Thermochimica Acta, 167 (1990) 129–138
Elsevier Science Publishers B.V., Amsterdam

THE RELATIONSHIP BETWEEN CHEMICAL COMPOSITION AND TRANSFORMATION TEMPERATURES, M_s AND A_s, IN POLYCRYSTALS AND SINGLE CRYSTALS OF Cu–Zn–Al SHAPE-MEMORY ALLOYS

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(Received 31 January 1990)

ABSTRACT

The present paper reports the results of a detailed study of M_s and A_s transformation temperatures of polycrystals and single crystals of Cu–Zn–Al shape-memory alloys as a function of chemical composition and electron to atom ratio, within the range $e/a = 1.46$–1.49. A flow calorimetric technique was used in the determination of the transformation temperatures.

INTRODUCTION

The alloy composition has been found to be the most important parameter determining the transformation temperature of shape-memory alloys. However, it must be remembered that for a given composition, shifts in transformation temperatures of up to several tens of degrees centigrade can occur as a consequence of thermal, microstructural, crystallographic or mechanical factors [1]. The influence of most of these factors on transformation behaviour is now understood and is increasingly controlled in commercial shape-memory alloys.

The same complex interplay of factors means that the graphs showing the compositional dependence on transformation temperatures, for example those of the M_s temperature of ternary Cu–Zn–Al alloys published by Delaey et al. [2] and Ahlers [3], can only be used as a first approximation. These studies are also limited by the fact that they only use polycrystals with a 1.48 electron to atom ratio.

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0040-6031/90/$03.50

EXPERIMENTAL PROCEDURE

Forty-two polycrystalline alloys with an average grain size of 900 μm and their corresponding single crystals obtained by the Bridgman method were used in this work [4]. The compositions of the polycrystalline alloys used were determined by standard chemical procedures: copper by gravimetric analysis and aluminium by atomic absorption spectroscopy. Table 1 lists the chemical compositions of the alloys. Energy dispersive X-ray analysis techniques did not reveal any appreciable systematic differences between the composition of the polycrystalline samples and the corresponding single crystals.

The samples, in the form of cylinders (diameter 5 mm, height 2 mm) with an average mass of 400 mg, were subjected to a heat treatment consisting of 10 min at 850 °C followed by quenching in water at room temperature. Transformation temperatures for the polycrystalline and single crystal samples were measured simultaneously 24 h after heat treatment during heating and cooling cycles.

The flow calorimeter measures differential signals (ΔT) by means of Melcor thermobatteries which consist of 32 thermocouples of P–N junctions made from Bi–Te–Se–Sb quaternary alloys connected in opposition. The working range of these thermobatteries is from -150 °C to 100 °C. Temperature was measured by means of a standard Pt-100 probe. All signals were digitalized through a multichannel recorder and linked to a microcomputer. The sensitivity of this calorimetric technique is approximately 100 × higher than other conventional methods such as DTA or DSC [5].

M_s and A_s transformation temperatures occur when there is a sudden increment in calorimetric signal. In the same way, the final temperatures, M_f and A_f, are determined as when the calorimetric signal returns to the baseline. The transformation temperatures were measured during the first heating and cooling cycle after heat treatment. No appreciable differences (± 1 °C) in transformation temperatures from these values were found if the sample was thermally cycled several times through the transformation temperature range.

RESULTS AND DISCUSSION

Transformation temperatures (M_s, M_f, A_s, and A_f) for 42 different alloys in both polycrystalline and single crystalline specimens are shown in Table 2, as well as their corresponding hysteresis values ($T_h = M_s - A_f$).

Ahlers has proposed an equation relating chemical composition to transformation temperature, M_s [3]. This linear function was the result of data from 24 polycrystalline alloys with an electron to atom ratio (e/a) of 1.48. Unlike Ahlers' work, the present paper determines a linear function relating

M_s not only to chemical composition but also to the value of the electron to atom ratio (from 1.46 to 1.49). Furthermore, a similar equation for the retransformation temperature, A_s, has been calculated.

