



THE JOHNSON-MEHL-AVRAMI MODEL APPLIED TO MARTENSITIC KINETICS IN AUSFORMED COOPER BASED SHAPE MEMORY ALLOY

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ABSTRACT

CuAlNi shape memory alloys which are used as sensors and actuators have also been investigated recently as materials for medicine devices. This study shows the influence of the thermo – mechanical treatments in CuAl13Ni4 shape memory alloy on martensitic transformation kinetics and microstructures. While maintaining a constant 20% degree of deformation, deformation temperature was varied between 800 °C and 1000 °C. The alloy was investigated by differential scanning Calorimetry (DSC) and optical microscopy. The validity of JMA model to the kinetics analysis was checked. The changes in the microstructure and kinetic transformations have been linked to the evolution of the rolling temperature that introduced high density dislocations in initial phase and changes fraction and interaction between the β_1 (18R) and γ_1 (2H) martensite coexisting in this shape memory alloy.

KEYWORDS: shape memory alloys, medicine devices, deformation

1. Introduction

Shape memory alloys belong to a class of so called smart material due to their unique properties of remembering the initial and cold shape. The shape modification is accounted on reversible, thermo-elastic transformation of the martensite. The martensitic transformation is a solid state heterogeneous transformation, produced not by diffusion but by atom displacement over smaller distances than the diffusion jump. Cu based SMAs, especially Cu-Al alloyed with Ni or Mn are commercially available. The temperatures characteristic to the martensitic transformations inside CuAlNi alloys are within the range -200 to +200 °C and depend on the content of Ni and Al. Cooper based systems were once the most attractive for industrial applications because of less difficult melting, cast and composition control, better stability of the two-way shape memory and not at least because of their lower costs as compared with the most popular Ti-Ni SMAs [1]. CuAlNi shape memory alloys have also been investigated recently as materials for medicine devices [2]. The main reason for studying the kinetics of thermo - mechanical treated cooper based SMAs

comes from engineering, from necessity to produce those alloys as finished products with defined memory proprieties and also good mechanical characteristics. Thermo – mechanically treatments provide ways to achieve those properties. Also sensor and actuator applications, in many cases, require high transformation temperatures and good thermal stability. Thermo-mechanical treatments represent a set of operations of plastic deformation, heating and cooling – made in certain sequence – and as a result of the final structure of the metallic material take place in a high density of lattice defects, associated with plastic deformation. In the case of SMA, the thermo-mechanical treatment involves plastic deformation of austenite (β). Through this plastic deformation at heating are introduced certain defects which will cause the change of the martensitic transformation parameters [3-4]. This study shows the influence of crystallization kinetics of the thermo – mechanical treated CuAl13Ni4 shape memory alloy.

2. Experimental research

The research program has used extruded wires of 4 mm in diameter, Cu Al Ni shape memory alloy



prepared by classical methods at Dunarea de Jos University of Galati. The extruded samples of 4 mm diameter have been heated in a vertical furnace type Nabertherm for 30 min. at 850 °C. The samples have been introduced into the furnace at the solubilization temperature. After heating they have been hot rolled on a double reversible rolling mill. Those samples have been hot rolled in three successive passes up to 2.6 mm thickness. The specimen had been thermo-mechanically treated at 1000°C, 950°C, 900°C, 850°C, 800°C and has been deformed with 20% deformation degree and cooled in the same conditions. The samples were noted as A1, A2, A3, A4 and A5.

The plastic deformations were done on a duo reversible rolling mill, home made, in one pass. The heating furnace was placed in front of the rolling mill.

The sample route has been protected by the ceramic tube.

The loss of heat through radiation is limited, aspect that posed more problems as the rolled sample thickness decreased. The rolling cylinders were preheated with methane gas burner.

The high thermo-mechanical treatment domain limits for the Cu Al Ni alloy were fixed according to the melting temperature and the minimum temperature was chosen to have no cracks in the sample.

$$800^{\circ}\text{C} \leq T < T_{\text{melting}}$$

The ausforming temperature was chosen in near high and low domain limit where the austenite is stable.

After rolling the subsequent quenching is essential. It can be considered that the alloy leaves the rolling mill at about the same temperature at which it entered to do adiabatic heating.

