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A Contribution to the Analysis of the Effects Observed on Heating Gold in Air. I

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High-resolution electron-diffraction techniques have been used to examine the products resulting from heating in air thin films of gold containing traces of copper in solid solution. It is shown that spines of CuO grow normal to the surface about screw dislocations, the axes of the spines being normal to the [110] axis of the compound.

Some observations on two hexagonal single-crystal patterns are described.

Introduction

The diffraction patterns obtained from thin films of gold of various degrees of purity heated in air and other gases have been studied by a number of workers (for instance, Finch, Quarrell & Wilman, 1935; Trillat & Oketani, 1937*b*). In particular, Trillat and his co-workers have described two types of pattern, the '*O*' and the '*B*', in considerable detail.

The purpose of this communication is to present further information on these and related patterns, the new information being largely obtained by epitaxial setting of the specimens in the electron beam.

The '*O*' pattern

Trillat and his co-workers described the conditions under which this pattern was obtained from gold containing small quantities of copper and silver (Trillat & Oketani, 1937*a*). They at first attributed this pattern to a compound containing gold and oxygen, but later pointed out that the interplanar spacings obtained from their ring patterns were in reasonable agreement with those obtained from the so called CuO′ ring pattern (Trillat, Oketani & Miyake, 1937).

In the present experiments nominally pure gold foil, which, however, on spectroscopic examination was found to contain approximately 3 parts per 1000 of copper, was used. This was thinned by etching and was washed with pure solvents in the usual manner. In all cases the films were examined with a high-resolution diffraction camera designed by Cowley & Rees (1953).

When thinned films supported on either nickel or platinum grids were heated in air at temperatures ranging from 200° C. to 400° C., and for periods of from 1 to 10 hr. the '*O*' pattern was observed both by itself and in conjunction with other patterns. Only ring patterns were observed throughout, despite the fact that observations were made both with the electron beam focused on the plate and on the specimen. Systematic use of these two methods of operation has proved valuable in a number of investigations and has been discussed in some detail by Cowley (1953). It is sufficient to remark here that the former method is favourable for the observation of fine structure, while the latter increases the probability of obtaining single-crystal patterns.

In the present experiments, however, focusing the beam on the plate yielded only traces of shape-function fine structure, while focusing the beam on the specimen produced only spotty rings. The evidence in no case was sufficient to provide any reliable information either on the constitution or the morphology of the specimen.

For reasons given later, films were placed on the {100} faces of freshly cleaved single crystals of sodium chloride and heated in air at temperatures ranging from 200° C. to 600° C., and for periods of from 1 to 50 hr. The films were then floated off the sodium chloride, washed and examined as before.

Under these conditions very different patterns were obtained. The typical pattern with the electron beam focused on the specimen was of the 'quasi-rotation' type (Fig. 1(*a*)). It was found that all such patterns could be completely indexed if interpreted as resulting

Table 1. *Comparison of the interplanar spacings on the zero, first and second layer lines obtained from a pattern of the type shown in Fig.* 1(*a*), *with those to be expected from an oscillation of a* CuO *crystal about the* [110] *axis*

Layer line	*d* (obs.) (Å.)	d_{hkl}(CuO) (Å.)	*hkl*
0	2·746	2·734	$1\bar{1}0$
	1·373	1·367	$2\bar{2}0$
1	2·746	2·734	110
	2·303	2·299, 2·308	200, 111
	1·704	1·695	020
	1·403	1·398	$3\bar{1}0$
	1·100	1·100	$\bar{1}30$
2	1·403	1·398	310
	1·373	1·367	220
	1·155	1·150, 1·154	400, 222
	1·104	1·100	130
	0·852	0·850	040