TABLE 1

Chemical compositions in weight

Alloy	%Cu	%Al	%Zn	e/a
1	72.6	6.07	21.33	1.458
2	72.9	5.86	21.24	1.449
3	73.2	6.22	20.58	1.457
5	76.2	7.69	16.11	1.472
6	76.4	8.04	15.56	1.480
8	76.6	7.99	15.41	1.477
9	77.2	8.15	14.65	1.470
10	71.8	4.94	23.26	1.432
11	68.9	4.66	26.44	1.451
12	72.4	6.27	21.33	1.465
13	77.0	8.14	14.86	1.477
14	72.3	6.66	21.04	1.470
15	73.0	6.15	20.85	1.457
21	76.4	7.81	15.79	1.473
22	78.9	8.54	12.56	1.471
24	76.7	7.62	15.68	1.465
49	74.8	6.99	18.21	1.464
50	74.8	7.38	17.82	1.475
52	74.3	7.33	18.36	1.478
54	74.3	7.42	18.28	1.481
55	75.5	7.17	17.33	1.463
58	75.6	7.77	16.63	1.488
59	76.5	8.00	15.50	1.478
60	75.8	7.93	16.27	1.482
61	76.2	7.82	15.98	1.475
63	76.5	7.92	15.58	1.475
64	76.3	8.08	15.62	1.481
65	76.5	7.86	15.64	1.474
66	73.1	7.07	19.83	1.482
67	73.8	7.37	18.83	1.484
69	73.5	7.27	19.23	1.484
70	73.8	7.39	18.81	1.485
71	73.4	7.54	19.06	1.492
72	73.8	7.45	18.75	1.486
73	73.8	7.47	18.73	1.487
74	74.5	7.34	18.16	1.477
75	74.8	7.68	17.52	1.484
76	75.5	7.97	16.53	1.487
79	75.0	7.88	17.12	1.487
80	74.9	7.70	17.04	1.484
81	75.8	7.81	16.36	1.478
82	75.1	7.77	17.16	1.484

TABLE 2

Transformation temperatures (°C)

Alloy	Polycrystals					Single crystals				
	M_s	M_f	A_s	A_f	T_h	M_s	M_f	A_s	A_f	T_h
1	0	−29	−19	10	10	0	−39	−23	13	13
2	18	−9	7	25	7	14	−10	6	25	11
3	27	−8	16	30	3	27	5	15	41	14
5	37	−5	15	35	2	35	−4	13	40	5
6	14	−13	0	19	5	4	−21	−4	10	6
8	38	0	29	46	8	28	1	15	35	7
9	40	0	25	49	9	28	5	18	33	5
10	41	2	28	42	1	34	8	27	52	18
11	−47	−77	−66	−45	2	−55	−74	−69	−46	9
12	−33	−54	−43	−23	10	−35	−57	−50	−25	10
13	47	19	33	57	10	43	25	30	46	3
14	−94	−107	−103	−87	7	−97	−110	−108	−93	4
15	10	−22	−15	15	5	−6	−22	−18	12	6
21	13	−18	−5	23	10	0	−20	−11	10	10
22	102	51	48	96	6	81	50	72	78	3
24	47	21	40	66	19	38	30	38	67	29
49	−9	−36	−22	−2	7	−9	−32	−22	18	27
50	−29	−48	−38	−22	7	−31	−45	−41	−25	6
52	−29	−56	−42	−25	4	−29	−53	−45	−18	11
54	−77	−105	−90	−68	9	−76	−98	−90	−71	5
55	26	1	14	30	4	26	4	14	36	10
58	21	−11	4	26	5	20	−10	2	33	13
59	18	−10	12	30	12	26	−6	12	37	11
60	−2	−27	−14	4	6	−7	−32	−21	0	7
61	13	−20	2	19	6	28	0	14	37	9
63	23	−7	11	29	6	19	−8	6	28	9
64	25	−11	13	28	3	25	0	13	50	25
65	33	6	25	44	11	32	1	21	37	5
66	−84	−100	−97	−79	5	−76	−103	−98	−72	4
67	−75	−89	−85	−68	7	−80	−107	−85	−79	1
69	−85	−100	−97	−76	9	−88	−102	−98	−82	6
70	−54	−88	−81	−47	7	−78	−104	−90	−66	12
71	−79	−110	−98	−72	7	−80	−108	−103	−74	6
72	−51	−81	−66	−48	3	−51	−74	−69	−48	3
73	−70	−91	−82	−62	8	−73	−93	−86	−67	6
74	−37	−67	−57	−32	5	−40	−60	−60	−33	7
75	−58	−84	−73	−54	4	−68	−84	−76	−62	6
76	−54	−76	−69	−50	4	−54	−79	−71	−47	7
79	−45	−62	−60	−43	2	−53	−78	−78	−52	1
80	−25	−52	−45	−20	5	−25	−58	−48	−20	5
81	6	−18	−4	12	6	6	−11	−4	10	4
82	−30	−60	−47	−28	2	−31	−57	−53	−27	4

