# A Brief Review of the Properties of Ordered Alloys

# J. B. COHEN

Department of Materials Science, Northwestern University, Evanston, Illinois, USA

# Received 25 April 1969

It is the purpose of this brief paper to review the understanding of many of the properties of ordered alloys, particularly with regard to critical problems which remain unsolved.

#### Introduction

There have been some very recent theoretical developments that suggest that it should now be possible to compare theory and experiment in a number of areas concerning ordering. It is hoped this review will stimulate this comparison.

In what follows it will be seen that most of the recent developments allow quantitative comparisons to the usual two parameters describing order, the long-range order parameter S and the local-order parameter a. For an ordered alloy with two sublattices:

$$S = r_1 - w_2 \tag{1}$$

where r is the fraction of sublattice 1 occupied by the correct kind of atoms and  $w_2$  is the fraction of sublattice 2 wrongly occupied.

$$a_{lmn} = 1 - \frac{P_{\rm AB}{}^{lmn}}{x_{\rm B}}$$

where  $P_{AB}^{lmn}$  is the probability of a B atom next to an A atom in the shell described by the translations  $l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$ , and  $x_B$  is the atomic fraction of B atoms—the random probability. ( $a_{lmn}$  is sometimes abbreviated as  $a_i$  where *i* is the number of a co-ordination shell.)

We shall discuss here only homogeneous alloys, although there are some very interesting effects associated with the presence of ordered particles in a disordered matrix. Also, longperiod superlattices will not be discussed.

There is extensive literature concerning the nature of ordering, including many reviews. These are listed in [1-38]. It is assumed that the reader is familiar with the general nature of ordering, and the concept of antiphase domain boundaries (APDB). Whenever possible, reference will be made to the reviews rather than the 1012

original paper, so that the reader can pursue any area more extensively. The bibliography is arranged according to topic.

#### 1. Plastic Deformation

## 1.1. Dislocation Arrangements

When an alloy with only local order is deformed, the passage of dislocations across a slip plane reduces the local order across this plane by about 20%, but does not destroy it completely. This is illustrated in fig. 1, which shows the neighbours to a slipping atom and the change in short-range order during slip. Because of the oscillations of the order parameters, the second dislocation through a region will move at a lower stress than the first for say, Cu-14 at. % Al, or it will release energy, as shown for Cu<sub>3</sub>Au. Hence, it will move more quickly under a given stress than the first; dislocations should appear in co-planar groups of two or three. This may well be the cause of co-planar groups of dislocation in many alloys, rather than a low fault energy [101]. When there is long-range order, the oscillations are identical, not damped, and this, of course, leads to the well known superlattice dislocation [34]. A sharp change in dislocation grouping is therefore not expected at the critical temperature. However, it is still not understood why dislocations in the  $DO_3$  structure,  $Fe_3Al$ , are not paired [37, 72].

For *local* order, the tendency of dislocations to be in pairs or groups *has* been verified experimentally, by Thomas [49] with *a*-brass, by Swann and Nutting on a Cu-Al alloy [44] and for Ni<sub>3</sub>Fe by Y. Calvayrac and M. Fayard [56] (see also [52, 57]). This grouping should not occur for clustering [50] and thus it could be a useful tool for detecting the presence of shortrange or long-range order. In alloys with long-

© 1969 Chapman and Hall Ltd.

range order, dislocation pairs (superdislocations) cross-slip and extend widely on planes with the lowest antiphase boundary energy [42, 53, 54, 55], fig. 2. This cross-slip process is thermally activated [59]; as shown in fig. 3 the amount of  $\{100\}$  boundary produced by deformation decreases with temperature. For the  $L1_2$  structure (Cu<sub>3</sub>Au) the lowest energy should be on a  $\{100\}$  plane, because no first-neighbour bonds are broken across such a plane [42]. Curiously, however, even for this superlattice the anisotropy of this energy varies from one alloy to another.



 $\begin{array}{c}
B\\
A\\
D\\
C\\
(111)\\
(100)\\
(100)\\
(111)\\
(111)\\
(111)\\
0:2\mu\\
\end{array}$ 

Figure 2 Electron micrograph showing paired dislocations in ordered Cu<sub>3</sub>Au after a tensile strain of 5% at 298° K. At A and D paired dislocations (super dislocations) move from {111} to {100} planes. From D. E. Mikkola, Ph.D. thesis, Northwestern University (1964).

It is large in  $Cu_3Au$  so that the boundaries produced on ordering are largely on {100}, but this is not the case for Ni<sub>3</sub>Al or Ni<sub>3</sub>Fe [56].



*Figure 1* Destruction of local-order by slip in fcc alloys. (a) The path followed by a slipping atom, and the neighbours to this atom before slip. (1 = first neighbour, etc.) (b) (c) Changes in  $\alpha_i$ , and  $\alpha_i$  across the slip plane ( $\alpha_i$ , sp) with number of units of slip, *n*. Calculations made with measured local-order parameters. From J. B. Cohen and M. E. Fine, *J. Phys. Radium* **23** (1962) 749.



