Determination of the cubic–orthorhombic transformation strain in Cu–Zn–Al alloys

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Abstract

The length change associated with the compression induced β-18R transformation for Cu–Zn–Al single crystals (SC) is measured. The results of deformation based on the invariant plane strain model and the phenomenological theory are in very good agreement with the experimental values. The invariant plane strain components, the dilatational and the shear component, are evaluated. The resulting relative volume change going from martensite to β is $\xi = -0.0016 \pm 0.0002$, and the shear component is $s = 0.1985 \pm 0.0004$.

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1. Introduction

Martensitic phase transformation occurs in a large number of alloys. Fundamental models of these transformations are offered by the phenomenological theories of Bowles and Mackenzie [1] and Wechsler, Lieberman and Read [2]. The transformation is formally described by a homogeneous Bain distortion plus a supplementary shear whose amount is determined by the condition of an undistorted habit plane existence. The Ahlers model describes the path of the atoms during the martensitic transformation, replacing the Bain distortion by a combination of essentially two transformation shears [3,4]. The salient crystallographic features for a quantitative description are the orientation of the interface plane separating the parent and martensitic phases, the orientation relationships between the lattices in the two structures and the magnitude and direction of the macroscopic strain related to the transformation.

The β to martensite stress induced transformation has been well studied in β-brasses. Starting from a β SC the 18R-martensite variant induced by tension or compression is the one with higher Schmid factor [5]. In this work, the length change associated with the compression induced β-18R transformation is measured, in order to ascertain the invariant plane strain components, the dilatational and the shear component. Compression tests in appropriate conditions permit to obtain a unique variant of 18R martensite along all the samples [6], and it can be retained at room temperature (RT) allowing the direct evaluation of the macroscopical strain involved. Moreover, the temperature and force dependence of the length, though expected to be small, does not have to be considered, being the measurement done at zero force and RT. A reliable determination of the transformation strain becomes important not only in order to test theoretical predictions. It is required for the calculation of fundamental magnitudes such as the transformation entropies [7] or the martensite fault density [8]. It is worth mentioning that the dilatational strain component is postulated as responsible for the dislocation formation in the martensitic transformation in Cu-based alloys [9,10]. These dislocations play a

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fundamental role in the shape memory effect and in the fatigue of the shape memory samples. The volume change accompanying a martensitic transformation is usually very small, and different procedures for its evaluation have been used [11–13].

2. The transformation strain—theory

The martensitic transformation can be described as an invariant plane (habit plane) strain deformation. As shown in Fig. 1, it can be considered as a combination of a shear on the invariant plane, $s\mathbf{d}$, with an expansion or contraction normal to that plane, $\xi\mathbf{n}$, giving an overall displacement $g\mathbf{e}$. Following the formalism given by Christian [14], this invariant plane strain transforms any unit vector $\mathbf{x}$ in $\mathbf{x}+(g\ \mathbf{e})\mathbf{n}\cdot\mathbf{x}=\mathbf{x}+(g\ \mathbf{e})\cos\chi$, where χ is the angle between $\mathbf{x}$ and the invariant plane normal $\mathbf{n}$. Since the square of the initial length is one, the square of the new length is $1+2s\cos\chi\cos\lambda+2\xi\cos^2\chi+(s^2+\xi^2)\cos^2\chi$, where λ is the angle between $\mathbf{x}$ and the direction of the shear component of the displacement $\mathbf{d}$.

Considering the $\mathbf{x}$ vector in the sample axis direction, the ratio between the final and initial length in the axial direction, l/l_0, is

$$\frac{l}{l_0} = \{1 + 2s\cos\chi\cos\lambda + 2\xi\cos^2\chi$$
$$+ (s^2 + \xi^2)\cos^2\chi\}^{1/2} \tag{1}$$

The transformation strain then is $\varepsilon = \Delta l/l_0$.