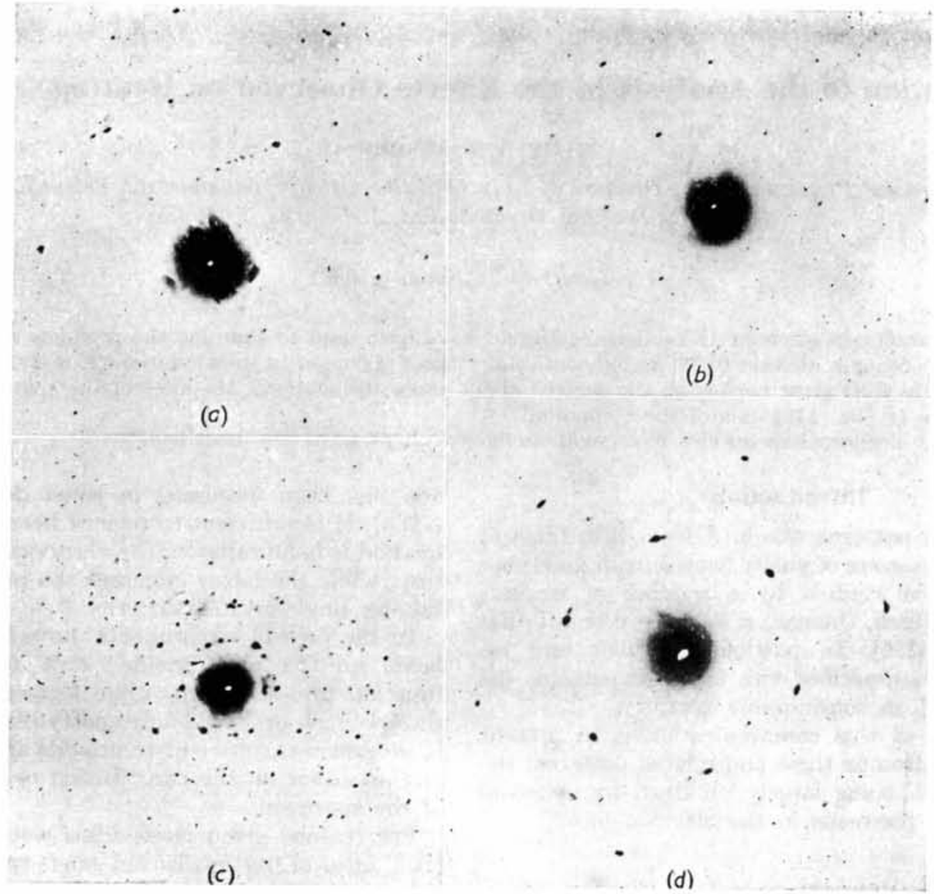

Fig. 1. (*a*) 'Quasi-rotation' pattern obtained from heated gold foil containing a trace of copper. Elongation of the spots along the higher layer lines is clearly evident in the original plate. As reproduced, $\lambda L = 3{\cdot}15$ Å cm.

(*b*) Single-crystal pattern of CuO obtained from heated gold foil containing a trace of copper. The intensities are anomalous and the orientation consistent with acicular growth about the [110] axis. As reproduced, $\lambda L = 3{\cdot}09$ Å cm.

(*c*) Elliptical ring pattern obtained from gold foil heated on rocksalt. As reproduced, $\lambda L = 2{\cdot}96$ Å cm.

(*d*) Hexagonal single-crystal pattern obtained from heated gold foil. As reproduced, $\lambda L = 3{\cdot}96$ Å cm.

from cupric oxide crystals oscillated about the [110] axis. This is in accord with Cowley's detailed analysis of the CuO′ pattern (Cowley, 1954). The observed values of the interplanar spacings on the first few layer lines of one typical pattern are compared in Table 1 with the values to be expected from a CuO crystal oscillated about the (110) axis. Many details of the patterns also agreed with Cowley's observations. Thus, spots were elongated along the layer lines, the effect being least for the zero layer line. This indicates an acicular morphology developed about a screw dislocation (Wilson, 1952).

A feature of these patterns contrasting with Cowley's observations was the accuracy of alignment of the spines, no appreciable arcing being evident in most patterns. Occasionally, however, two 'oscillation' patterns with approximately orthogonal layer lines were observed.

A limited number of single-crystal patterns were also obtained when the beam was focused on the specimen (Fig. 1(*b*)). These could be indexed as arising from cupric oxide crystals with [001] axes tilted at small angles to the electron beam. The diffraction spots were appreciably sharper than those in the rotation patterns.

