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Behaviour of electrical resistivity in single crystals of Cu-Zn-Al and Cu-Al-Be under stress

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Abstract. Electrical resistivity measurement (ER) has been one of the main experimental techniques used in researches that involve alloys with martensitic transformation, due to its susceptibly to detect crystalline structure modifications. In alloys that present shape memory effect, ER is mainly used to study thermal cycling and ageing. Recently, measures of electrical resistance have been coupled to mechanical tests during shape memory effect phenomena. Most of publications using ER at constant temperature in the stress-strain domain was done in polycrystalline alloys of Ti-Ni and Ti-Ni-Cu. In this work, single crystals of copper-based samples were tested at different temperatures to analyse the behaviour of stress and resistivity variation versus strain. During superelasticity test, ER variation presents a linear behaviour and an absence of hysteresis with strain. Mechanical tests are performed at different temperatures and with different orientations of the tensile axis. These results show that the martensite variants present an electrical anisotropy.

1. INTRODUCTION

Shape memory alloys (SMA) present different phenomena (one-way memory effect, two-way memory effect, superelasticity and rubber-like behaviour) which can be induced by temperature or stress. All those effects are characterised by crystalline structure modifications.

The electrical resistivity (ER) has been one of main techniques used in the study of the SMA. Its main application is the determination of phase transformation temperatures, due to its susceptibility to detect crystalline structure modifications [1,2]. ER has also been used to measure the evolution of SMA during ageing of parent phase and low temperature phase (stabilisation martensitic) [3-7].

Lately ER has been applied to investigate the mechanical behaviour of alloys submitted to shape memory effect phenomena (SME) [8]. The ER is affected in theses cases by strain, structural modifications, martensite variants reorientation process and micromechanisms related to introduction of linear defects [9,10]. The knowledge of ER behaviour in these events has special relevance for technological applications. Indeed, it can be used to program and to monitor the material performance from electronic control.

Resistivity measurement coupled with thermomechanical tests in polycrystalline alloys of Ti-Ni presents a linear variation of ER with strain. This variation cannot only be explained by geometric alterations of samples, but is also related to martensite variants reorientation process [11,12]. In these tests, a negative change of ER was attributed the presence of the R phase [13]. In the 50Ti-45Ni-5Cu and 50Ti-40Ni-10Cu alloys, alterations in slope of ER versus strain curves and formation of knees that are probably related to martensitic reorientation process are observed [14]. Behaviour of ER was analysed for the two-way memory effect (TWME) as a function of stress, strain and number of cycles during the training process [15-17].

A poly or a single variant of martensite can be induced from a beta phase (β) single crystal of copper-based SMA. A cooling without stress from the parent phase produces a martensite phase with different orientations of variants called polyvariant. Variants are self-accommodated and the shape of the

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sample does not change. It is also possible to obtain a single variant by stress induced martensitic transformation (SIM). From a single crystal of parent phase, each possible orientation of martensite corresponds to a different shear. For a fixed tensile axis, it is then possible to calculate a Schmid factor for each of the 24 possible variants. During the superelastic test (at T > A_f), the variant induced by the stress is the one which has the highest Schmid factor. Figure 1 shows the transformation strain obtained versus the crystallographical direction of tensile axis (in parent cubic phase coordinates) [17]. For Cu-Al-Ni alloy, the maximum recoverable strain by SIM is calculated to be near 8.6% with a Schmid factor close to 0.5.

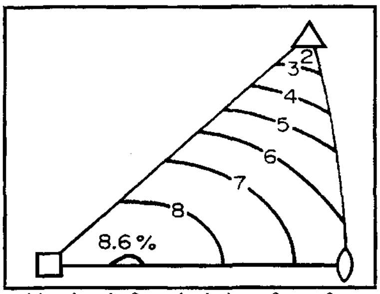

Figure 1. Stereographic triangle for calculation of transformation strain Cu-Al-Ni [17].

This work is concerned with tests in single crystals of the SMA Cu-Zn-Al and Cu-Al-Be, analysed by resistivity changes in the stress-strain domain. Tests were performed at different temperatures and for different crystallographical orientations along the tensile axis.

2. EXPERIMENTAL PROCEDURE

Cu-Zn-Al and Cu-Al-Be alloys were elaborated in an induction furnace. Single crystals were prepared by a modified Brigman method. *Table I* identifies nominal chemical compositions of the studied alloys and phase transformation temperatures, determined by DSC (Differential Scanning Calorimetry) and electrical resistivity.