From the transformation model given in [15], the shear and the normal components for the bcc to 18R can be calculated as:

$$s = [(\eta_2\eta_3)^2 + \eta_1^2 - 1 - (\eta_1\eta_2\eta_3)^2]^{1/2}$$
$$\xi = \eta_1\eta_2\eta_3 - 1$$

where ξ is the volume change upon transformation, $\Delta V/V = [V(\text{martensite}) - V(\text{beta})]/V(\text{beta})$, and it is in general very small. η_1, η_2, η_3 are the dilatation para-

meters, and can be written in terms of ξ and the tetragonal distortion of the basic fct martensitic lattice, $\psi = c/a$, as:

$$\eta_1 = \frac{1}{\sqrt{2}}\frac{\sqrt[3]{2(\xi+1)}}{\sqrt[3]{\psi}}$$

$$\eta_2 = \frac{\sqrt{1+2\psi^2}}{2}\frac{\sqrt[3]{2(\xi+1)}}{\sqrt[3]{\psi}}$$

$$\eta_3 = \frac{\sqrt{2}\psi}{18\sqrt{1+2\psi^2}}\frac{\sqrt[3]{2(\xi+1)}}{\sqrt[3]{\psi}}$$

The ψ value is related to the spontaneous transformation temperature to martensite M_s, being $\psi = (M_s(K) + 5413.5)/6021$ [16]. Note that $\sqrt[3]{2(\xi+1)}$ is the r parameter in [15].

The s component can be rewritten as a function of η_1 and ξ as:

$$s = \left[\left(\frac{\xi+1}{\eta_1}\right)^2 + \eta_1^2 - 1 - (\xi+1)^2\right]^{1/2} \tag{2}$$

In this way, the transformation strain ε can be evaluated as a function of the M_s, the axis orientation, and the normal component or volume change associated with the phase transformation.

3. Experimental procedure

The master ingots of the Cu–Zn–Al alloys were melted in quartz capsules under partial argon atmosphere from high-purity (all 99.999%) metals in a resistance furnace. The melt was vigorously shaken in order to obtain a homogeneous solution. Many pieces were cut from each alloy, cleaned in a solution of 50% HNO$_3$ in water, and vacuum-sealed in quartz tubes. Single crystals (SC) were then grown by the Bridgman method. After solidification, the crystals were kept for about 36000 s at 1070 K in order to homogenize them and afterwards were quenched in water to RT. The electron per atom ratio of the alloys was 1.48. The SC was spark machined to produce cylindrical samples of a diameter between 3.5 and 4 mm. A low speed diamond saw was used to cut these cylinders to a gauge length between 9 and 12 mm for the compression tests. Therefore, the slenderness relationship was between 2.6 and 3.0. From each crystal several samples could be cut. The parallelism of the end faces of the samples was ensured by a careful mechanical polish. The orientation of the SC was determined in the high temperature β phase using the X-ray Laue method. The 18R martensitic SC were induced from the β SC by applying compressive stresses at temperatures between $M_s + 20$ K and $M_s + 25$ K. The sample temperature was
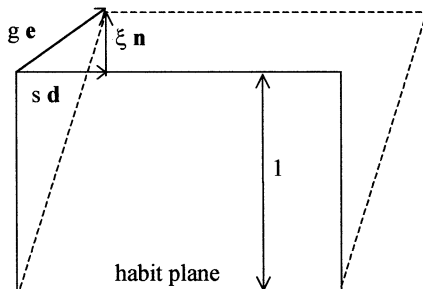

Fig. 1. Schematic illustration of the invariant plane strain. $\mathbf{e}$, $\mathbf{n}$ and $\mathbf{d}$ are the unit vectors specifying the direction of the displacement, the normal to the invariant plane, and the shear component. g, ξ and s are the magnitude of the displacement, the normal or dilatational component, and the shear component.

measured by a chromel-alumel thermocouple in contact with the sample. The composition, the spontaneous transformation temperature to martensite M_s, and the angles between the axis and the martensitic shear system of the SC used in this work are given in Table 1. M_s is a function of the composition and it was calculated as M_s $(K) = 3280 - 80C_{Zn} - 110C_{Al}$, with C_x the atomic concentration of the x atoms [17,18].

