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Formation of icosahedral phase by solid-state diffusion of alternating thin layers

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Thin alternating layers of Al–Cr were produced by sputtering. Heat treatment transforms them to the icosahedral phase. The effect of the layer thickness on their ability to transform to single-phase icosahedral film was examined and it was found that very thin alternating layers react completely to form a single icosahedral phase, while heat treatment of thicker layers always produced the icosahedral phase with residual aluminium. An attempt has been made to explain the results based on the crystallographic structure of the icosahedral phase.

1. Introduction

Since the discovery of the icosahedral phase [1], extensive investigations have been carried out on the quasi-periodic phases. These phases were first produced by rapid solidification methods, particularly melt spinning [1]. Another way of creating the quasi-periodic phases is by solid-state transformation of thin films. Many such methods have been used to date, among them ion-beam mixing of alternating thin layers or of co-evaporated alloys [2, 3], heat treatment of alternating thin layers or of co-evaporated alloys [4, 5] and sputtering of alloys at high temperatures [6].

We report here the production of icosahedral phase by annealing multilayers of poly-crystalline aluminium and chromium as well as on the role of the layers thickness in the formation of a single icosahedral phase without any residual aluminium. Single-phase icosahedral films are important for the accurate measurement of various properties of this phase.

2. Experimental procedure

Multilayers of aluminium and chromium were sputtered at room temperature on cleaved NaCl substrates and on silicon wafer covered with SiO_2. The thickness of the layers was determined by a known calibration of the sputtering machine (voltage, current and sputtering time). The total thickness of the sample was measured using an α step instrument. All the samples were examined by Auger spectrometry in order to ensure they contained only a minor amount of oxygen.

Heat treatments were performed in a vacuum furnace at 10^{-6} torr (1 torr = 133.322 Pa) in the temperature range 300–500 °C for periods of 1 h. The microstructure was studied by 200 kV transmission electron microscopy. Flat-on samples were made by dissolving the NaCl crystals in soft water and mounting the thin film on a copper grid. The cross-section samples were made by mechanically polishing a "sandwich" made of four pieces of the sample, down to a thickness of 40 μm, followed by ion-milling.

3. Results

3.1. Flat-on samples

Four different samples were sputtered with the same average composition of Al–15 at % Cr, but with different layer thicknesses. Table I shows the structure of the four as-sputtered samples.

The electron diffraction patterns (Fig. 1a and b) reflect the polycrystalline as-sputtered structure of aluminium and chromium. The dark-field image in Fig. 1c, taken from the two strongest rings marked in Fig. 1a, shows very small grains (about 10–15 nm) of aluminium and chromium.

In order to obtain the icosahedral phase, these layers were heat treated in a vacuum furnace at 400 °C for 1 h. Fig. 2a is a typical electron diffraction pattern of Samples 2, 3 and 4. All the rings in the diffraction pattern can be indexed according to the icosahedral phase (Fig. 2b), and no ring can be found which belongs to aluminium. The electron diffraction pattern of Sample 1, which has the thickest alternating layers, is shown in Fig. 2c, and its schematic diagram in Fig. 2d. Several rings which belong to aluminium can be seen. Fig. 3 is a dark-field image taken from the strongest doublet of Fig. 2a, and it shows an example of the small grains (≈ 10 nm) of the icosahedral phase produced in Samples 2, 3 and 4.

TABLE I The structure of the layers

Sample	Thickness of Al + Cr layer
1	$6x$
2	$3x$
3	$2x$
4	x

When $x = 2$ nm, and the total thickness is about 100 nm.