Figure 3  $\gamma$  ( $\blacktriangle$ ), the {111} antiphase domain boundary probability, and  $\eta$  ( $\blacksquare$ ) the {001} antiphase domain boundary probability, versus strain in tension of polycrystalline Cu<sub>3</sub>Au. The amount of {001} boundary decreases with the temperature of deformation, indicating that the presence of dislocations on {001} planes at room temperature is thermally activated. From D. E. Mikkola and J. B. Cohen, *Acta Met.* 14 (1966) 105.

For B2 structures ( $\beta$ -brass), the boundary energy is thought to be more isotropic than for  $L1_2$ , although the lowest antiphase boundary energy is on {110} planes [42], antiphaseboundary energy does not seem to control slip systems [60]. For  $L1_2$  structures, more random dislocation arrays are produced for moderate deformations than for pure metals, or locally ordered alloys [59], but for B2 alloys slip is less "wavy" on ordering [37].

Because a dislocation requires a considerable stress to extend in an alloy with order, either local or long-range order might be expected to increase the stacking fault energy [35]. However, there may be long-range energetics involved [40]; a fault is a hexagonal region and the associated Brillouin zone interacts with the fcc Fermi surface in directions where there are "necks". Ordering produces a new Brillouin zone within the first zone of the disordered alloy. This can be expected to reduce the necks, because more electrons have their energy lowered than raised. Then, this long-range interaction should reduce the fault energy. There is, in fact, a correlation of observed fault probability for pure metals and 1014

the "necks" in the Fermi surface [46]. Also, more faults are observed in Cu<sub>a</sub>Au with longrange order (which causes new Brillouin zones) than in Cu<sub>a</sub>Au with local-order, using to detect the faults both X-ray diffraction on heavily deformed samples [46] and electron microscopy on lightly deformed samples [48]. The measured fault energy is found to be lower in ordered  $Cu_aAu$  [63] and a transition to a  $\alpha$ -brass texture occurs at intermediate deformations of the ordered alloy, but not for quenched Cu<sub>3</sub>Au [74]. (Such a transition is thought to occur only when the fault energy is low.) However, more faults have been detected (with X-rays) in filings of Cu-14 at. % Al containing high local-order prior to filing than when the alloy has little local-order [46], but Tisone, Brittain, and Meshii [67] have shown that the measured fault energy is *highest* when local-order is greatest. (See also [58].) For fig. 4 (taken from their work), faults were produced by quenching from



Figure 4 Stacking fault energy vs. quenching temperature (quenching prior to creating faults by deformation at room temperature). Cu-14.4 at. % Al. From T. C. Tisone, J. O. Brittain, and M. Meshii, *Phys. Stat. Sol.* 27 (1968) 185.

various temperatures. There is a minimum in fault energy as a function of quenching temperature. It is well known in this alloy that localorder is lowest for a quench from an intermediate temperature. For higher quenching temperatures, vacancies cause extensive ordering during or just after the quench [85].

In  $Ni_3Mn$ , in contrast to  $Cu_3Au$ , the fault energy increases on ordering [43].

This state of confusion may indicate that effects other than changes in order are causing the variations in fault energy – changes in impurity level or losses in alloying elements on annealing, or simply more subtle effects than those so far considered.

# 2. Mechanical Behaviour

Numerous specific mechanisms have been proposed for the strength and work-hardening of ordered alloys and these are reviewed in [34–38]; but as yet the picture is far from complete. Only the yield drop seems to be connected with local-ordering according to work on Cu-Al and Ag-Au alloys (see [35, 75, 76]). In this connection Cohen and Fine [35] have derived an equation for the yield stress in terms of the short-range order parameters. This equation can be used for alloys with either longrange or short-range order and has the advantage that details of the atomic configuration, whether these are regions of ordering, antiphase domains etc, are automatically included. In effect, over the length of dislocation in a material it is the average atomic configuration (expressed by the alphas) that is important. Following Clapp and Moss's procedures for obtaining data on the interaction energies from  $T_c$  and measurements of local-order at one temperature [61], these parameters can be calculated for various temperatures, at least above  $T_c$ , to predict strength versus temperature.

There has not yet been a good test of the significance of this formulation. A study of the yield strength of an alloy single crystal whose local-order has been measured would be a useful contribution. Only data from different sources and different heat-treatments can be compared at the moment.

For alloys with long-range order, there are three proposed mechanisms for work-hardening: (i) In the presence of an antiphase domain structure, moving dislocations (even if they are paired) will create new domain boundaries, by cutting APDB on intersecting planes, and hence one might expect a contribution to workhardening [42]. However,  $L1_2$  type alloys (Cu<sub>3</sub>Au, Ni<sub>3</sub>Fe) appear to have a lower workhardening rate when the domain size is small [70]. Furthermore, as Schoeck has pointed out [77], considerable activity on secondary slip systems would be required to increase the boundary area on the primary system, and hence the work-hardening but very little slip on secondary systems has been detected in the deformation of these alloys [66, 70].

