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Observation of Size-Effect Diffuse Electron Scattering in Disordered α-CuAl Near the Critical Voltage

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Abstract

The detection is reported of two distinct types of diffuse electron diffraction pattern due to size-effect scattering (SES) in disordered Cu–16·7 at.% Al, observed near the critical voltage. The dynamical conditions for examining SES are discussed and it is concluded that the observed asymmetry switch due to annealing at 723 K for different periods of time followed by *in situ* quenching in the electron microscope may be kinematically interpreted and represents a change in the alloy's state of strain, rather than the result of a 'critical-voltage' Bloch-wave degeneracy in either the Bragg or diffuse scatter. One of the strain states is what would be expected in a homogeneously disordered alloy. The possibility that the other state is the result of a Suzuki lock solid-state reaction is briefly discussed.

Introduction

The copper-rich α phase of the Cu–Al alloy system has a low stacking-fault energy and is known to support homogeneous atomic short-range order (SRO) states when the concentration of aluminium atoms exceeds about 5% (Matsuo & Clarebrough, 1963; Borie & Sparks, 1964). In the same range it is also considered to undergo a Suzuki lock segregation reaction (Suzuki, 1952) in which solute atoms concentrate on {111} fault planes after brief heat treatment (Epperson, Fürnrohr & Ortiz, 1978).

When radiation is coherently diffracted from microscopic strain fields introduced into a homogeneous disordered alloy by the difference in radius of its atomic constituents, the resulting weak asymmetric diffuse scatter exhibits reciprocal-space maxima close to the usual Bragg diffraction peaks and, if intense enough, can appear to displace their centre of gravity. Known as size-effect scattering (SES), this is a well known phenomenon in X-ray and neutron diffraction (Warren, Averbach & Roberts, 1951; Mozer, Keating & Moss, 1968). In this paper we explain why the electron scattering analogue has escaped detection until now and present convergent-beam electron diffraction patterns containing SES contrast, taken near the critical voltage (V_c) for disordered specimens of α-CuAl approximately 3000 Å thick. We also discuss its behaviour under strong dynamical conditions and examine whether SES itself displays critical-voltage phenomena due to dynamical interactions between its main diffuse 'beams'.

The critical voltage effect

Consider electron diffraction from a perfect crystal of pure copper or from a perfectly ordered alloy in which the difference in atomic radii causes no microscopic strain, carried out in a high-voltage electron microscope (HVEM) with variable accelerating voltage, or, as in our case, with variable specimen temperature (Sellar, Imeson & Humphreys, 1980). If the crystal is tilted so that only the *hhh* row of diffraction peaks is appreciably excited (the one-dimensional 'systematics' case), and the second-order 222 peak is Bragg satisfied, then the only Bloch waves excited can be classed as either symmetric – with local intensity maxima at the operating atomic planes – or antisymmetric, with intensity minima at the atomic planes. For thick ordered specimens at a given temperature in this setting, the critical-voltage (CV) effect arises when an accidental degeneracy occurs between the kinetic-energy eigenvalues of the two principal Bloch waves (Metherell & Fisher, 1969). For a given HVEM accelerating voltage – 305 kV in our experiments – the degeneracy occurs at the critical voltage temperature $T_{\rm CV}$, and causes a near-total extinction of the 222 Bragg elastic peak and a reversal in the sense of asymmetry of Kikuchi lines, which can be considered to be elastically rediffracted diffuse scatter.

In the treatment of elastic dynamical diffraction from a perfect lattice, C_g^j, the *g*th Fourier coefficient of the *j*th Bloch wave of the Fourier sum representing the fast electron in a crystal, is determined by substitution into the Schrödinger equation yielding the set of