2.1 Analysis by Differential Scanning Calorimetry

The samples were analyzed by DSC. Differential Scanning Calorimetry was used to characterize the thermal effects associated with the direct and reverse martensite transformation. For DSC measurement were used small pieces weighting less than 0.100 g.

The differential calorimetric experiments were performed by means of SETARAM 92 instrument in air at a heating and cooling rate of 10°C/min between -50°C and 200°C.

The cooling treatment was acted by using liquid nitrogen. Endothermic and exothermic peaks on DSC profiles were taken from two consecutive thermal cycles. Prior to the investigation the specimen was etched in 1:1 HNO₃ solution in water.

The attack was seen as necessary for removing distortions that cut the oxide layer.

The martensite and austenite start and finish temperatures (Ms, Mf, As, and Af) were obtained using the base line method.

2.2 Microstructure characterization method

Optical specimens were prepared using standard methods. A color solution Klemm's III was used to etch CuAlNi alloys.

An Olympus microscope with digital image analysis system was employed to study martensite morphology and to characterize the thermo-mechanical effect on the microstructure.

3. Results and discussion

DSC measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes. DSC methods are quite popular for crystallization kinetics analysis where nucleation and growth mechanisms are involved. The crystallization behavior is determined by kinetics parameters. Johnson-Mehl-Avrami (JMA) model is valid for isothermal and isochronal transformation. In non isothermal cases the validity is ensured by a rate transformation which depends exclusively on temperature and the degree of deformation, but not on the thermo mechanical history [5].

This paper aims at setting temperature limits at which, the martensitic transformation taking place in the ausformed samples the JMA model can be applied. Germination and growth were studied by Johnson-Mehl-Avrami model:

$$y = 1 - e^{-kt^n} \quad (1)$$

Where: y is the transformed volume fraction, k is the reaction rate constant, independent of time but temperature dependent and related mechanism of constant transformation ($k=k_0e^{-E_a/RT}$, t the transformation time, n called Avrami exponent, a constant related to the behaviors of nucleation and growth). The transformation fraction y in a given time during isochronal transformation is determined by measuring the corresponding partial area of the endothermic and exothermic DSC processed peaks.

The above equation becomes:

$$\ln(1-y) = -kt^n \quad \text{respectively} \quad \ln[-\ln(1-y)] = \ln k + n \ln t. \quad (2)$$

The value of Avrami exponent n and the reaction constant k can be calculated from the slope straight line obtained by plotting $\ln(-\ln(1/1-y))$ vs. $\ln(dt)$. While maintaining a constant degree of deformation, deformation temperature was varied between 800°C and 1000°C. The DSC processed plots are illustrated in Fig. 1.

There is a good stability of critical points with a slight downward trend by the upper interval temperature chosen (Fig.2.). The critical temperature point martensite finish ranges around 80°C flourishing trend of increasing rolling temperature at 1000°C. By ausforming at 900°C, the critical point M_s undergoes a significant decrease compared to samples thermo-

mechanically treated at other temperatures, the breakpoint value was located at 67°C.

The critical transformation points austenitic finish remains stable at about 160°C, for all the samples plastically deformed with 20% and quenched subsequently.

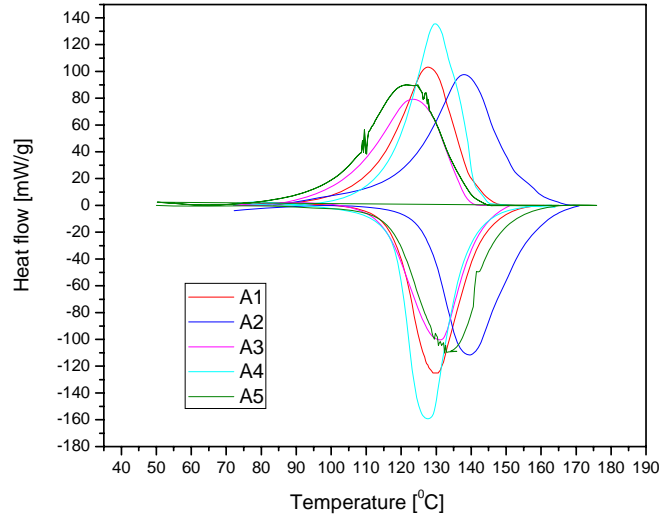


Fig.1. The DSC curves for thermo mechanical by treated samples with 20% degree of deformation, from austenitic temperature 1000°C-A1 980°C-A2, 900°C-A3, A4-850°C, respectively 800°C-A5