(ii) Movement of portions of superdislocations to planes of lower APDB energy has been

thoroughly documented and discussed [37, 38, 54, 59, 60, 64]. This should lock dislocations and make further deformation more difficult. In support of this, for FeCo, slip becomes less wavy on ordering, and for Cu<sub>3</sub>Au, slip lines are more uniformly distributed [37]. For Cu<sub>3</sub>Au, over the temperature range room temperature to  $77^{\circ}$  K, as discussed in the previous section, there is a very large decrease in the amount of such motion [59], and there is evidence for a *decrease* in work-hardening [60]. The presence of a "locked primary forest" at room temperature could explain the low activity of secondary systems. Since the yield stress of an ordered alloy with large domain size is lower than for an alloy with small domain size [39], for small sizes there will be more activity on the primary system before secondary systems become active, than when the size is large, and hence there are more strong barriers to secondary slip. Reduced activity on secondary systems will lead to lower workhardening for small domain sizes.

(iii) Non-aligned jogs in a superdislocation produce a tube of antiphase domain boundary [45, 47, 68, 70, 73]. Dark lines seem to trail behind dislocations in ordered alloys [59, 60], but a much more detailed study of these is required to know if they are indeed such tubes. This mechanism can explain the low activity of secondary systems and the variation in workhardening with domain size [71] as well as (ii). Both can also explain the large hysteresis in mechanical properties reported by Kear [53, 73].

It is interesting to remark that although we do not as yet know which of the two mechanisms, (ii) or (iii) is more important, the domain boundary itself does not seem to play a direct rôle.

Despite our lack of understanding of the mechanisms involved, there are many remarkable changes in mechanical properties of alloys associated with ordering. The ductile-to-brittle transition temperature of FeCo alloys (B2 structure) is raised 500° C [37, 38]. The variation of strength with grain size can increase almost by a factor of two in  $Ni_3Mn(L1_2 \text{ structure})$  [37]. Because of the more random dislocation arrays, this alloy's fatigue life is greater when long-range order is present as compared to only local-order, while the opposite is true of FeCo because of its more brittle behaviour on ordering [37, 68, 69]. The temperature dependence of the yield strength of FeCo alloys drops drastically on ordering [37], when easy cross-slip is no longer possible. There is a marked strain-aging effect in  $Ni_3Fe$  [36]. Recrystallisation is retarded [36].

For the hexagonal structure  $Mg_3Cd(DO_{19})$ the yield stress for basal slip increases on ordering, but that for prismatic slip decreases [65]. *The reasons for these opposite changes are not yet clear*. For polycrystalline specimens of this alloy, the texture produced in fabricating specimens produces basal planes parallel to the tensile axis. Because of this, and the larger number of prismatic slip systems compared to basal slip systems, ordering *reduces* the apparent strength of polycrystalline Mg<sub>3</sub>Cd. There is a large effect of order on diffusion [22], and hence creep properties are altered on ordering [36].

One of the features of changes in strength during long-range ordering is the maximum that occurs just below  $T_c$ , regardless of the crystal structure or whether the test is made at temperature or after quenching [36, 371. Originally this was explained by Cottrell [34] as being due to the creation of a domain boundary by dislocations. The work done to create a new boundary by slip intersecting the old boundary is proportional to the domain size ( $\epsilon$ ). The maximum work occurs for a slip distance half the domain size; further slip reduces the number of bonds broken. Equating this maximum work to the difference in volume of boundary before and after slip:

$$\sigma \, \frac{\epsilon}{2} = \frac{\gamma}{2} \, \left\{ 1 - \left[ 1 - \left( \frac{\epsilon - t}{\epsilon} \right)^3 \right] \qquad (1)$$

The above equation with an antiphase boundary energy ( $\gamma$ ) of 75 ergs/cm<sup>2</sup> leads to a rise for Cu<sub>3</sub>Au of about 5 kg/mm<sup>2</sup> to 6 kg/mm<sup>2</sup> on ordering at 350° C, before a fall to 3 kg/mm<sup>2</sup> at large domain sizes [39]. Correcting for variation in strength due to increase in longrange order with annealing time does not appreciably alter this domain size dependence [39]. This approach also assumes domains are all touching at short times – i.e. that all of the alloy is ordered to some degree. There is no conclusive evidence as yet for this, and some good electron microscopy or field ion-microscopy would be useful here.

Because of the fact that domain-intersection does not appear to be at all important in workhardening of ordered alloys, perhaps it has no large effect on the changes in yield strength during ordering. Stoloff and Davies [37] have suggested that the rise in strength with increasing degree of order is associated with unpaired dislocations (and with particle-hardening due to separate ordered regions), the fall in strength being associated with dislocation pairing to form superdislocations. This cannot be the case, because pairing occurs even where there is only local-order, above  $T_c$ , and also because in Fe<sub>3</sub>Al ( $DO_3$  structure) no pairs are observed even with full order, but the maximum in strength still occurs. At least six possibilities still remain:

(i) "Particle"-hardening: owing to the variation in APDB energy with order, cutting of ordered regions in a locally ordered matrix will become more difficult as order increases; strength will fall when the regions become large, and dislocations can bow between them (before impingement).

(ii) The strength of the locking of dislocations that have cross-slipped on to  $\{100\}$  planes will vary with the order parameter, S. It is not clear, however, how this would lead to a maximum in strength.

