The compilation and evaluation of data for the *NBS Crystal Data Identification File* has been a collaborative effort between the NBS Crystal Data Center and the following data centers: Cambridge Crystallographic Data Centre (England), the Metals Data Center (Canada), and the Inorganic Structural Data Center (Germany). The authors wish to thank Drs Judith Stalick and Antonio Santoro for critical comment on the subject matter.

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The Local Atomic Order of a Ni–12·7 at.% Al Alloy Quenched from 1323 K*

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Abstract

High-angle X-ray diffuse scattering has been measured in a volume element in reciprocal space for a Ni–12·7 at.% Al alloy single crystal quenched from 1323 K. The Cowley–Warren order parameters were determined after separation of the first- and second-order size effects, using a procedure based on the Borie–Sparks quadratic approximation of atomic displacements. The experimental order coefficients were used to reconstruct the real-space locally ordered distribution of atoms, from which the spectrum of nearest-neighbor atomic configurations was determined. Some 61% of the Al atoms were found to be in a planar ordered configuration consisting of a nickel atom and four nearest-neighbor aluminum atoms, the basic structural unit of Ni_3Al. These planar elementary ordered units were, of course, distributed on the three equivalent {100} planes. While most of the ordered 'domains' consisted of from one to three Ni_3Al rings, a few domains were found to contain on the order of a hundred such elementary ordered units. The larger ordered domains may be thought of as embryos of the ordered Ni_3Al phase which have formed during quenching of the bulk alloy single crystal. There is evidence that the spatial distribution of ordered domains is not random.

Introduction

The α-phase Ni–Al alloys are classical examples of a precipitation hardening system; there is a marked decrease in solubility of Al in Ni with decreasing temperature; a second phase forms upon suitable low-temperature heat treatment. These alloys may also properly be considered as the prototype of a class of Ni-base superalloys whose commercially desirable mechanical properties are in a large part attributable to the presence of ordered Ni_3Al-*type* precipitate par-

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ticles. The desirability and utility of understanding and being able to control the solid-state reactions in such alloy systems is apparent.

There has been some excellent work on the decomposition of the α-Ni–Al alloys; for example, see the papers by Williams (1959), by Phillips (1966) and by Ardell, Nicholson & Eshelby (1966). Nevertheless, some important gaps in our knowledge exist as illustrated by the fact that the mode of decomposition is presently not well understood. Since the work by Manenc (1957, 1959) and Bagariatskii & Tiapkin (1959) side bands have been observed in the decomposing α-phase Ni–Al alloys. While side-bands clearly signal the existence of a modulated microstructure, this observation alone is not sufficient to determine the nature of the modulations, as is sometimes erroneously assumed.

Most of the detailed research on this system has been done on samples annealed at rather elevated temperatures, say above 870 K. In this temperature regime, nucleation and growth are quite rapid. At lower temperatures, however, it is theoretically possible for decomposition to occur by a continuous process (Cahn, 1968).

Bagariatskii & Tiapkin (1959) reported occasionally seeing X-ray superlattice reflections from unaged (quenched) bulk, polycrystalline samples, and Ardell, Nicholson & Eshelby (1966) also found weak super-

X-ray diffuse scattering has been employed to characterize the local atomic structure in a Ni–12·7 at.% Al alloy single crystal quenched from within the single-phase solid-solution region (1323 K).

