DEVELOPMENT OF THE Cu-Al-Ni ALLOY BY POWDER METALLURGY AND CHARACTERIZATION OF ITS AGING AT TEMPERATURE

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Recently, Cu-Al-Ni shape memory alloys (SMA) have received special attention because of the shape memory phenomenon they present and the possibility of their applications at high temperature. Among several production methods, we have tried to explore a way of synthesizing these alloys by sintering under load preceded by a mechanical activation operation. The sintered alloys were subjected to a quenching and aging treatment at 250 ° C in order to highlight the structural modifications liable to degrade the phenomenon of shape memory which is a specific property of these alloys. The precipitates formed during aging block the growth of martensite and cause the formation of other variants of this phase. This phenomenon alters the thermoelastic martensitic transformation and thus degrades the shape memory of the alloy. For this, several techniques are used on the one hand to study the evolution of the material and on the other hand to characterize it before and after aging.

Keywords: Cu-Al-Ni shape memory alloys, powder metallurgy, SHS reaction, martensitic transformation, aging, precipitation

1. Introduction

Shape memory alloys (SMA) are materials capable of keeping in memory an initial shape and regaining it during a temperature variation, the application of a stress or both. The memory effect was found in the binary alloy Au-Cd for the first time in 1932 by the Swedish researcher Arne Olander **[1].**

Several binary alloys have similar properties but to a lesser extent like Cu-Zn brass whose memory effect was observed by Greninger and Mooradian **[2]** in 1938 and was found in the following years in several alloys: iron-platinum, indium- cadmium, iron-nickel, and nickel-aluminum. Researchers began to be interested in it from 1962 until the discovery of a memory effect in an

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intermetallic of the Ni-Ti system. Ni-Ti alloys with an equi-atomic content of Ni and Ti were the most widely used shape memory alloys **[3].**

They have an excellent shape memory up to 8% and are thermally stable. However, the reactivity of Ti limits their treatment in air and therefore all fusion operations must be carried out under vacuum.

Certain ferrous alloys also present SMA in certain conditions **[4]**. The Fe-Mn-Si alloys are the most important. There is a wide range of alloys which exhibit the shape memory effect, but the most commercially attractive are those which exhibit a substantial amount of stress recovery and generate significant force due to the shape change. Cu-Al-Ni shape memory alloys have received special attention due to their higher thermal stability than Cu-Zn-Al alloys **[5-6]**. The latter have maximum operating temperature of 120 ° C, but they show better ductility **[6]**. Otsuka has demonstrated the origin of the shape memory effect in the Cu-14.2Al-4.3Ni alloy **[7-8]**.

The characteristics of SMA come from the fact that they have two crystallographic phases, called by analogy to steels martensitic phase and austenitic phase. The mother austenitic phase (β) is divided into two types according to the composition ratio. The mother phase, designated by the β2 phase, exists as B2 type in Ni-Ti alloys and has an elementary composition in a ratio of approximately 50:50. The parent phase, designated by the β1 phase, exists as the DO3 type in Cu-based SMA and has approximately the elemental composition in a ratio of about 75:25 **[9]**.

The martensitic phase also has a superlattice like the mother austenitic β phase. During the martensitic transformation, the mother phase undergoes a shear deformation, and the resulting structure can be obtained by stacking the 6 atomic planes (A, B, C, A ', B', C '). Thus, depending on the stacking of these planes, different types of martensitic structures are obtained. The mother phase of B2 type is transformed into martensites 2H, 3R and 9R, while the mother phase of DO3 type is transformed into martensites 2H, 6R and 18R during quenching **[9]**.

The phase β transformation is done either by temperature change or by application of thermomechanical stress. The SMA advantage is that the phase transformation is displacive (small global displacements of atoms, therefore no change even local of the chemical composition) rather than diffusive. Shape memory materials are becoming more attractive for potential applications due to their reliability and multifunctionality. They have aroused great interest in a wide variety of applications such as: aeronautics **[10]**, automotive **[11],** robotics **[4]**, medical applications **[7]** etc.

