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On the impact of liquisol quenching on the structure of a double hcp gold-cadmium-indium alloy

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The effect of quenching from the liquid state a gold alloy containing 17.5 at.% cadmium and 5.0 at.% indium with the double hexagonal close-packed (dhcp) structure was investigated. With qualitatively differing cooling-rates three metastable close-packed layer structures, namely face-centred cubic, hexagonal close-packed and samarium-type, were obtained. On annealing, the metastable phases were observed to retransform to the equilibrium dhcp phase.

1. Introduction

The changes in structure and consequently in properties that are brought about as a result of quenching alloys in the solid state from high temperatures have been, and are being, studied in considerable detail. The results of these studies are not only of great academic interest but have been used commercially in a vital manner and fall under the classification of heat-treatment. Recent studies of states resulting from quenching the liquid (liquisol quenching) and the vapour (vaposol quenching) over the last decade have generated quite widespread interest as the resulting changes in the alloy structure are profound. Elaborate reviews of experimental results on liquid quenching [1] as well as vapour quenching [2] are available and document information on a variety of non-equilibrium phases such as those with extended solubilities, new intermediate phases and amorphous phases. The unusual properties observed in some of these products namely, high strength, superconductivity and ferromagnetism are some of the exciting developments which may yet be commercially exploited.

The present work is concerned with investigating the consequences of liquid quenching a gold alloy containing 17.5 at.% cadmium and 5.0 at.% indium. This alloy is characterized by a double hexagonal close-packed (dhcp) structure with the . . .ABACA. . . stacking sequence of close-packed layers. Imperfections, particularly stacking faults, in the dhcp structure form the subject matter of a research programme [3-7] in our Department and the choice of the ternary gold alloy was made in this context. Splat-cooling (gun technique), quenching the liquid droplets from the gun apparatus directly into water and filamentary casting technique were resorted to, yielding differing cooling-rates. Three distinct, but structurally related, non-equilibrium close-packed phases, namely face-centred cubic (fcc) hexagonal close-packed (hcp) and samarium-type were observed to result. The fcc, hcp and the Sm-type structures are characterized respectively by the stacking sequences of close-packed layers. The occurrence of these different close-packed layer structures in the same substance may be regarded as an interesting example of polytypism in alloys. A description of these non-equilibrium phases is offered here and the effect of annealing on their return to equilibrium is also reported.

2. Experimental

The alloy was prepared by melting the required quantities of the component metals (99.99+ %) under argon atmosphere in a sealed silica tube which had two interconnected chambers. One of these chambers contained a getter of molybdenum foil while the other was filled with the component metal pieces. The volume of the silica tube was maintained as small as possible to prevent evaporation of the low-melting constituents. The loss in weight as a result of melting was negligible and the composition is accurate to within ±0.1% in each component. Optical metallography of the homogenized button (homogenization consisted of annealing, wrapped in a molybdenum foil, in an atmosphere of argon at 600°C for 6 days) revealed single-phase grains. X-ray diffraction patterns obtained from annealed (400°C, 10 h) filings of homogenized ingot confirmed the presence of a homogeneous dhcp phase (Table I).

Different cooling-rates in quenching the liquid alloy were obtained in the following ways given in decreasing order of magnitude of cooling-rate. 1. Splat-quenching, using an apparatus similar to the gun technique developed by Duwez *et al* [8]. 2. Splat-quenching, using the same gun apparatus but with the copper substrate replaced by water held in a container. 3. Quenching the molten metal carried in a tapered silica capillary, resulting in a filamentary casting. The gun apparatus used in the present investigations has been described in detail elsewhere [9]. The filamentary casting was obtained by sealing a small quantity of the alloy ($\sim$ 3 g) in a double-chambered evacuated silica tube. The upper chamber carrying the getter (molybdenum foil) was connected to the lower chamber carrying the alloy via a constriction. The other end of the lower chamber was drawn out to have a progressively decreasing cross-section. The entire tube was heated to well above the melting point, and the liquid alloy was forced into the tapered portion by continuous agitation. The tube was then quenched by dropping it into water. In a typical experiment the diameter of the filament varied from 0.55 mm at the narrower end to 0.92 mm at the broader end. The filament had a circular cross-section at all points along the length.

X-ray powder patterns of the splat-cooled foils as well as the filamentary casting were obtained in a Philips 114.6 mm diameter camera using filtered Cu$K\alpha$ radiation. For the purpose of X-ray examination, the filament was sliced into pieces of about 5 mm length and Debye-Scherrer patterns were obtained from either end of each slice.

