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A metastable phase Al_3Cu_2

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A new metastable intermediate phase having a trigonal unit cell belonging to the space group $P\bar{3}ml$ has been detected in a rapidly solidified aluminium-45 at. % copper alloy. The unit cell dimensions are a = 4.106 and c = 5.094 Å. With five atoms per unit cell, the observed structure can be regarded as an isotype of Al_3Ni_2.

1. Introduction

In spite of copper being the most important constituent of many of the aluminium alloys in use for a long time, the aluminium-copper phase diagram is still a subject of investigation. Even though the terminal regions of the binary diagram are fairly well established, there is still uncertainty regarding the structure and constitution of alloys with near equiatomic compositions. The structure of the high temperature modification of Cu_3Al_{2+} and CuAl(r) were determined only recently by El-Boragy *et al* [1]. Cu_3Al_{2+}(h) was found to have a crystal structure of the partially filled NiAs-type while CuAl(r) has a monoclinic structure which is best described as a vacancy variant of the CsCl structure. Takahashi and Mihama [2], on the other hand, reported that a metastable CsCl type phase forms in vapour-deposited equiatomic alloys.

The present investigation deals with the influence of rapid solidification by the "gun" technique of splat-quenching on the structure of near equiatomic alumium-copper alloys. The large number of recorded investigations [3] to date on the rapid solidification of aluminium-copper alloys were primarily aimed at determining the limit of solid solubility of copper in aluminium or at relating the microstructural features, such as Al-$CuAl_2$ eutectic spacing and morphology, to the cooling rate. It is now established that the metastable solid solubility limit can be extended up to the eutectic composition by quenching the liquid alloys on to a diamond substrate at liquid nitrogen temperature [4]. The possibility of forming an amorphous phase has also been reported [5]. As a result of the pioneering investigation of Burden and Jones [6], the use of aluminium-copper eutectic alloys for evaluating the cooling rate in liquid quenching experiments is gaining popularity. However, no new metastable crystalline phases have so far been obtained as a result of splat-quenching aluminium-copper alloys. The present investigation is an extension of an earlier study [4] of the structure and constitution of splat-cooled aluminium-copper alloys and reports the formation of a new metastable intermediate phase in this system.

2. Experimental

Two alloys of aluminium containing 45 and 50 at. % copper were studied. The quenching technique and the procedure adopted in preparation of alloys have been described earlier [4]. Copper at room temperature served as the substrate. The product of the experiments was an agglomerate of thin flakes that were approximately circular ($\sim$ 1 to 3 mm diameter). The thickness of the flakes was found to vary considerably (up to a maximum of 50 μm) and in many areas there was superimposition of the flakes over one another. From the bulk of the splat, the thinnest flakes were isolated by visual inspection and were examined in a Siemens 114.6 mm diameter Debye-Scherrer camera with filtered Co$K\alpha$ radiation. For this purpose *single flakes* were utilized and these were carefully mounted on thin glass fibres with an appropriate adhesive. Typical exposures lasted 24 h. The bulk splats were used to obtain Guinier patterns using Cu$K\alpha$ radiation.

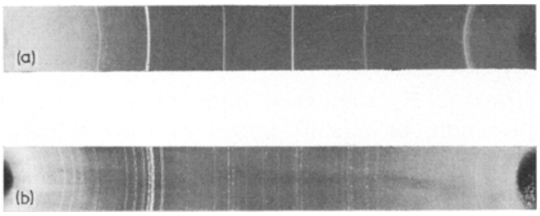

Figure 1 CoKα Debye-Scherrer patterns of an aluminium-45 at.% copper alloy: (a) immediately after splat quenching, (b) after slowly heating to 550° C and holding for 15 min.

