Characterization of Copper-Based Shape Memory Alloy with Zinc and Aluminum

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Abstract— Copper-based shape memory alloy with zinc and aluminum was manufactured, plastically deformed, heat treated and characterized in terms of physico-mechanical, structural and micro-structural investigation. Typical martensitic microstructure with twins is revealed by optical and electron microscopy. The presence of the martensite in the structure was further confirmed through X-ray diffraction. Toughness and hardness of the alloy are investigated too. Optimal properties are obtained for the condition of the alloy that was subjected to heat treatment according to the following scheme: annealing at 850 ^0C and 900 ^0C (10 min) + quenched in water + aging at 400 ^0C (1 hour) + air cooling.

Keywords— shape memory, SEM-EDS, hardness, copper-zinc-aluminum alloy, martensitic structure.

I. INTRODUCTION

The effect of shape memory is ability of some metals and alloys deformed in martensite state or at temperature interval of martensitic transformation to regain their original shape during the heating process due to complete or almost complete absence of deformation [1,2].

The heating process causes restoration of crystals in high-temperature phase called beta or parent phase and the removal of plastic deformation. In the same time, all physical and mechanical properties are restored.

During the shape recovering process, the alloys can produce a displacement or a force, or combination of the two, as a function of temperature. The starting force of recovering shape process is difference between free energies of parent and martensitic phases during the reverse transformation. The complete shape recovering is only notice if the martensitic transformation is crystallography reverses and if the deformation process is done without plane shearing [2,3].

Shape memory effect has been studied for many binary and ternary alloys, as well as for some pure metals. However, wide application can be found only for nitinol (Ni-Ti alloys) and copper-based alloys that show shape memory effect. Copper-based alloys, compared to nitinol alloys, possess somewhat lower mechanical properties due to their larger grain size and elastic anisotropy [4]. But, they can be improve, considerably without deterioration of shape memory effect, by small grain, method of rapid solidification, sinter metallurgy or by adding the elements such as Zr, V, B, Ti, Cr, etc. [5].

II. COPPER-BASED SHAPE MEMORY ALLOYS

Copper-based alloy with shape memory effect are very commercial and they are mainly alloys with zinc, aluminum and nickel. Figure 1 shows the liquidus projection in copper-based alloys with zinc and aluminum, while the Table 1 gives a review of the possible invariant reaction in the same system of alloy [6].

TABLE 1
CALCULATED INVARIANT REACTIONS IN Cu-Zn-Al SYSTEM OF ALLOY

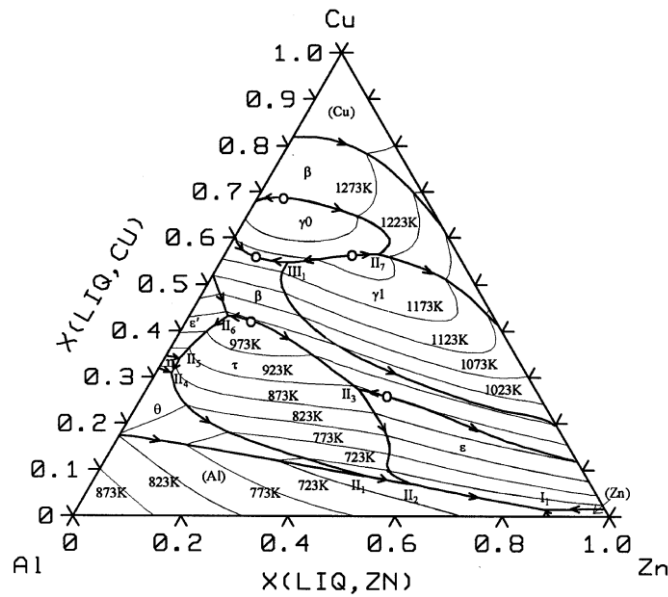| Reaction	Temperature, K	Composition of liquid phase
L+θ→(Al)+τ	698	Cu8,6Zn50,5Al40,9
L+τ→(Al)+ε	694	Cu6,8Zn60,1Al33,1
L→(Al)+(Zn)+ε	654	Cu1,6Zn87,2Al11,2
L+β→ε+τ	917	Cu27,4Zn39,5Al33,1
L+η→τ+θ	853	Cu31,2Zn2Al66,8
L+ε`→τ+η	893	Cu34,3Zn2Al62,8
L+β→τ+ε`	1010	Cu43,5Zn6,9Al49,6
L+γ°→β+γ	1226	Cu56,4Zn28,6Al15
L+γ+γ°→β	1197	Cu54,6Zn12,6Al32,8