Diffraction theory

Within the kinematic approximation, the total coherently scattered intensity in electron units (I_{eu}) at position k in reciprocal space is given by

$$I_{eu}(\mathbf{k}) = \sum_p \sum_q f_p\, f_q \exp\,(i\mathbf{k}\cdot\mathbf{R}_{pq}), \qquad (1)$$

where f_p and f_q are the scattering factors of atoms associated with lattice sites p and q, respectively, $\mathbf{k}$ is 2π times the diffraction vector and $\mathbf{R}_{pq}$ is the interatomic vector. The summation is over all atoms irradiated by the X-ray beam. In the general case when the atoms are not confined to the lattice sites, diffuse scattering in addition to that due to the local atomic order is produced, and this must be accounted for before a quantitative analysis of the short-range order can be carried out. Borie & Sparks (1971) showed that to a second-order approximation of the atomic displacements from the average lattice sites in binary substitutional f.c.c. or b.c.c. alloys, the coherent diffuse intensity is given by

$$
\begin{aligned}
I(h_1,h_2,h_3) = {}& NX_A\,X_B(f_A-f_B)^2 \sum_l \sum_m \sum_n \alpha_{lmn} \cos 2\pi h_1\,l \cos 2\pi h_2\,m \cos 2\pi h_3\,n \\[4pt]
& - NX_A\,X_B(f_A-f_B)^2 \sum_l \sum_m \sum_n [h_1\,\gamma^x_{lmn}\cdot \sin 2\pi h_1\,l \cos 2\pi h_2\,m \cos 2\pi h_3\,n \\[4pt]
& + h_2\,\gamma^y_{lmn}\cos 2\pi h_1\,l \sin 2\pi h_2\,m \cos 2\pi h_3\,n + h_3\,\gamma^z_{lmn}\cos 2\pi h_1\,l \cos 2\pi h_2\,m \sin 2\pi h_3\,n) \\[4pt]
& - 4\pi^2 N \sum_l \sum_m \sum_n [h_1^2\langle\delta^2\rangle^x_{lmn} + h_2^2\langle\delta^2\rangle^y_{lmn} + h_3^2\langle\delta^2\rangle^z_{lmn}] \cos 2\pi h_1\,l \cos 2\pi h_2\,m \cos 2\pi h_3\,n \\[4pt]
& + 8\pi^2 N \sum_l \sum_m \sum_n (h_1 h_2\langle\delta^2\rangle^{xy}_{lmn} \sin 2\pi h_1\,l \sin 2\pi h_2\,m \cos 2\pi h_3\,n + h_1 h_3\langle\delta^2\rangle^{xz}_{lmn}\sin 2\pi h_1\,l \\[4pt]
& \times \cos 2\pi h_2\,m \sin 2\pi h_3\,n + h_2 h_3\langle\delta^2\rangle^{yz}_{lmn}\cos 2\pi h_1\,l \sin 2\pi h_2\,m \sin 2\pi h_3\,n). \qquad (2)
\end{aligned}
$$

lattice reflections in electron diffraction patterns from unaged specimens. As will be seen, no superlattice reflections were observed in the present low-resolution wide-angle X-ray investigation of an alloy quenched from the single-phase region. In a study of the mode of decomposition, it is obviously desirable that the investigation commence with the earliest stage of phase separation attainable.

High-angle diffuse scattering techniques are well suited to investigating the local atomic configurations in the *very* early stages of alloy decomposition, even before it is possible to study the system with small-angle scattering. As a first step, in a more comprehensive effort to understand the decomposition process(es) in an α-phase Ni–Al alloy, high-angle

X_A and X_B are atom fractions of species A and B, respectively, and N is the total number of atoms irradiated. Relative to an arbitrarily chosen origin, the average interatomic vector is represented by

$$\langle \mathbf{R}_{lmn}\rangle = l\,\frac{\mathbf{a}_1}{2} + m\,\frac{\mathbf{a}_2}{2} + n\,\frac{\mathbf{a}_3}{2}, \qquad (3)$$

where the triplet of integers (l,m,n) specifies a lattice site relative to the arbitrary origin, and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are translation vectors of the cubic unit cell. The continuous variables in reciprocal space (h_1,h_2,h_3) are related to the diffraction vector by the relationship

$$\left(\frac{S-S_0}{\lambda}\right) = h_1\,\mathbf{b}_1 + h_2\,\mathbf{b}_2 + h_3\,\mathbf{b}_3, \qquad (4)$$