TABLE I

Sample	Cu (%wt)	Al (%wt)	Zn (%wt)	Be (%wt)	A_s (°C)	A_f (°C)	M_s (°C)	M_f (°C)
CZA-1	76.70	7.80	15.50	-	28.3	33.0	30.5	26.0
CAB-1	87.68	11.88	-	0.44	4.8	17	9.6	-6.5
CAB-2	87.54	12.00	-	0.47	-11.6	4.2	-6.7	-22.3

Tensile samples were prepared with dimensions: gauge length = 10 mm, width = 4 mm and thickness = 1 mm. The deformed superficial layer was eliminated by chemical attack with an aqueous solution with 15% HNO_3. Samples were then quenched from 850°C in water at room temperature and aged 1 hour at 100°C in order to eliminate excess vacancies and to stabilise the order of the β phase.

A specific tensile machine has been used [18]. Tests were performed at a strain rate of 0.2%.min^{-1} and constant temperature between -30 to 60°C. After each test the samples were heated up to 100°C for elimination of residual martensite. The strain was measured with an extensometer. ER measurements were carried out by conventional four terminals DC method. ER variation has two components: change of resistivity and geometrical alterations of sample. During thermoelastic martensite transformation the volume change is negligible. Then equation (1) can be applied (Ohm law):

$$\Delta\rho_\varepsilon/\rho_{\varepsilon 0} = \Delta ER_\varepsilon/ER_{\varepsilon 0} - 2.\varepsilon \quad (1)$$

where $ER_{\varepsilon 0}$ and $\rho_{\varepsilon 0}$ corresponding to the initial state just before test. All the measurements: stress, strain, ER, temperature were computer recorded.

3. RESULTS AND DISCUSSIONS

Figures 2 and 3 show thermal transformation and tensile tests for Cu-Zn-Al and Cu-Al-Be alloys obtained with samples CZA-1 and CAB-1, respectively.