The samples were compressed in a Shimadzu DSS-10T-S deformation universal machine. To reduce the stress inhomogeneities along the sample during the compression tests, the end faces were covered with a thin Teflon film and lubricated with grease. The stress–strain curves were registered in the paper recorder of the testing machine. For higher precision all measurements were recorded and stored for further computation of the length change using a high-speed digital acquisition system. The length and the diameter of the samples were also measured with a precision digital caliper, $\Delta = 5 \times 10^{-3}$ mm, in both phases. For surface observations the samples were electropolished in a solution of 10% HNO_3 in methanol at 277 K.

4. Results and analysis

The martensitic transformation was induced by applying compressive stress, Fig. 2 shows a typical stress–strain curve. Starting from a β SC, the martensitic transformation starts at a critical stress σ_M, after a certain deformation at nearly constant stress it is completed; cooling the sample below the transformation temperature to the β phase, As, the martensitic SC is retained on unloading. A_s is around 6 K above M_s in the brasses [19]. In samples with $A_s >$ RT, after cooling under stress to RT the martensite was retained on unloading. Samples with As near RT were previously

Table 1
Composition, M_s temperature, and angles formed by the compressive axis with the habit plane (χ) and with the martensitic shear direction (λ) of the SC used in this work

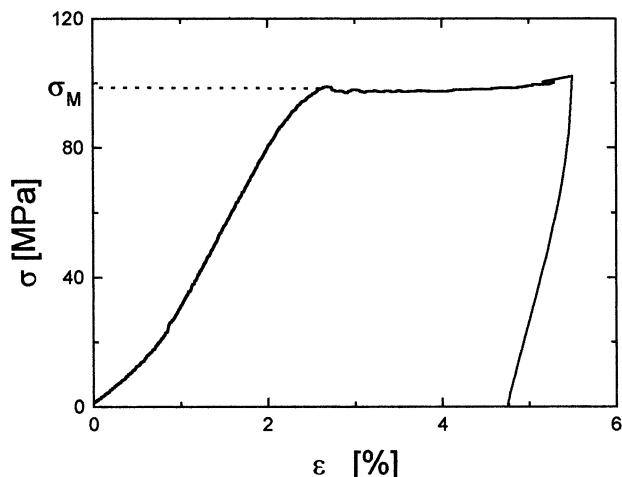| SC	C_{zn} (at.%)	C_{Al} (at.%)	M_s (K)	χ	λ
1	13.357	17.321	306	58	239
2	13.755	17.123	296	41	247
3	12.167	17.917	336	59	234
4	12.167	17.917	336	45	244
5	12.167	17.917	336	58	232
6	12.167	17.917	336	48	239
7	12.167	17.917	336	55	234
8	12.167	17.917	336	60	226
9	13.748	17.125	296	46	239
10	12.167	17.917	336	55	229
11	13.755	17.123	296	54	236
12	13.357	17.321	306	55	227
13	13.357	17.321	306	47	231

Fig. 2. Stress–strain curve for the β-18R transformation. The transformation starts at σ_M. An 18R SC is obtained after certain deformation, and it is retained on unloading.

subject to a short stabilization treatment under stress in order to increase the A_s [20]. The induced 18R variant is that with the highest Schmid factor. In the stereographic projection of Fig. 3 the habit plane normal P and the direction d of the martensite shear for the compression-induced 18R variant are plotted, as well as the 18R axis of the orthorhombic lattice. By optical microscopy with polarized light analysis it was made certain that a single martensitic variant existed along the whole crystal. The Laue diffraction pattern of the 18R basal plane was obtained in each case to verify that the induced 18R variant was the predicted one.