The lattice parameters from X-ray powder patterns were calculated in all cases by means of a graphical extrapolation technique, utilizing the well-known Nelson-Riley function. Separate extrapolation plots were made for a and c parameters where necessary. For points close to $\theta = 90°$ in such cases, a method [10] whereby high-angle reflection could be utilized for extrapolation of a (or c) by eliminating c (or a) found from reflections with $h = k = 0$ (or $l = 0$), was employed.

3. Results and discussion

The X-ray line positions in $2\theta°$, observed intensities (qualitative) and interplanar spacings (d_{obs}) of the equilibrium alloy are given in Table I. The powder pattern has been indexed on the basis of the dhcp structure with lattice parameters: $a_0 = 2.909$ and $c_0 = 9.557_5$ Å found by extrapolation as described earlier.

The foil obtained by splat-cooling using the gun apparatus produced a metastable homogeneous fcc phase (Table II). The foils so obtained, were also malleable at room temperature and in this they were typical of the fcc structure and unlike the brittle equilibrium alloy. As foils thinner than 1000 Å can be produced by splat-cooling and readily retransformed (annealing at 300°C for 2 h) to the equilibrium dhcp structure, this provides an excellent means of preparing the otherwise difficult thin foils of the dhcp alloy for transmission electron microscopic studies.

Splatting the molten alloy directly into water produced a two-phase fcc + hcp mixture in which the fcc phase was predominant (Table III). Filamentary casting of the alloy produced two distinct phases, one at the thin end of the capillary which was hcp (Table IV) and another at its thick end which was samarium-type (Table V). Regions of the filament in between the ends showed powder patterns typical of mixtures of the hcp and Sm-type phases.

The lattice parameters of the different metastable phases are summarized in Table VI. The metastable fcc and Sm-type phases were observed to retransform to the equilibrium dhcp phase on annealing at 300°C for 2 h. However, the hcp phase obtained at the thin end of the filamentary casting was found to yield, on annealing under the above conditions, a Sm-type phase which was analogous to the one obtained at the thicker end of the filament. It was only on annealing this intermediate product at 300°C for a further 2 h that the equilibrium dhcp phase was recovered. This leads us to conclude that the sequence of transformations fcc $\rightleftharpoons$ dhcp $\rightleftharpoons$ Sm $\rightleftharpoons$ hcp observed in high-pressure studies [11], is perhaps also valid in the present studies. Interesting correlations in terms of the electronic structure

TABLE I Interplanar spacings in the equilibrium dhcp phase

No.	*hkil*	$2\bar{\theta}^\circ$	Obs. Int.*	*d*(Å)	
				Obs.	Calc.
1	$10\bar{1}0$	36.04	ms	2.492	2.519
2	$10\bar{1}1$	37.30	vs	2.411	2.436
3	0004	38.08	s	2.363	2.390
4	$10\bar{1}2$	40.85	vvs	2.209	2.228
5	$10\bar{1}3$	46.34	s	1.960	1.976
6	$10\bar{1}4$	53.16	w	1.723	1.734
7	$10\bar{1}5$	61.12	ms	1.516	1.523
8	$11\bar{2}0$	64.31	s	1.449	1.455
9	$10\bar{1}6$	70 06	s	1.343	1.346
10	$20\bar{2}0$	—	no	—	1.260
11	$20\bar{2}1$	—	no	—	1.249
12	$11\bar{2}4$	76.86	s	1.240	1.242
13	$20\bar{2}2$	78.67	ms	1.216	1.218
14	$10\bar{1}7$	—	no	—	1.200
15	0008	80.95	w	1.189	1.195
16	$20\bar{2}3$	82.48	w	1.169	1.171
17	$20\bar{2}4$	88.20	vw	1.108	1.114
18	$10\bar{1}8$	91.45	vw	1.077	1.079
19	$20\bar{2}5$	94.46	w	1.050	1.052
20	$20\bar{2}6$	102.74	ms	0.987	0.988
21	$10\bar{1}9$	104.25	w	0.977	0.979
22	$21\bar{3}0$	—	no	—	0.952
23	$21\bar{3}1$	109.12	ms	0.946	0.947
24	$21\bar{3}2$	$111.33\alpha_1$ $111.73\alpha_2$	ms w	0.933 0.933	0.934
25	$20\bar{2}7$	$112.78\alpha_1$	vw	0.925	0.926
26	$11\bar{2}8$	$113.31\alpha_1$ $113.81\alpha_2$	ms w	0.922 0.922	0.923
27	$21\bar{3}3$	$115.53\alpha_1$	w	0.911	0.912
28	$10\bar{1},10$	$119.36\alpha_1$ $119.88\alpha_2$	ms w	0.892 0.892	0.894
29	$21\bar{3}4$	$121.26\alpha_1$	vw	0.884	0.885
30	$20\bar{2}8$	$125.58\alpha_1$	vvw	0.866	0.867
31	$21\bar{3}5$	$129.37\alpha_1$ $129.97\alpha_2$	w vw	0.852 0.852	0.852
32	$30\bar{3}0$	$133.29\alpha_1$ $133.87\alpha_2$	ms w	0.839 0.839	0.840
33	$10\bar{1},11$	$139.66\alpha_1$ $140.44\alpha_2$	w vw	0.821 0.821	0.821
34	$21\bar{3}6$	$141.12\alpha_1$ $141.95\alpha_2$	w vw	0.817 0.817	0.817
35	$20\bar{2}9$	$143.38\alpha_1$ $144.53\alpha_2$	w vw	0.811 0.811	0.812
36	000,12	$150.63\alpha_1$ $151.78\alpha_2$	w vw	0.796 0.796	0.796
37	$30\bar{3}4$	$153.07\alpha_1$ $154.22\alpha_2$	s ms	0.792 0.792	0.792
38	$21\bar{3}7$	$161.15\alpha_1$ $162.98\alpha_2$	ms w	0.781 0.781	0.781