(iii) A change in the facility of APDB tube production with order.

(iv) A change in the energy (and/or the type) of antiphase boundary with degree of order. There is evidence for both effects [78, 79].

(v) The order at APD boundaries produced by annealing is quite different from that at a thinner APD boundary produced by slip, as has been pointed out. As a result of this difference in order, Brown [41] showed that there is drag on a dislocation. Popov *et al* [62] estimated this for  $Cu_3Au$ , and for temperatures just below  $T_c$ obtained an increase in strength of 4 kg/mm<sup>2</sup>, the right order of magnitude.

(vi) There is an atomic displacement at antiphase boundaries – both those produced by annealing and those produced by slip [22, 59]. The material is divided into regions whose boundaries have a different lattice parameter. As it turns out, Cahn [51] has developed equations for strengthening for a similar situation-spinodal decomposition: Let A be the maximum change in composition at the boundary  $\approx 0.75^*$ ,  $\eta =$  $\partial \ln a_0/\partial x_A$ ,  $\beta = 2\pi/D$  where D/2 is the domain diameter. Then dislocations can curl around the boundary if  $A\eta/b\beta > 1$ . Beyond this value the yield stress will fall as  $\beta$  decreases. For less than this value, the dislocation will not conform to the strain at the domain boundaries, but will

\*The boundary for  $Cu_3Au$  could be all Au, compared to an average atomic fraction of Au = 0.25. 1016 only bend slightly. Maximum strength occurs when this quantity = 1. For Cu<sub>2</sub>Au,  $b \simeq 2.65$  Å. Therefore the critical value of D/2 is about 80 Å. This is of the right magnitude, although an excessive concentration at the boundary has been assumed.

Much work is also needed before we can understand the role of order in determining the yield strength.

# 3. Internal Friction

Welch and LeClaire [82] have recently reexamined the explanation for Zener relaxation, for alloys with local-order (or clustering). Under stress, certain directions are thought to become more favourable for local-ordering than other directions. These authors utilised a theory involving local-order parameters rather than the first-neighbour quasichemical approach first employed, and showed that the anisotropy of relaxation strength and its temperature dependence could be qualitatively explained, considering first and second neighbour bonds rather than just the first. This agrees with a suggestion by Nowick and co-workers [80, 81]. If only first neighbours were important in a bcc alloy, there should be no relaxation for a tensile stress in a  $\langle 100 \rangle$  direction; this direction makes equal angles with all  $\langle 111 \rangle$  directions between first neighbours and therefore one direction is not made more favourable than any other. For a stress in a  $\langle 111 \rangle$  direction there should be a relaxation. The opposite asymmetry has been found [80, 81] which can be qualitatively explained by the new treatment.

For quantitative comparisons, this treatment of Welch and LcClaire requires knowledge of the "alphas" and  $(\partial V_i/\partial r)^*$ . From the theory of Clapp and Moss [61], an X-ray study could provide both pieces of data, and this should be an interesting experiment!

# 4. Electrical Behaviour

There are now well-developed theories for the change in electrical resistivity with long-range and short-range order [83, 84]. The results of Asch and Hall [84] are in terms of the local-order parameters, and some of the complicated integrals required have been evaluated [86]. There has been very little in the way of experimental work to test or utilise these developments. Ordering can, however, increase or decrease the resistivity [83], although clustering will always  $*V_i$  is the bond energy of pairs  $i^{\text{th}}$  shell apart.

lead to an increase for small cluster sizes.

# 5. Magnetic Effects

In many ordered alloys involving transition elements it appears that magnetic behaviour can be reasonably well understood in terms of a near-neighbour ferromagnetic coupling between like atoms, and a higher-neighbour superexchange when another species intervenes between the two. Ordered  $Pt_3Fe(L1_2)$  is antiferromagnetic, but as extra Fe is added, and there is a reasonable chance for Fe atoms to be near neighbours, the alloy becomes ferromagnetic [91]. FeAl alloys are ferromagnetic until a composition of 28 at. % is reached. Above 33 at. %, alloys are antiferromagnetic at low temperatures, but paramagnetic at room temperature. In the transition range alloys are ferromagnetic at room temperature and antiferromagnetic at low temperatures [89]. In this system, antiferromagnetism occurs only in the ordered alloys, and only in those with the B2structure, not in those with the  $DO_3$  structure. Furthermore, the alloys can be made partially or completely ferromagnetic at room temperature by deformation [94], which increases the number of Fe-Fe pairs.