The length of each sample was measured in both phases with the caliper. The sample length change was confirmed with the strain register of the paper recorder and the digital data. The measured strains $\varepsilon = \Delta l / l$, between 4.5 and 7.6%, were compared with the calcu-
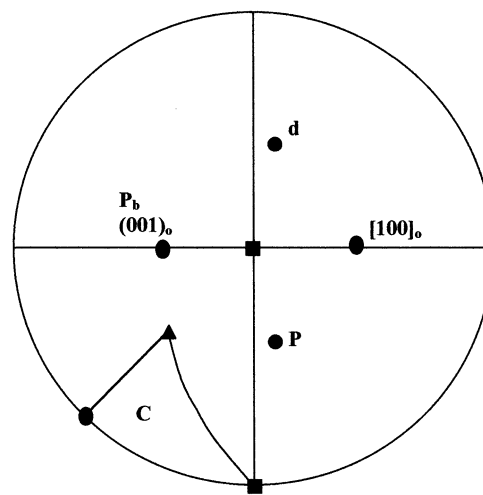

Fig. 3. Stereographic projection showing the martensitic shear system (P, d) for the 18R variant induced by compression (tensile axis in C). $(001)_o$ and $[100]_o$ are the 18R axis of the orthorhombic lattice.

lated ones. Values of the displacement normal component ξ between $+0.1$ and -0.3% were used to evaluate the shear component s and the transformation strain, Eqs. (2) and (1), for the different samples. The relative difference between the measured and the calculated strain, $\delta = [\varepsilon(\text{calculated}) - \varepsilon(\text{measured})]/\varepsilon(\text{measured})$, was determined for the different ξ values. Table 2 shows the obtained mean values of δ for the different ξ values. The standard deviation of the δ mean value is 0.9% in all the cases.

Considering the δ expected mean value is zero, the best approximation for the volume change going from β to martensite is -0.16%. Fig. 4 shows the distribution of δ for $\xi = -0.16\%$. It can be reasonable fitted with a Gaussian distribution with center 0.2 apart from zero, and standard deviation of the mean $\sigma_{\bar{\delta}} = 0.5$. Considering an expected value $\bar{\delta}$ equal 0, the acceptability of the measured value can be evaluated. The t-variable defined as $t = |\bar{\delta} - 0|/\sigma_{\bar{\delta}}$ [21] gives a discrepancy level of 0.40 $\sigma_{\bar{\delta}}$, this value is well inside the standard acceptance boundaries and shows an excellent agreement between the predicted and the experimental results. The data analysis did not evidence systematic deviations because of differences in the sample chemistry. Moreover, the alloys used here have actually a very close composition. Hence, a composition dependence of the results, if exists, is not expected to be detected.

Fig. 5 shows the experimental strain against the calculated one with $\xi = -0.16\%$, the least-square fitting gives a slope of 0.97 ± 0.07. The uncertainty in ξ determination can be evaluated considering the uncertainty in the lengths ratio measurement is around 0.1%. This conduces to a value of $\xi = -0.0016 \pm 0.0002$. Although the shear component s is composition dependent through the tetragonal distortion ψ, Eq. (2), a mean value becomes significant considering there are no large differences in the alloy composition used here. The obtained mean s value is $\bar{s} = 0.1985 \pm 0.0004$. Stabilization does not lead to changes in the molar volume of martensite but it does in ψ [22]. The consequent deviation in s was evaluated and it is far inside the experimental scatter.

The Schmid factor for the martensitic shear system μ is maximum when the compressive axis is in the $[001]_\beta$ orientation, and it decreases going to the $[111]_\beta$ pole. A
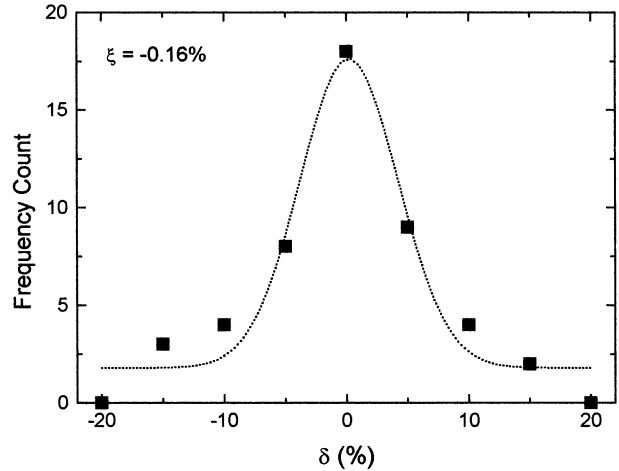