3. Results and discussion

Under equilibrium conditions, the two alloys studied are composed of the tetragonal phase $CuAl_2$ (a = 6.066, c = 4.874 Å) and the low-temperature modification of the η phase, CuAl [7]. The Guinier patterns obtained by utilizing a fair amount of each splat had a large number of diffraction lines. An analysis of the patterns revealed the presence of reflections which could not be interpreted in terms of the equilibrium phases. On the other hand, the Debye-Scherrer photographs recorded from thin single flakes (Fig. 1a) contained only those diffraction lines which cannot be accounted for in terms of the equilibrium phases. In these patterns reflections from the equilibrium phase were rare and very faint, if present. The differences noticed between the Guinier patterns and the Debye-Scherrer patterns can be understood in terms of the variations in cooling rate arising as a result of changes in the thickness of the splat. Regions solidifying at slow cooling rates result in equilibrium phases, while those solidifying at a rapid rate lead to the formation of the metastable phase. These differences also highlight the importance of careful selection of splat foils for

TABLE I Observed and calculated $\sin^2\theta$ values and intensities of the reflections from the metastable phase Al_3Cu_2

S. No.	$hkil$	$\sin^2\theta_{calc}$	$\sin^2\theta_{obs}$	$I_{calc} \times 10^{-2}$	I_{obs}*
1	$10\bar{1}0$	0.0634	0.0637	1056	m
2	$10\bar{1}1$	0.0950	0.0947	869	m
3	$10\bar{1}2$	0.1898	0.1903	5286	vs
4	$11\bar{2}0$	0.1902		2173	
5	$11\bar{2}1$	0.2218	0.2224	420	mw
6	$20\bar{2}0$	0.2536	0.2572	130	w
7	0003	0.2845	0.2845	17	vw
8	$20\bar{2}1$	0.2852		118	
9	$10\bar{1}3$	0.3479	—	252	n.o
10	$20\bar{2}2$	0.3800	0.3797	295	mw
11	$21\bar{3}0$	0.4438	—	102	n.o
12	$11\bar{2}3$	0.4747	0.4748	80	w
13	$21\bar{3}1$	0.4754		71	
14	0004	0.5056	—	53	n.o
15	$20\bar{2}3$	0.5381	—	35	n.o
16	$10\bar{1}4$	0.5690	—	3	n.o
17	$21\bar{3}2$	0.5702	0.5704	1583	ms
18	$30\bar{3}0$	0.5706		414	
19	$30\bar{3}1$	0.6022	—	100	n.o
20	$11\bar{2}4$	0.6958	0.6977	278	mw
21	$30\bar{3}2$	0.6970		6.8	
22	$21\bar{3}3$	0.7283	—	256	n.o
23	$20\bar{2}4$	0.7592	0.7590	698	m
24	$22\bar{4}0$	0.7608		419	
25	0005	0.7901	—	2	n.o
26	$22\bar{4}1$	0.7924	—	80	n.o
27	$31\bar{4}0$	0.8242	—	52	n.o
28	$10\bar{1}5$	0.8535	0.8527	20	vw
29	$30\bar{3}3$	0.8551	—	61	n.o
30	$31\bar{4}1$	0.8558	—	153	n.o
31	$21\bar{3}4$	0.9494	0.9486	126	m

*vs, very strong; ms, medium strong; m, medium; mw, medium to weak; w, weak; vw, very weak; n.o, not observed.

X-ray diffraction studies aimed at isolating metastable phases. The observed reflections from the metastable phase could be successfully interpreted in terms of a trigonal cell with $a = 4.106$ Å and $c = 5.094$ Å (Table I). There is a striking resemblance of the pattern obtained from the metastable phase to the pattern of Al_3Ni_2 which has a trigonal unit cell of comparable parameters belonging to the space group $P\bar{3}m1$ [8].

The calculated intensities recorded in Table I were arrived at by replacing nickel atoms in the unit cell of Al_3Ni_2 with copper atoms. Thus the assumed atomic positions are:

Al (1) 000
Al (2) $\frac{1}{3}\,\frac{2}{3}\,z;\ \frac{2}{3}\,\frac{1}{3}\,z$, with $z = 0.352$
Cu $\frac{1}{3}\,\frac{2}{3}\,z;\ \frac{2}{3}\,\frac{1}{3}\,z$, with $z = -0.149$.