TABLE 3

Differences between experimental and calculated M_s temperature in polycrystals

Alloy	e/a	M_s (exp.) (°C)	M_s (calc.) (°C)	$\lvert\Delta M_s\rvert$ (°C)
1	1.458	0	−7	7
2	1.449	28	25	3
3	1.457	27	9	18
5	1.472	37	31	6
6	1.480	14	10	4
8	1.477	38	25	7
9	1.470	40	30	10
10	1.432	41	49	8
11	1.451	−47	−56	9
12	1.465	−33	−36	3
13	1.477	47	31	16
14	1.470	−94	−87	7
15	1.457	10	6	4
21	1.473	13	29	16
22	1.471	102	90	12
24	1.465	47	61	14
49	1.464	−9	21	30
50	1.475	−29	−13	16
52	1.478	−29	−33	4
54	1.481	−77	−41	36
55	1.463	26	40	14
58	1.488	21	9	12
59	1.478	18	19	1
60	1.482	−1	−10	8
61	1.475	13	18	5
63	1.475	23	24	1
64	1.481	25	0	25
65	1.474	33	31	2
66	1.482	−84	−70	14
67	1.484	−75	−62	13
69	1.484	−85	−67	18
70	1.485	−54	−62	8
71	1.492	−79	−97	18
72	1.486	−51	−68	17
73	1.487	−70	−70	0
74	1.477	−37	−24	13
75	1.484	−58	−38	20
76	1.487	−54	−27	27
79	1.487	−45	−47	2
80	1.484	−25	−11	14
81	1.478	6	1	5
82	1.484	−30	−33	3

TABLE 4

Differences between experimental and calculated A_s temperature in polycrystals

Alloy	e/a	A_s (exp.) (°C)	A_s (calc.) (°C)	$\lvert\Delta A_s\rvert$ (°C)
1	1.458	−23	−26	3
2	1.449	6	7	1
3	1.457	15	−9	24
5	1.472	13	13	0
6	1.480	−4	−8	4
8	1.477	15	6	9
9	1.470	18	17	1
10	1.432	27	31	4
11	1.451	−69	−87	18
12	1.465	−50	−53	3
13	1.477	30	13	17
14	1.470	−108	−100	8
15	1.457	−18	−13	5
21	1.473	−11	11	22
22	1.471	72	71	1
24	1.465	38	42	4
49	1.464	−22	2	24
50	1.475	−41	−32	9
52	1.478	−45	−51	6
54	1.471	−90	−60	30
55	1.463	14	22	8
58	1.488	2	−17	19
59	1.478	12	0	12
60	1.482	−21	−29	8
61	1.475	14	0	14
63	1.475	6	7	1
64	1.481	13	−18	31
65	1.474	21	12	9
66	1.482	−98	−89	9
67	1.484	−85	−81	4
69	1.484	−98	−87	11
70	1.485	−90	−82	8
71	1.492	−103	−116	13
72	1.486	−69	−87	18
73	1.487	−86	−89	3
74	1.477	−60	−43	17
75	1.484	−76	−57	19
76	1.487	−71	−47	24
79	1.487	−78	−65	13
80	1.484	−48	−33	15
81	1.478	4	−17	21
82	1.484	−53	−51	2