Fig. 4. Frequency distribution of the relative difference between strain values given by [1] and the experimental ones, $\delta = \Delta\varepsilon/\varepsilon$. Dot line corresponds to the Gaussian fit.
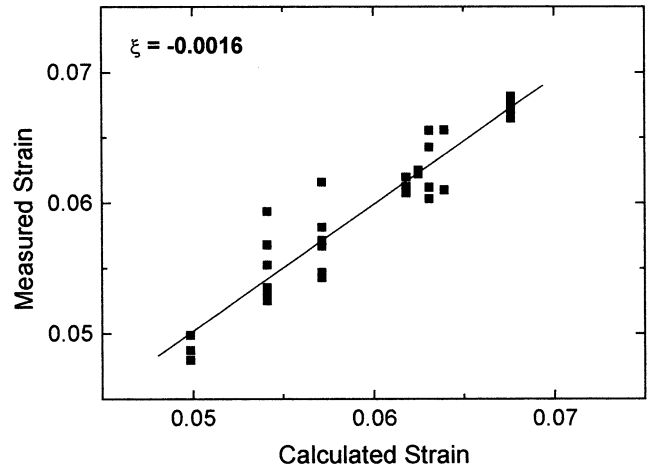

Fig. 5. Measured strain (■) vs. calculated strain according to Eq. (1). Least-square fitting (full line).

second martensitic variant or a variant different for the predicted one could appear as the Schmid factor of the predicted one decreases. The orientation relationship of the Schmid factor and the relative difference between the measured strain and the predicted strain δ versus μ are shown in Fig. 6. No systematic dependence with the axis orientation is observed for the several samples orientation tested here. The results are solidly indicating that a single variant of 18R martensite is obtained by compression under carefully experimental conditions. Moreover, optical microscopy observations via the remarkable optical anisotropy of martensite variants and X-ray Laue patterns of the basal plane confirm the presence of the 18R single variant oriented according to Fig. 3. The appearance of a second martensite variant at the last stage of transformation has been reported in [23], but this does not occur in our case.

Table 2
Mean value of $\delta = \Delta\varepsilon/\varepsilon$ ($MV\delta$) vs. the normal component ξ

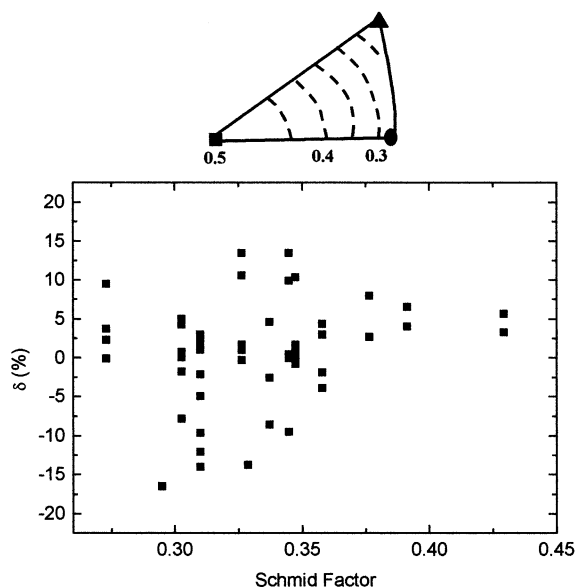| ξ (%)	$MV\delta$ (%)
0.10	-1.0
0	-0.7
-0.10	-0.3
-0.16	0.01
-0.20	0.2
-0.40	1.1

Fig. 6. Equal Schmid factor lines for the compression martensitic shear system, and relative difference between measured strain and the predicted one, δ ($\xi = -0.16\%$), vs. the Schmid factor.

