Domain Structure in Sodium Tungsten Bronzes

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No satisfactory explanation has been advanced for the striking colours of the tungsten bronzes and their variation with sodium content. Using the microscopical technique of reflectivity measurement, five bronzes varying in composition from $Na_{0.59}WO_3$ to $Na_{0.76}WO_3$ have been studied. It has been found that these bronzes have reflectivity curves in the visible spectrum of comparable shape. There is a progressive shift of the prominent peak to higher wavelengths with decreasing sodium content. The shape of the reflectivity curves and the opacity and other properties of the bronzes suggest that the colour could result from interference effects. Two kinds of mutually parallel lamellae exist. One has a periodicity of some tens of ångström units, the other of some thousands of ångström units. The former appears to be the effective unit cell thickness while the latter results from the regular intercalation of a second phase which leads to the interference effects and intense colours observed.

Introduction

In the present study, an attempt has been made to find a structural basis for the striking colours which are characteristic of sodium tungsten bronzes of general formula Na_xWO_3 in which x varies from about 0.05 to about 0.95. The samples studied were within the range of composition $Na_{0.59}WO_3$ to $Na_{0.76}WO_3$.

There is an extensive literature on the tungsten bronzes, which were first prepared by Wöhler in 1824. In recent reviews, Dickens and Whittingham (*1*) and Banks and Wold (*2*) summarized much of the work which has been published on this family of nonstoichiometric compounds.

Previous Work—Structure

The complete set of phase relations for the sodium tungsten bronzes was first given by Ribnick, Post, and Banks (*3*). They found that the cubic (or pseudocubic) range extended from $x = 0.43$ to $x = 0.95$. At lower x values, tetragonal and orthorhombic phases occur. The cubic phase has the structure of perovskite. The unit cell has a tungsten atom at the centre of a cube octahedrally surrounded by six oxygen atoms at the face centres; there are eight "interstitial" sites at the cube corners, some of which are occupied by sodium atoms. For Na_xWO_3 within the cubic range the structure is intermediate between the hypothetical $NaWO_3$ and WO_3

structures in which a fraction $1 - x$ of sodium atoms are missing from the cube corners of the $NaWO_3$ unit cell (*1*). Brown and Banks determined the variation of lattice constant with nominal bronze composition (*4*). Atoji and Rundle (*5*) carried out a neutron diffraction study of the cubic sodium tungsten bronzes and found that the occupancy of sodium sites follows a regular pattern. Thus for $x = 0.75$, no sodium atom is found at (000) or at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ (on the basis of the unit cell chosen by them). Atoji and Rundle also observed the twinning which had earlier been reported by Ingold and de Vries (*6*). The latter observed a birefringent twinned phase over a well-defined but limited temperature range, and concluded that there was a distortion from cubicity of less than 0° 35′ with c/a in the range 0.990–1,000.

Previous Work—Colour

The colour of the bronzes is closely related to their composition. The sequence presented in Table I was given by Dickens and Whittingham for the sodium tungsten bronzes and the stoichiometric end member compounds. Others had previously reported rather similar patterns of colour variation with varying sodium content, although the bronzes with composition about $Na_{0.6}WO_3$ were reported (e.g., by Ingold and de Vries) as violet rather than purple in colour.

TABLE I

COLOURS OF SODIUM TUNGSTEN
BRONZES

Composition	Colour
WO_3	Green; dark grey
$Na_{0.2}WO_3$	Dark blue
$Na_{0.4}WO_3$	Royal blue
$Na_{0.6}WO_3$	Purple; brick red
$Na_{0.8}WO_3$	Orange
$NaWO_3$	Yellow

Brown and Banks (4) measured the reflectance of pellets of powdered bronzes in a Beckman quartz spectrometer with a diffuse reflectance attachment. They obtained broad absorption peaks, the maximum absorption for all their bronzes exceeding 95%, and the absorption throughout the range studied (3350–12,500 a.u.) always exceeding 50%. With decreasing sodium content the position of the absorption peaks shifted to lower wavelengths and the breadth of the peaks increased. For $x < 0.20$ the bronzes no longer had a metallic luster and the absorption spectrum was of an entirely different character. Brown and Banks also observed that there was a linear relation between position of absorption peak and x for much of the range of x, but for compositions where $x > 0.75$, the scattering of points away from the curve became large. The deviation is in the sense that the position of absorption peaks is at *lower* wavelengths than would be expected if the linear relation held for compositions where $x > 0.75$.