TABLE 5

Differences between experimental and calculated M_s temperature in single crystals

Alloy	e/a	M_s (exp.) (°C)	M_s (calc.) (°C)	$\lvert\Delta M_s\rvert$ (°C)
1	1.458	0	−12	12
2	1.449	14	18	4
3	1.457	27	4	23
5	1.472	35	26	9
6	1.480	4	6	2
8	1.477	28	20	8
9	1.470	28	22	6
10	1.432	34	40	6
11	1.451	−55	−72	17
12	1.465	−35	−39	4
13	1.477	43	25	18
14	1.470	−97	−92	5
15	1.457	−6	1	7
21	1.473	0	23	23
22	1.471	81	81	0
24	1.465	38	53	15
49	1.464	−9	14	23
50	1.475	−31	−18	13
52	1.478	−29	−36	7
54	1.481	−76	−44	32
55	1.463	26	33	7
58	1.488	20	8	12
59	1.478	26	14	12
60	1.482	−7	−14	7
61	1.475	28	13	15
63	1.475	19	19	0
64	1.481	25	−4	29
65	1.474	32	25	7
66	1.482	−76	−72	4
67	1.484	−80	−64	16
69	1.484	−88	−70	18
70	1.485	−78	−64	14
71	1.492	−80	−97	17
72	1.486	−51	−70	19
73	1.487	−73	−71	2
74	1.477	−40	−29	11
75	1.484	−68	−42	26
76	1.487	−54	−30	24
79	1.487	−53	−52	1
80	1.484	−25	−14	11
81	1.478	6	−3	9
82	1.484	−31	−36	5

TABLE 6

Differences between experimental and calculated A_s temperature in single crystals

Alloy	e/a	A_s (exp.) (°C)	A_s (calc.) (°C)	$\lvert\Delta A_s\rvert$ (°C)
1	1.458	−19	−23	4
2	1.449	7	8	1
3	1.457	16	−7	23
5	1.472	15	13	2
6	1.480	0	−7	7
8	1.477	29	7	22
9	1.470	25	14	11
10	1.432	28	32	4
11	1.451	−66	−82	16
12	1.465	−43	−50	7
13	1.477	33	13	20
14	1.470	−103	−98	5
15	1.457	−15	−10	5
21	1.473	−5	12	17
22	1.471	48	70	22
24	1.465	40	42	2
49	1.464	−22	4	26
50	1.475	−38	−29	9
52	1.478	−42	−48	6
54	1.481	−90	−55	35
55	1.463	14	23	9
58	1.488	4	−9	13
59	1.478	12	2	10
60	1.482	−14	−26	12
61	1.475	2	1	1
63	1.475	11	7	4
64	1.481	13	−16	29
65	1.474	25	13	12
66	1.482	−97	−83	14
67	1.484	−85	−75	10
69	1.484	−97	−81	16
70	1.485	−81	−76	5
71	1.492	−98	−109	11
72	1.486	−66	−82	16
73	1.487	−82	−83	1
74	1.477	−57	−39	18
75	1.484	−73	−53	20
76	1.487	−69	−42	27
79	1.487	−60	−61	1
80	1.484	−45	−28	17
81	1.478	−4	−15	11
82	1.484	−47	−48	1

These equations for M_s and A_s (°C) are:

Polycrystals

$$M_s = 11.76 - 204.12(\text{wt.\% Al}) - 65.93(\text{wt.\% Zn}) + 1800.93(e/a) \quad (1)$$

with a multiple correlation coefficient of 0.94.

$$A_s = 270.10 - 186.11(\text{wt.\% Al}) - 60.83(\text{wt.\% Zn}) + 1463.57(e/a) \quad (2)$$

with a multiple correlation coefficient of 0.91.