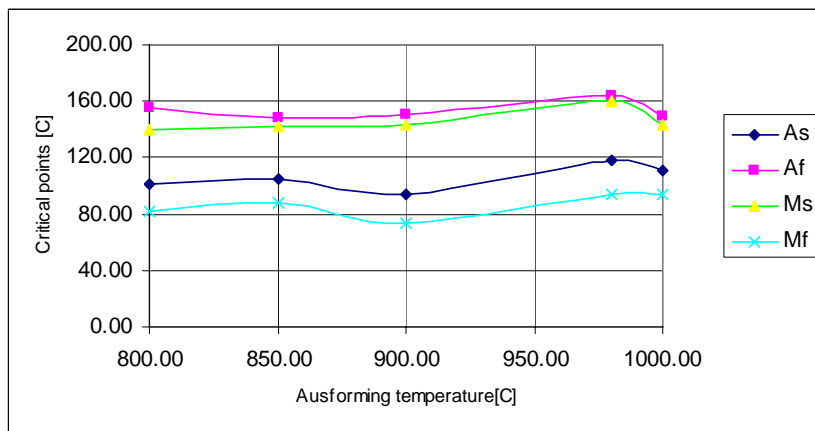


Fig.2. Variation of reverse martensitic transformation critical points for the samples subjected to thermomechanical treatment

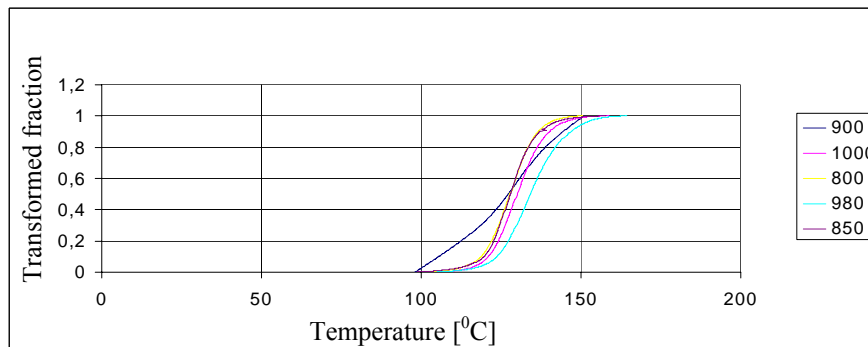


Fig.3. Reverse martensitic transformation kinetic curves for samples deformed with the same degree of deformation at different temperatures

The Reaction Mechanism of the reversible martensitic transformation alloy thermo-mechanically treated at different temperatures follows the model of deformation Johnson-Mehl-Avrami (JMA). Most of them have the classical sine transform both direct and reverse martensitic transformation at cooling and heating. Figures 3 and 4 are the kinetic curves for samples deformed with a deformation degree of 20% at temperatures ranging from 1000°C to 800°C.

With one exception represented by alloys deformed under low temperature condition, other curves are grouped in the range of phase transformation temperatures in the range of 100°C to

170°C. Ausforming alloy after the same degree of deformation of 1000°C to 850°C shows a sine curve and emphasizes the processes of nucleation and growth.

The sample deformed at 850°C has a linear transformation which no longer fits with Avrami exponent determined by kinetic type used for analysis. The first stage is a linear increase followed by an inflection point at which the slope decreases. The kinetic plot curves for the transformed volume fraction highlight that for the sample deformed at 850°C the slope is the largest achieved.