FIGURE 1. CALCULATED LIQUIDUS PROJECTION IN Cu-Zn-Al SYSTEM OF ALLOY

The possibility of shape memory effect depends upon the alloy ability to undergo the thermo-elastic martensite deformation. The alloy is first cooled and transferred to the martensitic phase, when there is possibility of mechanical deformation. As long as the lower temperature, the alloy is deformed or if heated, martensite again deformed into the austenite and the alloy returns to its original shape.

Martensitic transformation does not occur at a certain temperature, yet there is whole temperature range which is different for each monitored system.

Various deformation temperatures and the corresponding voltage curves for copper-based alloy with zinc and aluminum are shown in Figure 2.
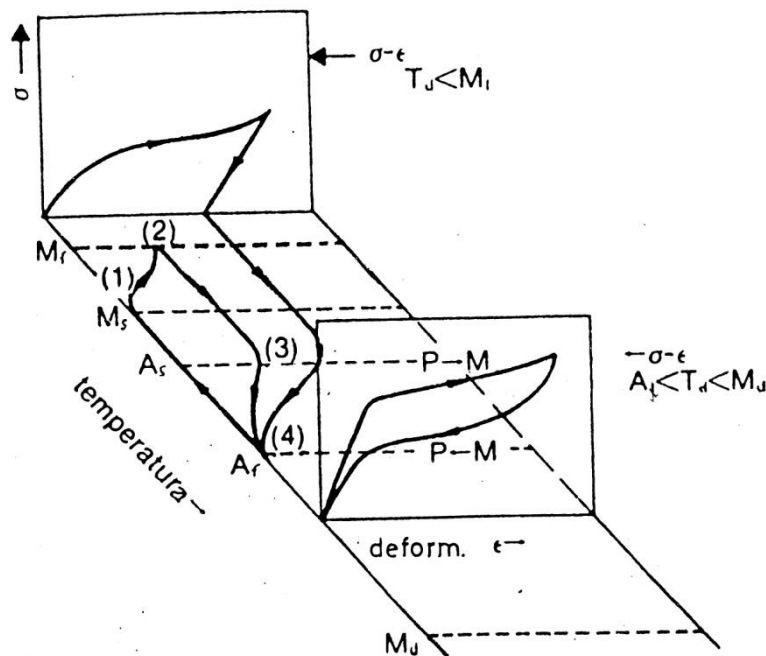

FIGURE 2. SCHEMATIC OVERVIEW OF THE VOLTAGE CURVES DEPENDING ON DEFORMATION TEMPERATURE (MS-TEMPERATURE OF BEGINNING MARTENSITE FORMATION AT COOLING; MF-TEMPERATURE OF THE MARTENSITIC TRANSFORMATION ENDING; AS-STARTING TEMPERATURE OF HIGH TEMPERATURE PHASE FORMATION; AF-ENDING TEMPERATURE OF HIGH TEMPERATURE PHASE FORMATION AT HEATING; MD-BELOW THIS TEMPERATURE MARTENSITE CAN BE REVERSED INTO THE ORIGINAL PHASE)

In the upper left corner in Figure 2, the alloy deformation below the Mf temperature is shown, while alloy is fully in martensitic condition. For a relatively low stress there is a possibility when the deformation can be deposited in the martensite structure at certain stress. When unloading once, the elastic distance can be observed in any metal. Heating to Af temperature, martensite with added deformation disappears and the original structure returns.