The powder metallurgy route has emerged as an important alternative to the conventional continuous casting and rolling route for the preparation of metal strips. The starting materials are pure or alloyed metal powders. The different variants of the powder metallurgy route for the production of metal strips were

discussed by Dube **[12]** and quite recently in detail by Agrawal and all. **[13]**. It is well established that such a route can reduce energy requirements and equipment costs and provides better control of the composition during processing and a fine grain compared to the conventionally produced material. In recent years, attempts have been made to develop Cu-Al-Ni alloys by powder metallurgy from elementary powders or from pre-alloyed powders. In particular, mechanical grinding has emerged as a promising method for producing a variety of nanocrystalline and ultrafine powders. The consolidated Cu-Al-Ni preforms were densified by sintering, isostatic pressing or hot pressing.

Our study concerns the Cu-Al-Ni alloy which was produced by hot pressure sintering the mixture of elementary powders. Its dilatometric analysis revealed a rapid reaction of the elements in the vicinity of the aluminum smelting which results in a sudden swelling of the sample. This SHS (Self-propagating High-temperature Synthesis) type reaction is highly exothermic. The phases formed were identified by X-ray diffraction and examined with a scanning electron microscope (SEM). The sintered product was subjected to a quenching heat treatment followed by long aging at temperature.

The transmission electron microscope (TEM) was used to identify an intermetallic precipitate responsible for a deterioration of the shape memory effect.

2. Experimental procedure

The raw materials used are commercial powders of copper, aluminum and nickel with a purity of 99.5%. The composition studied is Cu-13% Al-4% Ni close to the eutectoid predicted by the pseudo-binary phase diagram **[14]**.

In order to choose the optimal sintering temperature, a pellet is subjected to an anisothermal dilatometry up to 950 °C using a vertical dilatometer of the SETARAM type, under argon with heating and cooling rates of 5 °C per minute. After activation for 15 minutes under argon using a Spex 8000 type grinder, the powder is poured into a cylindrical graphite mold 15 mm in diameter after having covered the walls with a thin layer of boron nitride (BN) to avoid any reaction between the powder and mold. The treatment was carried out under argon in an oven equipped with a hydraulic compression system. The sintering operation was carried at 900 °C, under argon for 2 hours. A pressure of 150 MPa was applied from 800 °C and maintained until the end of the treatment. The heating and cooling rates were set at 10 °C per minute. The sintered material was characterized by X-ray diffraction using the BRUKER D8 type diffractometer. The analyses were carried out under a wavelength of 1.54 Å, with a step of 0.02 degree and an exposure time of one second per step.

The material was then subjected to a quenching heat treatment at 850 °C followed by tempering at 120 °C to remove the stresses. The quenched and tempered material was subjected to an aging operation at 250 °C for different durations.

In order to avoid oxidation, the samples were sealed under secondary vacuum in quartz ampoules. The aged material was then examined by scanning electron microscopy (SEM). A phase identification was carried out by electron diffraction using transmission electron microscopy (TEM).

3. Results and discussion

3.1 Anisothermal dilatometry

A dilatometric study was carried out on pure copper and the Cu-13% Al-4% Ni mixture, the dilatograms are shown in Fig.1.

The dilatogram of pure copper (curve 1) showed thermal expansion up to 580 ° C followed by shrinkage at higher temperature due to the phenomenon of densification by solid phase sintering. Above the temperature in the region of 860 °C, the relative shrinkage reached a maximum value of around 2% which remained almost constant during cooling.

The Cu-13% Al-4% Ni mixture showed a relatively brutal swelling marked on curve 2 by an almost vertical straight line at the temperature close to 580 °C reflecting a rapid expansion of the sample up to 5.25%. The very rapid increase in sample size is the result of an SHS-type reaction between the mixture components. A.P. Savicki and G.N. Romanov have shown a reaction between copper and aluminum by dilatometry **[15]**. This violent reaction is strongly exothermic as evidenced by the differential thermal analysis (ATD) which revealed an exothermic peak in the vicinity of 580 °C (Fig.2).