where b_1, b_2 and b_3 are a set of vectors reciprocal to $a_1/2$, $a_2/2$, $a_3/2$, respectively, λ is the X-ray wavelength and S and S_0 are unit vectors in the directions of the scattered and incident beams, respectively. The structural information of principal interest here is contained in the Cowley–Warren order coefficients (Cowley, 1950) which are defined as follows:

$$\alpha_{lmn} = 1 - \frac{P^{A|B}_{lmn}}{X_B}, \qquad (5)$$

where $P^{A|B}_{lmn}$ is the conditional probability of finding a B-type atom at site (l,m,n) after having specified that there is an A-type atom at the local origin. The γ^i_{lmn}, $\langle \delta^2 \rangle^i_{lmn}$ and $\langle \delta^2 \rangle^{ij}_{lmn}$ ($i \neq j = x, y, z$) are the size-effect coefficients, and these contain additional structural information, provided separation of the various components represented by (2) can be performed with sufficient accuracy.

Experimental procedure

A single-crystal rod of Ni–12·6$_9$ at.% Al (chemical analysis determined following crystal growth), approximately 1 cm in diameter and 5 cm long, was grown by a modified Bridgman technique. The crystal was grown in a high-purity Al_2O_3 crucible under a protective atmosphere of argon in a high-frequency induction furnace. The starting materials were 99·998% Ni and 99·999% Al. After homogenizing for two days at 1373 K, a 3 mm thick slice with parallel (520) surfaces was prepared by spark machining. The disturbed surface layer was removed by standard mechanical polishing procedures and by etching in boiling aqua regia.

In preparation for the diffraction experiment, the sample was annealed for 1 h at 1323 K in flowing H_2 and drop quenched into water at room temperature. Again, the single-crystal sample was polished mechanically through the lapping wheel, and the final surface preparation consisted of electropolishing at 243 K in a vigorously stirred bath composed of two parts methanol and one part concentrated nitric acid by volume, with an applied potential of 25 V.

The diffuse X-ray scattering measurements were made in parallel geometry at room temperature on a partially automated Siemens diffractometer equipped with an evacuated sample chamber mounted on an Eulerean cradle. An incident-beam Warren (1954)–Chipman (1956)-type doubly bent LiF monochromator was utilized to select the Cu $K\alpha$ radiation. The detecting equipment comprised an Ortec Si(Li) solid-state counter and associated electronics with an overall energy resolution of just under 200 eV. This resolution permitted the Ni-fluorescence radiation, and other wavelength-dependent parasitic effects outside this 200 eV range, to be discriminated electronically from the Cu $K\alpha$ scattered by the sample.

The diffusely scattered intensity was measured at 1671 positions on an equally spaced rectangular grid in a volume of reciprocal space chosen so as to permit separation of the first- and second-order size effects from the local atomic order component of the diffuse intensity; the procedures used in this investigation are described more in detail by Epperson, Fürnrohr & Ortiz (1978).

Analytical procedure

The observed diffuse scattering data were converted to absolute units (electron units atom^{-1}) by comparison with the total scattering from amorphous polystyrene at $\sin \theta/\lambda = 0·5$ Å^{-1} by use of the relationship

$$\frac{I_{eu}}{N} = \left(\frac{I_{eu}}{M}\right)_p \frac{M_s(\mu/\rho)_s P_p}{M_p(\mu/\rho)_p P_p I_p} I_s, \qquad (6)$$

where I_{eu}/M is the theoretical total scattering in electron units per 'molecule' of polystyrene (C_8H_8), M_s and M_p are the molecular weights, $(\mu/\rho)_s$ and $(\mu/\rho)_p$ are mass absorption coefficients, P_s and P_p are polarization factors, and I_s and I_p are measured intensities in counts per unit time. The subscripts s and p denote sample and polystyrene, respectively. A correction for Compton-modified scattering was computed with the incoherent scattering data from Cromer (1969) and Freeman (1959) for Ni and Al, respectively. The coherent scattering factors were taken from Doyle & Turner (1968), and anomalous dispersion was corrected by using the parameters computed by Cromer (1965). Following the procedure of Warren & Mozzi (1966), a correction of 6·80%, due to double diffuse scattering, was added to the computed total single scattering from polystyrene.

