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DIFFERENCES IN THE SINGULAR TEMPERATURES OF MARTENSITIC TRANSFORMATION MEASURED BY CALORIMETRY AND STRESS–STRAIN METHODS IN SINGLE CRYSTALS OF SHAPE-MEMORY Cu–Zn–Al ALLOYS

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ABSTRACT

From the linear equations relating transformation stresses ($\beta \rightleftharpoons$ stress-induced martensite) to temperature, $M_s^{\sigma \to 0}$ and $A_s^{\sigma \to 0}$ temperatures were calculated at zero stress for different single-crystal alloys. The transformation stresses were corrected by the Schmid factor.

Comparing these values with the M_s^c and A_s^c temperatures measured by calorimetry, it can be observed in all cases that M_s^c (calorimetric) is higher than $M_s^{\sigma \to 0}$ (extrapolated to zero stress) and A_s^c (calorimetric) is lower than $A_s^{\sigma \to 0}$ (extrapolated to zero stress).

INTRODUCTION

It is well known that the martensitic transformation can be induced even above the M_s temperature if an external stress is applied. The stress necessary to initiate martensite decreases linearly with temperature, becoming zero at M_s, the temperature at which martensite forms spontaneously on cooling.

The variation of stress with temperature can be calculated from a Clausius–Clapeyron-type equation applicable to stress-induced martensite (SIM)

$$d\sigma/dT = \Delta H/T_0\ \Delta V \qquad (1)$$

where ΔH is the heat of transformation, ΔV is the change in volume when the transformation to martensite has been completed and T_0 is the temperature at which the matrix and martensite phases are in equilibrium at zero stress. It assumes that both matrix and martensite are always in equilibrium and does not take into account any hysteresis in the stress–strain curve. Hence, for any real system the formula is only an approximation [1].

Under cooling conditions, the martensite will not produce an external shape change of the specimen because differently oriented martensite plate variants form in such a way that the individual shape changes cancel each

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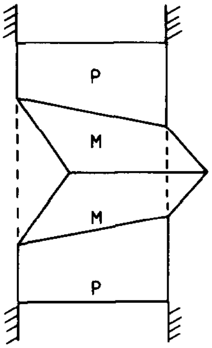

Fig. 1. Idealised representation showing no macroscopic shape change when two self-accommodating variants are formed [2].

other out, that is, the transformation proceeds in a self-accommodating manner. Figure 1 shows an idealised representation of this behaviour for two variants [2,3].

The martensitic transformation normally proceeds by forming six groups of four self-accommodating variants and the four variants in each plate group have their habit plane normals clustered around one of the six {110} β-poles (Fig. 2) [4].

It has been found experimentally that the martensite variant which forms on stressing is the one for which the resolved shear stress of the applied stress in the habit plane and in the shear direction, is a maximum. There are 24 possible planes and so there is always one fairly closely oriented with respect to the plane of maximum shear.

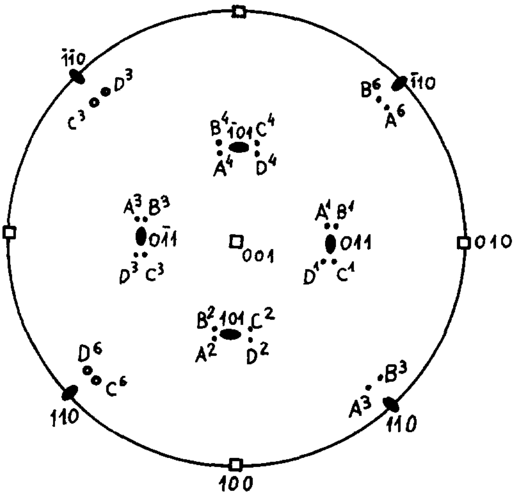

Fig. 2. Stereographic projection showing the calculated habit plane poles of the 24 variants of martensite with respect to the parent phase. Note the clustering of four habit plane poles about each {100} pole [4].