Although the evidence appeared, at this stage, to offer strong support to the belief that the '*O*' pattern arose from cupric oxide, it was felt for a number of reasons that it did not completely exclude the possibility that the patterns were produced by an isomorphous gold–oxygen system. Thus, even with rotation, single-crystal and powder patterns, determination of the parameters of a monoclinic unit cell with the precision possible in X-ray work poses considerable experimental difficulties in electron diffraction. Further, the morphology which the diffraction patterns reveal is surprising in view of the extreme dilution of the alloy. In fact, previous workers had advanced a tentative explanation based on the hypothesis of a substantially uniform film (Trillat *et al.*, 1937).

The intensities of the spots in the least-tilted single-crystal pattern were therefore estimated approximately and compared with those to be expected on a kinematic basis from cupric oxide and from an isomorphous gold compound. In particular, the intensities of those reflexions to which only oxygen contributed clearly eliminated the latter possibility. However, agreement with the calculated intensities for cupric oxide was very poor. This is scarcely surprising. The morphology is acicular, the diffraction spots on the single-crystal pattern indicate a minimum linear dimension of the order of 1000 Å, and hence the beam must traverse the same order of thickness. Appreciable dynamic effects might therefore be expected. It might be noted that Cowley (1954) also found evidence of dynamic scattering effects in the $(h0l)$ section.

Patterns obtained with the electron beam focused on the plate again differed from those obtained from specimens heated on a grid. In general, ring patterns were observed as before, but in this case shape-function effects were pronounced and clear. Further, the form of the shape functions was consistent with the morphology deduced from the rotation patterns.

It would therefore appear to be definitely established that when gold containing small quantities of copper in solid solution is heated in air at temperatures ranging from 200° C. to 500° C., normal cupric oxide is formed on the surface, that this compound grows in the form of spines about screw dislocations, the axis of the spine being parallel to the [110] axis of the compound, and that the range of spine diameter extends at least from the order of 1000 Å to the order of 100 Å.

The importance of the morphology of the rocksalt surface in the above experiments was pointed out by Dr A. L. G. Rees, and on this basis the following more detailed interpretation of the above results is suggested. A (100) face of sodium chloride exposed by cleavage is known to contain a number of steps of varying height. If a thin film of gold is placed on such a face and the whole is heated the film will follow the details of the surface morphology. If now a small amount of copper is present in the gold in the form of a solid solution it will diffuse preferentially to and in grain boundaries, screw dislocations or other imperfections, since grain-boundary diffusion is known to proceed at a rate differing by several orders from bulk diffusion. Consequently, a high concentration of copper will develop at a limited number of very small areas on the surface. Spines of cupric oxide grow from these areas about screw dislocations.

The film, when floated off the crystal of sodium chloride, will be an accurate replica of the surface, carrying, in turn, on its surface, spines of cupric oxide.

On examining such a film by transmission the electron beam will frequently be parallel to the sides of steps. Providing that the angle is not too small, any preferred orientation between the cupric oxide spine and the plane of the gold film will then be revealed by a sufficiently small exploring electron probe. In fact, the results obtained with the electron beam focused on the specimen indicate that the [110] axes of cupric oxide, and hence the axes of the spines, are aligned within two or three degrees of the normal to the plane of the gold film. Confidence in the above interpretation is increased by the occasional observation of two rotation patterns with layer lines approximately at right angles. This pattern would be produced when the electron beam passes close to the intersection of two steps.

When the electron beam is focused on the plate a considerably greater area of the specimen will be covered and an oriented ring pattern will be observed. Since the axes of the spines will be normal to the beam, a high-resolution instrument will reveal the shape-function effects characteristic of spine-like growth.

In contrast to this, when a film heated on a grid is examined by transmission the greater part of the pattern will be produced by spines oriented approximately parallel to the beam. Thus those patterns which, with least ambiguity, characterize the constitution and morphology of the specimen, will be rarely if ever observed. Further, mere tilting of the specimen is unlikely to prove helpful, since the film will almost certainly be deformed on the macroscopic scale.