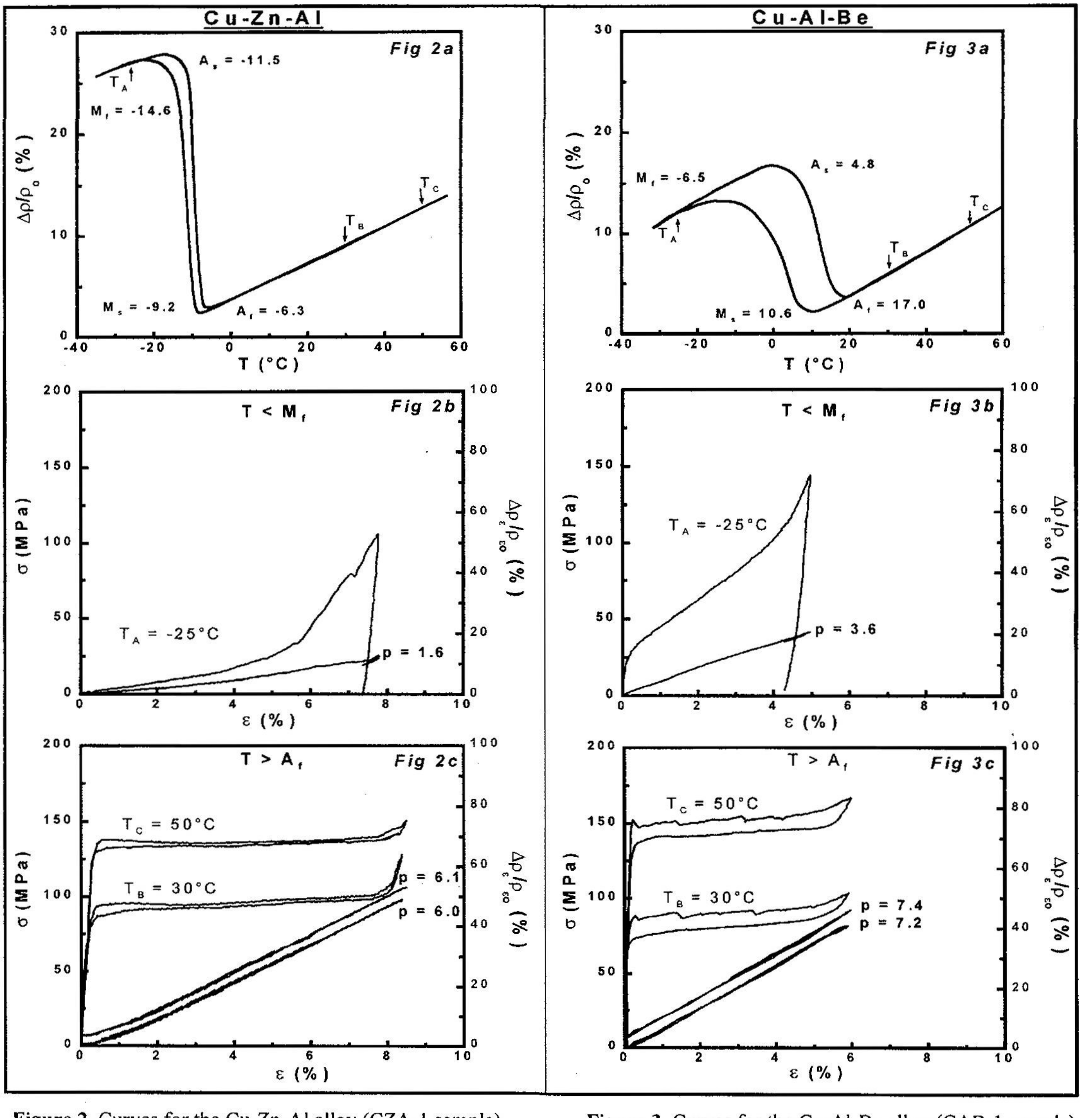

Figure 2. Curves for the Cu-Zn-Al alloy (CZA-1 sample). **Figure 3.** Curves for the Cu-Al-Be alloy (CAB-1 sample). **a)** thermal transformation ($\sigma = 0$), **b)** tensile test in martensitic phase ($T < M_f$), *c)* superelastic test ($T > A_f$).

3.1. Thermal Martensite

Figures 2a and 3a show the variations of resistivity versus temperature under no stress, in which transformation temperatures are indicates. The arrows indicate temperatures chosen for traction tests in each sample. Comparison of these two figures shows for the two alloys that the resistivity is higher for the martensite phase than for the austenitic phase. After transformation by cooling, the electrical resistivity is increased of about 27% for Cu-Zn-Al and 16% for Cu-Al-Be. This variation of resistivity corresponds to the formation of randomly oriented polyvariant martensite. It can also be noticed that the hysteresis of Cu-Zn-Al is smaller (≈ 6°C) than the hysteresis of the Cu-Al-Be alloy.

3.2. Martensitic Phase Test

Figures 2b and 3b show the results obtained at $T < M_f$ in the martensite phase. In this case, the initial state of the sample is a polyvariant of martensite. During the traction test, the volume of the variant that has the highest Schmid factor increases to the expense of other variants. Electrical resistivity variation ($\Delta\rho_\varepsilon/\rho_{\varepsilon o}$) is then only due to the reorientation of the variants of martensite. The maximum values obtained for $\Delta\rho_\varepsilon/\rho_{\varepsilon o}$ are about 14% for Cu-Zn-Al and 21% for Cu-Al-Be.

3.3. Superelastic Test

Figures 2c and 3c show the superelasticity curves and electrical resistivity variation measured at $T > A_f$. During superelasticity test, the martensite phase is induced by the stress (SIM). As for thermal martensite, the hysteresis of stress induced martensite transformation is higher for the Cu-Al-Be than for Cu-Zn-Al. In case of tests of figures 3c and 4c, the obtained recoverable maximum strain (ε_{max}) is about 7.8% for Cu-Zn-Al and 5.8% for Cu-Al-Be. The observed variation of resistivity corresponds to the formation of these single variants of martensite. These variations are higher than the variation corresponding to the formation of polyvariant thermal martensite (figures 3a and 4a). We have obtained $\Delta\rho_\varepsilon/\rho_{\varepsilon o}$ about 45% for the Cu-Zn-Al alloy and 40% for the Cu-Al-Be alloy. Theses values, as well as the slopes of the $\Delta\rho_\varepsilon/\rho_{\varepsilon o}$ curves do not change with temperature ($T > A_f$). It can also be noticed that the hysteresis of $\Delta\rho_\varepsilon/\rho_{\varepsilon o}$ versus ε is negligible. Then for the same alloy, $\Delta\rho_\varepsilon/\rho_{\varepsilon o}$ depends only on superelastic strain. This can be explained by the fact that strain and ER variation are directly proportional to the amount of stress induced martensite.