*vvs: very very strong; vs: very strong; s: strong; ms: medium strong; w: weak; vw: very weak; vvw: very very weak; no: not observed.

TABLE II Interplanar spacings in the metastable fcc phase

No.	*hkl*	$2\bar{\theta}^\circ$	Obs. Int.*	*d*(Å)	
				Obs.	Calc.
1	111	37.85	vs	2.377	2.380
2	200	43.95	vs	2.060	2.061
3	220	63.99	s	1.457	1.457
4	311	76.65	vs	1.243	1.243
5	222	80.77	ms	1.190	1.190
6	400	97.05	ms	1.029	1.031
7	331	109.29	s	0.945	0.946
8	420	113.61	s	0.921	0.922
9	422	$132.54\alpha_1$	s	0.841	0.841
10	333,511	$152.33\alpha_1$ $153.61\alpha_2$	s w	0.793 0.793	0.793

*vs: very strong; s: strong; ms: medium strong; w: weak.

TABLE III Interplanar spacings in the metastable fcc + hcp phase mixture

No.	*hkl*/*hkil*	$2\bar{\theta}^\circ$	Obs. Int.*	*d*(Å)	
				Obs.	Calc.
1	$10\bar{1}0$	35.62	vvw	2.520	2.522
2	111	37.83	vs	2.378	2.380
3	$10\bar{1}1$	40.33	w	2.236	2.233
4	200	43.95	s	2.060	2.061
5	$10\bar{1}2$	52.81	vw	1.734	1.740
6	220	63.86	ms	1.458	1.457
7	$10\bar{1}3$	69.53	w	1.352	1.352
8	311	76.70	vs	1.242	1.243
9	$20\bar{2}1$	77.96	vvw	1.216	1.220
10	222	80.67	ms	1.191	1.190
11	400	96.72	ms	1.032	1.031
12	$20\bar{2}3$	102.47	vvw	0.989	0.991
13	331	109.21	s	0.946	0.946
14	$21\bar{3}1$	111.04	vvw	0.935	0.935
15	420	113.53	s	0.922	0.922
16	422	$132.69\alpha_1$	s	0.841	0.841
17	$21\bar{3}3$	$140.46\alpha_1$	vvw	0.819	0.819
18	333- 511	$152.38\alpha_1$ $152.79\alpha_2$	s w	0.793 0.793	0.793

*vs: very strong; s: strong; ms: medium strong; w: weak; vw: very weak; vvw: very very weak.

[12, 13] have been proffered as explanations for the above sequence, which is the same as is observed in the sequence of phases in phase diagrams involving pairs of rare earth metals [12]

The observation that all the metastable phases returned to the dhcp structure with a lattice parameter differing only in the fourth decimal place (within experimental error) from that of the equilibrium parent alloy, is important. This