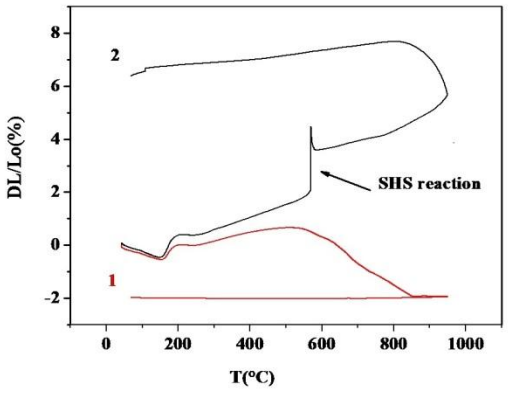


Fig.1. Dilatogram of Cu-13% Al-4% Ni mixture

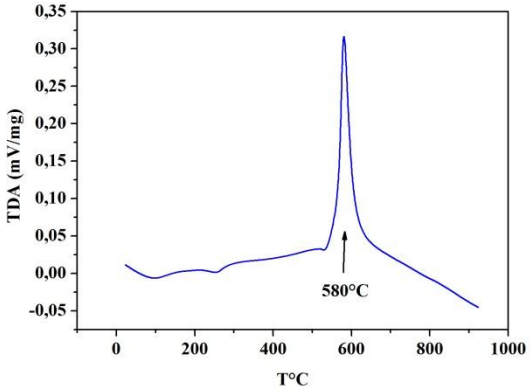


Fig.2. Differential thermal analysis of the Cu-13% Al-4% Ni mixture

3.2 X-ray diffraction

The diffractogram of the Cu-13% Al-4% Ni mixture, sintered at 900 °C, revealed the formation of 2 phases, including a solid solution α as well as an intermetallic compound of the Cu_9Al_4 type (Fig.3).

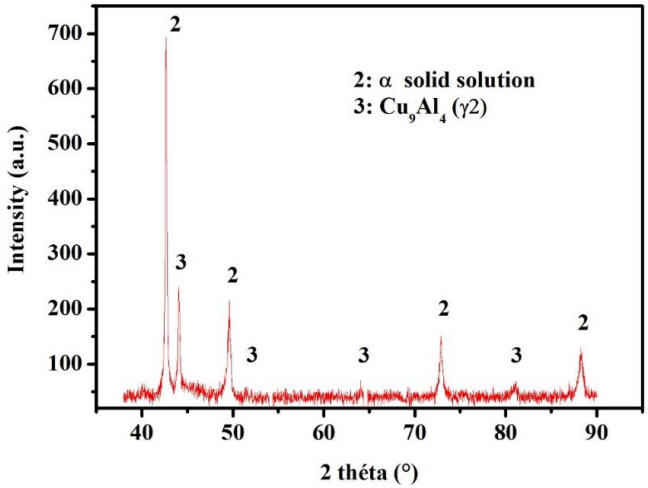


Fig. 3. Diffractogram of Cu-13% Al-4% Ni sintered at 900 °C for 2 hours

It appears that the diffraction peaks of the solid solution are shifted towards the small angles, which explains an increase in the lattice parameter by dissolution of the aluminum and nickel atoms in the copper lattice. In addition, the compound Cu_9Al_4 (γ_2) is the product of the SHS reaction between copper,

aluminum and nickel which is at the origin of the swelling of the sample observed by dilatometry.

3.3 Quenching and aging treatment

The sintered material was heated to the austenitic single-phase range at 850 °C and maintained for 30 minutes to ensure the dissolution of the compound Cu_9Al_4 (γ_2) in the β phase. Water quenching was then carried out to ensure the martensitic transformation. The quenched material was examined with a scanning electron microscope which revealed a martensitic structure shown in Fig.4a. Fine martensite needles with different orientations have been highlighted by TEM (Fig.4b)