In contrast, in the lower right corner in Figure 2, the curve corresponding to the alloy deformed between the temperatures the Af and Md is shown, while the alloy is in the initial phase at high temperature. Here is a tensile martensite before the applied deformation (P→M). After release, martensitic structure is unstable and is converted to the original phase (P←M). During this reversible process each deformation which was incorporated into the tensile-martensite disappears and the material returns to its original shape. This behavior of materials was called the pseudo-elasticity.

Copper-based shape memory alloys with zinc and aluminum are widely used in the industry as thermostats, control equipment, connectors, etc. The most obvious examples are the various types of springs with different systems for remote regulation and control. The shape memory alloys based on copper also have wide applications in home use as constitutive elements of various assemblies. Their great advantage over the other types of smart materials alloys is low price, as well as the role of environmental friendly materials.

III. EXPERIMENTAL

The copper-based shape memory alloy with zinc and aluminum are usually obtained by classical method of melting, casting and manufacturing. Generally, all alloys with martensite structure have heavy plastically deformation, which is consist of few cycles of rolling at hot and drawing at cold with series of intermediate annealing treatments, from ingots to rods and wires of small cross-section. However, it is necessary to keep chosen composition of alloy during the production process, which is difficult by zinc evaporation during casting process. Also, plastically deformation of these alloys is heavy, with a lot of operations of rolling, drawing and intermediate annealing treatments.

Because of that, the copper-based shape memory alloy with zinc and aluminum is obtained by using technology of continuous casting of wire and profiles of small diameters, which is developed in Mining and Metallurgy Institute Bor for some pure metals [7].

The principle of this method of continuous casting is used the procedure of crystallization above the melt for directly obtaining of the copper-based shape memory 8 mm wire. The principle of technology is as follows [7]: The cooler for copper-based shape memory wire casting is dipped into the melt to the depth of h. The protection shell made of heat-resistant material, which does not react with molten alloy and layer of heat-insulation material, protect the cooler from the influence of the melt and high temperatures. Hydrostatic pressure of surrounding melt drives the molten alloy into graphite crucible. The molten alloy hardens in the crucible by heating exchange through primary part of the crystallizer, which is water-cooled. Hardened wire leaves graphite crucible at a high temperature. For prevention of oxidation of cast wire caused by high temperature on its surface, vacuum is used. Apart from above mentioned role, vacuum serves also for provision of required differential pressure inside cooler, which enables penetration of molten alloy into graphite crucible. For prevention of oxidation of cast wire after leaving the cooler, temperature on its surface should be below 60 ^{0}C. Cooling provides this cast wire in the secondary part of crystallizer. Cast wire drawing is done according to the drag-pause schematic. Process stability is ensured by adjustment of wire drawing speed and heat removal from its side surface.

IV. RESULTS AND DISCUSSION

The chemical composition of obtaining 8 mm wire is: Cu-69.7%, Zn-26.3% and Al-4%. The samples of wires are treated in the aim to obtain the wire of 1.8 mm with the shape memory effect as follows: 2 h of homogenization at 800 ^{0}C in low oxidation atmosphere, then drawing to the dimension 4x4, with thermal treatment: 15 min of annealing at 400 ^{0}C, quenching in water, 120 min annealing at 550 ^{0}C, cooling in furnace to 450 ^{0}C and air cooling and drawing to the dimension 1.8 mm. In the aim to reach the martensite structure, samples are heating 5 min in nitrogen atmosphere at 800 ^{0}C and quenched in cold water and in martensite state the alloy was memorized.

In the aim to determine the characteristics of obtained shape memory alloy, investigations of mechanical properties, structural and micro-structural analysis, as well as SEM-EDS and X-ray are done. Obtained results are shown in Table 1 and Figs 3-8 respectively.