The agreement between observed and calculated intensities appears to support the assumption regarding the atomic positions. On the basis of this arrangement, Al(1) has as neighbours 6Al(2) at 2.973 Å and 6Cu at 2.490 Å. Al(2) has as neighbours 6Al at 2.973 and 2.815 Å. It also has 5Cu at 2.547 and 2.586 Å. Copper has (3 + 2) almost equidistant neighbours at 2.490 Å and three more at a somewhat larger distance of 2.586 Å. These interatomic distances are marginally larger than the corresponding values for Al_3Ni_2. Such an increase is to be anticipated owing to the relatively larger size of copper atoms compared to nickel atoms.

The observed metastable phase was found to occur in both 45 and 50 at. % copper alloys. It is, however, predominant at lower concentrations as shown by the comparative intensities of equilibrium and metastable phase lines in the Guinier patterns. It is interesting to note that Al_3Ni_2 also occurs over a relatively wide range of compositions [7]. On the basis of these observations, the formula Al_3Cu_2 appears to be appropriate to this phase.

The volume of the proposed unit cell is 74.35 Å^3. With five atoms per unit cell the atomic volume works out to be 14.87 Å^3 and is in fair agreement with a value of 13.96 Å^3 calculated for a 45 at.% copper alloy by assuming linear variation of atomic volume as a function of composition.

The metastability of the phase was established by annealing the flakes at high temperatures. For example, it was observed that slowly heating the same flake which gave rise to the pattern shown in Fig. 1a to 550° C and holding it at that temperature for 15 min was sufficient to completely decompose it to equilibrium phases (Fig. 1b).

It is likely that even more drastic rates of quenching or a shift in composition towards higher copper concentrations will result in a CsCl-type phase as detected by Takahashi and Mihama [2] in vapour-deposited films of CuAl stoichiometry. On the other hand, it is important to note that Takahashi and Mihama have used electron diffraction patterns obtained from extremely fine crystallites (ring patterns) to arrive at the CsCl-type structure for CuAl films. If only the alternate intense and weak reflections were taken into account (namely, reflections 2, 3, 7, 10, 17 and 23 of Table I) the pattern obtained in present study could also be indexed on the basis of a CsCl-type structure. Careful examination of more closely spaced alloy compositions by X-ray as well as electron diffraction techniques will help to confirm the identity of structures in this composition range. It will also be useful if the atomic movements necessary for transforming the metastable phase to equilibrium phase can be worked out from crystallographic considerations.

4. Conclusions

The present work has shown that splat-quenching aluminium alloys containing 45 and 50 at. % copper results in the formation of a metastable intermediate phase. The phase is found to be isotypic with Al_3Ni_2. The observed intensities of X-ray reflections could be satisfactorily explained on the assumption that copper atoms take up the positions occupied by nickel in a unit cell of Al_3Ni_2 type.

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References

1. M. EL-BORAGY, R. SZEPAN and K. SCHUBERT, *J. Less Common Metals* 29 (1972) 133.

2. N. TAKAHASHI and K. MIHAMA, *Acta Metallurgica* **5** (1957) 159.
3. H. JONES and C. SURYANARAYANA, *J. Mater. Sci.* **8** (1973) 705.
4. P. RAMACHANDRARAO, M. LARIDJANI and R. W. CAHN, *Z. Metallk.* **63** (1972) 43.
5. H. A. DAVIES and J. B. HULL, *Scripta Met.* **6** (1972) 241.
6. M. H. BURDEN and H. JONES, *J. Inst. Metals* **98** (1970) 249.
7. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958).
8. A. J. BRADLEY and A. TAYLOR, *Phil. Mag.* **23** (1937) 1049.

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