The coherent diffuse scattering data were separated into the various components according to the method of Borie & Sparks (equation 2), and the order and size-effect coefficients were obtained by Fourier inversion of the appropriate separated data arrays. A computer model (the GC structure) depicting the real-space local atomic arrangements represented by the experimental α_{lmn} was generated by use of the program by Epperson (1979), which is based generally on a concept first demonstrated and used by Gehlen & Cohen (1965). The spectrum of nearest-neighbor atomic configurations was determined by use of another program described by Epperson (1979), and the ordered 'Ni$_3$Al domains' were characterized by the method given by Epperson & Fürnrohr (1980).

Results and discussion

There is a considerable degree of short-range order present in the bulk Ni–12·7 at.% Al alloy single-crystal quenched from 1323 K as is readily apparent from Fig. 1. Shown here are iso-intensity contours of the total diffuse scattering (in Laue monotonic units) measured in the $h_3 = 0$ plane of reciprocal space. Long-range-ordered Ni_3Al has the Cu_3Au-type structure ($L1_2$), and elements of this character are reflected in diffuse maxima seen near positions (100), (210), etc. In view of comments in the Introduction it is worth noting, however, that these diffuse maxima are characteristic of local atomic order, and clearly no superlattice reflections indicative of long-range order are present.

Using the procedures outlined in the previous section, the three-dimensional coherent diffuse intensities were separated into the short-range-order and size-effect components represented by the four triple summations in (2). The size-effect coefficients are given in Table 1 and the Cowley–Warren order coefficients in Table 2. While, in principle, the size-effect parameters contain information about the structural details, there is currently no straightforward general method to extract this information from the set of coefficients obtained by the present method of separation. Because of this, and recognition of the fact that the experimental size-effect parameters tend to be somewhat less reliable than the order coefficients, no detailed analysis of the former will be attempted.
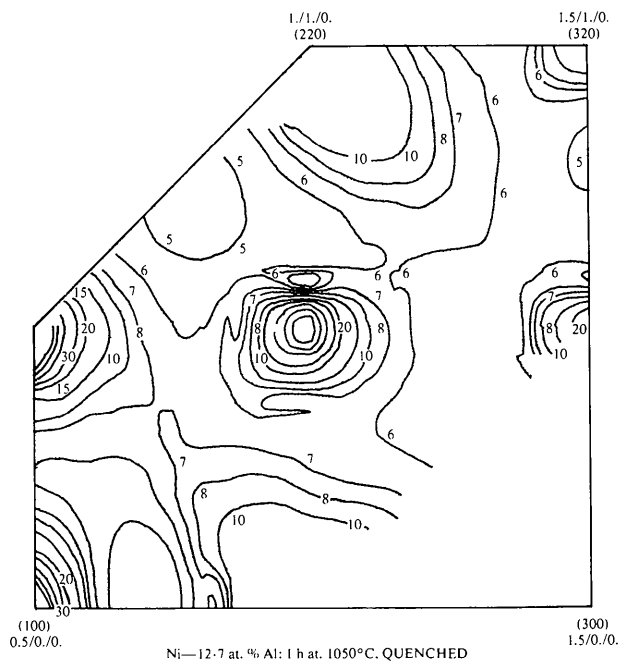
From Table 2, we see that the experimental value of α_{000} exceeds the theoretical value of unity by an appreciable amount, even though the identical correction procedures and/or separation routines as used by Epperson, Fürnrohr & Ortiz (1978) in investigating some Cu–Al alloys were utilized. To be sure, the α-phase Ni–Al system is more complex in that, with proper heat treatment, decomposition proceeds until rather massive ordered precipitates of a second phase (Ni_3Al) form; whereas in α-phase Cu–Al alloys, the equilibrium state was found to be short-range ordered. Exactly how the presence of submicroscopic ordered clusters (chemical inhomogeneities) manifest themselves in the separation process is not known; however, the recent work by Auvray, Georgopolous & Cohen (1981) on an Al–Cu alloy well known for the formation of GP zones indicates that the most up-to-date separation scheme is capable of handling this state of aggregation. The origin of the anomalously large α_{000} is probably traceable to the condition just related and is taken as an indication of the need to make use of a more sophisticated separation procedure, e.g. the procedure implemented by Georgopoulos (1978).