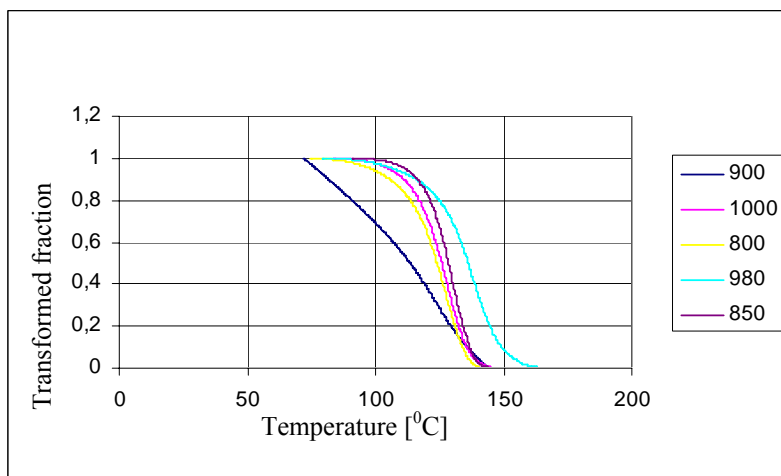


Fig.4. Forward martensitic transformation kinetic curves for samples deformed with the same degree of deformation at different temperatures

JMA fits with constant kinetic parameter n , E_a and k_0 is only applicable for the extreme cases where pure continuous nucleation or pure site saturation prevails. Reversible martensitic transformation is considered site saturation because of the number of supercritical nuclei which occurs in the first moment of transformation ($t=0$) and does not change during the transformation [6, 7, 10, 11]. The martensite crystals is growing up instantaneous, probably the germination are based on statistical composition fluctuation and crystal defects especially dislocation introduced by ausforming in initial phase.

Thermo mechanical treatments applied in temperature interval 1000°C and 850°C allows for transformation analysis based on JMA model with minimum error. Fig.5 shows plot $\ln(-\ln(1/1-y))$ vs. $\ln(dt)$ using the data for transformed volume fraction between 15%-85% at different rolling temperatures. A slight deviation from linearity is provided by interactive double nucleation β_1 monoclinic type martensite (18R) and type γ_1 orthorhombic (2H) coexisting in CuAlNi alloys.

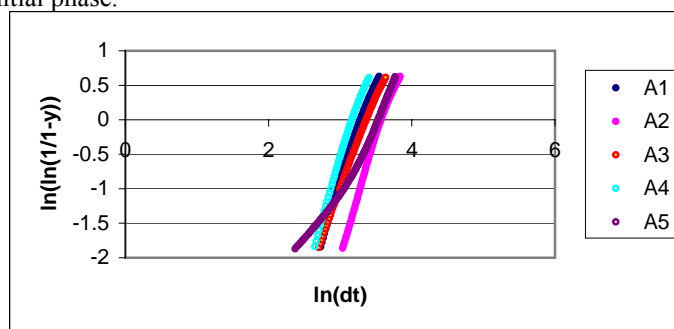
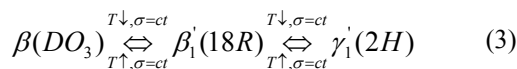


Fig.5. Isochronal JMA plots of forward martensitic transformation of thermo mechanical treated $CuAl_{13}Ni_4$ samples at different rolling temperature and 20% deformation degree

The simultaneous nucleation and their mutual interaction affected complete forward martensitic transformation [6-7]. Ausforming from 800°C does not respect the condition of pure site saturation being an intermediate case and JMA model fits in much higher error.

3.2 Microstructural analysis of thermo-mechanically treated CuAlNi samples

As it is well known, CuAlNi alloys exhibit by quenching or stress-induced, a first-order diffusionless martensitic reverse transformation such as:



The starting point of most direct martensitic transformation is the initial phase (austenite) a solid solution generally denoted β . Elementary cell of this phase for Cu Al Ni obtained by annealing treatment has cubic symmetry, DO3 type. Complex ordering DO3 structure is initially obtained by substituting atom in the center of basic cell and then increasing the degree of ordering by replacing two atoms of two parallel sides of the cube which are on opposite corners of it, but not parallel diagonal. Thus the atoms of a species are isolated among them and raise very different packing possibilities.

The initial phase β , a solid solution based on the electronic component Cu_3Al by rapid cooling undergoes a martensitic transformation. The β_1

martensite has a monoclinic structure with packing orders 18R. It is a typical structure of martensite with a coarse needle zigzag occurring even after plastic deformation by hot extrusion. On this martensite germinate orthorhombic orders, 2H packing. Orthorhombic martensite plate looks thick alternating with thin plates. For this particular alloy composition the presence of the both martensitic phases is simultaneous.