It is clear, however, that in both cases the morphology is such that intense diffraction patterns from limited parts of the specimen can result even when the amount of copper present is quite small.

The occurrence of oscillation rather than complete rotation patterns is presumably a consequence of the limited amount of copper available. The whole process appears to be so lacking in uniformity, however, that elementary calculations of the number and size of spines to be expected are invalid. Thus, not only is the range of spine size considerable, but comparatively large areas (at least of the order of hundreds of square microns), yielding single-crystal patterns of gold without any trace of the cupric oxide pattern, are of fairly frequent occurrence.

Finally, Trillat & Oketani indexed the smallest observed spacing in their ring patterns as the forbidden 011 reflexion, an observation at variance with the interpretation advanced above (Trillat *et al.*, 1937). In the present series of experiments, however, this spacing was never observed, the smallest observed spacing being identified within the limits of experimental error as the 110. While these spacings are similar they would have been readily distinguishable under the present experimental conditions.

Hexagonal spot patterns and related patterns

Single-crystal patterns in the form of hexagonal nets have been obtained by Trillat from specimens of pure gold heated under a variety of conditions (for instance, Trillat & Oketani, 1937*b*). There has been considerable speculation as to the origins of the pattern, but, to the best of the author's knowledge, the unit cell has not been determined.

The difficulty, which occurs frequently in electron diffraction, arises from the tendency of the crystals to adopt a preferred orientation relative to the film. Attempts to tilt such small crystals at predetermined angles relative to the beam are usually unsuccessful because of the imperfections of practical specimen holders. Further complications can also arise if, as is usual, the film is not planar, and if there is appreciable extension of the reciprocal-lattice points.

In an attempt to overcome some of these difficulties, films were heated in contact with the {100} faces of freshly-cleaved sodium chloride single crystals. It was hoped that thereby either, or both, of the following two advantages might accrue: (*a*) That well-defined reference planes might be established over small areas. This would increase the probability of obtaining 'elliptical ring' patterns, and hence of establishing the unit cell. The experiments described in the previous section indicate that even after stripping, the gold films preserve the surface details of the sodium chloride crystals at least over small areas. (*b*) That new orientations of the phase might be induced by epitaxy. In fact, it was hoped that the sodium chloride lattice might act as a setting template.

While unsupported films had yielded hexagonal nets similar to those described by Trillat, specimens prepared as above gave a variety of spotty patterns related to the typical elliptical ring pattern (Fig. 1(*c*)). Which of the two effects was the more important in producing these patterns is not clear. In any case the patterns were consistent with a hexagonal unit cell having $a = 5{\cdot}29 \pm 0{\cdot}05$, $c = 11{\cdot}0 \pm 0{\cdot}1$ Å. A more precise value could not be assigned to the c axis because of the considerable extension of the reciprocal-lattice spots. Approximately the same parameters had been obtained from tilted, unsupported films, but the patterns were ill-defined, and the interpretation was correspondingly doubtful. These latter patterns were, however, useful at the outset in indicating that at least a certain degree of order did exist normal to the plane of the film. Some results of a more detailed examination of those patterns from a structural point of view will be presented in a later publication.

Under the conditions described above, another pattern was observed, although very infrequently. This may be related to patterns of the type reported by Quarrell (1937). This took the form of a hexagonal net having a parameter, within the limits of experimental error, of $d\sqrt{3}$, where d is the gold 220 spacing (Fig. 1(*c*)). The pattern tended to occur near or in conjunction with gold in a [111] orientation. No obvious impurity which might produce such a pattern could be found.

The intensity variation in the pattern is approximately monotonic. This, combined with a parameter of $d\sqrt{3}$, would be the result expected from an $ABAB$ stacking of the densest planes. This effect might be explained either by the occurrence of limited regions of stacking disorder, or by the formation of a new lattice induced by the intrusion of atoms of low scattering power. A value of approximately 5 Å for the c axis deduced from an arc pattern lent some support to the latter interpretation, but the evidence is not considered sufficiently reliable to make this interpretation more than speculative.

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