materials Processing Technology*, 2009, 209(7), p 3657-3664

[xvi] J. M. Jani, M. Leary, A. Subic and M. A. Gibson, A review of shape memory alloy research, applications and opportunities, *Materials & Design*, 2014, 56(0), p 1078-1113

[xvii] K. Otsuka and X. Ren, Recent developments in the research of shape memory alloys, *Intermetallics*,1999, 7(0), 511-528

[xviii] U. S. Mallik and V. Sampath, Influence of quaternary alloying additions on transformation temperatures and shape memory properties of Cu–Al–Mn shape memory alloy, *Journal of Alloys and Compounds*, 2009, 469(1–2), p 156-163

[xix] H. H. Kuo, W. H. Wang, Y. F. Hsu and C. A. Huang, The corrosion behavior of Cu–Al and Cu–Al–Be shape-memory alloys in 0.5M H_2SO_4 solution, *Corrosion Science*, 2006, 48(12), p 4352-4364