Constitutional Defect Structure of CuAl₂

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Abstract

The equilibrium phase CuAl₂ contains a small excess of Al atoms at all temperatures. From accurate X-ray and density measurements, it was found that the simplest defect structure model consistent with the experimental results is substitutional, Cu₁-xAl₂+x (x = 0.005 - 0.022 at room temperature). Such a defect type appears to be very unfavourable energetically because of the short Cu-Cu-site bond length of CuAl₂ compared to other C16 compounds, and would be in contrast to that of the other known C16 compounds.

Introduction

The b.c. tetragonal C16 (AB₂-type) structure may be described as two interpenetrating orthogonal honeycomb nets of B atoms parallel to (110) and (110), with the remaining channels parallel to the c axis filled by chains of A atoms. The prototype phase of this structure, θ-CuAl₂, crystallizes directly from the melt [some authors claim that it forms peritectically (Schürmann & Löblisch, 1977; Eshelman, 1975)] and its ‘stability index’, i.e. the melting point compared to the melting points of the components, lies in the midrange of other C16-type compounds (Raynor, 1974).

However, CuAl₂ has unique structural properties which have not been found in other C16 compounds. The stability range of CuAl₂ lies outside the exact stoichiometric composition: ‘CuAl₂’ is slightly deficient in Cu at all temperatures. An exact determination of the homogeneity range was made by Stockdale (1933); it extends from 67.07 to 68.09 at.% Al at 548 °C, and from 66.83 to 67.40 at.% Al at 400 °C.

In an extensive work, Havinga, Damsma & Hokkeling (1972) prepared all known (~50) and some new binary and pseudo-binary C16-type compounds and determined their crystallographic parameters. CuAl₂ was found to lie at the limit of stability plots which are based on the distance between nearest neighbours (Havinga & Damsma, 1972). For CuAl₂, the c/a ratio is so small (0.8036) that the Cu–Cu distances overlap and Havinga’s reduced stress parameter

\[ y = \frac{(d_A - c/2 - r_A)}{r_B} \]

\( d_A - c/2; r_A, r_B = \text{atomic radii of A and B atoms}, \)

which determines the relative separation between A atoms, becomes negative, \( y = -0.022 \), for the composition CuAl₂₀.₆ used by these authors. The other bonds, A–B and B–B, have normal lengths. According to Havinga et al. only three other C16 compounds, SiTa₂, GaHf₂ and GeHf₂, also having negative \( y \) values, lie in the same corner of these stability plots. SiTa₂ is not stable — the composition found for the stable compound was SiTa₁.₈₆ — whilst GaHf₂ and GeHf₂ could not be prepared as single phases and are probably also deficient in B. However, ‘CuAl₂’ is the opposite in that there are excess B atoms. Originally, it was suggested that some of the Cu sites were occupied by Al (Stockdale, 1933), but this defect structure should be unstable in the light of Havinga’s work because the larger Al atoms would then be located in the unfavourable small space around Cu sites. Thus, it would be more realistic if vacancies on the Cu sublattice balanced the excess Al atoms.

Experimental

Several single crystals were grown by a modified Bridgman technique. Polycrystalline rods, prepared from 99-99% Al and electrolytic Cu, were remelted in vacuo in high-purity graphite crucibles and pulled through a temperature gradient at a rate of 3 mm h⁻¹. The samples were then annealed in vacuo for 12 d at 530 °C and slowly cooled (~4 d) to room temperature. Spectroscopically determined impurity contents of these samples yielded:

Fe<0.003, Si<0.003, Mg<0.003, Ca<0.01 (wt.%).

Some of the as-grown crystals contained a few η-AlCu precipitates at the bottom and some α(Al)/θ(CuAl₂) eutectic at the top due to segregation.

Metallographic examination showed no microcracks. A few inclusions other than α or η were also found, but were not identified because their volume fraction was very small (<0.3%).

From two of these crystals, thin slices were cut from different sections in such a manner that samples of approximately constant composition, but covering the whole homogeneity range of θ-CuAl₂, were obtained.

Powdered samples were examined by X-ray analysis using monochromatized Co Kα and Cu Kα radiation. A least-squares fit program was used to calculate the lattice parameter \( a \), the c/a ratio and to take account of a systematic error proportional to \( \cos^2 \theta \).