Fuchs (7) concluded that "perhaps it is dangerous to base any conclusion whatsoever on the optical absorption, because typical samples have a surface layer deficient in sodium, which may modify the optical properties in an unknown way."

Dickens, Quilliam, and Whittingham (8) reinvestigated the reflectance spectra of the sodium tungsten bronzes with the object of distinguishing between specular and diffuse components (9) "in an attempt to resolve the apparent disagreement between spectral and other electronic properties." They used a spectrometer with unspecified powder reflectance attachment and made measurements in the range 20,000–2500 a.u., observing their samples first as pure samples and secondly after dilution with a tenfold excess of a reference substance. They reported a considerable difference between the reflectance spectra of diluted samples and those of the pure materials, and concluded (contrary to the present results) that the true absorption spectra were approximated to by diffusion reflectance measurements on diluted samples.

Present Studies

The bronzes used in the present studies are listed in Table II. The crystals grow in the form of cubes (Bronzes Nos. 1, 2, and 5) or prisms (Bronzes Nos. 3 and 4). Many of the crystals are intergrown. They have the appearance of interpenetrating twins, but as a rule the two crystals are quite readily parted.

On the basis of X-ray diffraction data, the bronzes (except perhaps No. 4) are cubic so far as can be determined using modern instrumental refinements. Bronze No. 4 is less certainly cubic and may actually be tetragonal.

TABLE II

LIST OF BRONZES STUDIED

Bronze No.	Composition	Lattice Constant (a.u.)	Colour and Luster	Crystal Form
1	$Na_{0.76}WO_3$	3.8477	Orange to yellowish green; dull to metallic luster[a]	
2	$Na_{0.73}WO_3$	3.8433	Orange; metallic luster[a]	Intergrown cubes
5	$Na_{0.70}WO_3$	3.8419	Red to orange; metallic luster	
4	$Na_{0.65}WO_3$	3.8391	Purple to deep red; sub-metallic luster	Prisms with pyramidal terminations intergrown in part
3	$Na_{0.59}WO_3$	3.8333	Purple to deep red sub-metallic luster	

[a] Some crystals of Bronzes 1 and 2 showed patchy yellow-green areas of tarnish.

There is a slight suggestion of a second phase in the diffraction pattern of Bronze No. 2. The extra peaks would be consistent with the presence of a small amount of $Na_{0.10}WO_3$. Low-angle X-ray diffraction examination showed a weak peak corresponding to a spacing of about 80 a.u.

Reexamination of Colour in Tungsten Bronzes

The crystals varied from less than one, to several millimeters across. In the uncrushed state, each of the samples was predominantly of one colour. Even between bronzes Nos. 1, 2, and 5 there were marked colour differences, although all were more or less orange. For some crystals variations in colour in a single face could be observed with the unaided eye. A small change in colour could commonly be observed in a particular face when the crystal was rotated.

When the crystals are crushed the powder appears quite a uniform distinctive colour for each bronze. Bronzes Nos. 1, 2, and 5 are still of rather metallic luster in the powdered form, Nos. 3 and 4 less so. If the powder after mechanical crushing is placed in water or alcohol it quickly settles, and has a similar appearance as in the dry state but there is usually a slight change in colour. Bronzes Nos. 1, 2, and 5 appear slightly lighter in colour when immersed, while the two purple bronzes appear deep red. If the powders while in a liquid—either water or organic solvents—are placed in an ultrasonic bath for a few minutes, the supernatant liquid does not, as previously, clear quickly on standing, but for all five bronzes remains a deep blue for hours or even days. The colour is due to particulate material, since the liquid does eventually clear, and the fine material can be readily dispersed again. Crushed grains tend to be tabular in shape.

The absorption spectrum of Bronze No. 2 was obtained in the infrared region using a Perkin-Elmer Model 621 spectrophotometer and in the ultraviolet using a Perkin-Elmer Model 4000A spectrophotometer. The finely ground sample was dispersed in a KBr disk for this purpose—0.025 wt. % in a ~200 mg disk. Weak featureless absorption in the infrared region increased with decrease in wavelength from 150,000 a.u., increasing more rapidly in the visible and then more slowly in the ultraviolet to reach a maximum near 2250 a.u. Below this wavelength the absorption decreased abruptly.