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dispersion equations

$$[K^2-(k+g)^2]C^j_g+\gamma \sum_{h\neq g} U_{g-h}C^j_g=0,$$

where g is a reciprocal-lattice vector, k the incident-beam vector and K the mean wave vector (Bethe, 1928). $\gamma=m/m_0$ and $U_g=(2m_0e/h^2)V_g$, where V_g is the effective Fourier coefficient of the local elastic scattering potential including the effect of the Debye–Waller factor, and m is the relativistic electron mass (Watanabe, Uyeda & Fukuhara, 1968). Detailed computations are required for wave functions (David, Gevers & Stumpp, 1985), but useful approximate values of V_c (or T_{CV}) may be quickly obtained by solution of Bethe's second approximation

$$U(2)-Rd^2[U(1)^2-\tfrac{2}{3}U(1)U(3)-\tfrac{1}{4}U(2)U(4)\ldots]=0, \quad (1)$$

in which all relativistic dependence is absorbed in R, where $R=1+eV_c/m_0c^2$, $U(h)=U_{hhh}$, and d is the lattice spacing for the first-order reflection.

For our experiments, detailed n-beam scattering calculations show that only Bloch waves 2 and 3 contribute significantly to the 222 convergent-beam elastic rocking curve, which is a map of intensity as a function of tilt angle. The other Bloch waves are effectively damped by absorption processes which can be treated phenomenologically.

Experimental

(*a*) *Strain-free case*

All the experiments described in this paper were conducted on the AEI EM7 electron microscope at the Department of Metallurgy and Science of Materials at Oxford University, England, operated in a non-standard convergent-beam mode. This results in a spot size of not less than 1000 Å in radius (Moodie, Sellar, Imeson & Humphreys, 1977). Similarly, all our results refer to the 222 rocking curves of 305 kV electrons diffracted from undeformed electropolished samples of Cu–16·7 at.% Al with wedge angles of approximately 10^{-2} rad. In none of these (nor in similarly prepared foils of copper and other α-CuAl alloys) could gross bending effects be noticed after heat treatment. We experienced none of the rocking-curve asymmetries described by Bird, Walmsley & Vincent (1984). For further experimental details, see Sellar, Imeson & Humphreys (1980).

In order to bring out more clearly the SES intensity profile and reveal the extent of the temperature 'window' on the 222 reflection which the CV degeneracy allows, we first examine the convergent-beam rocking curve from an alloy crystal without strain. At 305 kV, with a slow-cooled ordered specimen of Cu–16·7 at.% Al in the HVEM, the Kikuchi line switches asymmetry and the elastic peak begins to reappear at the 222 reflecting position as the specimen temperature is varied above and below T_{CV}, as in Fig. 1. Near the degeneracy (Fig. 1*b*) the Bragg peak and the Kikuchi line are extinguished and away from the exact reflecting position the near-sinusoidal subsidiary elastic maxima are mirror symmetric, owing to wave-mechanical reciprocity (Sellar, Imeson & Humphreys, 1980). No asymmetric SES contrast is visible in the dark extinction band astride the reflecting position, since the size-effect strain may be considered to be released by the formation of long-range-order domains in ordered Cu–16·7 at.% Al, based on a faulted Cu_3Au model (Epperson, Fürnrohr & Ortiz, 1978).

(*b*) *Quenched-alloy case*

For a disordered alloy with a comparatively small atomic size disparity (6%) as in α-CuAl, such that the scattering potential can be separated into an average-lattice (AL) part and a small strain-dependent deviation term, the 222 SES 'peak' and the corresponding diminution ('trough') of intensity on the other side of the reflecting position can be made visible near the extinction band, since the 222 Bragg peak and the Kikuchi line both depend on diffraction from the average lattice, and, as we have seen, can be made to vanish by judicious choice of temperature and accelerating voltage. The measurements of Borie & Sparks (1964) suggest that static atomic displacements of up to 0·5 Å may be possible in Cu–16·0 at.% Al annealed at 420 K for 54 h. Metherell & Fisher (1969) have shown that the symmetric average-lattice Bloch wave (Bloch wave 2 when below V_c and 3 when above) is near its intensity minimum when at a distance of 0·5 Å from the {111} planes and so is scattered only a little by the strain field of the deviation. The strain is sampled instead by the antisymmetric Bloch wave which is near its maximum at 0·5 Å. Quite apart from being nearly two orders of