In addition to the experimental α_i, Table 2 also presents those determined from the 8000-atom GC

Fig. 1. Iso-intensity diagram of the total diffuse intensity, in Laue monotonic units, in the $h_3 = 0$ plane of reciprocal space for a Ni–12·7 at.% Al alloy single crystal annealed for 1 h at 1323 K and quenched to room temperature in water.

Table 1. *Size-effect coefficients for the* Ni–12·7 *at.% Al alloy single crystal quenched from* 1323 K

i	lmn	γ^y_{lmn}	$\langle \delta^2 \rangle^y_{lmn}$	$\langle \delta^2 \rangle^{xy}_{lmn}$
0	000	0·000	−9·478	0·000
1	011	−0·105	−1·334	0·000
2	002	0·000	−0·892	0·000
3	112	−0·029	−0·535	−0·225
4	022	0·020	−0·466	0·000
5	013	−0·031	−0·620	0·000
6	222	0·030	−0·238	−0·309
7	123	−0·011	−0·344	−0·141
8	004	0·000	−0·412	0·000
9a	114	−0·008	−0·340	−0·063
9b	033	−0·030	−0·242	0·000
10	024	0·006	−0·282	0·000

Table 2. *Experimental* (*expt.*) *and modelled* (*mod.*) *Cowley–Warren order coefficients for a* Ni–12·7 *at.% Al alloy annealed for* 1 h *at* 1323 K *and quenched to room temperature*

i	lmn	α_{lmn}(expt.)	α_{lmn}(mod.)
0	000	1·426	1·0000
1	011	−0·147	−0·1453
2	002	0·343	0·3429
3	112	−0·031	−0·0310
4	022	0·186	0·1861
5	013	−0·082	−0·0820
6	222	0·112	0·1120
7	123	−0·035	−0·0320
8	004	0·085	0·1575
9a	114	−0·010	−0·0004
9b	033	−0·035	−0·0545
10	024	0·049	0·0984

structure which was synthesized using the first six experimental order coefficients as boundary conditions. No statistical improvement in the CG structure could have been realized without extending the fitting to higher coordination shells. A segment of the GC

```
                    PLANE    2
     0    0    0    0    0    0    0    0    0    0
  0    0    0    1    1    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    1    1    0    0    0    0    1
     0    0    0    0    0    0    0    0    0    0
  1    0    0    1    1    0    1    0    0    1
     0    0    0    0    0    0    0    0    0    0
  1    0    0    1    1    0    0    0    0    1
     0    0    0    0    0    0    0    0    0    0
  0    0    1    1    1    0    0    0    0    1
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    1    1    1    0    0    0    1    0    0
     0    0    0    0    0    0    0    0    0    0
  1    1    1    1    1    0    0    1    0    0
     0    0    0    0    0    0    0    0    0    0
  1    0    0    1    1    0    0    0    0    0

                    PLANE    3
  0    0    1    0    0    1    1    0    0    1
     1    0    0    0    0    0    0    0    0    0
  0    0    1    0    0    1    1    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    1    1    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    1    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    1    0    0
     0    1    1    1    1    0    0    0    1    0
  0    0    0    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  1    0    0    0    1    1    1    0    0    1
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    1    1    0    1    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    1    0    0    0
     0    0    0    0    0    0    0    0    0    0

                    PLANE    4
  0    0    0    0    0    0    0    0    0    0
  0    0    0    1    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    1    0
  1    0    0    1    1    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    1    1    0    0    0    1    1
     1    0    0    0    0    0    0    0    0    0
  0    0    0    1    1    1    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    1    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    0    0    0    0    0    0    0    0    0
     0    0    0    0    0    0    0    0    0    0
  0    1    0    1    0    0    0    1    0    0
     0    0    0    0    0    0    0    0    0    0
  0    1    1    1    0    0    0    1    0    0
     0    0    0    0    0    0    0    0    0    0
  0    1    1    0    0    0    0    1    0    0
     0    0    0    1    1    0    0    0    0    0
  0    1    0    0    0    0    0    1    0    0
```