Bunge and Müller [87], Chikazumi and coworkers [88, 90] and Chin [93, 95] have studied the effects of slip, in creating like pairs, on magnetic anisotropy, for L1<sub>2</sub> and B2 structures. From the state of stress and the known slip systems, predictions can be made as to the directions of easy magnetisation. This is particularly important, for example, in Permalloy tapes (Ni-base alloys with about 17 % Fe and 4% Mo). Either a hard axis or a soft axis along the tape is desired for a square hysteresis loop, and whether this will occur can be predicted, knowing the initial texture, the mode of deformation, any intermediate anneals, etc. The theory predicts different effects when either long-range or short-range order is present. For example, when an FeNi alloy is cut to a (110) plane and deformed in plane compression so that the material can extend in a  $[\overline{1}12]$  direction, the predicted easy direction of magnetisation should be near [111] for alloys with long-range order but near [110] for alloys with only local-order [93]. This has been confirmed by experiment [95]. Just as with stress, the application of a magnetic field during annealing apparently leads to magnetic anisotropy (see [36] for a more extensive discussion of this phenomenon.) However a direct proof of this being due to ordering in preferred directions, through, say, the change in diffuse X-ray scattering, is still lacking.

It has been demonstrated that atomic pictures of the regions of local-order or clustering can be obtained directly from only the first two to three measured local-order coefficients, without any assumptions [92]. Such three-dimensional maps provide a simple understanding of the nature of short-range or partial long-range order [22], and can be particularly useful in understanding magnetic properties. To illustrate this, one of my associates, Mr Pronob Bardhan, made a detailed analysis of such pictures for Cu<sub>0.525</sub> Ni<sub>0.475</sub>; a careful study of local-order (clustering in this case) has been carried out [96] to provide the input data. There is considerable interest in the magnetic behaviour of this solid solution, and in a recent paper, Hicks et al claimed to have found large magnetic clusters which were regions of like spin [98]. They felt that these could not be Ni clusters, because only  $\alpha_1$  was appreciably different from zero. The fact that  $a_2, a_3$ , etc, were near zero meant, they suggested, that the only clusters of Ni present did not extend beyond the first-neighbour shell around any Ni, whereas the spin clusters they found were much larger. Unfortunately, the local-order parameters are not so easy to interpret directly [22].

Most of the quantitative results from the computer pictures for this alloy are presented in table I and fig. 5. The alloy contains rods and two and three dimensional plate-like clusters of Ni on {111} planes, two such regions often crossing (see [22] for such a picture). The average Ni cluster contained 27 atoms compared to 14 to 15 found by Hicks et al from the magnetic neutron scattering and initial moment (about 8 to 9  $\mu_{\beta}$  per cluster, divided by 0.6  $\mu_{\beta}$  per Ni atom. The actual number would be higher and in better agreement as the surface atoms have a lower moment (see [99] for detailed calculations based on this idea).\* They estimated the spacing of clusters at 48 at. % Ni to be 13.5 Å. From the computer pictures, there are  $6 \times 10^{20}$  Ni clusters/cm<sup>3</sup> which means an average spacing of 11.7 Å.

Kidron [97] has reported small-angle X-ray scattering from about the same alloy composition

 TABLE I Results on Cu<sub>0.525</sub>Ni<sub>0.475</sub> from computer simulation of local-order with 4000 atoms

Shell	Experimental short- range order parameters [96]	From computer (406 jumps from a random alloy) given only $\alpha_1$ ,
		a <sub>2</sub> , a <sub>3</sub>
1	+0.121	+0.1210
2	0.007	-0.0068
3	+0.011	+0.0114
4	+0.011	+0.0602
5	-0.0025	+0.0139
6	+0.004	+0.0003
	· · · · · · · · · · · · · · · ·	
	Number of first-neighbour triplets and	
	Cu-Cu-Cu-4860	
	Cu-Ni-Ni-11068	

Ni-Ni-Ni-6096 Cu-Cu-Cu-Cu-780 Cu-Cu-Cu-Ni-1740 Cu-Cu-Ni-Ni-2378 Cu-Ni-Ni-Ni-2104 Ni-Ni-Ni-Ni-998

and the spacing from the maximum in his reported small-angle pattern is 30 Å. The radius of spherical particles estimated from his data is 4.9 Å. If the computer results are used to synthesise a small-angle pattern, assuming the rods and plates would appear as spheres generated by their largest dimension (due to multiple orientations of the regions to the X-ray beam) a radius of 13.7 Å results. It appears that the magnetic behaviour of this alloy can be well explained by Ni clusters, although more work of this kind at other compositions is needed. The computer models predict that the diffuse scattering from this alloy should contain streaks in  $\langle 111 \rangle$ , and there should be same magnetic anisotropy.

The combined study of magnetic phenomena and local atomic arrangements through these atomic pictures promises a more thorough understanding of superparamagnetism and other magnetic phenomena in alloys and ceramics.

## 6. Corrosion

It seems appropriate, in a sense, to finish at the beginning, as the main purpose of this review was to highlight areas we are only beginning to

\*For the same alloy run in the computer to near randomness ( $\alpha_1 = \alpha_2 = \alpha_3 = 0.00$ ) there were, of course, clusters, and many of these were plates. But they were always two-dimensional and with an average of 9 to 10 atoms. 1018