TABLE 2
RESULTS OF PHYSIC-MECHANICAL PROPERTIES TOUGHNESS AND HARDNESS BY VICKER'S METHOD

N^0	Condition of materials	Toughness	Hardness
		J/cm^2	HV
0	As-cast condition	20	314
1	Hot-rolled at 850 ^{0}C	40	354
2	Annealing at 850 ^{0}C (10 min), quenched in water	34	379
3	Annealing at 900 ^{0}C (10 min), quenched in water	33	368
4	(2.) + ageing at 400 ^{0}C (1 h) + air cooling	22	492
5	(2.) + ageing at 450 ^{0}C (1 h) + air cooling	16	475
6	(2.) + ageing at 500 ^{0}C (1 h) + air cooling	26	448
7	(2.) + ageing at 450 ^{0}C (1 h) + cooling in furnace	21	454
8	(3.) + ageing at 400 ^{0}C (1 h) + air cooling	20	504
9	(3.) + ageing at 450 ^{0}C (1 h) + air cooling	19	478
10	(3.) + ageing at 500 ^{0}C (1 h) + air cooling	18	464
11	(3.) + ageing at 450 ^{0}C (1 h) + cooling in furnace	23	479

According to the results of mechanical investigation shown in Table 2, it is noticed that optimal characteristics of alloy are obtained for the follow state of materials: annealing, quenched in water, ageing at 400 ^{0}C 1 hour, and then air cooling. This conclusion is verified by metallography, Figs. 3-8.

FIGURE 3. MICROSTRUCTURE OF AS-CAST ALLOY, (X960)

FIGURE 4. MICROSTRUCTURE OF ALLOY, HOT DEFORMED (X960)

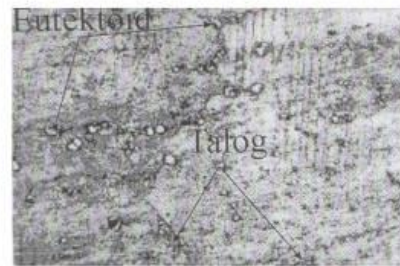**FIGURE 5. MICROSTRUCTURE OF ALLOY, ANNEALED AT 850 ^{o}C FOR 10 MIN AND WATER QUENCHED (X960)**

FIGURE 6. MICROSTRUCTURE OF ALLOY, ANNEALED AT 900 ^{o}C FOR 10 MIN AND WATER QUENCHED (X960)

FIGURE 7. MICROSTRUCTURE OF ALLOY QUENCHED FROM 850 ^{o}C AND AGED AT 400 ^{o}C FOR 1h (X960)

FIGURE 8. MICROSTRUCTURE OF ALLOY QUENCHED FROM 900 ^{o}C AND AGED AT 400 ^{o}C FOR 1h (X960)

Microstructure of cast alloy consists of a lot of big bright crystal α-solid solution in the dark basically β-crystals (Fig. 3). In appearance, this structure corresponds with the martensite structure with notable locality Widmanstatten structure. This structure is not favourable for cold plastic deformation, because the present structure is very brittle, and therefore the only possible deformation is at elevated temperatures.

Hot-processed alloy sample consists of bright crystals of α-solid solution surrounding the crystals of dark β-phase. Between the crystals of α-solid solution in the dark based β-phase particles extracted notice precipitate, but in a very small volume shares (Fig. 4). Compared to as-cast structure, the microstructure is somewhat finer, because the α-solid solution is better deployed in the β-base as a result of deformations in hot condition.

The microstructure of annealed state of alloy is given in Figures 5 and 6. It is noted that the large polygonal grains formed with the present of eutectoid and precipitate deposited on the grain boundaries. Due to higher temperatures (Fig. 6) there was a complete transformation of martensite structure.

Microstructure of aging state of alloy consists of large polygonal grains with separate participate and eutectoid on the grain boundaries. In the sample of alloy that is quenched in water from 850 ^{0}C observed the appearance of residual martensite structure with a fine needle (Fig. 7), while the sample quenched from 900 ^{0}C and subsequently ageing at 400 ^{0}C, noted the presence of residual martensite and eutectoid, but there has been a phenomenon of thermal deposition in the grain boundaries and within each grain (Fig. 8). In this sample the observed martensite structure with Widmanstatten schedule, since the α-solid solution separated in the form of martensitic needles.