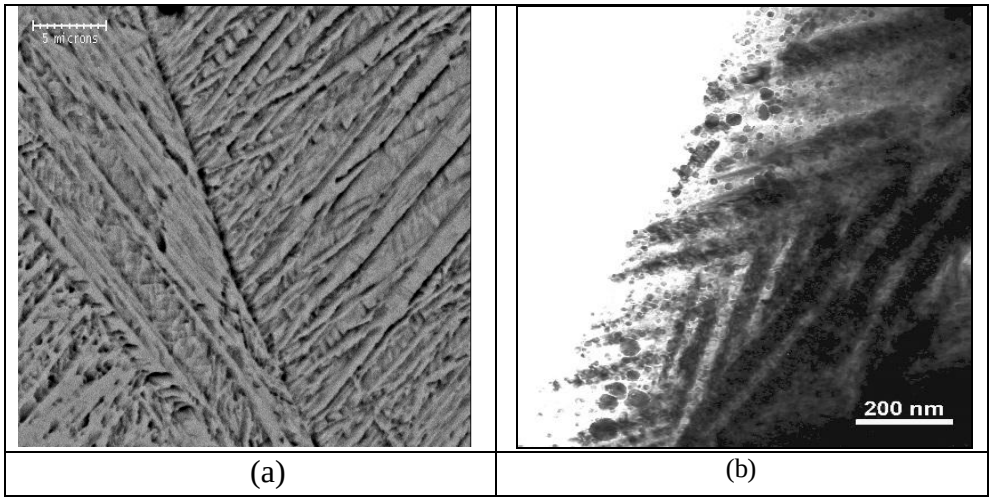


Fig.4. (a) SEM micrograph of the several variants of the martensite
(b) Different orientations of the martensite needles observed by TEM

3.4 Aging effect

The quenched and tempered material was subjected to aging at 250 ° C for different durations. The structure of the aged material, examined by SEM, revealed precipitates inside the martensite after 180 days of aging. These precipitates come from the supersaturated and metastable residual austenite β. A similar phenomenon has been reported in the case of ternary alloys CuAlBe **[16]** and CuAlAg **[17]**. The precipitates formed during aging was observed after a long period because the kinetic of the transformation is very slow at 250 ° C. Fig. 5 shows a precipitate within the martensitic matrix after 180 days of aging.

During cooling after aging, at 250 ° C, the residual metastable austenite must be transformed into martensite. It has been shown for SMA that the

martensitic transformation has a thermoelastic character whose process provides that the last martensite plate which disappears on heating is the first to be reconstituted on cooling **[18]**. On the other hand, in the presence of precipitates, the process is disturbed during a transformation, the martensite plates meet the precipitate and stop growing.

The action of the pressure exerted by the precipitate modifies the martensite variants by the formation of new self-adapting variants around the precipitate. The micrograph of Fig.5 reveals, in fact, a reorientation of the martensite plates in the neighboring layers of the precipitate. This phenomenon alters the thermoelasticity of martensitic transformation and thus degrades the shape memory property of the alloy.