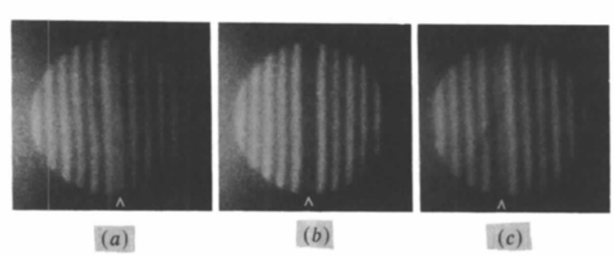
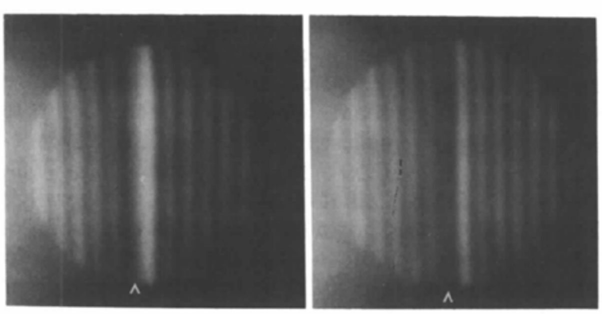


Fig. 1. Strain-free case. Mirror-symmetric 222 rocking curves for the slow-cooled Cu–16·7 at.% Al specimen near the average-lattice (AL) CV degeneracy, demonstrating Kikuchi-line asymmetry. (*a*) $T=348$ K, (*b*) $T=399$ K $\simeq T_{CV}$, (*c*) $T=451$ K. The temperature window is approximately 100 K wide. At T_{CV} the otherwise bright Bragg-satisfied 222 beam is extinguished at the exact reflecting position (arrowed). Note absence of SES. Intensity halo on low-angle side of disc is due to diffuse scattering from 111 rocking curve (not shown). Wavevector increases from left to right.

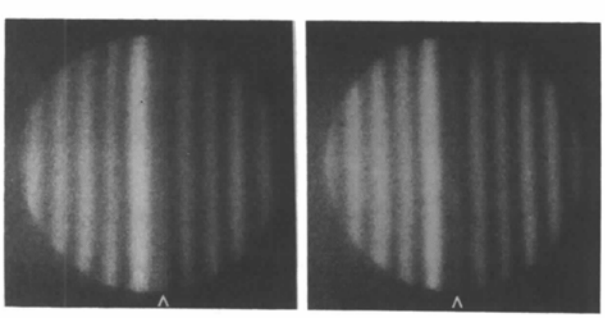
magnitude dimmer than the brightest Bragg peaks, the SES is suppressed when the incident beam is in a principal orientation since [for example, in copper (Metherell & Fisher, 1969)] the asymmetric waves then vanish by symmetry (see also Cowley, 1965; Cowley & Fields, 1979). This explains its not being detected previously, and the need to conduct experiments in the one-dimensional systematics orientation.

If Cu–16·7 at.% Al is annealed at 723 K for 20 min and the induced disorder 'quenched' by turning off the heating coils, the 222 rocking curves in Fig. 2 result, when the temperature is returned to a setting near the AL T_{CV} (approximately 399 K). The subsidiary maxima retain their mirror symmetry but have the SES superimposed, which displays an intensity maximum on the high-angle side of the reflecting position, corresponding to the X-ray determination of Borie & Sparks (1964). After annealing a similar specimen at 723 K for 2 min and again quenching, however, the asymmetric intensity maximum observed at 399 K appears on the low-angle side (Fig. 3). This appears to indicate strain of a sense opposite to that described by Borie & Sparks (1964).



(a) (b)

Fig. 2. 222 rocking curve for quenched specimen after 20 min at 723 K. Asymmetric SES superimposed with peak on high-angle side of reflecting position corresponds to X-ray determination of Borie & Sparks (1964). (a) $T = 444$ K. Note Kikuchi line and weak Bragg peak in extinction band. (b) $T = 398\ \mathrm{K} \simeq T_{CV}$.



(a) (b)

723 K near AL CV, with superimposed SES peak now on the low-angle side. (a) $T = 451$ K. (b) $T = 387\ \mathrm{K} \gtrsim T_{CV}$.