The blue suspension obtained by the ultrasonic treatment of Bronze No. 2 in spectroscopic-grade ethanol was examined in the ultraviolet and visible regions (PE4000A—alcohol reference). This showed a transmission maximum between 4500 and 4750 a.u. which is consistent with the colour. (Note that there is also a sharp cutoff in absorption below about 2250 a.u.) The infrared spectrum of the residue obtained by evaporating off the ethanol from a suspension and dispersing it in a KBr disk exhibited two sharp absorption doublets at 1380/1400 and 1040/1080 cm^{-1}.

Under the microscope the variation in colour within each of the bronze samples was clearly related to the presence of steps which occurred on all crystal surfaces. Thus, for one planar cleavage surface the colour tended to be constant, while changes, usually small, might occur between one cleavage step and the next (see Fig. 1).

The grains after normal crushing were opaque in transmitted light, even on very thin edges and even when placed in media of very high refractive index. After ultrasonic treatment the finer grains appeared blue—usually deep royal blue—in transmitted light and many of the larger grains had dark blue margins. For some small grains the number of steps could be counted. Crystals up to three steps thick were translucent to some extent [Fig. 2(a)]. Rare grains of No. 2 Bronze, which had broken across rather than along the cleavage, could be observed edge-on; they appeared colourless to pale yellow and translucent. In such grains fine dark bands were observed at intervals of about 0.5 μm [see Fig. 2(b)].

Grains of bronze were embedded in polyester resin and polished. These polished grains showed the colours characteristic of each of the bronzes, with a small amount of variation within grains and from grain to grain. Thus, a single grain of No. 2 Bronze varied from a deep orange to a distinctly yellowish orange. The variation in colour was gradual and unrelated to the shape of the grain. For the most part the grains showed no internal reflexions in doubly polarized vertically incident light. However, when two grains were adjacent, lemon yellow internal reflexions were sometimes observed near the margins of one or both grains (see Fig. 3). These polished grain mounts were used to obtain reflectivity curves using a microscope photometer (10). In this technique the vertically incident light is reflected from a polished surface through the microscope optics to a photomultiplier. The absolute value of the reflectivity from regions down to a few microns in diameter is obtained by comparison with the reflectivities of polished standard substances at each of the wavelengths used. The quantity being measured is thus specular reflectivity (9) in the visible region. Well-polished

FIG. 1. Typical cubes of Bronze No. 1. Note the steps on some cube faces. Most of these edges are sharp, but some cubes have fissures where cube faces do not quite meet. Magnification 20 (approx.).

planar surfaces away from edges of grains (to avoid relief effects) were chosen.

Figure 4 shows typical curves obtained for the reflectance spectra of the bronzes. The bronzes are weakly anisotropic and the two curves for Bronze No. 2 represent the extreme cases observed in about one hundred grains.

Because the conclusions of Dickens, Quilliam, and Whittingham (8) were surprising, and, if correct, of importance in interpretation, Reid (11) obtained diffuse reflectance spectra of diluted and pure
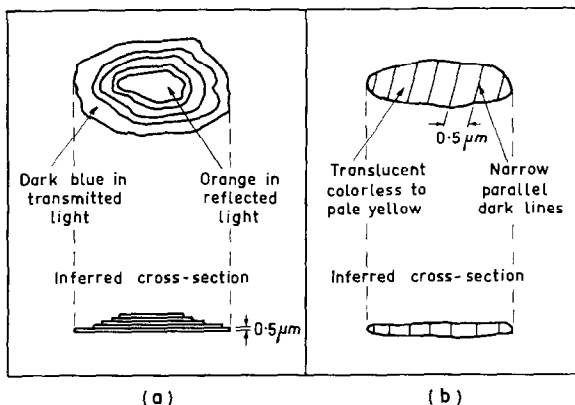

FIG. 2. Appearance of grains in microscope after mechanical crushing and ultrasonic treatment: (a) is the usual case; (b) is extremely rare since most breakage is along plane of lamination.
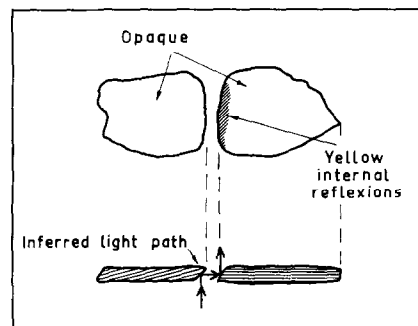