As the composition of the compound deviates from
exact stoichiometry, we tried to detect forbidden lines, \( h+k+l \) odd or \( h\ell l \) with \( l \) odd, due to altered occupancies of the corresponding planes, but no such lines were observed in the entire range of measurement \((15^\circ \leq \theta \leq 164^\circ)\). Therefore, if they exist, their intensity must lie below our detection limit.

Densities were measured by weighing polished pieces in air, water and dibromethane. The density of the dibromethane used was accurately determined \((\rho_{22^\circ C} = 2.169 \text{ g cm}^{-3})\). It was carefully checked that no systematic errors due to incomplete wetting occurred. With different pieces of the same composition but of unlike mass \((\sim 0.5-8 \text{ g})\) and correspondingly different surface/volume ratios, the reproducibility was found to be better than 0.02%.

The exact chemical compositions were determined by electrolytic separation of Cu from at least three different pieces with an accuracy of better than 0.2 at.% Cu.

**Results**

In all cases, it was found that the Cu content decreased, the lattice parameter \( a \) increased, and the density decreased monotonically when successive samples were analyzed, taken from the bottom to the top of the ingots.

Fig. 1(a) shows measured lattice parameter \( a \) and the \( c/a \) ratio at room temperature (22°C) as a function of the Al content, \( c_{Al} \). The error bars of \( a \) and \( c/a \) are given according to the least-squares fit program. The values obtained from samples containing \( \alpha \) or \( \eta \) inclusions are placed on the \( \alpha-\theta \) or \( \theta-\eta \) phase boundaries, respectively. The compositions of these boundaries were taken from Stockdale (1933) for the lowest temperature (400°C) given by him. The results of Havinga et al. (1972) and Bradley & Jones (1933) are also included in the figure.*

If we assume that Stockdale’s values for the phase boundaries are also applicable at room temperature, the compositional change of the lattice parameter \( a \) may be expressed by linear interpolation as

\[
a = (6.0591 \pm 0.0008) + (0.36 \pm 0.04)x \text{ Å}
\]

\([x = 3(c_{Al}/100 - \frac{1}{3})]\) whereas \( c/a \) remains approximately constant:

\[
c/a = (0.80372 \pm 0.00006) - (0.005 \pm 0.003)x.
\]

Fig. 1(b) shows the measured densities of the single-phase samples. The error bars include both the experimental scatter using different samples with the same composition and an upper limit for the systematic error caused by the inclusions already mentioned. Also included are linear interpolations of calculated densities from the experimental X-ray data and from three different defect-type models: (i) A pure vacancy model, \( \text{Cu}_{1-x}\text{Al}_2 \), where all excess Al is compensated by vacancies on the Cu sublattice, (ii) a pure substitution model, \( \text{Cu}_{1-x}\text{Al}_{2+x} \), with the excess Al atoms on Cu sites and (iii) a model in which the excess Al atoms form interstitials, \( \text{CuAl}_2 + \text{Al}^+. \)

Some high-temperature X-ray work was performed at \( T=555^\circ C \), but owing to the limited resolution of the high-temperature goniometer used, it was not possible to resolve a change in \( a \) or \( c/a \) as a function of composition. For this temperature, we found: \( a = 6.118 \pm 0.003 \text{ Å}, c/a = 0.8070 \pm 0.0006 \). When this \( c/a \) value is compared with the room-temperature values, it follows that the lattice expands \( \sim 50\% \) more strongly in the \( c \) than in the \( a \) direction. Calculation of average thermal expansion coefficients \((22-555^\circ C)\) yields \( \tilde{\alpha}_a = (16 \pm 1) \times 10^{-6} \text{ deg}^{-1} \) and \( \tilde{\alpha}_c = (24 \pm 4) \times 10^{-6} \text{ deg}^{-1} \) in the \( a \) and \( c \) directions respectively.† The weighted mean of these values, \( \tilde{\alpha} = \frac{1}{2}(2\tilde{\alpha}_a + \tilde{\alpha}_c) = (18.7 \pm 2) \times 10^{-6} \)

* Bradley & Jones (1933) described the Cu-rich sample as two-phase, but the sample with 67.6 at.% Al as single-phase.
† For these calculations, the room-temperature values of \( a \) and \( c/a \) were taken at the Al-rich boundary, as the homogeneity range is shifted towards higher Al contents at 555°C.
Cu-rich and the Al-rich phase boundary (as deduced from the slope of the V region at \( n = \frac{3}{2} \)) would be expected, whereas the experimental change is less than \( 1 \times 10^{-4} \).