TABLE IV Interplanar spacings in the metastable hcp phase

No.	*hkil*	$2\bar{\theta}^\circ$	Obs. Int.*	d(Å) Obs.	d(Å) Calc.
1	$10\bar{1}0$	35.83	ms	2.506	2.522
2	0002	37.71	ms	2.385	2.403
3	$10\bar{1}1$	40.70	vs	2.217	2.233
4	$10\bar{1}2$	52.89	ms	1.731	1.740
5	$11\bar{2}0$	64.19	ms	1.451	1.456
6	$10\bar{1}3$	69.73	s	1.349	1.352
7	$20\bar{2}0$	75.58	w	1.258	1.261
8	$11\bar{2}2$	76.71	s	1.242	1.245
9	$20\bar{2}1$	78.64	s	1.217	1.220
10	0004	80.07	w	1.198	1.201
11	$20\bar{2}2$	87.58	w	1.114	1.116
12	$10\bar{1}4$	90.79	w	1.083	1.085
13	$20\bar{2}3$	102.47	w	0.989	0.991
14	$21\bar{3}0$	108.24	ms	0.951	0.953
15	$21\bar{3}1$	$111.17\alpha_1$	w	0.934	0.935
		$111.67\alpha_2$	vw	0.933	
16	$11\bar{2}4$	$112.60\alpha_1$	ms	0.926	0.927
		$113.03\alpha_2$	w	0.926	
17	$10\bar{1}5$	$118.20\alpha_1$	ms	0.898	0.898
		$118.73\alpha_2$	w	0.897	
18	$21\bar{3}2$	$120.96\alpha_1$	ms	0.885	0.886
19	$20\bar{2}4$	$124.72\alpha_1$	w	0.869	0.870
20	$30\bar{3}0$	$132.85\alpha_1$	ms	0.840	0.841
		$133.73\alpha_2$	w	0.840	
21	$21\bar{3}3$	$140.23\alpha_1$	s	0.819	0.819
		$141.23\alpha_2$	ms	0.819	
22	0006	$148.18\alpha_1$	w	0.801	0.801
		$149.24\alpha_2$	vw	0.801	
23	$30\bar{3}2$	$152.30\alpha_1$	s	0.793	0.793
		$153.65\alpha_2$	ms	0.793	

*vs: very strong; s: strong; ms: medium strong; w: weak; vw: very weak.

TABLE V Interplanar spacings for the metastable Sm-type phase

No.	*hkil*	$2\bar{\theta}^\circ$	Obs. Int.*	d(Å) Obs.	d(Å) Calc.
1	$10\bar{1}1$	36.60	w	2.455	2.504
2	$10\bar{1}2$	36.93	vvw	2.434	2.455
3	0009	37.91	vs	2.373	2.398
4	$10\bar{1}4$	39.82	ms	2.264	2.284
5	$10\bar{1}5$	41.85	ms	2.159	2.177
6	$10\bar{1}7$	46.87	vw	1.938	1.952
7	$10\bar{1}8$	49.86	ms	1.829	1.842
8	$10\bar{1},10$	56.44	ms	1.630	1.640
9	$10\bar{1},11$	60.14	vvw	1.539	1.548
10	$11\bar{2}0$	64.35	ms	1.448	1.456
11	$10\bar{1},13$	67.81	ms	1.382	1.387
12	$10\bar{1},14$	72.15	ms	1.309	1.315
13	$20\bar{2}1$	76.01	w	1.252	1.259
14	$20\bar{2}2$				1.252
15	$11\bar{2}9$	76.87	ms	1.240	1.244
16	$20\bar{2}4$	77.92	vvw	1.226	1.228
17	$20\bar{2}5$	78.77	vvw	1.215	1.210
18	000,18	80.28	vvw	1.196	1.199
19	$10\bar{1},16$	81.08	ms	1.186	1.189
20	$20\bar{2}7$	82.95	vvw	1.164	1.167
21	$20\bar{2}8$	81.10	vvw	1.140	1.142
22	$10\bar{1},17$	85.94	vvw	1.131	1.134
23	$20\bar{2},10$	90.44	vvw	1.086	1.089
24	$20\bar{2},11$	93.54	vvw	1.058	1.061
25	$10\bar{1},19$	96.55	w	1.033	1.036
26	$20\bar{2},13$	100.56	w	1.002	1.004
27	$10\bar{1},20$	—	no	—	0.992
28	$20\bar{2},14$	104.68	w	0.974	0.976
29	$21\bar{3}1$	108.27	w	0.951	0.952
30	$21\bar{3}2$	—	—	—	0.949
31	$21\bar{3}4$	110.62	w		0.938
32	$21\bar{3}5$	111.80	w	0.931	0.931
33	$11\bar{2},18$	—	no	—	0.926
34	$20\bar{2},16$	—	no	—	0.921
35	$10\bar{1},22$	115.02	w	0.914	0.914
36	$21\bar{3}7$	—	no	—	0.910
37	$21\bar{3}8$	—	no	—	0.899
38	$20\bar{2},17$	—	no	—	0.895
39	$10\bar{1},23$	122.56	w	0.879	0.879
40	$21\bar{3},10$	—	no	—	0.872
41	$21\bar{3},11$	—	no	—	0.857
42	$20\bar{2},19$	—	no	—	0.844
43	$30\bar{3}0$	$132.97\alpha_1$	w	0.840	0.840
		$133.62\alpha_2$	vw	0.840	
44	$20\bar{2},20$	$140.52\alpha_1$	w	0.818	0.819
45	$10\bar{1},25$	$141.45\alpha_1$	w	0.816	0.817
46	$21\bar{3},14$	$143.96\alpha_1$	w	0.810	0.811
47	000,27	$148.45\alpha_1$	ms	0.799	0.799
		$149.67\alpha_2$	w	0.799	
48	$30\bar{3}9$	$152.54\alpha_1$	ms	0.793	0.793
		$153.42\alpha_2$	w		
49	$10\bar{1},26$	—	no	—	0.788
50	$21\bar{3},16$	—	no	—	0.778
51	$20\bar{2},22$	—	no	—	0.774

