A15 TYPE STRUCTURE OF CHROMIUM FILMS AND PARTICLES*

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We have observed a metastable structure of chromium, being of the A15 type, both in thin granular films and in fine single crystal particles. The new phase is not superconducting above 0.5 K.

It has been shown by Kimoto and Nishida [1] that if small particles of chromium are produced by evaporation in an argon pressure of a few torr a new crystal structure may be stabilized. Their analysis, employing both electron and X-ray diffraction concluded that the new phase was of the A15 (αW) type. The results were not due to an oxide as proved [1] by a stoichiometric investigation of the oxidation of Cr particles, having the new structure, to Cr₂O₃. This observation is important because Cr₂O₃ with an A15 structure has been reported [2]. Subsequent work has demonstrated that the same structure occurs as a high temperature phase in bulk specimens [4], as well as a growth phase [5,6] when chromium is evaporated onto a substrate under good vacuum conditions; for film thicknesses exceeding a few nanometers only the normal bcc structure was found.

As seen from our measurements, reported in table 1, the thickness range where the A15 structure may be stabilized can be increased appreciably if the films are evaporated in an argon pressure of the order of 10⁻² torr. The films were produced in a diffusion pumped bell jar system that was evacuated to < 10⁻⁶ torr before admitting 99.999% pure Ar. Chromium (99.996% purity) was evaporated with perpendicular incidence onto amorphous carbon substrates located 8 cm from the source (W spiral). The deposited films

Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure [torr]</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>2 x 10⁻⁵</td>
<td>only bcc</td>
</tr>
<tr>
<td>Ar</td>
<td>2 x 10⁻⁴</td>
<td>bcc + trace A15</td>
</tr>
<tr>
<td>Ar</td>
<td>4 x 10⁻²</td>
<td>A15 + trace bcc</td>
</tr>
<tr>
<td>air</td>
<td>4 x 10⁻²</td>
<td>bcc + A15</td>
</tr>
</tbody>
</table>

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† The structure analysis was questioned on the basis of more recent work [3].
Annealing results.

<table>
<thead>
<tr>
<th>Temp. [K]</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>A15 + trace bcc</td>
</tr>
<tr>
<td>400</td>
<td>bcc + trace oxide</td>
</tr>
<tr>
<td>500</td>
<td>oxide + trace bcc</td>
</tr>
<tr>
<td>620</td>
<td>oxide + trace bcc</td>
</tr>
</tbody>
</table>

were studied with an AEI electron microscope. Films produced at the highest background pressures were found to be highly granular, with an average grain size of about 5 nm.

Fig. 1 shows diffraction patterns for films produced at argon pressures of \(4 \times 10^{-2}\) torr and \(2 \times 10^{-5}\) torr. The upper curve agrees in detail with data by Kimoto and Nishida [1], showing that the crystal structure is, indeed, of the A15 type. The cubic lattice parameter is found to be 0.458 nm, in good agreement with previous determinations [1,5] as well as with extrapolation from measurements on Cr-Pt, Cr-Ir and Cr-Si in bulk form [7]. The lower curve in fig. 1 indicates that only the bcc phase is present. A small peak, reminiscent of the (200) reflection in the bcc lattice, can be seen in fig. 1a; this signifies that only about 10% of the volume of the film does not have the A15 structure. In films with thicknesses of about 100 nm or larger X-ray diffractograms showed that only the bcc phase is present.

The A15 structure is metastable and transforms back to bcc below 400°C. The data of table 2 were obtained by keeping a thin film, produced at an Ar pressure of \(4 \times 10^{-2}\) torr, at the reported temperatures for one hour under a vacuum of \(<10^{-5}\) torr. At the higher temperatures diffraction rings, presumably due to an oxide with the approximate composition Cr\(_2\)O\(_3\), became increasingly dominant.

It is well known [8] that the A15 structure is the most favorable one for occurrence of superconductivity. To check whether the new phase of Cr is superconducting the granular films were not considered satisfactory, because fluctuations of the superconducting order parameter as well as other size dependent effects may seriously alter the transition temperature from its bulk value. Therefore we produced fine particles by evaporation in Ar or Xe at pressures of 1.5 to 25 torr and collecting the soot-like deposit on a glass surface partially surrounding the resistive source. The particles were found to be of two types: cubes having a bcc lattice, or complex polyhedra with and A15 structure — this is in agreement with the results of ref. [1]. Thick powder deposits were strongly pyrophoric, and rapid exposure to air of the freshly produced particles resulted in an ignition of the A15 particles, presumably due to the strongly exothermic nature of chemisorption of O\(_2\). However, by making sufficiently thin deposits we were able to produce powder samples with more than 50 vol.% of A15 crystallites with diameters exceeding 100 nm. About 0.2 g of this powder was inserted into the narrow tail section of a sample chamber that was thermally linked to a pumped \(^3\)He refrigerator. Magnetization versus temperature plots were taken with a high resolution superconducting quantum flux detection (SQUID) system.

Measurements on a powder specimen, before and after an annealing to transform all of the sample into the bcc phase, yielded no significant difference of the magnetic susceptibility. Hence the A15 type structure is non-superconducting down to 0.5 K. An extremely small discontinuity in the susceptibility was observed reproducibly at about 1.15 K in powers produced by evaporation in Ar. The effect is not due to contamination with aluminum, as proved by neutron activation studies, but is most likely of the same nature as the superconducting behavior found previously [9] in ion beam sputtered chromium thin films with the bcc structure.

References