Using measurements of the length and diameter of the samples prior and after the compression induced transformation, the β volume V_β and the martensite volume V_M were determined and the volume change could be evaluated. The frequency distribution of the relative difference of volume $\Delta V/V = (V_M - V_\beta)/V_\beta$ is shown in Fig. 7. The distribution is centered in $(-0.3 \pm 0.2)\%$, being 0.2% the mean value error. While each V_M/V_β value has an important uncertainty, 0.6%, because of the product and quotient error propagation, the statistic mean value has a lower error. Despite the roughness of the measuring method, it is interesting to remark that both the sign as well as the magnitude of $\Delta V/V$ are in accordance with the obtained from the evaluation of the length change, considering $\xi = -0.16\%$ is well inside the 68% confidence interval.
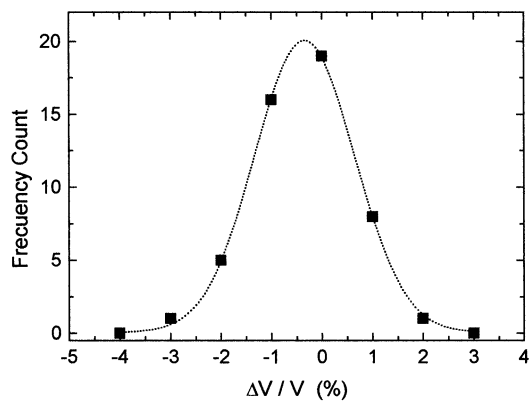

Fig. 7. Relative volume change between 18R phase and β phase determined via the samples length and diameter measurements. Dot line corresponds to the Gaussian fit.

Table 3
Volume change for the martensitic transformation obtained here and by different methods and systems

Number	Alloy (at.%)	$\Delta V/V$ (%)	Experimental technique
1	Cu–13.75Zn–17.12Al	−0.08	Density measurement [11]
2	Cu–26.78Al–4.56Ni	−0.09%	Pressure–temperature [12]
3	Cu–26.80Al–4.10Ni	−0.12%	Pressure–temperature [12]
4	Cu–28.8Al–3.2Ni	−0.11%	Pressure–temperature [25]
5	Cu–27.7Al–3.8Ni	−0.29%	Phenomenological theory [26]
6	Cu–15Zn–17Al	−0.26%	Lattice parameters [27]
7	Table 1, this work	−0.16; −0.3%	This work

The volume change associated with the martensitic transformation obtained here can be compared with that obtained by different methods and systems, Table 3. The values for Cu–Al–Ni (2, 3, 4) have been calculated from the reported pressure dependence of the critical transformation temperatures according to the relation $dT_0/dp = \Delta V/\Delta S$, where T_0 is the equilibrium temperature between martensite and the parent phase, $1/2(M_s + A_f)$, and ΔS is the entropy difference between both phases calculated according to [24], ΔS [J K^{-1} mol^{-1}] $= 2.87e/a - 2.80$ with e/a the electron atom ratio.

The influence of pressure and temperature on the transformation entropy and the volume change has to be considered in pressure–temperature determinations. In Cu-based alloys the Debye temperature is around RT [24], and taking into account that T_0 was near RT and it only changes about 5 K [12,25], the temperature contribution to ΔS temperature dependence can be neglected. The pressure dependence of ΔS can also be neglected because $[\partial \Delta S(P, T)/\partial P]_T = [\partial \Delta V(P, T)/\partial T]_P \approx 10^{-11}$ m^3 mol^{-1} K^{-1}. Besides, it is not expected that ΔV can be strongly influenced by the pressure. However, from Table 3 the values of $|\Delta V/V|$ determined by this method are lower than those obtained by the other experimental techniques (excluding density measurements). Within the experimental scatter it is not possible to determine if this effect is a real one. A β SC transforms to polyvariant martensite in density measurements [11]. As the authors discussed, the measured density includes interfaces and defects and could be not a real martensite density.