FIG. 3. Appearance of internal reflexions from tabular grains when appropriately oriented. Where there is no adjacent grain no internal reflexion is observed.
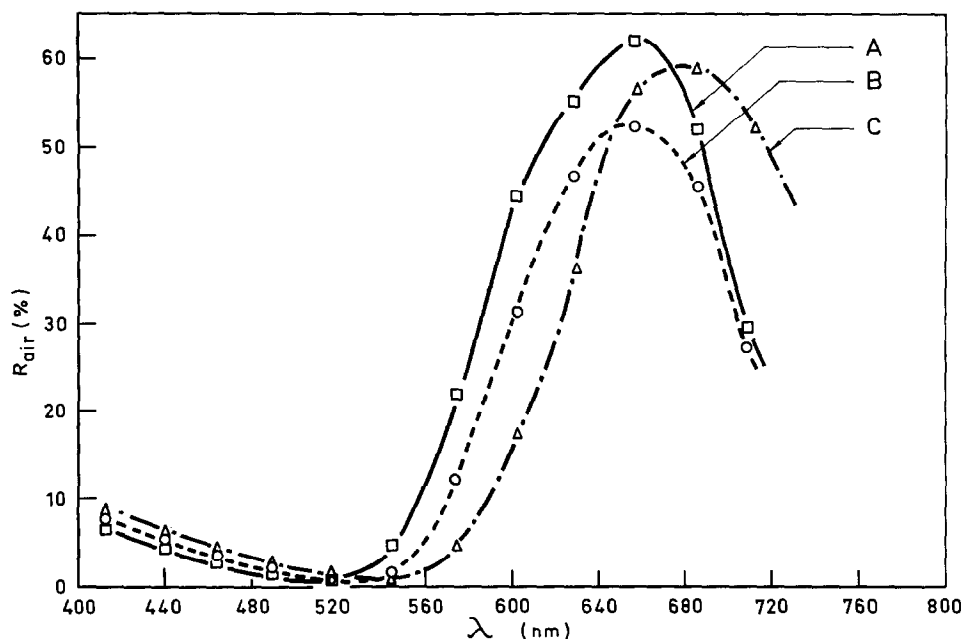
FIG. 4. Reflectance spectra for Bronzes Nos. 2 and 4. For No. 2 two curves (A and B) are shown representing the highest and lowest peak reflectance found in approximately 100 grains. Only the maximum curve (C) has been shown for Bronze No. 4.

samples of the sodium tungsten bronzes used in the present study, with a Beckman DK-2A spectrophotometer in which the reflectance arrangement employs an incident beam normal to the sample surface and detects the diffusely reflected light inside an MgO-coated sphere which is itself diffusely reflecting. Apart from the effects of dilution in reducing the intensities of absorption, no difference was observed between the diffuse reflectance spectra of the pure and the diluted material. The spectra consisted of single broad peaks at all dilutions, without changes such as were observed by Dickens, Quilliam, and Whittingham, whose results appear to be an instrumental artifact.

Structural Features of Tungsten Bronzes

The crystals are frequently better developed on some faces than others, the less well-formed faces being irregular and less lustrous than the remainder. The edges and corners of the crystals used in the present studies are often imperfectly formed, with irregular cracks or fissures where adjacent faces do not meet (Fig. 1). On these exposed edges the crystals can be observed to have a regular cleavage developed parallel to the prominent faces. Thus, the cubic crystals exhibit cleavage parallel to the well-formed cube faces. The cleavage is thus not constant throughout one cube but forms three sets

of planes which diminish in area from the cube faces in towards the centre of the cube to give a "Chinese box" configuration. The same regular sets of planes can be observed in crushed grains and in grains which have been polished (Fig. 5). In polished surfaces of correctly oriented grains it is possible to measure the spacing of the planes, which appear as narrow dark lines across the coloured bronze surface. The grains in polished mounts are randomly oriented; the minimum spacing therefore approximates the true spacing. For the No. 2 Bronze this was determined as approximately 0.48 μm—it is difficult to be precise because the interval between planes approaches the limit of resolution of the light microscope.

During microscopic examination the "twinning" referred to by Ingold and de Vries (6) was observed in polished surfaces. However, it disappeared gradually from at least some preparations over a period of several weeks, following which it could not be observed even after the grain mount had been repolished.