*Figure* 5 Distribution of Ni atoms in  $Cu_{0.525}Ni_{0.475}$  having *n* Ni atoms as first neighbours, for a computer model of 4000 atoms, compared to the random distribution. The techniques in [92], with the data in [96] were employed. The distribution for a random alloy was calculated from the binomial theorem: the number of Ni atoms in a 4000 atom mode having *n* first neighbour Ni atoms,  $N_{Ni}^{n}$ , is:

$$N_{\rm Ni}^{\ n} = 1900 \left( X_{\rm Cu} \right)^{12-n} \left( X \right)_{\rm Ni}^{\ n} \begin{pmatrix} 12 \\ n \end{pmatrix}$$

understand. Tammann suggested long-range order as an explanation for the peculiar resistance to acids of certain CuAu alloys [100]. Today, local-order is thought to play an important role in stress-corrosion. As is well known, any phenomenon that causes planar arrays of dislocations in an alloy, increases its susceptibility to stress-corrosion cracking. Low fault energy leads to planar arrays. But even if the fault energy is high, planar arrays may be produced by local-order as was explained in section 2.1. This *may* explain the susceptibility of some of the stainless steel alloys [101].

## Acknowledgement

It is a pleasure to acknowledge the support of the US National Science Foundation in preparing this review. Professor P. A. Beck stimulated our interest in the magnetic behaviour of Cu/Ni alloys.

#### References

## Reviews

Books

- 1. E. W. ELCOCK, "Order-Disorder Phenomena" (Methuen, London, 1956).
- 2. M. A. KRIVOGLAZ and A. A. SMIRNOV, "The Theory of Order-Disorder in Alloys" English edition (American Elsevier Publishing Co, New York, 1965).
- Proc. 3rd AIME Bolton Landing Conference (Sept. 1969) to be published.

#### Introductory Articles

- 3. F. C. NIX, J. Appl. Phys. 8 (1937) 783.
- 4. C. S. BARRETT, Metals and Alloys 8 (1937) 251.
- 5. F. C. NIX and W. SHOCKLEY, Rev. Mod. Phys. 10 (1938).
- 6. F. SEITZ, "The Modern Theory of Solids" (McGraw-Hill, New York, 1940).
- 7. C. E. BIRCHENALL, in "Thermodynamics in Physical Metallurgy" (ASM, Cleveland, Ohio, 1950) pp. 144-160.
- 8. H. LIPSON, Progr. in Metal Phys. 2 (1950).
- 9. s. SIEGEL, in "Phase Transformations in Solids" edited by R. Smoluchowski (Wiley, New York, 1950) pp. 366-386.
- C. S. BARRETT and T. B. MASSALSKI, "Structure of Metals" 3rd edition (McGraw-Hill, New York, 1966) ch. 11.

#### Particularly Non-Metallics

- 11. M. J. BUERGER, Anais., Acad. Brasil, Cienc. 21 (1949) 245.
- 12. R. COLLONQUES, Ann. Chim. 8 (1963) 395.
- H. JAGODZINSKI, in "Advanced Methods of Crystallography" (Academic Press, New York, 1964) p. 181.

## Mainly Thermodynamics

- 14. R. H. FOWLER and E. A. GUGGENHEIM, "Statistical Thermodynamics" (Cambridge University Press, London, 1949).
- 15. E. A. GUGGENHEIM, "Mixtures" (Oxford University Press, New York, 1952).
- 16. G. H. WANNIER, Rev. Mod. Phys. 25 (1953) 353.

- 17. G. F. NEWELL and E. W. MONTROLL, *ibid* 25 (1953) 353.
- 18. T. MUTO and Y. TAKAGI, Solid State Physics 1 (1955) 194.
- 19. L. GUTTMAN, ibid 3 (1956) 145.
- 20. C. DOMB, Adv. in Phys. 9 (1966) 149.
- 21. H. SATO, to be published in Physical Chemistry 10.
- 22. J. B. COHEN, in "Phase Transformations" (ASM, Cleveland, Ohio, in press).

#### Antiphase Domains

 M. J. MARCINKOWSKI, in "Electron Microscopy and Strength of Crystals" (John Wiley, New York, 1963) p. 333.

#### Long Period Superlattices

- 24. H. SATO and R. S. TOTH, in "Alloying Behavior and Effects in Concentrated Solid Solutions" edited by T. B. Massalski (Gordon and Breach, New York, 1965).
- 25. H. SATO, R. S. TOTH, and G. HONJO, J. Phys. Chem. Solids 28 (1967) 137.
- 26. H. SATO and R. S. TOTH, Bull. Soc. Fr. Miner. Cryst. 91 (1968) 557.

#### Primarily Diffraction Studies

- 27. B. W. WARREN and B. L. AVERBACH, in "Modern Research Techniques in Physical Metallurgy" (ASM, Cleveland, Ohio, 1953).
- B. L. AVERBACH, in "Theory of Alloy Phases" (ASM, Cleveland, Ohio, 1956).
- 29. W. W. BEEMAN *et al*, in "Handbuch der Physik" edited by S. Flugge, Vol. 32 (Springer, Berlin, 1957) p. 321.
- 30. V. GEROLD, Ergebn. exakt. Naturwiss. 33 (1961) 105.
- 31. B. E. WARREN, Trans. Met. Soc. AIME 233 (1965) 1802.
- 32. C. J. SPARKS and B. BORIE, in "Local Atomic Arrangements Studied by X-ray Diffraction" edited by J. B. Cohen and J. E. Hilliard (Gordon and Breach, New York, 1966).