Fig. 2. Three adjacent planes from the GC structure of the Ni–12·7 at.% Al alloy quenched to room temperature from 1323 K. 0 denotes a Ni atom and 1 an Al atom.

structure is shown in Fig. 2 which demonstrates the type and three-dimensional character of the local atomic order. As a means of gaining more insight about the short-range order of this alloy, the CG structure has been searched for all possible nearest-neighbor atomic configurations, using the procedure and computer code described by Epperson (1979). The abundances of the first 17 species of the resulting spectrum of configurations of Al about Ni atoms are given in Table 3 for the quenched alloy, along with similar information determined for a random alloy of the same composition. Note that the C16 configuration is the basic unit of the Ni$_3$Al structure and consists of a planar array of four nearest-neighbor Al atoms about a Ni atom. There is a surprising degree of antiphase character in the order, as evidenced by the fact that some 2·25% of the Ni atoms have the C17 configuration; this is comprised of a tetrahedral arrangement of four nearest-neighbor Al atoms about a central Ni atom.

That there is some agglomeration of the Ni$_3$Al rings is obvious from Fig. 2 and can also be seen from Table 3. If there were no agglomeration, the maximum abundance of Ni atoms having this local environment would be 3·64%, whereas 6·40% is found to be present. It is perhaps worth pointing out that, in the GC structure for the random alloy, only two each of the C16 and C17 configurations were found to be present (0·03%).

As we have indicated earlier, low-temperature annealing of this alloy results in precipitation of a second phase and fragments of two sizeable domains of Ni$_3$Al can be seen in the three cube planes of the GC structure shown in Fig. 2. The long-range-ordered Ni$_3$Al structure can be visualized as consisting of two types of layers which alternate along the [100] direction; one layer consists of only Ni atoms, and the second-type layer consists of alternate rows of Ni and Al atoms. The result is that there are no nearest-neighbor Al–Al bonds and in the mixed plane each atom has first nearest neighbors only of the other type.

The Ni$_3$Al-type ordered domain structure has been further characterized by making use of the search procedure devised by Epperson & Fürnrohr (1980), and the results are summarized in Table 4. Some 61% of the Al is already contained in these ordered domains, and this comprises about 31 vol % of the microstructure of the quenched alloy. This procedure also affords a convenient means of estimating the number density of ordered domains. For the bulk Ni–12·7 at.% Al alloy from 1323 K to room temperature in water, we find the density of domains having Ni$_3$Al-type order to be about 0·47 G m^{-3}. As seen in Table 4, most of the 'domains' consist of either isolated* Ni$_3$Al rings or

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* By definition, Ni$_3$Al rings are considered to be 'associated' if their central Ni atoms are either first- or second-nearest neighbors.

small agglomerates consisting of two or three such units. It is considered far more significant, however, that a few much larger domains are present; one was found to consist of 115 of the basic Ni_3Al rings. While the mean diameter of the domains is only 9 Å, the largest one present in the GC structure exceeds 22 Å in diameter. The latter value is still below the critical size for a thermodynamically stable nucleus in this alloy, but it would appear to be correct to consider the larger ordered domains as being embryos, which presumably have been formed during the quench,† it is not difficult

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† The other alternative is that the observed 'embryos' are heterophase fluctuations retained by the quench from the solution temperature.