When the surfaces were replicated and the shadowed replicas examined in the electron microscope, it became apparent that in addition to the planes which could be observed with the light microscope there was a mutually parallel system of regular steps which, for No. 2 Bronze, were 70 a.u. apart, as estimated from the shadowing angle
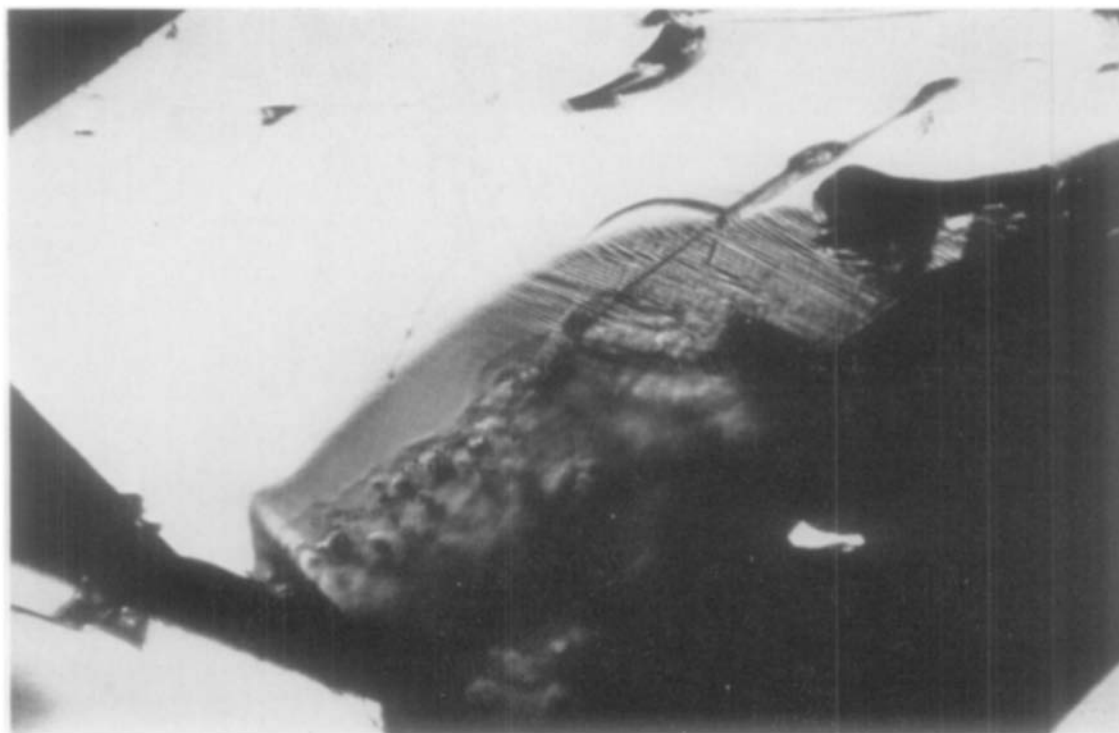
FIG. 5. Photomicrograph of part of the surface of a grain of No. 2 Bronze. The regular steps are clearly visible and are about 0.48 μm apart. The slight apparent irregularities are caused by a slightly irregular fracture surface.

defined during replica preparation (Fig. 6). These were observed by Ingold and de Vries, who referred to them as "steps in the atomic layers and crystal structure irregularities which form as the crystal grows."

Finely comminuted bronze powder itself was examined by electron microscopy. Many thin platelets were sufficiently thin to be transparent to the electron beam, and dislocations could commonly be observed to move in the beam. The platelets showed no tendency to charge up, consistent with their reported high conductivity (1). The bronzes were heated while in the electron microscope, and electron diffraction patterns observed continuously during cycling from room temperature to 300°. No phase transformation such as had been reported (6) was observed.

