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The Structure of Co_4Al_{13}

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The structure of the intermetallic compound Co_4Al_{13} is similar to that of '$FeAl_3$' with which it forms a complete series of solid solutions. Refinement of the structure reveals certain differences in detail.

1. Introduction

As a contribution to the general study of aluminium-rich transition-metal alloys in progress in this Laboratory a part of the Al–Co system has been re-examined by metallographic and X-ray methods and its relationship with the Al–Fe system has been clarified (Hudd, 1959). In the Al–Co system the existence of the phases $\eta(Co_4Al_{13})$ and $\varepsilon(CoAl_3)$ has been established, and the η phase has been shown to form a complete series of solid solutions with the phase '$FeAl_3$'. These studies are described in detail elsewhere (Hudd, 1961). The present paper reports the structure-analysis of the phase Co_4Al_{13}, which is very similar to, but not identical with, $FeAl_3$ (Black, 1955*a*, *b*).

2. Experimental

Alloys were prepared by melting together super-pure Al (supplied by the Northern Aluminium Co. Ltd.) and a Co–Al master alloy (kindly presented by British Aluminium Laboratories Ltd.) under analar sodium chloride as flux; the melt was cooled to 900 °C., held at this temperature overnight, then quenched; the alloy was then annealed at 600 °C. for two weeks. The single-phase ingot from which crystal fragments were obtained for X-ray measurements contained 43·85 wt.% Co (chemical analysis by Messrs. Johnson, Matthey & Co. Ltd.); the density of the crystals, determined by displacement in bromoform, was $3{\cdot}81 \pm 0{\cdot}05$ g.cm.$^{-3}$.

The base-centred monoclinic unit cell

$$a = 15{\cdot}183 \pm 0{\cdot}002,\ b = 8{\cdot}122 \pm 0{\cdot}001,$$
$$c = 12{\cdot}340 \pm 0{\cdot}002\ \text{Å};\ \beta = 107^\circ\ 54' \pm 0{\cdot}5'$$

is very similar to that of $FeAl_3$ (Black, 1955*a*) and contains 24·4 Co and 68·3 Al atoms. As with $FeAl_3$, the pseudo-orthorhombic symmetry is accentuated by twinning. The diffraction patterns of the two alloys are very similar though not identical. The possible space groups are $C2$, Cm, $C2/m$.

Intensities of reflexions up to $\sin \theta/\lambda \sim 0{\cdot}8$ were estimated visually on Weissenberg photographs, obtained with Mo $K\alpha$ radiation using the multiple-film technique. The crystal fragments used were approximately cubic in form, with edge 0·15 mm., and no correction for absorption was applied to individual reflexions. No truly single crystal was found; difficulties due to overlapping of reflexions were overcome by measuring the twin ratio for one of the crystals used; a set of intensity measurements obtained from another crystal with one twin-component very small was used in the final stages of refinement. In the course of the structure analysis the effects of extinction became obvious, and an empirical correction was applied. Details of the experimental procedures are available elsewhere (Hudd, 1959).

3. Analysis and refinement of the structure

The '$FeAl_3$' structure, as described by Black (1955*a*), is based on $C2/m$ with 24 Fe sites and 78 Al sites (one set of 4 sites, numbered Al 7, only 70% occupied); the unit-cell content, directly determined, was 23·4 Fe and 76·6 Al—in close agreement. The ideal structural composition of the phase was therefore taken as Fe_4Al_{13}.

The similarity between the Co–Al phase and '$FeAl_3$' suggested as a trial structure 24 Co and 78 Al atoms placed in the Fe and Al sites in the space group $C2/m$, but since the cell actually contains only about 68 Al, either vacant or partially-occupied Al sites were thought probable. The [110] projection was used to refine the structure by means of difference syntheses (cf. Black, 1955*a*); at the end of this process the R-factor was 15% for all reflexions in the zone. Partial occupation of three sets of sites was strongly indicated —Al 9, 30%; Al 10 and Al 14, 70%; the corresponding Al-content of the unit cell, 72·8 atoms, is more nearly in accordance with the chemical composition 24·4 Co and 68·3 Al.