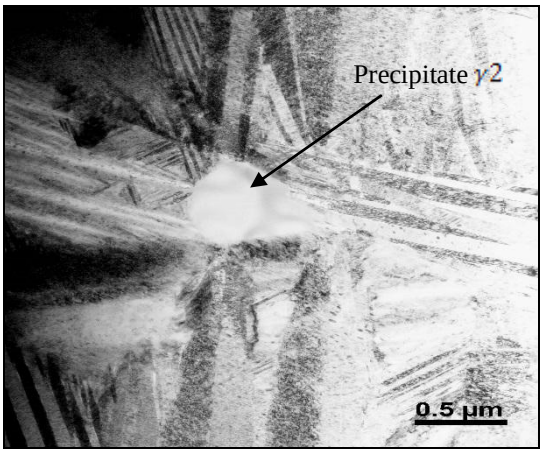


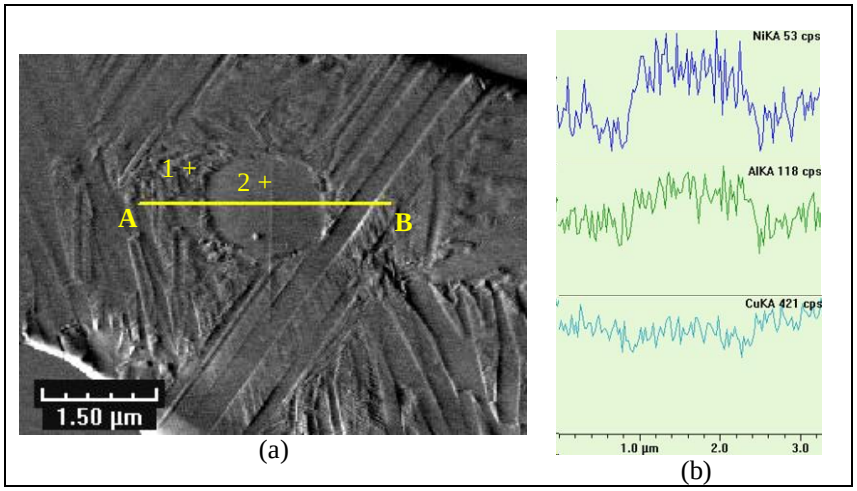
Fig. 5. Precipitate γ_2 reveled by TEM in the martensitic phase

3.4.1 EDS-X analysis

The concentration profile, obtained by EDS-X, shows clearly the difference in concentration of Al and Ni of the martensitic matrix and of the precipitate (Fig.6).

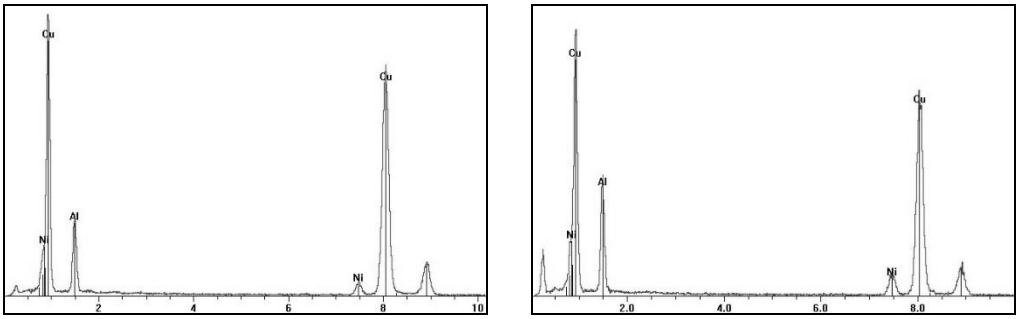
Indeed, the formation of the precipitate mobilizes a significant amount of nickel and aluminum and depletes the mother phase in these elements.

This is confirmed by point analyzes (EDS-X) carried out in points 1 and 2 respectively indicating the martensitic matrix and the precipitate. The results are presented in Fig. 7 and given in Table 1.



(a) (b)

Fig.6. (a) Micrograph of martensite around the precipitate
(b) Concentration profile according to AB across the precipitate



a) Point 1 b) Point 2

Fig.7. EDS-X analyzes of the martensitic matrix (point 1)
and the precipitate (point 2)

Table 1

Analysis results of the mother phase (point 1) and of the precipitate (point 2)

Point 1				
Element	**Line**	**keV**	**Wt%**	**At%**
Ni	KA1	7.477	3.85	3.54
Cu	KA1	8.046	83.51	71.09
Al	KA1	1.487	12.65	25.36
Total			100	100
Point 2				
Ni	KA1	7.477	7.33	6.31
Cu	KA1	8.046	74.11	58.93
Al	KA1	1.487	18.56	34.76
Total			100	100

The decrease in the concentration of the austenitic mother phase in Al and Ni consequently raises the martensitic points Ms and Mf towards the high temperatures. The increase in the temperatures of the martensitic points Ms and Mf has also been reported in the literature as a function of the aging duration **[19]**. On cooling, the residual austenite transformed into martensite whose orientation and growth disturbed by the precipitate itself. This phenomenon affects the thermoelastic character of the transformation and the shape memory of the alloy.

3.4.2 Precipitate analysis by TEM

The precipitate obtained after an aging treatment of 180 days was analyzed by electronic diffraction with TEM. Fig.8 shows the electron diffraction images with the zone axes [001], [110] and [111].

