Spherical Monocrystals for X-ray Work Obtained by Plasma Remelting of Alloy Powder

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(Received 25 October 1977; accepted 28 November 1977)

Spherical crystals of alloy phases too hard and brittle for grinding can be obtained by partial remelting and solidification of a powder sample. The alloy powder is blown through an argon-plasma jet melting the surface material of individual fragments, which solidify again as nearly perfect spheres. The yield is a mixture of different materials in which it is possible, however, after heat treatment to find good single crystals of the original composition. Spherical single crystals of Cu₉Al₄ have been produced by this method and used for a high-precision X-ray investigation described elsewhere.

Introduction

For several years we have been engaged in a study of the ordering of component atoms and point defects in the class of alloy structures related to γ-brass (Westman, 1972). We have not been able to reach very high levels of precision in these studies, however, and other research groups seem to have met with similar difficulties. The typical R value for a γ-brass structure determination lies around 10% (Arnberg & Westman, 1978).

We therefore decided to try to carry out, with high precision, an X-ray diffraction determination of the Cu₉Al₄ γ-brass structure and to use the determination, among other things, as a test for various possible sources of error and obscurity in previously collected data.

Obvious effects to be compensated for in the computations are X-ray absorption and extinction. The alloy samples have usually been prepared by arc-melting or induction-melting of mixtures of the components, and single crystals have been obtained from the crushed ingots as irregular fragments for which quantitative determination of extinction and absorption factors has been virtually impossible.

A most efficient way to avoid anisotropy and to provide the best geometry for quantitative calculation would be the use of spherical single crystals in the diffraction experiments. Several earlier attempts at grinding spherical crystals of this type of alloy had failed, however; the materials are hard and brittle, and the crystal fragments tended rather to grind up the apparatus. This time we tried instead to partially remelt already formed single crystals and to have them solidify again as spherical droplets. One attempt to accomplish this by induction heating of alloy fragments dispersed in graphite powder was unsuccessful. Eventually, we obtained the desired result by rapidly blowing a powdered alloy sample through a jet of plasma, as described in the following.

Synthesis

A batch of 5 g of Cu₉Al₄ was prepared by induction melting of the components (Al, VAW, 99.999%; and Cu, Kebo elektrolytkoppar pa, 99.95%) at ~1100°C in a graphite crucible under a flux of cryolite. The induction furnace was filled with argon of atmospheric pressure to exclude oxygen and to reduce evaporation losses. Nevertheless, some evaporation did occur: the weight loss upon melting was 0.02 g.

Metallographic examination of the ingot revealed micro-segregation. The alloy sample was crushed to a powder in a steel mortar, so that the diameters of most fragments would lie in the interval 0.01–0.1 mm, i.e. suitable for single-crystal X-ray work. A Guinier photograph taken at this stage was rather diffuse, also proving that the alloy was poorly equilibrated.

The sample was therefore heated in vacuo at 750°C for 3 weeks and subsequently quenched in water. After this treatment a Guinier photograph of the powder showed exclusively sharp lines of the Cu₉Al₄ phase.

Fig. 1. Photomicrograph of a section of a partially oxidized sphere showing two metallic phases (light) and an oxide phase (dark).
A plasma furnace was then used to partially remelt the individual crystal fragments. The powder was injected downward into a vertical stream of argon gas, ionized by electromagnetic induction. The plasma jet had a length of 5 cm and a diameter of 3 cm. Most of the alloy fragments remained unaffected; several became oxidized, but some melted and solidified again to form metallic spheres with diameters between 0.02 and 0.1 mm.

From metallographic examination and from the appearance of oscillation and rotation photographs we concluded that these particles were not good single crystals. Renewed heating in vacuo, for 3 months at 750°C, of some 20 of them collected under the microscope did eventually yield the desired product: a few spheres which were, as far as could be ascertained, true monocrystals of the Cu₉Al₄ phase.