The typical martensite twins were also observed on scanning electron microscope image (Fig. 9 and Fig. 10), while the elemental analysis (EDS) detailed in Fig. 11 locates the manufactured alloy in the compositional range for the shape memory alloys in the Cu-Zn-Al system.
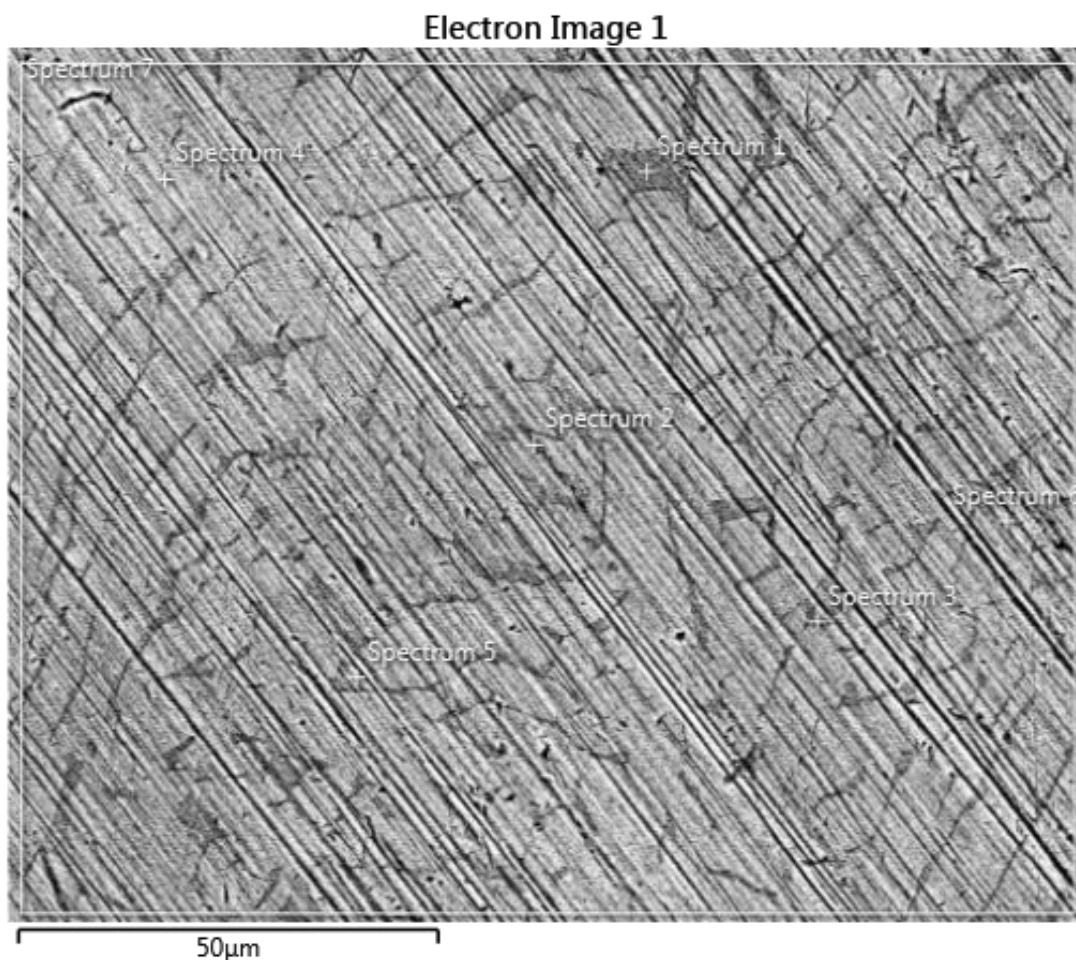