For the present, we shall still refer to it as a variety of size-effect scattering: its appearance suggests the existence of a disordered, perhaps inhomogeneous, state in the alloy, possibly with {111} planes slightly further apart on average than those of the matrix. In an inhomogeneous state, the 'matrix' critical voltage may be a more relevant term than that of the average lattice, since an average lattice may be difficult to identify.

In these experiments the possibility exists of confusing the SES with the Kikuchi line: that is why we present rocking curves both near and far from the critical voltage in Figs. 2 and 3, in order to demonstrate the persistence of the SES peak and its implied independence from the average-lattice degeneracy. If the scattering in Fig. 3 is indeed evidence of a Suzuki lock reaction, the finesse of the present series of experiments was insufficient to detect segregation to {111} planes through the measurement of changes in the critical voltage from the ordered strain-free value. The change predicted would have been approximately 1 kV per unit percentage of solute remaining in the matrix. Quenching from 870 K results in a return to a rocking curve with lack of asymmetry corresponding to the ordered state suggested by Fig. 1, except that heavier diffuse scatter is evident, consistent with the deductions of Matsuo & Clarebrough (1963) that, as the quenching temperature rises, ordering recurs with a concomitant increase of retained vacancies.

It should be noted that the intensity halo on the low-angle (left-hand) edge of each 222 disc in Figs. 2 and 3 is due to strong diffuse scattering from the high-angle side of the 111 rocking curve (not shown). Beyond the high-angle (right-hand) edge of the 222 discs no corresponding halo is visible from the 333 elastic and diffuse scattering, which is weak at these temperatures.

Dynamical scattering

In order to judge whether the asymmetry switch should be interpreted kinematically or whether it is produced solely by dynamical scattering effects, it is necessary to estimate the relative importance of several interactions between the diffuse and the Bragg scatter.

(a) *Effect of the average-lattice CV degeneracy on the SES asymmetry switch*

Considered, for example, as another form of diffuse radiation dynamically rescattered by the Bragg planes of the average lattice, the behaviour of SES should bear some similarity to that of Kikuchi lines, and therefore be affected by the AL degeneracy.

Using the reciprocity theorem, Thomas & Humphreys (1970) devised a method for calculating an intensity series whose sum approximates the Kikuchi-line contrast to be expected from thick specimens, including cases near the AL critical voltage, where the Kikuchi asymmetry switches. By similar reasoning, the largest term of a series for the intensity profile of the SES near the 222 position is governed by the AL CV behaviour of the 000 beam. It is as if the weak 222 SES beam has become the incident electron beam, so that the main contribution arises from the product in reciprocal space of the 222 SES profile and the 000 elastic rocking curve reversed about the reflecting position. Dynamical calculations of the asymmetry switch in the AL 000 rocking curve near T_{CV} show that over the range of the temperature window this reversal causes intensity variations of approximately 10%, not enough to bring about the large difference in symmetry evident between Figs. 2 and 3. In any case, with increasing thickness, multiplicative dynamical factors in reciprocal space always show reducing fluctuations (Cowley & Fields, 1979). This appears to rule out intensity modifications due to the AL CV degeneracy as the source of the observed gross changes in the SES profiles, although even for parallel incident illumination a full dynamical (diffuse plus Bragg) calculation would be necessary to extract the Warren-Averbach-Roberts 'Fourier' coefficients for a homogeneous random solid solution.

(b) CV degeneracy in the size-effect diffuse scatter

Another possibility which should be considered is a SES asymmetry switch brought about by an elastic diffuse-diffuse interaction in which the strain-deviation part of the total scattering potential may produce its own critical voltage effect. Such a dynamical diffuse interaction would be small but possibly decisive for switching behaviour in the SES. We can examine this possibility using the following approximate argument. If, for a small atomic-size disparity in a homogeneous disordered alloy, we assume that the SES arises principally from nearest-neighbour-shell strains, then, crudely speaking, the strain field would resemble the average lattice in outline, so CV behaviour in some ways similar to that for a perfect lattice might be expected. In our present tilt setting, the effective size-effect-strain scattering potential would be arrayed in broadened distorted 'planes' somewhat analogous to the operating average-lattice (111) planes, with corresponding SES 'scattering factors'.