# 33. L. H. SCHWARTZ, *ibid*.

#### Mechanical Behaviour

- 34. A.H. COTTRELL, in "Properties and Microstructure" (ASM, Cleveland, Ohio, 1954).
- 35. J. B. COHEN and M. E. FINE, J. Phys. Radium 23 (1962) 749; Acta Met. 11 (1963) 1106.
- 36. R. W. CAHN, in "Local Atomic Arrangements Studied by X-ray Diffraction" edited by J. B. Cohen and J. E. Hilliard (Gordon and Breach, New York, 1966).
- 37. N. S. STOLOFF and R. G. DAVIES, Progr. Materials Sci. 13 (1966).
- N. S. STOLOFF, in "Strengthening Methods in Crystals" edited by A. Kelly and R. B. Nicholson (Elsevier Publishing Co, in press).

#### **Dislocations, Mechanical Properties**

39. G. J. ARDLEY, Acta Met. 3 (1955) 525. 1020

- 40. A. SEEGER, in "Report of the Conference on Defects in Crystalline Solids" (The Physical Society, London, 1955) p. 328.
- 41. N. BROWN, Phil. Mag. 4 (1959) 693.
- P. A. FLINN, *Trans. Met. Soc. AIME* 218 (1960) 145;
   S. G. CUPSCHALK and N. BROWN, *Acta Met.* 16 (1968) 657.
- 43. M. J. MARCINKOWSKI and D. S. MILLER, *Phil.* Mag. 6 (1961) 871.
- 44. P. R. SWANN and J. NUTTING, J. Inst. Met. 90 (1961) 133.
- 45. A. E. VIDOZ and L. N. BROWN, *Phil. Mag.* 7 (1962) 1167.
- 46. D. E. MIKKOLA and J. B. COHEN, J. Appl. Phys. 33 (1962) 892.
- 47. C. I. VASILYEV and A. N. ORLOV, *Fiz. Met. Metall.* 15 (1963) 481.
- 48. M. J. MARCINKOWSKI and L. ZWELL, Acta Met 11. (1963) 373.
- 49. G. THOMAS, *ibid* 1369.
- 50. J. B. COHEN and M. E. FINE, *ibid* 1106.
- 51. J. W. CAHN, *ibid* 1275.
- 52. W. BELL, W. R. ROSER, and G. THOMAS, *ibid* 12 (1964) 1247.
- 53. B. H. KEAR, *ibid* 845.
- 54. B. H. KEAR and H. G. WILSDORF, *Trans. Met. Soc.* AIME 224 (1962) 382.
- 55. B. H. KEAR, Acta Met. 12 (1964) 555.
- 56. Y. CALVAYRAC and M. FAYARD, Compt. rend. 258 (1964) 4531; Y. CALVAYRAC, Ph.D. Thesis, University of Paris, 1965.
- 57. W. BELL, P. OKAMOTO, and G. THOMAS, Acta Met. 13 (1965) 559.
- 58. K. NAKAJIMA, J. J. SLADE, and S. WEISSMANN, Trans. ASM Quarterly 58 (1965) 14.
- 59. D. E. MIKKOLA and J. B. COHEN, in "Local Atomic Arrangements Studied by Plastic Deformation" edited by J. B. Cohen and J. E. Hilliard (Gordon and Breach, New York, 1966); *Acta Met.* 14 (1966) 105.
- 60. B. H. KEAR, Acta Met. 14 (1966) 659.
- 61. P. C. CLAPP and S. C. MOSS, *Phys. Rev.* 142 (1966) 418; 171 (1968) 754, 764.
- 62. L. E. POPOV, E. V. KOZLOV, and N. S. GOLOSOV, *Phys. Stat. Sol.* 17 (1966) 903.
- 63. I. COMANZI, G. SCHIANCHI, and R. RIMINI, *Phil. Mag.* 16 (1967) 144, 1207.
- 64. S. M. COPLEY and B. H. KEAR, *Trans. Met. Soc.* AIME 239 (1967) 977, 984.
- 65. J. H. KIRBY and F. W. NOBLE, *Phil. Mag.* **16** (1967) 1009; F. W. NOBLE and J. H. KIRBY, to be published.
- 66. M. P. VICTORIA and A. E. VIDOZ, Acta Met. 15 (1967) 676.
- 67. T. C. TISONE, J. O. BRITTAIN, and M. MESHII, *Phys. Stat. Sol.* 27 (1968) 185.
- 68. K. R. JORDAN and N. S. STOLOFF, IMD-AIME Annual Meeting (1968).
- 69. C. E. FFLTNER, IMD-AIME Annual Meeting (1968).