Discussion and Conclusions

Electron-microscope examination and low-angle X-ray diffraction provide strong evidence for a 70 a.u. layering parallel to the larger-scale, microscopically observed layering with a period of about 4800 a.u. The fact that a crystal at a particular position cleaves readily along one of the cubic

directions, and with difficulty or not at all along the other two, also indicates highly developed anisotropy of structure, although to date X-ray diffraction has been unable to detect it. As Ingold and de Vries pointed out, and as the present author has confirmed, the deviation if any from orthohombicity must, however, be vanishingly small. The repeating layer interval of 70 a.u. is believed to be the effective "unit cell" dimension in the x-axis direction. This is a high multiple of the sub-cell lattice spacing of about 3.84 a.u. (cf. Table II) or of the value found by Atoji and Rundle, who preferred $a = 2\acute{a}$ where $\acute{a}$ is the X-ray lattice constant. Other pseudocubic substances with distorted perovskite structure have quadrupled super-cells which, it has been suggested, "might be associated with cation deficiencies which may sometimes be distributed in a regular manner throughout the structure" (12). The sodium tungsten bronzes, with gross cation deficiencies, appear to have super-cells which are still higher multiples of the X-ray lattice constant, at least in the unique crystallographic direction, and which are indicative of long-range ordering.

There are thus about 70 super-cells to each of the gross or microscopically visible (half-micron) layers, although the number of 70 a.u. cells, and so the
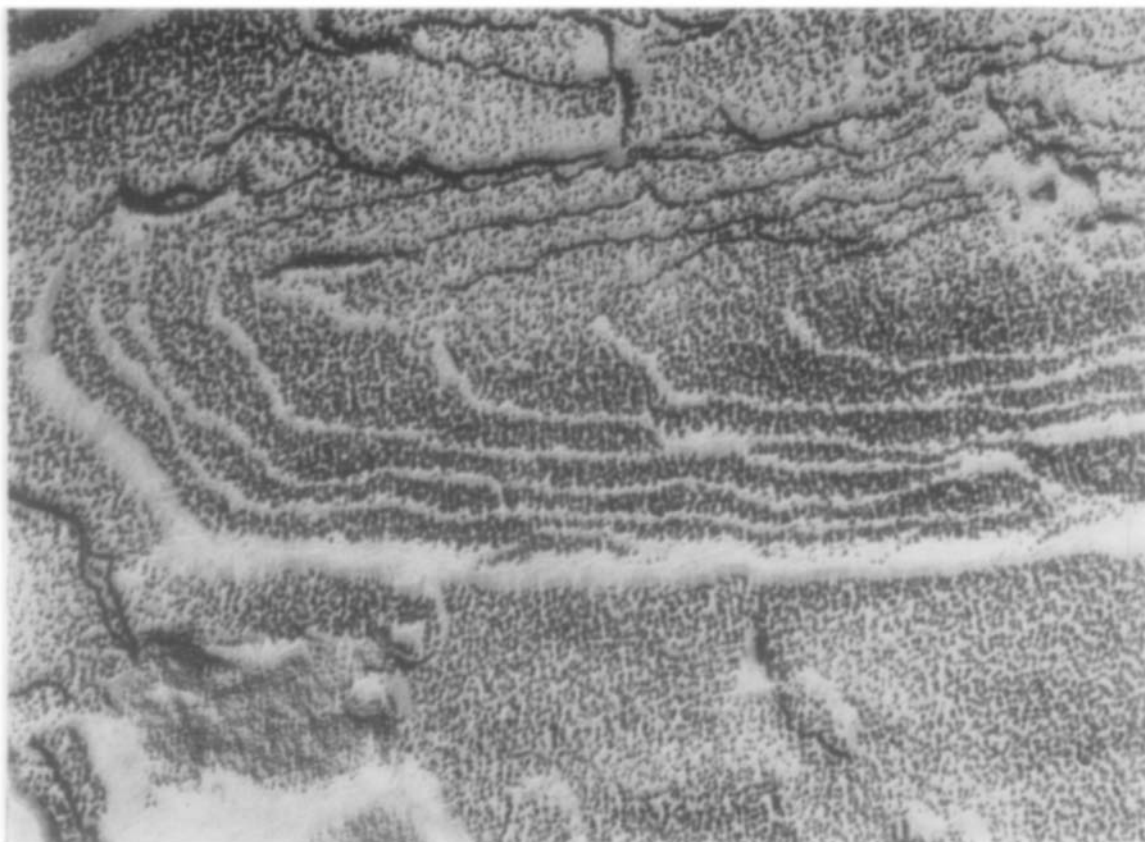
FIG. 6. Electron micrograph of the surface of Bronze No. 2 after ultrasonic treatment. Regular steps, 70 a.u. apart, can be seen. Shadowed replica X98,000.

thickness of the gross layers, is not absolutely constant. The surface formed by one gross step in a particular crystal tends to be fairly constant in colour and may vary slightly from another step even on the same face. For No. 2 Bronze, microscopic observations indicated that the thickness of the gross layering varies from about 4800 a.u. to about 5600 a.u., with a mean figure of about 5200 a.u.