Since at these temperatures the SES in the 333 disc is very weak, we assume the SES is at its maximum near the 222 reflecting position. Using Bethe's second approximation, we now demonstrate how the Bragg elastic term $U(1)$ may be combined with $U_s(1)$ and $U_s(2)$ to give a SES degeneracy, where these represent the 111 and 222 SES scattering factors.

In this notation, if we truncate the Bethe series after the second term (giving 15% accuracy for the V_c prediction), the condition for the AL 222 CV degeneracy [(1)] now reads $U(2) = Rd^2[U(1)]^2$. The simplest combination of diffuse and Bragg beams giving a 222 SES degeneracy is displayed in Fig. 4. The corresponding Bethe-series expression is then

$$U_s(2) = Sd^2 U_s(1) U(1), \qquad (2)$$

where $S = 1 + eV_s/m_0c^2$ and V_s is the SES critical voltage.

If we use Cowley's (1965) expression for the scattering potential of the strain field and take its Fourier transform, $U_s(g)$ will be proportional to $gU(g)$ (Cowley & Fields, 1979), so that from substitution into (2) we obtain $2U(2) = Sd^2[U(1)]^2$ and $S = 2R$. Since for the average lattice $V_c = 305$ kV, the SES degeneracy would set in at a voltage in excess of 1 MeV, well outside the 25 kV 'window' near 305 kV. So, while CV degeneracy appears a possibility for the SES, it does not affect our present experiments. The foregoing discussions regarding degeneracies in the average-lattice and SES diffuse scatter appear to indicate, then, that the observed gross asymmetry switch (but not the relative intensities) may be interpreted kinematically.

Discussion

The SES switch, it seems, must reflect a transition of some kind between the two states of strain. The asymmetry result for the 20 min anneal appears to agree with the corresponding X-ray determination for size-effect scattering in this alloy (Borie & Sparks, 1964). In the present preliminary experiments, however, we are not in a position to identify with certainty the state of the Cu-16·7 at.% Al specimens after annealing for 2 min, except to say that it is consistent with several other investigations indicating that Suzuki atmospheres may occur in this alloy after similar heat treatments. In such a Suzuki atmosphere, the average {111} interplanar spacings would probably be slightly

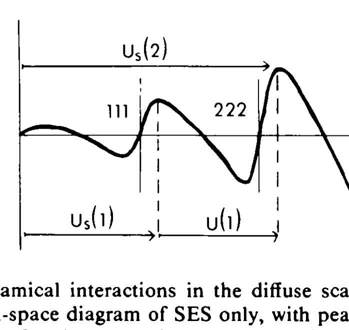


Fig. 4. Dynamical interactions in the diffuse scatter. Schematic reciprocal-space diagram of SES only, with peaks on the high-angle side of each Bragg reflecting position (continuous vertical lines). Abscissa corresponds to increasing wave vector in [*hhh*] direction: ordinate is arbitrary intensity scale. $U(g)$ and $U_s(g)$ values represent strength of respective contributing Bragg elastic and diffuse interactions in truncated Bethe-series expression.

larger than that of the matrix owing to their higher aluminium concentrations, so the diffuse scattering peak would be found at a slightly lower angle than the Bragg reflection position, in agreement with our observation. This accords with the Suzuki lock interpretation of Epperson, Fürnrohr & Ortiz (1978) for their X-ray results, and with the transitory increase in mechanical strength noticed by Saarinen (1968) and Chirikov (1972) on subjecting α-CuAl to heat treatments similar to our 2 min anneal.

Quenching from 723 K was found to be sufficient to produce plastic deformation in a Cu-14·76 at.% Al alloy specimen 22 mm wide and 3 mm thick (Epperson, Fürnrohr & Ortiz, 1978) but may not be when an imperfect *in situ* 'quench' is made of an electron-microscope specimen, as in our case.