EXPERIMENTAL PROCEDURE

Single crystals were obtained by the Bridgman method from polycrystals of the same casting [5].

Fifteen single-crystal alloys showing β or $\beta +$ martensite structures were studied, the compositions of which are shown in Table 1. The samples were cylindrical (diameter 5 mm and thickness 6.5 mm).

The transformation temperatures (M_s^c and A_s^c) in these single crystal samples were determined by calorimetry, 24 h after a heat treatment consisting of 10 min at 850 °C and water quenching at 25 °C.

A non-conventional calorimeter was used which measures differential signals by means of thermobatteries. These are made up of 32 thermocouples of the quaternary alloy (Bi–Te–Se–Sb) with the P–N junctions connected in opposition. The temperature was measured by a Pt-100 standard probe.

Compression tests at different temperatures were carried out on the same samples using a Houndsfield W testing machine. The compression clamps were inside a tank filled with water at different temperatures.

RESULTS AND DISCUSSION

Transformation stresses ($\beta \rightarrow$ stress-induced martensite, SIM) as well as retransformation stresses (SIM $\rightarrow \beta$) were evaluated at different temperatures.

Stress values increase linearly when the temperature increases (as expected). The modified stress–temperature equations, according to the Schmid correction, (factor around 0.4) are shown in Table 2.

$M_s^{\sigma \rightarrow 0}$ and $A_s^{\sigma \rightarrow 0}$ temperatures at zero stress were calculated from those linear equations by extrapolation; values for each single crystal are given in Table 3.

TABLE 1

Chemical compositions

Alloy	Cu (wt.%)	Al (wt.%)	Zn (wt.%)	e/a
1A1	72.6	6.07	21.33	1.458
6A1	76.4	8.04	15.56	1.480
15A2	73.0	6.15	20.85	1.457
21N	76.4	7.81	15.79	1.473
49A	74.8	6.99	18.21	1.464
51A1	74.5	7.44	18.10	1.480
56A1	74.8	7.68	17.52	1.484
81A1	75.8	7.81	16.36	1.478

TABLE 2

Temperature dependence of the stress required to induce and revert stress-induced martensite with Schmid correction

Alloy	Equations: $\sigma(MN/m^2) - T\,(^\circ C)$
1	$\sigma_{SCH}^{\beta\to M} = 13.46 + 0.90T$
	$\sigma_{SCH}^{M\to\beta} = 7.28 + 0.90T$
2	$\sigma_{SCH}^{\beta\to M} = 2.79 + 1.06T$
	$\sigma_{SCH}^{M\to\beta} = -0.53 + 1.07T$
6	$\sigma_{SCH}^{\beta\to M} = 8.00 + 1.37T$
	$\sigma_{SCH}^{M\to\beta} = -1.62 + 0.95T$
8	$\sigma_{SCH}^{\beta\to M} = -25.40 + 1.45T$
	$\sigma_{SCH}^{M\to\beta} = -16.27 + 0.98T$
9	$\sigma_{SCH}^{\beta\to M} = -20.63 + 1.13T$
	$\sigma_{SCH}^{M\to\beta} = -26.76 + 1.09T$
15	$\sigma_{SCH}^{\beta\to M} = 16.87 + 1.25T$
	$\sigma_{SCH}^{M\to\beta} = 4.47 + 1.05T$
21	$\sigma_{SCH}^{\beta\to M} = 3.68 + 0.91T$
	$\sigma_{SCH}^{M\to\beta} = -3.32 + 0.83T$
49A1	$\sigma_{SCH}^{\beta\to M} = 23.20 + 1.15T$
	$\sigma_{SCH}^{M\to\beta} = 6.38 + 0.94T$
49A2	$\sigma_{SCH}^{\beta\to M} = 32.13 + 1.29T$
	$\sigma_{SCH}^{M\to\beta} = 7.26 + 1.03T$
49A3	$\sigma_{SCH}^{\beta\to M} = 34.97 + 1.21T$
	$\sigma_{SCH}^{M\to\beta} = 8.21 + 0.78T$
51	$\sigma_{SCH}^{\beta\to M} = 12.77 + 1.30T$
	$\sigma_{SCH}^{M\to\beta} = 0.71 + 0.88T$
56	$\sigma_{SCH}^{\beta\to M} = 11.91 + 1.26T$
	$\sigma_{SCH}^{M\to\beta} = -3.13 + 0.80T$
59	$\sigma_{SCH}^{\beta\to M} = -10.48 + 1.29T$
	$\sigma_{SCH}^{M\to\beta} = -18.13 + 0.84T$
61	$\sigma_{SCH}^{\beta\to M} = -14.84 + 1.43T$
	$\sigma_{SCH}^{M\to\beta} = -17.35 + 0.83T$
81	$\sigma_{SCH}^{\beta\to M} = -5.21 + 1.12T$
	$\sigma_{SCH}^{M\to\beta} = -12.72 + 0.90T$