There are several indications of the effective presence in these tungsten bronzes of two regularly intergrown phases which could hardly have been present at the time of initial deposition. Direct microscopic observation by transmitted light shows the presence of a major phase which is translucent and yellow and a minor phase which is dark blue to opaque. X-ray diffraction suggests that the major phase has a composition close to that of the composite "crystal" while the minor phase could be a bronze highly deficient in sodium. Electrochemical measurements by Koch and Becker (13) also suggest a two-phase system.

If the colour of the bronzes was due to a homo-

geneous phase of uniform refractive index, then in the present special case of perpendicular incidence the Fresnel equation should apply and the reflectivity in air would be

$$R = \frac{(n-1)^2 + n^2 K^2}{(n+1)^2 + n^2 K^2},$$

where n is the refractive index and K is the absorption index (9). For media other than air, of refractive index n_0,

$$R_0 = \frac{(n-n_0)^2 + n^2 K^2}{(n+n_0)^2 + n^2 K^2}.$$

The reflectivities of Bronze No. 2 were measured in air and in oil of refractive index 1.515, at thirteen wavelengths throughout the visible spectrum. On solving for n, however, unacceptable values (<1) were obtained, especially at wavelengths where the reflectivity was high. Other opaque materials give $n \gg 1$ from this procedure. The fact that the Fresnel equation does not apply is confirmation that the colour of bronzes is not simply related to the optical

properties which normally govern reflection at a plane surface.

It is concluded that interference effects are the only possible explanation for the colour of these bronzes. The curves shown in Fig. 4 are quite unlike the reflectance spectra of metals or minerals. The most striking features of the curves are the height and limited extent of the peak and the low minimum-reflectivity values. Even for a comparatively highly coloured metal like copper, the reflectivity as a percentage of incident light is always in the tens rather than near or below unity, as for the minima of the bronzes. Even poorly reflecting materials such as glass, or minerals of low refractive index, have appreciably higher reflectivities than, say, Bronze No. 2 at a wavelength of 5000 a.u. Further, the spectra for different bronzes are of similar form, there being a progressive shift to higher wavelengths as the sodium content of the bronze falls. Thus, the purple bronzes actually are purple—a mixture of red and blue—and not violet. If the powdered bronzes are immersed in a substance of higher refractive index than air, there is comparatively little effect on the main peak and the minimum, but the reflectivities at lower wavelengths are considerably reduced. Thus, the purple bronze appears distinctly more red when immersed in liquids.

There is also an important relation between the positions of the minimum and of the maximum in the spectrum. For the curve A' in Fig. 4, the peak is at about 6600 a.u. and the minimum at about 5000 a.u.—similarly for the other bronzes. This wavelength ratio of nearly 4:3 is accounted for as follows. For reinforcement to occur as a result of constructive interference of light reflected from two superposed planes, the path difference must be $(n + \frac{1}{2})\lambda$, the half-wavelength being necessary to allow for the phase jump on reflection (9). For the path difference to be $(n + \frac{1}{2})\lambda$, that is $3\lambda/2$ for $n = 1$, the interplanar spacing must be $3\lambda/4$ (assuming vertical incidence). Thus, for reinforcement of light of $\lambda = 6600$ a.u. (as for Bronze No. 2) the interplanar spacing must be $3\lambda/4$ or 4950 a.u., which corresponds closely to the spacing actually observed and measured microscopically. Since the least favourable conditions for the reinforcement and reflection of light occur when the wavelength of light equals the interplanar spacing, there should be a reflectivity minimum at about 4900 a.u. for Bronze No. 2, as indeed is found

For a spacing of about 4900 a.u. (using the same example) another peak resulting from interference would be expected at 3900 a.u. (for $n = 2$). While this is beyond the limits of detection using present equipment, the shape of the curve at the blue end of

the spectrum is consistent with another smaller peak in this position. Peaks for $n = 3$ and higher orders are well outside the range studied. A similar sort of relation appears to hold for each of the bronzes examined.

The generation of colours by interference also explains the variation in colour which sometimes occurs when a bronze crystal is rotated to bring a given face into a new orientation. The effective path length is varied slightly by rotation of the crystal, and the position of the interference maxima is thus altered.