From the results of their analysis of the temperature behaviour of Shockley partial dislocations in Cu-13·43 at.% Al, Saka, Sueki & Imura (1978) concluded that no definitive evidence could be found for the existence of a Suzuki effect, but their annealing times were all much longer than 2 min, which is thought to correspond to the time constant of the 'rapid process' observed in this alloy system in the study of the order/disorder kinetics of notionally inhomogeneous phases conducted by Trieb & Veith (1978).

A careful series of electron diffraction patterns from several short-anneal specimens taken near the matrix critical voltage (possibly including imaging and energy filtering) is likely to help clarify the situation.

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References

BETHE, H. A. (1928). *Ann. Phys. (Leipzig)*, **87**, 55-129.

BIRD, D. M., WALMSLEY, J. C. & VINCENT, R. (1984). *Inst. Phys. Conf. Ser. No.* 68, pp. 41-42.

BORIE, B. & SPARKS, C. J. (1964). *Acta Cryst.* **17**, 827-835.

CHIRIKOV, N. V. (1972). *Phys. Met. Metallogr. (USSR)*, **33**, 161-163.

COWLEY, J. M. (1965). *Proc. Int. Conf. Electron Diffraction and the Nature of Defects in Crystals, Melbourne*, paper J-5. Australian Academy of Science, Melbourne.

COWLEY, J. M. & FIELDS, P. M. (1979). *Acta Cryst.* **A35**, 28-37.

DAVID, M., GEVERS, R. & STUMPP, H. (1985). *Acta Cryst.* **A41**, 204-206.

EPPERSON, J. E., FÜRNROHR, P. & ORTIZ, C. (1978). *Acta Cryst.* **A34**, 667-681.

MATSUO, S. & CLAREBROUGH, L. M. (1963). *Acta Metall.* **11**, 1195-1206.

METHERELL, A. J. F. & FISHER, R. M. (1969). *Phys. Status Solidi*, **32**, 551-562.

MOODIE, A. F., SELLAR, J. R., IMESON, D. & HUMPHREYS, C. J. (1977). *J. Electron Microsc. Suppl.* **26**, 191-194.

MOZER, B., KEATING, D. T. & MOSS, S. C. (1968). *Phys. Rev.* **175**, 868-876.

SAARINEN, A. V. A. (1968). *Acta Polytech. Scand. Chem. Ind. Metall. Ser. A*, **77**, 7-86.

SAKA, H., SUEKI, Y. & IMURA, T. (1978). *Philos. Mag.* **A37**, 273-289.

SELLAR, J. R., IMESON, D. & HUMPHREYS, C. J. (1980). *Acta Cryst.* **A36**, 686-696.

SUZUKI, H. (1952). *Sci. Rep. Tohoku Univ.* **A4**, 455-463.

THOMAS, L. E. & HUMPHREYS, C. J. (1970). *Phys. Status Solidi A*, **3**, 599-615.

TRIEB, C. & VEITH, G. (1978). *Acta Metall.* **26**, 185-196.

WARREN, B. E., AVERBACH, B. L. & ROBERTS, B. W. (1951). *J. Appl. Phys.* **22**, 1493-1496.

WATANABE, D., UYEDA, R. & FUKUHARA, A. (1968). *Acta Cryst.* **A24**, 580-581.

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Grain Boundaries in Sintered $YBa_2Cu_3O_{7-\delta}$

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Abstract

High-resolution electron microscopy has been carried out on grain boundaries of 92% dense $YBa_2Cu_3O_{7-\delta}$ in the tetragonal form. Grain boundaries were found to be predominantly parallel to (001) of one of the adjacent grains. No amorphous interlayer was observed at the grain boundaries. At some grain boundaries highly localized strains were detected.

Introduction

$YBa_2Cu_3O_{7-\delta}$, prepared using different routes (oxides, nitrates, oxalates), shows a density in the range of 50-70%. Because this material is very brittle an obvious goal is to densify the material as much as possible. Another reason for densification is a decrease in decomposition which was found to start at the surface (Zandbergen, Gronsky & Thomas, 1988).

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