There are some advantages of our determination compared with the obtained by other methods, essentially consisting of the possibility of measuring the strain associated with the transformation from a matrix SC to a martensite SC, and to do this at the same temperature and atmospheric pressure. In comparison with compression test, tensile tests present some problems in measur-

ing the elongation accurately even using an extensometer [26]. Since the habit plane is not parallel to the knife edges in general, it is not clear how to define the completion of the transformation between the knife edges.

5. Conclusions

According to the experimental results, we can conclude that: (i) A SC of 18R martensite, or a unique 18R variant, can be obtained from a β SC by compression, this under strict control of the slenderness relationship of the samples, alignment of the end faces and an appropriate lubrication between the surfaces of contact as established in [6]. In this way, the β-18R transformation strain is direct and precisely achieved, allowing the evaluation of the shear and dilatational strain components. (ii) The results of deformation based on the invariant plane strain model and the phenomenological theory are in very good accordance with the experimental values for the β-18R transformation. The resulting relative volume change going from martensite to β is $\xi = -0.0016 \pm 0.0002$, and the shear component is $s = 0.1985 \pm 0.0004$.

Acknowledgements

References

[1] J.S. Bowles, J.K. Mackenzie, Acta Metall. 2 (1954) 129, 138, 224.
[2] M.S. Wechsler, D.S. Lieberman, T.A. Read, Trans. AIME 197 (1953) 1503.
[3] M. Ahlers, Z. Metallkde. 65 (1974) 636.
[4] M. Ahlers, Philos. Mag. A 82 (2002) 1093.
[5] W. Arneodo, M. Ahlers, Acta Metall. 22 (1974) 1475.
[6] J.L. Pelegrina, R. Romero, Mater. Sci. Eng. A 221 (1996) 63.
[7] P. Wollants, J.R. Roos, K. Otsuka, Z. Metallkde. 82 (1991) 182.
[8] F.C. Lovey, Acta Metall. 35 (1987) 1103.
[9] K. Marukawa, Philos. Mag. A 55 (1987) 85.
[10] J. Pons, F.C. Lovey, E. Cesari, Acta Metall. Mater. 38 (1990) 2733.
[11] A. Caneiro, M. Chandrasekaran, Scr. Metall. 22 (1988) 1797.
[12] V.A. Chernenko, J. Phys. IV (París) 5 (1995) C2–C77.
[13] V.A. Chernenko, V.A. Livov, Philos. Mag. A 73 (1996) 999.
[14] J.W. Christian, Metall. Trans. 13A (1982) 509.
[15] J. De Vos, E. Aernoudt, L. Delaey, Z. Metallkde. 69 (1978) 438.
[16] M. Ahlers, Scr. Metall. 8 (1974) 213.
[17] H. Pops, Trans. Met. Soc. AIME 236 (1966) 1532.
[18] H. Pops, N. Ridley, Metall. Trans. 1 (1970) 2654.
[19] M. Ahlers, Prog. Mater. Sci. 30 (1986) 135.
[20] A. Abu Arab, M. Ahlers, Acta Metall. 36 (1988) 2627.
[21] J.R. Taylor, An introduction to error analysis, in: The Study of Uncertainties in Physical Measurements, University Science Books, Sausalito, CA, 1996, p. 149.
[22] F. Saule, M. Ahlers, E.B. Rivero, Acta Metall. Mater. 40 (1992) 3229.
[23] A. Vivet, L. Orgéas, C. Lexcellent, D. Favier, J. Bernardini, Scr. Mater. 45 (2001) 33.
[24] R. Romero, J.L. Pelegrina, Phys. Rev. B 50 (1994) 9046.
[25] T. Kakeshita, T. Saburi, K. Shimizu, Mater. Sci. Eng. A273 (1999) 21.
[26] K. Otsuka, C.M. Wayman, K. Nakai, H. Sakamoto, K. Shimizu, Acta Metall. 24 (1976) 207.
[27] S. Chakravorty, C.M. Wayman, Acta Metall. 25 (1977) 989.