The main purpose of these experiments is to obtain fine structure by thermo mechanical treatments applied to designing sensors and actuators with this shape memory alloy family. Variation of thermo mechanical treatment parameters, temperature - degree of deformation leads to specific structures reversible martensitic transformation with different grain size and two types martensitic structure coexisting in different proportion.

Optical microscopy of samples after quenching reveals two types of martensite reverse, namely β_1 , monoclinic type of martensite (18R) and type γ_1 orthorhombic (2H). Monoclinic martensite morphology is a typical zigzag and the orthorhombic type martensite is laths.

The hot plastic deformation morphology of the two types of thermoelastic martensite is enriched with forms described as:

- Parallel plates
- Saw
- Small arrow
- Large arrow

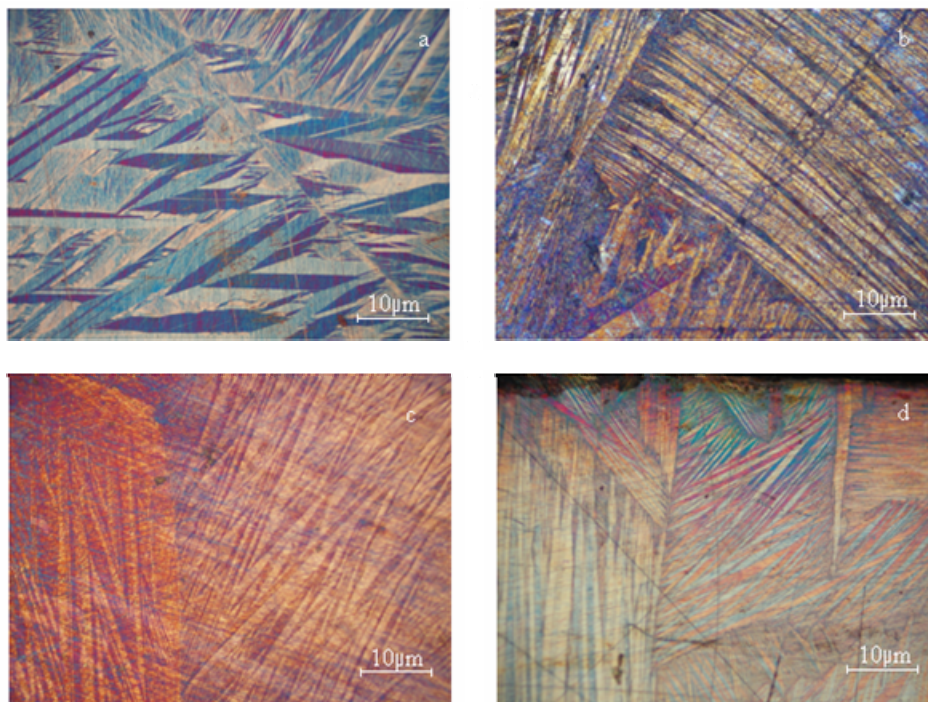


Fig. 6. Optical microstructures CuAl₁₃Ni₄ alloy after ausforming with 20% deformation degree, from temperature: a-1000°C, b. 980°C, c 850°C, d 800°C. Metallographic Attack Klemm's III.

The parameter that was varied in the thermo mechanical treatment was the rolling temperature which had values between 1000°C and 800°C. The metallographic structure, highlights the finishing of the initial grain shape and the martensitic needles are oriented to a perpendicular direction to rolling direction. This aspect is more evident with the decrease in the deformation temperature. The proportion of monoclinic martensite (fig.6.a) decreases with decreasing temperature as a share of the rolling condition. Specific fine structure of lath martensite typical orthorhombic accompanied by numerous packing defects is found in cold-rolled samples (fig.6.c). Metallographic observation for samples after rolling at 1000°C temperature and 20% degree of deformation shows specific martensite shapes: small arrowhead, arrowhead large, parallel plates and saws. Long-range order structure is maintained. The initial grain size is rough. Specific to the degree of deformation in the boundary grain is occurring of very fine structures and short needles that make the transition to the next seed grain martensitic phase which germinated. Grain boundaries are polygonal, have smooth and regular shape. Decreasing temperature leads to a decrease in grain size. The martensitic microstructure morphology highlights mostly small arrowheads and those become finer. The grain boundaries of the initial phase lose their smoothness and start to fringes, packing more obvious defects.