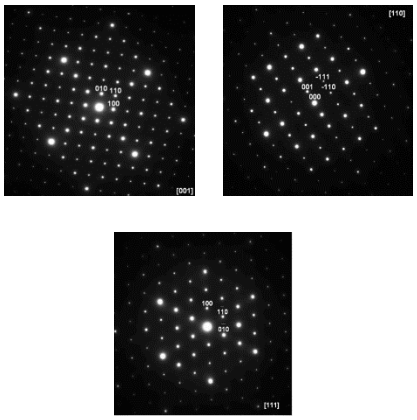


Fig. 8. Electronic diffraction of the precipitate with the zone axes [001], [110] and [111] after 180 days of aging at 250 ° C

This precipitate has the same crystal structure as the intermetallic Cu_9Al_4 (γ2) with a lattice parameter of 8.704 Å. However, the point analysis of the precipitate has revealed a presence of nickel as shown in Fig.7 as well as the analysis results given in Table 1. As copper and nickel form a solid solution with total miscibility, it is very likely that the atoms of Ni replace those of copper in the compound γ2 by forming the compound of the Cux Niy Alz type. Indeed, analysis by XRD after heat treatment reveals the martensite phase β_1' and the presence of the compound Al_7Cu_4Ni whose diffraction peaks coincide with those of the compound γ2 for certain families of diffracting planes as shown in Fig. 9.
This analysis revealed the precipitates Al_7Cu_4Ni and Cu_9Al_4. The diffraction peaks of the compound Al_7Cu_4Ni coincide partly with those of the compound Cu_9Al_4. The presence of martensite is due to the high cooling rate unlike the

sintered sample that reveals an equilibrium structure (solid solution and the compound Cu_9Al_4) as shown in Fig. 3.

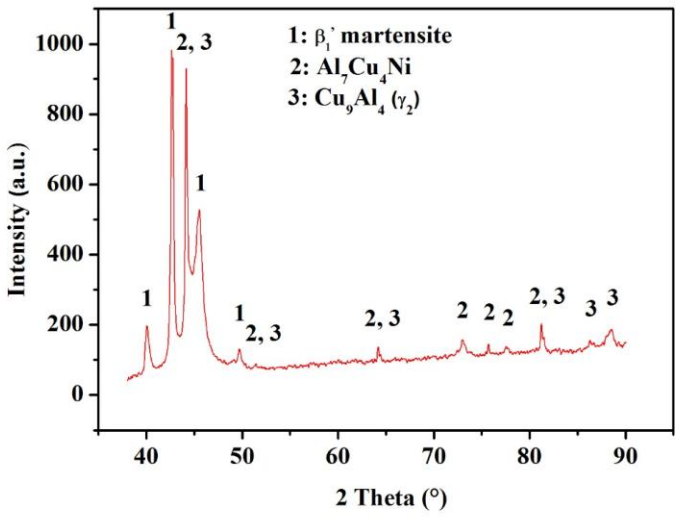


Fig. 9. Diffractogram of Cu-13% Al-4% Ni after heat treatment

4. Conclusions

The hot pressure sintering of the mixture of elementary Cu-Al-Ni powders previously mechanically activated makes it possible to obtain an alloy of fixed composition with biphasic structure ($\alpha + \gamma_2$). A SHS type reaction was initiated at 580°C between the 3 elements, giving rise to the Cu_9Al_4 type intermetallic compound.

The compound Cu_9Al_4 was formed in α solid solution whose lattice parameter increases due to the dissolution of Al and Ni in the copper lattice. The densification of the material requires the application of a load at a temperature higher than that of the SHS reaction. The quenching treatment of the sintered material generates a martensitic structure revealed by TEM with a multitude of needle orientations. It is known that this transformation is reversible thermoelastic.

The aging treatment at 250 ° C leads to the formation of a precipitate from the residual metastable austenitic β phase. The formation of this precipitate decreases the concentration of the mother phase in Al and Ni which raises the martensitic points Ms and Mf and allows martensitic transformation in the areas surrounding the precipitates.

During this transformation, the growth of the martensite plates was blocked and generated a self-accommodation of the martensite needles which develop in privileged directions. This phenomenon disturbs the thermoelasticity of the transformation and degrades the shape memory process of the alloy.