Table 3. *Percentage of* Ni *atoms having the indicated configurations in* Ni–12·7 *at.% Al quenched from* 1323 K *and in a* 12·7 *at.% random alloy*

The notation is that used by Epperson (1979). The C16 configuration is the basic structural unit of Ni_3Al, consisting of a planar array of four nearest-neighbor Al atoms about a Ni atom.

Configuration	Configuration abundance (%)	
	Quenched	Random
C1	15·85	19·61
C2	29·43	34·77
C3	16·38	5·01
C4	1·92	2·43
C5	9·56	9·33
C6	0·00	9·69
C7	10·51	0·64
C8	6·84	1·52
C9	0·86	0·43
C10	0·00	3·09
C11	0·00	2·83
C12	0·00	1·63
C13	0·00	1·39
C14	0·00	1·39
C15	0·00	0·49
C16	6·40	0·03
C17	2·25	0·03

Table 4. *The distribution of ordered domains found in* Ni–12·7 *at.% Al quenched from* 1323 K

A pair of Ni_3Al rings are considered to be connected provided the central Ni atoms are mutual first- or second-nearest neighbors.

n (Number of Ni_3Al rings in the ordered cluster)	N(n) (Number of ordered clusters in the 8000-atom GC structure having n Ni_3Al rings)
1	19
2	6
3	5
4	1
6	1
9	1
11	2
19	1
26	1
54	1
65	1
81	1
115	1

to imagine that the decomposition of this alloy would be strongly dependent on the sample size and other details of the quench. The subsequent phase separation in this alloy will be reported in a forthcoming publication.

If one examines the composition in the various coordination shells averaged about all the C16 configurations (Ni_3Al rings) in the GC structure, one notes that the composition of the shells does not converge rapidly to the mean composition of the alloy, as shown in Fig. 3(a). This is in marked contrast to the behaviour observed in α-Cu—Al by Epperson & Fürnrohr (1980) as shown in Fig. 3(b). The latter is the behaviour to be expected if the ordered domains are randomly dispersed in the matrix. The behavior observed for the Ni–Al alloy is interpreted as being due to a slightly non-random dispersion of the ordered domains. That is, a modulated microstructure is evolving from the very earliest experimentally accessible stages of alloy decomposition, presumably due to elastic interactions between the Ni_3Al embryos as has been proposed by Ardell, Nicholson & Eshelby (1966) for advanced-stage coarsening in these alloys. Because of this
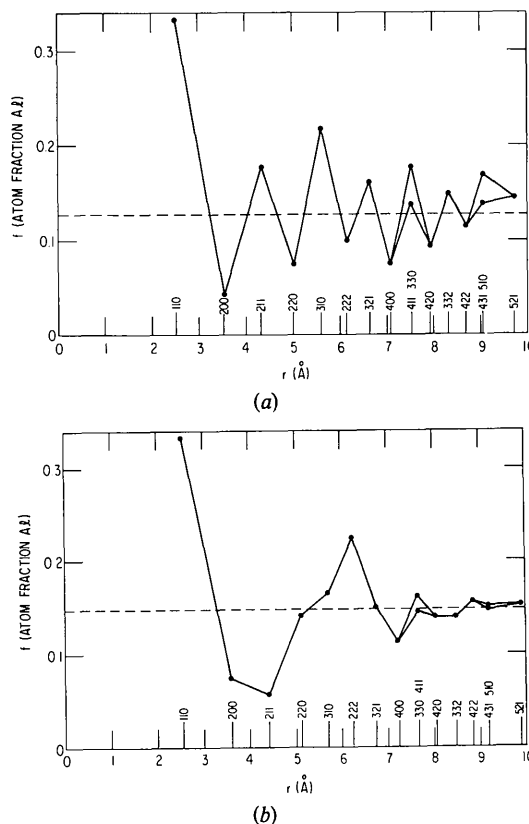