The structural parameters of CuAl\(_2\) would fit those of the other C16 compounds much better if CuAl\(_2\) were of the vacancy-defect type or if its \( c/a \) ratio were greater by at least 3\%. As a pure vacancy-defect structure does not agree with our experimental results, the actual \( c/a \) ratio of CuAl\(_2\) might, therefore, be explained by very strong directional bonds between (001) Al planes or by a smaller 'atomic size' of Cu in the [001] directions due to other strong directional bonds.

Some evidence for strong directional bonds was found by Knoop hardness measurements on single-crystal faces (Table 1). These observations are consistent with the assumption of stronger directional bonds in [001] directions than in other directions, but, of course, no detailed conclusions can be drawn from these measurements.

<table>
<thead>
<tr>
<th>Face</th>
<th>( H_k ) (100 g load)</th>
<th>Anisotropy on this face when the indenter is turned</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>250 ± 10</td>
<td>No anisotropy found, must be less than 4%</td>
</tr>
<tr>
<td>(100)</td>
<td>135 ± 6</td>
<td>No anisotropy found, must be less than 4%</td>
</tr>
<tr>
<td>(110)</td>
<td>127 ± 6</td>
<td>Long diagonal of indenter parallel to [001]</td>
</tr>
<tr>
<td></td>
<td>137 ± 6</td>
<td>Long diagonal of indenter parallel to [112]</td>
</tr>
<tr>
<td></td>
<td>148 ± 6</td>
<td>Long diagonal of indenter parallel to [110]</td>
</tr>
</tbody>
</table>

On the other hand, elastic data of single crystals of CuAl\(_2\) do not indicate a pronounced anisotropy of the single-crystal elastic constants (Eshelman, 1975), hence, it does not seem likely that strong anisotropic directional bonds play an important role.

Thus, structural information and structure chemical arguments do not yield a consistent explanation for the substitutional defect-type model. If this model is not accepted, more complicated models must be considered:

(iii) A mixed substitution–vacancy model, \textit{viz.} \( \text{Cu}_{1-x-y}\text{Al}_{2+y} \) is consistent with the measured densities. To account for the X-ray results, the corresponding unit-cell volume must be estimated. With hard-sphere models,

\[
V = \frac{(2+x)r_{\text{Al}}^3 + (1-x)r_{\text{Cu}}^3 + yr_{\text{vac}}^3}{2r_{\text{Al}}^3 + r_{\text{Cu}}^3},
\]

where \( r_{\text{Al}} \) and \( r_{\text{Cu}} \) are the metallic radii of Al and Cu respectively, \( r_{\text{vac}} \) the radius of a vacancy and \( V_0 \) the unit-cell volume of the (hypothetical) ideal CuAl\(_2\) composition. Only the \textit{width} of the single-phase field is needed, but no absolute chemical compositions, if this equation is used for comparison with the experimental increase between the Cu- and Al-rich phase boundaries, if \( \Delta V/V_{\text{exp}} = 3.0 \pm 0.5 \% \).

For \( y = 0 \), \textit{i.e.} for model (ii), this estimate yields \( \Delta V/V_0 = 2.4 \% \) in good agreement with the experimental value. For \( y = \frac{1}{4}x \) and with
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$r_{\text{vac}}$ set as high as 1.25 Å (=r_{\text{Cu}}), a change $\Delta V/V_0 = 2.0\%$ is obtained. This change is still smaller than the experimental one and would further decrease if more realistic values for $r_{\text{vac}}$ were used. Therefore there are good reasons to assume that the vacancy fraction in such a model would be too low to remove the discrepancies discussed above for the pure interstitial model, even if the width of the homogeneity field of θ-CuAl₂ used is incorrect within rather wide margins.

(v) Of course, the experimental results can be explained with still more complicated defect-structure models. These models would have to involve interstitials, vacancies on the Al sublattice or a density of vacancies at Cu sites which does not depend proportionally on the compositional deviation from stoichiometry.

Conclusions

(1) A dominant vacancy defect type structure, Cu₁₋ₓAl₂ would fit the properties of the other C16 compounds, but does not agree with the experimental results.

(2) A dominant substitutional-defect structure, Cu₁₋ₓAl₂₊ₓ, is consistent with the experimental data, but cannot be understood on the basis of structure chemical or electronic arguments.

(3) If such a substitutional-defect structure is denied, only much more complicated defect-structure models involving interstitials or vacancies with densities which are not proportional to the deviation from the stoichiometric composition would be consistent with the experimental facts, as well as with generally accepted structural arguments.

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References