R E F E R E N C E S

[1] *A. Ölande, The* crystal structure *of* AuCd, *Zeitschrift für Kristallographie-cristalline materials,* 83 A, 1932, pp. 145–148

[2] *A.B.* Greninger *and V.G.* Mooradian, Strain transformation in metastable beta copper-zinc and beta copper-Ti alloys, *Trans.* Metall. Soc. *AIME*, **vol. 128**, 1938, pp. 337–341

[3] *W. J. Buehler, J. V. Gilfrich, and R. C. Wiley*, Effect of Low-Temperature Phase Changes on the Mechanical Properties of Alloys near Composition TiNi, *Journal of Applied Physic*, **vol. 34**, 1963, pp. 1475-1477

[4]. *A. Sato, E. Chishima, K. Soma and T. Mori*., Shape memory effect in $\gamma \rightleftarrows \epsilon$ transformation in Fe-30Mn-1Si alloy single crystals, *Acta. Metall.*, **vol. 30**, 1982, pp. 1177-1183.

[5]. *T. Tadaki*. Cu-based shape memory alloys, *Shape memory materials*, (ed. K. Otsuka and C. M. Wayman), Cambridge Univesity Press, 1998, pp. 97–116.

[6]. *T. W. Duerig, K. N. Melton, D. Stockel and C. M. Wayman,* Engineering Aspects of Shape Memory Alloys, *Butterworth Heinemann Publishing, London*, 1990, pp. 3-20.

[7]. *K. Otsuka and K. Shimizu,* Morphology and Crystallography of Thermoelastic γ' Cu-Al-Ni Martensite, Jpn. *J. Appl. Phys.*, **vol. 8**, issue 10, 1969, pp. 1196-1204.

[8*]. K. Otsuka*, Origin of Memory Effect in Cu-Al-Ni Alloy, Jpn. J. Appl. Phys., **vol. 10**, issue 5, 1971, pp. 571-579.

[9]. *S. Miyazaki, K. Otsuka*. Development of Shape Memory Alloys, *ISIJ International*, **vol. 29**, issue 5, 1989, pp. 353-377.

[10]. *M. Chinaud, J. Scheller, J.F. Rouchon, E. Duhayon and M. Braza*, Solid State Phenomena, *Trans. Tech. Publications, Switzerland,* **vol. 198**, 2013, pp. 200-205.

[11]. *T.W. Duerig,* Applications of Shape Memory, *Materials Science Forum*, **vol. 56/58**, 1990, pp. 679-692.

[12]. *R.K. Dube*, Metal strip via roll compaction and related powder metallurgy routes, *International Materials Review*, **vol. 35**, 1990, pp. 253-292.

[13]. *A Agrawal, RK Dube*, Methods of fabricating Cu-Al-Ni shape memory alloys, *Journal of Alloys and Compounds*, **vol. 750**, 2018, pp. 235-247.

[14]. *B. Kosec, M. Bizjak*, Microstructure of rapid solidified Cu-Al-Ni shape memory alloy ribbons, Journal of materials processing technology, vol. 162/163, 2005, p. 220-229

[15]. *G.N. Romanov*, Liquid-phase sintering of aluminum-based powder alloys, Russian journal of Non-Ferrous Metals, vol. 51, 2010, pp. 347–351

[16]. *SM. Chentouf, M. Bouabdallah, H. Cheniti, A. Eberhardt, E. Patoor, A. Sari,* Ageing study of Cu–Al–Be hypoeutectoid shape memory alloy, *Mater. Char.* **vol. 61**, 2010, pp. 1187–93.

[17]. *S. Rag, A. Aeat, R. Aejo,* Influence of Ag addition on the thermal behavior of the Cu–11 mass% Al alloy, *J. Therm. Anal. Calorim.* **vol. 97**, 2009, pp. 117–21.

[18]. *J. Ortinh, A. Planes*, thermodynamic analysis of thermal measurements in thermoelastic martensitic transformations, *Acta Metall. Vol.* 36, 1988, pp. 1873-1889.

[19]. *M. Bouabdallah, G. Cizeron*, evolution of the martensitic transformation by ageing in a Cu-Al-Ni shape memory alloy, *Annales de Chimie Science des Matériaux, Vol.* 28, 2003, pp. 31-39