Single crystals

$$M_s = -425.85 - 204.12(\text{wt.\% Al}) - 66.66(\text{wt.\% Zn}) + 2131.49(e/a) \quad (3)$$

with a multiple correlation coefficient of 0.95.

$$A_s = 977.30 - 170.10(\text{wt\%. Al}) - 57.81(\text{wt.\% Zn}) + 865.46(e/a) \quad (4)$$

with a multiple correlation coefficient of 0.94.

These equations adjust fairly well to a linear function as can be seen from the values of the multiple correlation coefficient.

Experimental M_s and A_s temperatures are compared with M_s and A_s values calculated from the above equations in Tables 3 and 4. An average error for polycrystals of 11°C for M_s and of 12°C for A_s was obtained. In single crystals, the average error was about 12°C for both M_s and A_s temperatures, as shown in Tables 5 and 6.

The relationships shown in Table 7 are obtained from eqns. (1)–(4) for an electron to atom ratio of 1.46, 1.47, 1.48 and 1.49. It should be noted that in these equations the relation between the aluminium and zinc coefficients has a constant value of 3 : 1. This implies that the influence of the aluminium content on transformation temperatures is three times higher than that of the zinc content.

TABLE 7

Equations for an electron to atom ratio of 1.46, 1.47, 1.48 and 1.49

e/a	Polycrystals	Single crystals
1.46	$M_s = 2641.2 - 65.9\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$M_s = 2686.1 - 66.7\,[3.2(\%\text{Al}) + (\%\text{Zn})]$
1.47	$M_s = 2659.0 - 65.9\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$M_s = 2707.4 - 66.7\,[3.2(\%\text{Al}) + (\%\text{Zn})]$
1.48	$M_s = 2678.8 - 65.9\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$M_s = 2728.8 - 66.7\,[3.2(\%\text{Al}) + (\%\text{Zn})]$
1.49	$M_s = 2695.3 - 65.9\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$M_s = 2750.1 - 66.7\,[3.2(\%\text{Al}) + (\%\text{Zn})]$
1.46	$A_s = 2407.0 - 60.8\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$A_s = 2240.9 - 57.8\,[2.9(\%\text{Al}) + (\%\text{Zn})]$
1.47	$A_s = 2421.6 - 60.8\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$A_s = 2249.5 - 57.8\,[2.9(\%\text{Al}) + (\%\text{Zn})]$
1.48	$A_s = 2436.2 - 60.8\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$A_s = 2258.2 - 57.8\,[2.9(\%\text{Al}) + (\%\text{Zn})]$
1.49	$A_s = 2450.8 - 60.8\,[3.1(\%\text{Al}) + (\%\text{Zn})]$	$A_s = 2266.8 - 57.8\,[2.9(\%\text{Al}) + (\%\text{Zn})]$

Thus chemical composition produces large variations in transformation temperatures as can be seen from the following examples: for the same aluminium composition and the same electron to atom ratio, an increase of 0.1% in weight of zinc (0.1 at.% Zn) causes a decrease in both M_s and A_s temperatures of about 7 °C in polycrystals as well as in single crystals; for the same zinc composition and the same electron to atom ratio, an increase of 0.05% in weight of aluminium (0.1 at.% Al) causes a decrease in both M_s and A_s temperatures of about 10 °C in polycrystals as well as in single crystals.

The difference in transformation temperatures of polycrystalline and single crystalline samples of the same composition will be published at a later date [6].

ACKNOWLEDGEMENTS

The authors are grateful to Drs. J. Muntasell and J.L. Tamarit from Universitat Politécnica de Catalunya and E. Cesari from Universitat Illes Balears. The present research was supported by CAICYT project PA 0085-84.

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