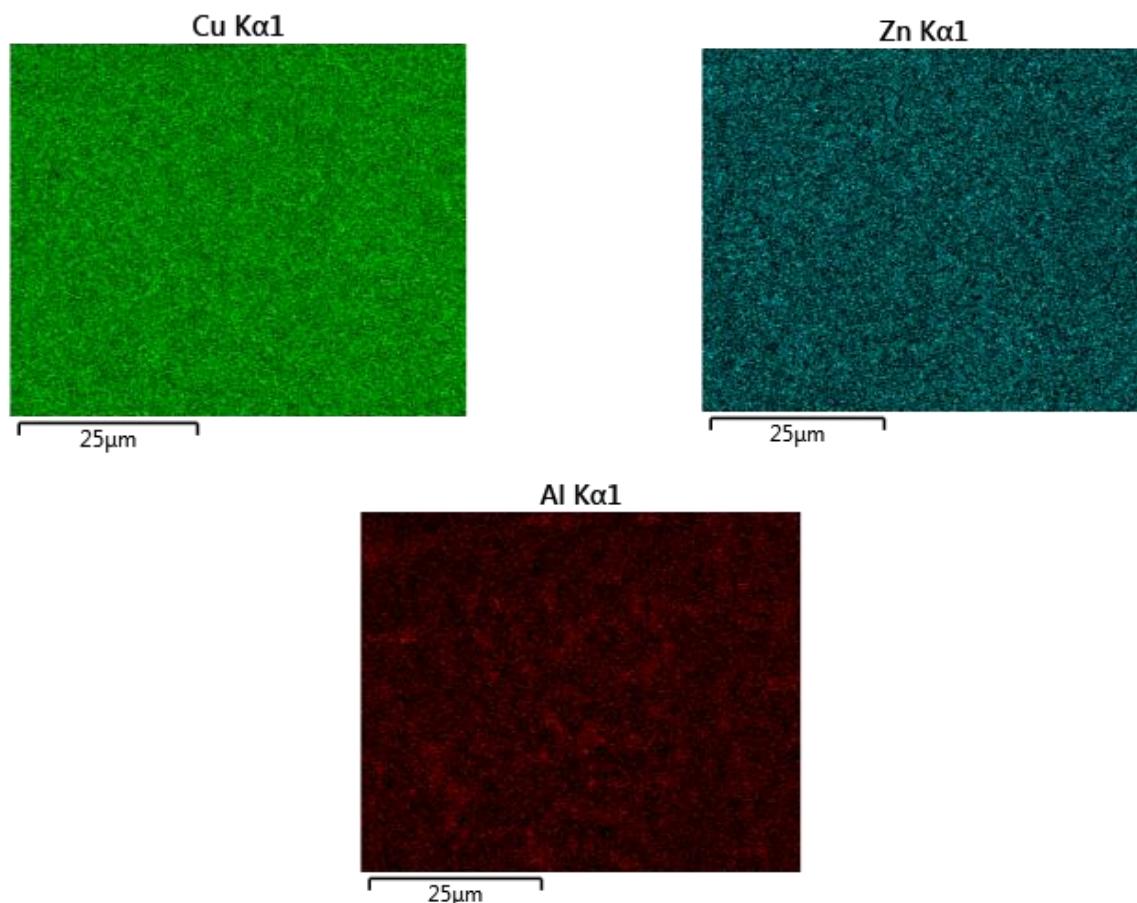**FIGURE 9. SEM OF ALLOY QUENCHED FROM 900 ^{0}C AND AGED AT 400 ^{0}C FOR 1 h**