At this stage the [110] difference synthesis showed typical 'split-atom' effects near both positions of Co 5 and—less well-defined—near Al 16. Since the effects appear only near these atoms, it was thought unlikely that they arose as a consequence of inadequate correction for absorption. An explanation in terms of marked anisotropy of thermal vibration was also rejected as improbable; the large vibration amplitude of Co 5

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Table 1. *Atomic parameters in* Co_4Al_{13}

Atom	No. in cell	*x*	*y*	*z*
Co 1	2	0·086$_3$	0	0·382$_7$
Co 2	2	0·604$_5$	0	0·373$_2$
Co 3	2	0·909$_4$	0	0·012$_9$
Co 4	2	0·597$_8$	0	0·018$_0$
Co 5	4	0·318$_5$	0·292$_5$	0·277$_4$
Al 6	2	0·055$_0$	0	0·174$_5$
Al 7	2	0·329$_6$	0	0·280$_3$
Al 8	2	0·767$_5$	0	0·469$_0$
Al 9	2 × 0·3	0·923$_0$	0	0·424$_0$
Al 10	2 × 0·7	0·754$_8$	0	0·031$_0$
Al 11	2	0·522$_4$	0	0·169$_0$
Al 12	2	0·502$_0$	0	0·499$_6$
Al 13	2	0·702$_0$	0	0·230$_7$
Al 14	2 × 0·7	0·905$_2$	0	0·212$_0$
Al 15	4	0·185$_4$	0·217$_6$	0·111$_9$
Al 16	4	0·364$_1$	0·210$_7$	0·111$_6$
Al 17	4	0·176$_9$	0·219$_2$	0·334$_0$
Al 18	4	0·491$_9$	0·224$_7$	0·331$_0$
Al 19	4	0·367$_8$	0·210$_3$	0·477$_0$
Al 20	2	0·498$_5$	0·248$_5$	0
Co 21	2	0·913$_7$	0	0·617$_1$
Co 22	2	0·395$_4$	0	0·626$_9$
Co 23	2	0·090$_3$	0	0·987$_0$
Co 24	2	0·402$_0$	0	0·982$_0$
Co 25	4	0·182$_7$	0·229$_7$	0·722$_6$
Al 26	2	0·945$_5$	0	0·825$_0$
Al 27	2	0·670$_2$	0	0·720$_0$
Al 28	2	0·232$_9$	0	0·532$_0$
Al 29	2 × 0·3	0·077$_0$	0	0·576$_0$
Al 30	2 × 0·7	0·245$_2$	0	0·966$_0$
Al 31	2	0·477$_0$	0	0·831$_3$
Al 33	2	0·297$_5$	0	0·769$_3$
Al 34	2 × 0·7	0·095$_0$	0	0·788$_0$
Al 35	4	0·314$_3$	0·282$_6$	0·888$_0$
Al 36	4	0·124$_1$	0·271$_7$	0·888$_4$
Al 37	4	0·322$_6$	0·280$_6$	0·666$_0$
Al 38	4	0·008$_7$	0·279$_3$	0·669$_0$
Al 39	4	0·131$_9$	0·289$_8$	0·523$_0$

Sites Al 9, Al 10, Al 14, Al 29, Al 30, Al 34 are partially occupied to the extents shown.

would be along the shortest bond in the structure, there is no corresponding effect in adjacent atoms, and moreover no such effect was observed with atom Fe 5 in $FeAl_3$. (No low-temperature measurements were available to check this conclusion.) It was therefore decided that the true space group must be *Cm*, instead of *C*2/*m*, the relaxation in symmetry-requirements permitting the separation of the set of 8 atoms Co 5 into two sets of 4 each, now numbered Co 5 and Co 25 (Table 1) and no longer exactly superposed as they must be in the centrosymmetrical space group *C*2/*m*. (Similarly for 8 Al 16 now split into 4 Al 16 and 4 Al 36.) Ambiguities in selecting the correct directions of displacement in these splittings were resolved by comparing [110] and [010] projections.

Further cycles of refinement, based on space group *Cm*, led to final *R*-factors 12·2% for [110] and 14·2% for [010] projections. The atomic parameters are listed in Table 1. Values of F_o and F_c are available elsewhere (Hudd, 1959). Standard deviations in atomic positions, $\sigma(x)$, computed from Cochran's relation (Lipson & Cochran, 1953, p. 308) and the final F_o and F_o-F_c syntheses are 0·008 Å for Co and 0·018 Å for Al.

4. Discussion

Comparison of the atomic parameters in Table 1 with those for '$FeAl_3$' (Black, 1955*a*, Table 2), confirms the close similarity of the two structures. For a general account of the important features of the structure, reference may be made to Black (1955*b*); complete tabulations of interatomic distances in Co_4Al_{13} are available (Hudd, 1959), as are detailed discussions of the differences which distinguish one structure from the other.

In considering the significance to be attached to structural detail, it is essential to bear in mind the extreme complexity of the problem of analysis of a structure such as $FeAl_3$—with 43 atomic parameters, and one set of sites partially occupied; even more is caution necessary in the case of Co_4Al_{13}–with 88 parameters, three sets of sites partially occupied, and a non-centrosymmetrical space group. We do not think it justifiable, in the circumstances, to devote the large amount of space which would be essential for clarity to an exposition of features of this structure in isolation. Instead, this structure will be included in a more general treatment of the characteristics of phase structures of this type which are gradually emerging as more structures are analysed.

5. Conclusion

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