Thus, the colour in these bronzes appears to be a direct result of the structure—in that the layering which can be observed in the light microscope is responsible for all or most of the colour displayed by the crystal. For reflection, and so for interference to occur, there must be discontinuities of some sort in the structure. The kind which the present evidence supports is the formation of two phases by a sort of disproportionation, although it is not easy to see why such regularity in the distribution of the second phase would exist or indeed why any disproportionation should occur at all. Another possible type of regular discontinuity is a set of periodic dislocations. While remarkably regular arrays of dislocations do occur in metals (14), these are likely to be very small in areal extent compared with the planar discontinuities which exist in the bronzes. Moreover, the bronzes apparently possess the same colour whether prepared by vapour phase reaction, electrolytic reduction, or solid state reaction, and whether the crystals are cooled slowly or quenched rapidly on being taken from the reaction vessel (13).

The "twinning" which was observed by Ingold and de Vries and which the present author found to disappear with time is almost certainly due to stress, possibly resulting from the unoccupied sodium sites and a consequent tendency to deformation. The structure of perovskite itself has been considered by Naray-Szabo (15) to be monoclinic with $a \simeq b \simeq c = 7.62$ a.u. and $\beta \simeq 90°$. Megaw (16) gave $a = c = 7.654$ a.u., $b = 7.645$ a.u. and $\beta = 90° \, 40'$; with suitable choice of axes an orthorhombic symmetry could be obtained. It seems probable that deformation in the sodium tungsten bronzes would follow the same pattern and that there is a real likelihood of angular stress developing as the sodium atoms diffuse from random to regularly distributed occupancy of some of the available sites. From the work of Ingold and de Vries and from observations on perovskite itself the direction of stress is the (101) or (011) direction, so that the unit cell becomes a rhombus instead of a square when viewed along the

a or *b* axis, depending on the direction along which distortion has occurred.

The present symmetry of the bronzes being so nearly cubic, it seems probable that the initial lattice planes build up with cubic symmetry. Since Atoji and Rundle found that there were preferred sites for sodium occupancy, any sodium atoms not initially deposited in such sites presumably diffuse to these positions shortly after deposition. As deposition proceeds accumulated stress or tendency to deform increases. There is, apparently, a preferential collapse perpendicular to the plane of deposition, to form a unique axis perpendicular to this plane and thus to the layering. Also, the angle β tends to exceed 90°; this tendency can perhaps be resisted providing the thickness of crystal is not too great, but eventually this stress exceeds the strength of bonding between two super-cells and is relieved by the adoption of a new angle β. Crystallographic continuity is then lost between the adjacent super-cells where failure has occurred. The periodicity of such failure is evidently related to the degree of occupancy of sodium sites. Over the range $x = 0.6$–0.9 the stress resulting in formation of gross layers apparently increases as the occupancy of sodium sites increases. This may be because a high occupancy of sodium sites limits the relief of stress by uniaxial distortion (uniaxial compaction), leading to a greater tendency to angular distortion. It may also be that for these purposes the anisotropy of stress resulting from sodium site occupancy is more important than the total degree of occupancy.

The available evidence suggests that the region in the immediate neighbourhood of the plane of slip is depleted in sodium atoms, presumably by migration to sites within a domain of the major phase. Whatever the mechanism, the result is a layer with a high population of free electrons at the margin of each layer or domain. It is this zone which is the effective minor phase with its characteristic properties of metallic luster, high degree of reflection of light, and strong light absorption except in the blue region of the visible spectrum.

The metallic conductivity of the bronzes is almost certainly related to the presence of the electron-rich zones, and it would be expected that bronze crystals would exhibit very marked anisotropy of electrical conductivity. Because the cubes actually contain three crystallographic orientations, with the "metallic" zones lying parallel to each of the six crystal faces in a "Chinese box" configuration, this cannot be measured without cutting out a section having a single crystallographic orientation. Such a section would be expected to behave very similarly to the cleavable platelets of blue potassium molybdenum bronze which were studied by Perloff, Vlasse, and Wold (*17*). They found an anisotropy in the electrical resistivity of approximately $1\frac{1}{2}$–2 orders of magnitude. The change from semiconducting to metallic behaviour was also found to be sensitive to sample orientation.

Although only some of the sodium tungsten bronzes have been examined in this study, it seems probable that other bronzes are analogous as to the origin of their colour and other properties.

Acknowledgments

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