In conclusion experimental results obtained in figures 2 and 3 can be summarise (see *table II*):

A - Thermal transformation of β phase in non oriented variants of martensite (figures 2a and 3a)
B - Reorientation of existing variants at $T < M_f$ (figures 2b and 3b)
C - Induced single variant at $T > A_f$ (figures 2c and 3c)

Result of operation ***C*** (single crystal of austenite → single variant of martensite) is very close to the sum of the two operations ***A*** and ***B*** (single crystal of austenite → stress oriented martensite). In line ***D*** of *table II* has been reported the sum of ER variation corresponding to the two operations ***A*** and ***B***. This sum is close to the variation of resistivity of operation ***C***. Differences can be due to the fact, in operation ***B***, the reorientation of variants is not completed.

These measurements show in two ways that the resistivity of a single variant obtained in a particular direction can be larger than the resistivity of the martensite phase with variant randomly oriented. The martensitic crystal therefore presents a large resistivity anisotropy.

TABLE II

Operation	***Process***	***Resistivity Variation - $\Delta\rho/\rho_o$ (%)***	
		Cu-Zn-Al	***Cu-Al-Be***
A	Thermal Martensite	27	16
B	Orientation of Variants ($T < M_f$)	14	21
C	Induced Single Variant ($T > A_f$)	45	40
D	$A + B \approx C$	41	37

3.4. Superelasticity Tests for Different Orientations of the Tensile Axis

Figure 4 shows three superelasticity tests obtained at 40°C with samples manufactured in the same austenite single crystal, but with different orientations of the tensile axis (CAB-2 alloy, samples: ***a***, ***b*** and ***c***). The curves present the maximum transformation strain that can be obtained. At the maximum strain plotted on the curves, the samples are completely martensitic and we have optically checked that only one variant is present.

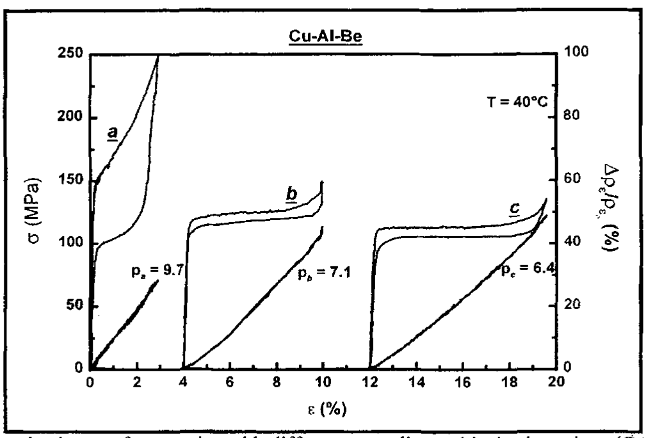

Figure 4. Superelastic tests for samples with different crystallographical orientations (CAB-2 alloy).

The sample ***c*** presents a maximum recoverable strain about 7.0%, this means that the Schmid factor of the induced variant is near 0.5. For the sample ***a***, the maximum strain is about 2.8%. The Schmid factor of the induced variant is then lower. It is significant that the stress necessary to reach this low strain is higher than for sample ***c***.

We have thus obtained three samples in martensitic single variant state with different crystallographical orientations in respect to the tensile axis and the direction of resistivity measurement. Results of maximum transformation strain and resistivity variation are indicated on the *table III* for the three samples. These results show that the difference between resistivity of austenite and martensitic single variant is dependent of the crystallographical orientation of the variant. This also clearly indicates that martensitic crystal presents an anisotropy of resistivity.

TABLE III

Sample	***a***	***b***	***c***
Maximum of Recoverable Strain - ε_{max} (%)	2.8	5.4	7.0
Variation of Resistivity - stress induced martensite (SIM) - $\Delta\rho_\varepsilon/\rho_{\varepsilon o}$ (%)	28	42	49

4. CONCLUSIONS

This work studied the behaviour of resistivity in single crystals of the copper-based alloys under stress in specific conditions. It was verified that the resistivity of the martensitic phase is larger than the one of austenitic phase. In the superelasticity tests, resistivity variation depends directly on the amount of stress induced martensite. The curves of resistivity versus strain present a small hysteresis and the slope is independent of the temperature tests. During deformation of a polyvariant of martensite, it was observed that variants reorientation process promotes a variation of resistivity with strain. The sum of the variation of resistivity produced by thermal martensite and variants reorientation process is near to the one obtained by SIM. In tests of single crystals with different crystallographical orientations, the martensite resistivity obtained by SIM varies for each orientation. These results can be interpreted as a dependence of resistivity with the direction of measurement in the martensitic phase (anisotropy resistivity).

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