FIGURE 10. SEM MAP OF BASED ELEMENTS OF ALLOY QUENCHED FROM 900 ^{0}C AND AGED AT 400 ^{0}C FOR 1 h
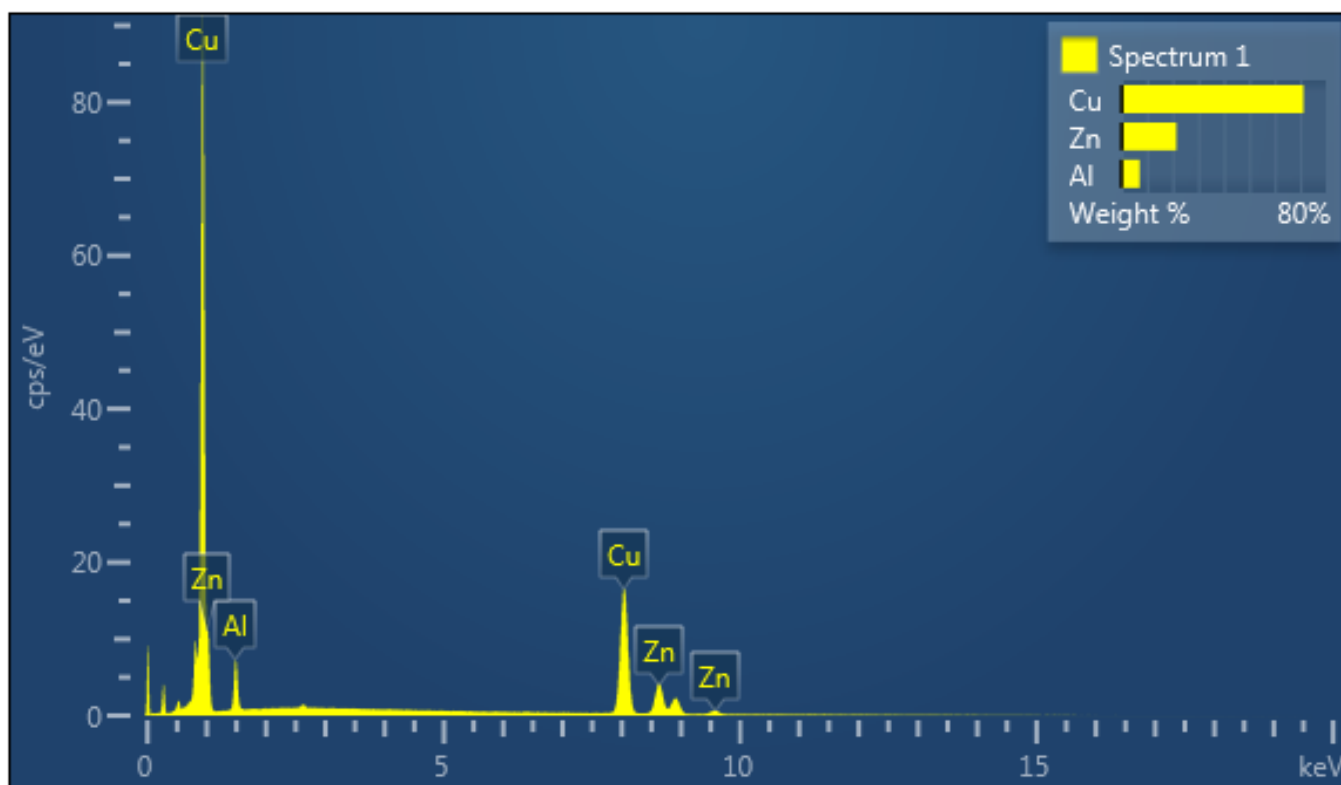