Fig. 3. Average composition of the various coordination shells about all the C16 configurations (Ni_3Al or Cu_3Al rings) in the GC structure; (a) Ni–12·7 at.% Al quenched to room temperature from 1323 K, (b) Cu–14·75 at.% Al annealed for 1580 h at 423 K. Cu–Al figure from Epperson & Fürnrhor (1980).

interaction and the fact that a majority of the Al atoms are already in the elementary Ni_3Al rings after quenching from 1323 K, it is reasonable to anticipate that phase separation will proceed by a type of biased rearrangement and/or coarsening at lower temperatures where diffusion is possible. This process should result in an even less random dispersion of embryos, and consequently side bands near the matrix reflections should become visible due to the quasi-regular dispersion of ordered zones whose elastic properties differ from those of the matrix (Khachaturyan, 1979).

It has been assumed, without proof, that the dispersion of ordered Ni_3Al embryos observed in this solution-treated Ni–12·7 at.% Al alloy was formed during the quench. Establishing this point as baseline information would aid in understanding changes associated with subsequent phase separation.

The existence of a dispersion of Ni_3Al embryos in the solution-treated alloy supports the proposal by Starke, Gerold & Guy (1965) as to the origin of the K effect. They found that subjecting a solution-treated Ni-11·3 at.% Al alloy to 40% deformation by cold rolling resulted in a 6% decrease in electrical resistivity. Such behaviour is opposed to the 'normal' behavior for metals and alloys in which deformation results in an increase in resistivity, attributed largely to a higher dislocation density. It was proposed that deformation tends to destroy the embryos, resulting in a more nearly random alloy; embryos in the size range found in this investigation are thought to be strong scatterers of the conduction electrons.

Summarizing comments

The local atomic structure of a bulk Ni–12·7 at.% Al alloy single crystal quenched to room temperature from 1323 K was investigated by analysis of the diffusely scattered X-rays. The diffuse scattering was measured in a volume of reciprocal space in order that the size-effect contributions could be separated from the local order component, and the Cowley–Warren order coefficients were obtained by Fourier transforming the local-order diffuse intensity. These coefficients contain information about the statistical distribution of atoms on the nodes of the average lattice. In order to recover some details of the real-space ordered structure, an 8000-atom model was computer generated, using the experimental order coefficients as boundary conditions. This synthesized GC structure was first characterized in terms of the spectrum of nearest-neighbor atomic configurations, and subsequently the Ni_3Al ordered domain structure was investigated.

Some 61% of the Al atoms were found to be contained in Ni_3Al rings, a planar configuration consisting of four nearest-neighbor Al atoms about a central Ni atom. Numerically, most of the ordered 'domains' contained from one to three such units, but a

few domains were found to be much larger, containing on the order of a hundred such elementary Ni_3Al rings. The ordered domains in this quenched alloy have not attained the size necessary to be stable thermodynamically, hence the larger ones should be regarded as embryos, and not nuclei, of the Ni_3Al phase. It was argued that these ordered domains, estimated to be about 0·47 Gm^{-3}, are not randomly dispersed in the matrix; in a strict sense, the structure of the Ni–12·7 at.% alloy quenched as described should be classified as a modulated microstructure.

Because of the sophistication with which it is now possible to investigate routinely the local atomic configurations in alloy systems, high-angle diffuse-scattering techniques should be more widely used, especially in combination with small-angle scattering and transmission electron microscopy, in systematically investigating alloy decomposition. Fortunately, high-angle diffuse-scattering techniques are most useful in a stage of decomposition where the other techniques mentioned are least applicable.

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