Characterization of the material

Even though Al has the higher vapour pressure, this Cu-rich preparation seems to have lost Cu preferentially during the initial induction melting of the mixed components. The composition aimed at was exactly Cu₉Al₄, with the mole fraction $x_{\text{Al}} = 0.308$ and the unit-cell content Cu₃₅Al₁₆. The Guinier photograph taken of the heat-treated crystal powder yielded $a = 8.7068 \pm 3$ Å, however, which corresponds to $x_{\text{Al}} = 0.320$ and the unit-cell content Cu₃₅.₄Al₁₆.₆ (Westman, 1965). If the weight loss during melting is used for calculating the composition it becomes $x_{\text{Al}} = 0.314$, corresponding to Cu₃₅.₇Al₁₆.₃. The substitution of Al for Cu in the ideal structure, then, is approximately $\frac{1}{8}$ atom per unit cell. The lattice parameter of the spherical monocrystal obtained from the plasma melting and used in the diffractometer experiment was found to have the lattice parameter $a = 8.707 \pm 1$ Å, and thus the same composition as that derived above, within the limits of experimental error. The remelting of the alloy powder in the plasma furnace resulted in a rather heterogeneous mixture of products. As mentioned earlier, most fragments were not affected at all, and of those melted several became oxidized. Fig. 1 is a photomicrograph of a polished section of such a droplet containing two metallic phases and one oxide phase.

The melted crystals that remained metallic showed other defects: polishing and etching [FeCl₃(aq)+ HCl(aq)] of the metallic spheres revealed a micro-segregation pattern (Fig. 2).

After the renewed equilibration at 750°C some of the 20 selected spheres proved to be two-phase aggregates. A photomicrograph of a polished and etched section of one of these is shown in Fig. 3(a). Examination in polarized light revealed (Fig. 3b) that each
phase was polycrystalline. The minor phase had a yellowish colour, indicating a higher Cu content than Cu₉Al₄. This finding indicates preferential evaporation of Al during the plasma heating, which is consistent with the higher vapour pressure of Al, but at variance with the observation that Cu evaporated during the induction melting.

The single-phase spheres were often polycrystalline, however (cf. Fig. 4), and some also contained voids. Oscillation and rotation photographs showed that two out of six examined spheres were good single crystals. The one finally selected for diffractometry had a diameter of 0.05 ± 0.01 mm.

**Single-crystal-data quality**

We collected data from the spherical crystal on a PW 1100 automatic X-ray diffractometer with monochromatized Cu Kα radiation. The 2416 reflections recorded could be averaged to 150 independent \( I_0 \) values which we corrected for absorption assuming the crystal to be an ideal sphere with \( \mu r = 90 \). The absorption factors calculated ranged between 2.8 and 3.6.

After removal of the 36 weakest reflections, which were found not to be determined with the required precision, we could refine a 32-parameter structure model together with a scale factor and an isotropic extinction parameter to reach a value of \( R = 2.44\% \). The extinction factors then lay in the range 1.00–1.40.

In order to test the perfection of the crystal by means of the anomalous dispersion effect we also collected intensity data with monochromatized Mo Kα radiation. We determined the structure amplitudes of ten reflections, \( |F_o(hkl)| \), and of their Friedel pairs, \( |F_o(hkl)| \), selected for the relatively large expected values of the differences \( \Delta_o = |F_o(hkl)| - |F_o(hkl)| \), and compared \( \Delta_o \) with \( \Delta_c = |F_c(hkl)| - |F_c(hkl)| \) calculated for different degrees of coherent twinning. The lowest value of the reliability index \( R_a = \sum |\Delta_o| - |\Delta_o| / \Sigma |\Delta_o| = 22\% \) was obtained for a model without twinning.

The refinement of the structure, the final structure model, including anisotropic thermal parameters, and the tests for various modes of twinning are described in detail in a separate article (Arnberg & Westman, 1978).

**Conclusion**

This investigation has shown that excellent X-ray diffraction data, amenable to accurate absorption and extinction corrections, can be obtained from a spherical alloy crystal. Our experience is that such data collected from irregular crystal fragments generally do not have the quality required, for example, for the refinement even of meaningful isotropic temperature factors, let alone anisotropic thermal parameters. When a high-precision determination of an alloy crystal structure is desired one may therefore have recourse to the method we have described, which produces almost perfectly spherical single crystals of good quality, albeit in very limited quantity. Greater experimental difficulty may be expected with systems of more dissimilar components; we intend, nevertheless, to try producing crystals of a structurally rather complicated Pd–Zn phase (20% Pd) by this method.

This investigation has been carried out within a research program sponsored by the Swedish Natural Science Research Council. Professor Arne Magnéli is most cordially thanked for his encouragement of our research and for critical evaluation of this report.

**References**