*vs: very strong; ms: medium strong; w: weak; vw: very weak; vvw: very very weak; no: not observed.

is strong support for the implicit premise that no compositional changes occurred in the various quenching operations.

The formation of the different metastable phases is undoubtedly related to the differing cooling-rates. In general, the fcc phase appears to form at the fastest cooling-rate, then the hcp phase and finally the Sm-phase at the slowest

TABLE VI Metastable phases produced on quenching from the liquid state the $Au_{77.5}Cd_{17.5}In_{5.0}$ alloy (lattice constants of the equilibrium dhcp alloy: $a_0 = 2.909$ Å; $c_0 = 9.557_5$ Å; $V_0 = 17.51_1$ Å^3)

No.	Mode of quenching	Structure	a_{cubic} (Å)	Hexagonal a and c (Å)	$\Delta a/a_0$	$\Delta c^*/c_0$	100 $\Delta V/V_0$
1	Splatted onto a copper substrate	fcc	4.122_1	2.914_8 7.139_7	+0.0020	−0.0040	0
2	Filamentary casting (thin end)	hcp		2.911_8 4.805_8	+0.0010	+0.0056	+0.26
3	Filamentary casting (thick end)	Sm-type		2.911_4 21.582_5	+0.0008	+0.0036	0.53

*Δc represents change in interlayer spacing along the c-axis.

cooling-rates used in the present experiments. It is interesting to point out that at cooling-rates in between those at which the above homogeneous phases were formed, mixtures of the relevant phases were observed. As an illustration, Table III shows that splatting directly into water, with a cooling-rate conceivably between splat-quenching onto a copper substrate and filamentary casting, resulted in a mixture of fcc and hcp phases. Similarly, the regions of the filamentary casting in between the ends resulted in a mixture of hcp and Sm-phases. These observations have relevance to the cooling-rate versus composition diagrams innovated by Anantharaman *et al* [14] to represent the influence of cooling-rate on the constitution of alloys. The diagrams constructed so far do not show the existence of more than one crystalline phase at any point along the cooling-rate axis at a fixed composition, whereas the present results indicate this state of affairs as a distinct possibility. Such a possibility needs to be explored in all investigations directed towards the establishment of cooling-rate versus composition diagrams.

While it is difficult to pinpoint the mechanism by which the different close-packed phases have been obtained, it is likely that the low stacking-fault energy (SFE) is an important factor. The equilibrium dhcp alloy, even on mild cold work, develops a high fault-density [7] (the intrinsic-ch fault probability was found to be 0.045 in mechanically-ground samples) and filings of the alloy, the conventional form of samples used in such X-ray studies, produced diffractograms with so much broadening of the X-ray reflections with $h - k \neq 3N$ (where N is zero or an integer) that no meaningful analysis could be carried out. This is evidence for a low SFE of the alloy. It is also relevant to add that splat-cooling is known to cause formation of stacking faults, as observed in the work on silver-germanium alloys [15, 16].

The fractional changes in the a and c lattice parameters (or lattice vectors equivalent to these) as well as the atomic volume (V) of the metastable phases in relation to the equilibrium dhcp phase are also recorded in Table VI. The order of magnitude of these quantities is comparable to a recent calculation of similar quantities made by Kayser [17] for cases involving fcc $\rightleftharpoons$ dhcp and hcp $\rightleftharpoons$ dhcp transformations.

4. Conclusions

The present work has shown that quenching from the liquid the $Au_{77.5}\,Cd_{17.5}\,In_{5.0}$ alloy at differing cooling-rates results in the formation of different polytypic structures. This constitutes a new feature in the interesting array of results obtained in liquid quenched alloys. This result is also analogous to polytypism observed in transformations induced by high pressure [11], silicon carbide [18], and in certain martensites [19].

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