FIGURE 11. EDS ANALYSIS OF THE INVESTIGATED ALLOY QUENCHED FROM 900 ^{0}C AND AGED AT 400 ^{0}C for 1 h

The X-ray diffraction data collected for the quenched sample of alloy, showed in Fig. 12 indicates a predominantly martensitic structure, with the relevant peaks in the 40o to 45o 2θ range.
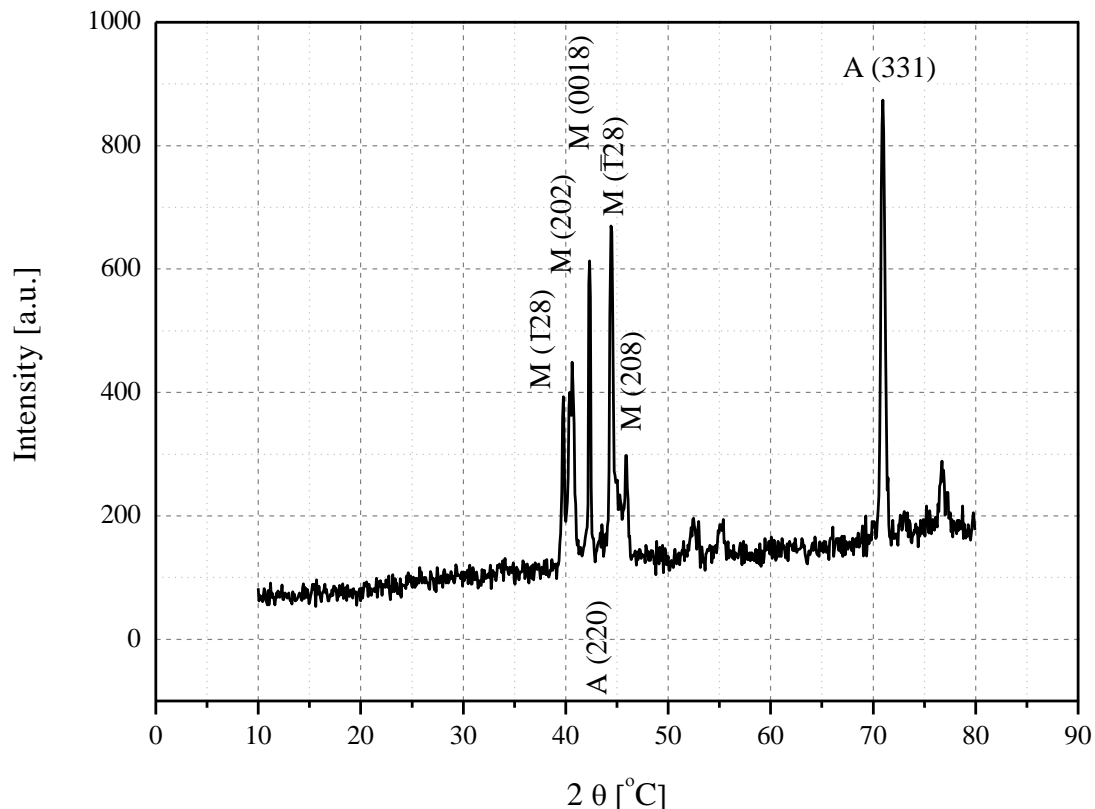

FIGURE 12. X-RAY DIFFRACTOGRAM OF THE QUENCHED ALLOY

V.   CONCLUSION

The copper-based shape memory alloys with zinc and aluminum was manufactured, plastically deformed, heat treated and characterized in terms of physic-mechanical, structural and micro-structural analysis.

Quenching in water, following heating at 850 ^{0}C and 900 ^{0}C, lead to the observation of a typical martensitic microstructure, with twins revealed by optical and electron microscopy.

The presence of the martensite in the structure was further confirmed through X-ray diffraction.

Severe plastic deformation lead to an increase of the the hardness compared to the undeformed samples, a more pronounced increase was observed for the quenched samples.

Establishing a correlation between the state of the material, microstructure and mechanical properties it can be concluded that the combination of thermo-mechanical processing regime, can achieve such a state of the material that provides good mechanical properties.

By reducing the particle size α-solid solution of hot processing increases the hardness and impact toughness compared to the as-cast state.

Heat treatment of hot-processed alloy increases the hardness, while the impact toughness gradually decreases as the microstructure can be explained by the appearance of brittle phases, as a result of thermal deposition.

Optimal properties are obtained for the condition of the material that was subjected to heat treatment according to the following scheme: annealing at 850 ^{0}C and 900 ^{0}C (10 min) + quenched in water + aging at 400 ^{0}C (1 hour) + air cooling.

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