- 70. M. P. VICTORIA and A. E. VIDOZ, *Phys. Stat. Sol.* 28 (1968) 131.
- 71. A. E. VIDOZ, *ibid* 145.
- 72. P. MORGAND, P. MOUTURAT, and G. SAINFORT, Acta Met. 16 (1968) 867.
- 73. G. SCHOECK, Scripta Met. 2 (1968) 283.
- 74. E. A. STARKE JR, J. C. OGLE, and C. J. SPARKS JR, in "Advances in X-ray Analysis" Vol. 12 (Plenum Press, New York, 1969) p. 372; *Trans. Met. Soc.* AIME, 245 (1969) 169.
- 75. J. J. SVITAK and R. M. ASIMOW, *Trans. Met. Soc. AIME* 245 (1969) 209.
- 76. R. A. KLOSKE and M. E. FINE, ibid 217.
- 77, G. SCHOECK, Acta Met. 17 (1969) 147.
- 78. G. E. POQUETTE and D. E. MIKKOLA, *Trans. Met.* Soc. AIME 245 (1969) 743.
- 79. J. R. BEELER JR, in "Int'l. Conf. on Phys. Met. of Ti" (1968), to be published.

#### Internal Friction

- 80. C. Y. LI and A. S. NOWICK, Acta Met. 9 (1961) 49-
- 81. A. S. NOWICK and D. P. SERAPHIM, ibid 40, 85.
- 82. D. O. WELCH and A. D. LECLAIRE, *Phil. Mag.* 16 (1967) 981.

#### **Electrical Resistivity**

- 83. J. B. GIBSON, J. Phys. Chem. Solids 1 (1956) 27.
- 84. A. E. ASCH and G. L. HALL, *Phys. Rev.* **132** (1963) 1047.
- 85. s. MATSUO and L. M. CLAREBOUGH, Acta Met. 11 (1963) 1195.
- 86. A. A. KATSNEL'SON and L. M. SCHEVCHUK, Fiz. Met. Metall. 24 (1967) 97.

## Magnetic Behaviour

- 87. H. J. BUNGE and H. G. MÜLLER, Z. Metallk. 48 (1957) 26.
- 88. S. CHIKAZUMI, K. SUZUKI, and H. IWATA, J. *Phys. Soc. Japan* 12 (1957) 1259; 15 (1960) 250.
- 89. A. ARROTT and H. SATO, *Phys. Rev.* **114** (1959) 1420, 1427.
- 90. N. TAMAGAWA, Y. NAGAKAWA, and S. CHIKA-ZUMI, J. Phys. Soc. Japan 17 (1962) 1256.
- 91. G. E. BACON and J. CRANGLE, Proc. Roy. Soc. A272 (1963) 387.
- 92. P. GEHLEN and J. B. COHEN, *Phys. Rev.* **139** (1965) A844.
- 93. G. Y. CHIN, J. Appl. Phys. 36 (1965) 2915; Materials Science and Eng. 1 (1966) 77.
- 94. G. P. HUFFMAN and R. M. FISHER, J. Appl. Phys. 38 (1967) 735.
- 95. G. Y. CHIN, E. A. NESBITT, J. H. WERNICK, and L. L. VANSKIKE, *ibid* 2623.
- 96. B. MOZER, D. T. KEATING, and S. C. MOSS, *Phys. Rev.* **175** (1968) 868.
- 97. A. KIDRON, *Phys. Rev. Lett.* **26a** (1968) 593; but see comments on this work by S. C. MOSS, *ibid*, in press.
- 98. T. J. HICKS, B. RAINFORD, J. S. KOUVEL, G. G. LOW, and J. B. COMLY, *ibid* **22** (1969) 531.
- 99. C. G. ROBBINS, H. CLAUS, and P. A. BECK, *ibid* 22 (1969) 1307.

#### Corrosion

- 100. G. TAMMAN, Z. anorg. Chem. 107 (1919) 1.
- 101. D. L. DOUGLASS, G. THOMAS, and W. R. ROSER, Corrosion 20 (1964) 15.

# Letters

An Electron Microscope Examination of Deformed Polycrystalline Magnesium Oxide

Metallic oxides have a wide potential in many high-temperature applications, and it is therefore important that methods are developed for the microstructural examination of these materials in the deformed state. Transmission electron microscopy has been widely used to observe dislocation configurations in ceramic single crystals; only a few reports have been published on the application of this technique to polycrystals, however, since the production of suitable thin foils is often difficult under such conditions due to substantial porosity and/or weak second phases. Argon-ion bombardment has been employed to thin some polycrystalline ceramics [1, 2] but, whilst this only slightly enlarges any © 1969 Chapman and Hall Ltd.

pores, a recent study suggests that it introduces some radiation damage [3].

In the present work, polycrystalline magnesium oxide, available from a previous investigation [4], was produced by hot-pressing MgO powder with 3 wt % LiF for 3 h at 1000° C and annealing for 3 h at 1300° C. The average grain size was  $12\mu m$ , the density was > 99.8%theoretical, and the purity was 99.98% of which the major impurity was 75 ppm Li resulting from the use of LiF as a densifying additive. To permit a study of the dislocation configurations in the deformed state, three specimens were tested in compression at temperatures of 600, 1000 and 1400° C respectively, under a constant force rate of  $1.38 \times 10^6$  dynes/cm<sup>2</sup> sec. The deformed and fractured specimens were sectioned on a diamond saw into strips of  $\sim 0.5$  mm thickness, and discs of 2.5 mm diameter were cut out ultrasonically.