Plastic deformation achieved at low temperatures (800°C and 850°C) leads to untypical curved martensite grown on the perpendicular rolling direction (fig.7). Explaining the formation of very fine martensite curves is attributed to how the germination and growth of martensitic crystals take place. The previous experiments highlighted that although two-dimensional centres of crystallization are formed in the nodes of the dislocations they are not growing. Martensitic curved plate growth occurs between individual dislocations and dislocations networks. Their expansion is hampered by the grain boundary and sometimes by sub grain boundary [4]. At low temperature of deformation a fine scale martensite originates. The size is limited by the dimension of the deformed initial grain. Grain boundaries are never crossed by martensite needles or curved plate, but sub boundaries are. Thermo mechanically treated samples at 850°C with 20% deformation degree show fine primer cracks.

The monoclinic to orthorhombic interacting nucleation had been carefully observed by the forward study only for quenched and stress induced martensitic transformation [7]. Due to this interaction, the martensitic nucleation is strongly affected throughout the cooling process, leading to very different crystal microstructures.

The result observed in both cases in thermal and stress induced MT concludes that proportion of monoclinic and orthorhombic martensite strongly depends on very local nucleation conditions.



Fig. 7. Optical microstructures CuAl₁₃Ni₄ alloy after ausforming with 20% deformation degree, from 800°C. Curved martensite

It was ascertained lack of reproducibility of any crystal property throughout the transformation process. Some authors take for granted that aging in the parent phase favors the formation of γ_1 phases [8]. In this study of ausforming a β copper based alloy through the process introduced a high defect density before transformation. Ausforming at selected temperatures did not change the bulk nature of the martensitic reaction. The changes in the deformation temperature have been linked to the slight evolution of the critical martensitic transformation points, different fraction of monoclinic and orthorhombic martensites and grain size. At this amount of deformation a martensite reorientation takes place, based on massive network dislocation introduced in initial phase that maintains a state of tension more pronounced as the deformation temperature approaches the instability of austenite.

From microstructure observation, it is seen that β_1 (18R) and γ_1 (2H) martensite phases coexist at different fractions also in the thermo mechanical state at different temperatures rolling. The most obvious effect of the dropping deformation temperatures are the increasing fraction of orthorhombic martensite. According to a recent study this result indicates that the conditions of ausforming cause changes between two types martensite coexisting in alloy, and additional transformation β_1 to γ_1 occurs during the ausforming at temperatures lower than 900°C [7,9].



4. Conclusions

1. The JMA model can be valid in isochronal reverse martensitic transformation kinetics showing that nucleation is completed before the beginning of the reaction.

2. Kinetic curves plotted for the alloys studied are specific to the JMA model; curves have the classical sine wave.

3. Points of shape memory alloy transformation $\text{CuAl}_{13}\text{Ni}_4$ and kinetic curves have been determined with minimum error using JMA model.

4. Transformation points (M_f , M_s , A_s , A_f) vary depending on the parameters studied of thermo mechanical treatments applied.

5. Kinetic curves of ausforming samples at the same degree of deformation are grouped with critical temperatures approximately constant.

6. The mechanism of reversible martensitic transformation follow the Johnson –Mehl- Avrami model also for thermo-mechanically treated alloy not only for quenched samples.

7. β_1' (18R) and γ_1' (2H) martensite phases coexist at different fraction also in the thermo mechanical state at different rolling temperatures. The most obvious effect of the dropping deformation temperatures is the increasing fraction of orthorhombic martensite. Additional transformation β_1' to γ_1' occurs during the ausforming at temperatures lower than 900°C

8. Ausformed samples after the same degree of deformation rolled at 1000°C to 850°C show sine curves and emphasize the processes of nucleation and growth.

9. The interval phase transformation temperature ranges between 67°C to 170°C for thermo-mechanically treated alloy that is an important point in choosing and designing sensor and actuators from this SMA_s family.

10. The sample deformed at 850°C is a linear transformation which no longer meets Avrami type kinetics.

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