Comparing the values of the M_s^c and A_s^c temperatures measured by calorimetry with those extrapolated at zero stress, it can be observed that, in all the cases, the extrapolated values of M_s are lower and of A_s are higher. In addition, the increment between the two M_s values is lower than 18 °C; the same applies to the A_s values. The variation between the M_s^c and $M_s^{\sigma\to 0}$ temperatures can be explained by the following.

(a) The thermal transformation ($\beta \to$ martensite) gives rise to 24 self-accommodating martensitic variants. Therefore, this requires less energy than a stress-induced martensitic transformation where only a few preferred variants are formed.

(b) The stress-induced martensitic transformation ($\beta \to$ SIM) takes place by applying a stress and produces more defects than quenching. These defects will inhibit plate growth.

TABLE 3

Singular temperatures (°C) of martensitic transformation measured by calorimetry and by extrapolation to zero stress

Alloy	M_s^c [a]	$M_s^{\sigma\to 0}$ [b]	$\lvert\Delta M_s\rvert$	A_s^c [a]	$A_s^{\sigma\to 0}$ [b]	$\lvert\Delta A_s\rvert$
1	0	−14	14	−23	−8	15
2	14	3	11	−10	0	10
6	4	−6	10	−4	2	6
8	28	18	10	15	24	9
9	28	18	10	18	25	7
15	−6	−13	7	−18	−4	14
21	0	−4	4	−11	4	7
49A1	−9	−20	11	−22	−7	15
49A2	−9	−25	16	−22	−7	15
49A3	−9	−28	19	−22	−11	11
51	6	−9	15	−9	0	9
56	1	−9	10	−14	4	18
59	26	8	18	12	21	9
61	28	11	17	14	20	6
81	6	4	2	−4	14	18

[a] M_s^c and A_s^c measured by calorimetry.

[b] $M_s^{\sigma\to 0}$ and $A_s^{\sigma\to 0}$ temperature calculated at zero stress.

In fact, these differences between both temperatures must be higher than the evaluated ones, because there is a different sensitivity in the measurement techniques. It has been noticed that when the start of the transformation is detected calorimetrically, there are no changes in the stress–strain curve.

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REFERENCES

1 J.M. Guilemany and F.J. Gil, Rev. Anal. de Fis., in press.
2 B.G. Mellor, Martensitic transformation and the shape-memory effect, Project COMETT 87/2 C-2 00863, Proceedings of the Course 274-332, Barcelona, 1989.
3 L. Delaey, R.V. Krishnan, M. Tas and H. Warlimont, J. Mater. Sci., 9 (1974) 1521.
4 T.A. Shroeder and C.M. Wayman, Acta Metall., 25 (1977) 1375.
5 J.M. Guilemany, F.J. Gil and J.R. Miguel, Rev. Metall., 24 (3) (1988) 175.