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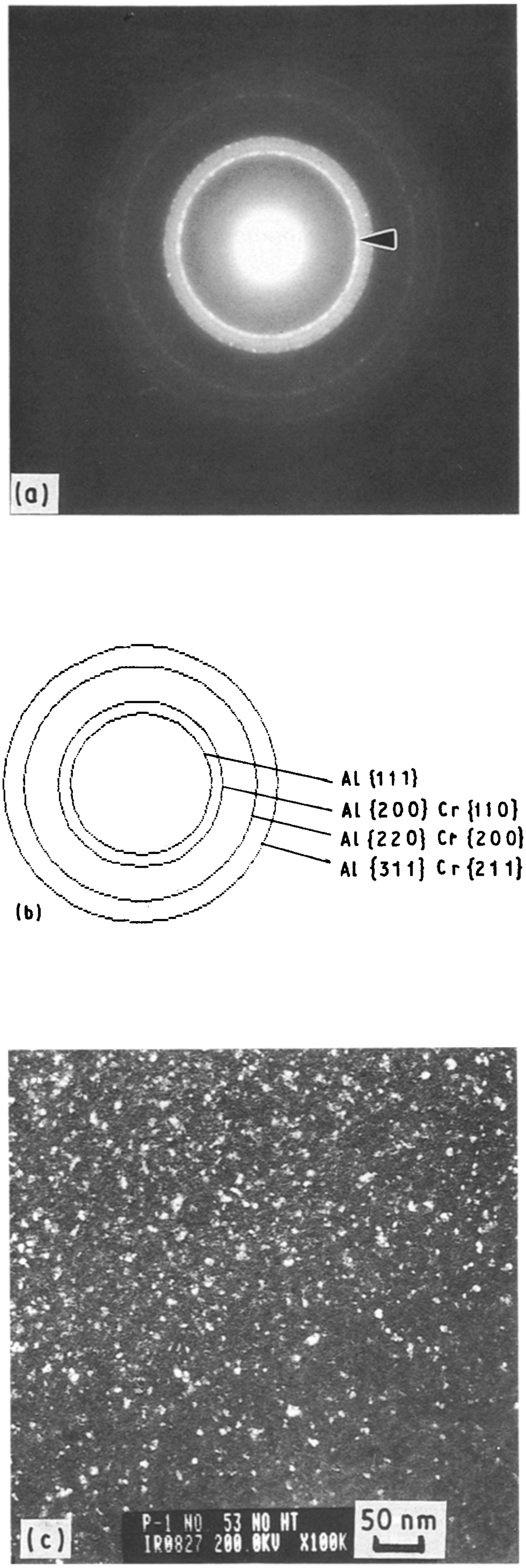

Figure 1 Structure of the flat-on samples before heat treatment. (a) Electron diffraction pattern showing the polycrystalline structure of aluminium and chromium. (b) Schematic diagram of (a). (c) Dark-field image taken from the two strongest rings marked in (a): small grains of aluminium and chromium.

3.2. Cross-section samples

Two sets of aluminium and chromium layers were sputtered on silicon wafer covered with SiO_2. The first set constitutes 20 pairs of 3 nm Al and 0.5 nm Cr; above them is a second set made of 10 additional pairs of 6 nm Al and 1 nm Cr.

Fig. 4 shows a cross-section image of these two sets before the heat treatment, and the various alternating layers may be seen. A sample of this film was heat treated in a vacuum furnace at 300 and 480 °C for 1 h.

After annealing at 300 °C for 1 h, the thinnest layers were completely mixed, as can be seen in Fig. 5a. The thicker layers were partially mixed, as can be seen if one compares the thickness of these layers before and after the heat treatment (Figs 4 and 5a, respectively). The electron diffraction pattern (Fig. 5b) shows the coexistence of the icosahedral phase with aluminium. Fig. 6a is a cross-section image of the layers after annealing at 480 °C for 1 h. As can be seen, all the layers are mixed at this temperature, and, as is shown in the diffraction pattern (Fig. 6b), the layers are transformed into a periodic intermetallic compound. No aluminium remains after this heat treatment.

4. Discussion

The solid-state transformation of alternating thin layers requires diffusion of one or more of the elements. A comparison of the diffusion constants of aluminium and chromium [7] shows that aluminium diffuses much faster than the chromium. This is true in particular at the moderate temperatures used in this study. As a consequence, it can be assumed that only the aluminium atoms are diffusing during the transformation, and that the transformation to the icosahedral phase is done just on one interface, between the chromium and the icosahedral phase.

Grushko and Shechtman [8] claim that formation of metastable phases can be achieved in systems which contain complicated stable crystalline phases. In such cases, the metastable phase should form by a smaller interfacial diffusion length.

In the Al–Cr system, at the composition range of our study, there are several stable intermetallic compounds: θ, η and ε. The crystal lattices of these phases have not yet been completely determined, because there are many variations of each one (see, for example, [9–11]). All these variations have complicated crystal structure, with several tens of atoms per unit cell, and lattice parameters of the order of 0.5–3 nm. Cooper [10], gives the most detailed description of θ, and shows that it has a monoclinic structure with icosahedral motifs.

A comparison of the structure of θ, as given by Cooper [10] and the structure of the icosahedral phase, shows that the latter is composed of the same motifs as θ, but these motifs are arranged randomly, with a long-range orientational order [1, 12] and not at the lattice points of a bravais lattice. This means that in order to create the crystal lattice of θ, the atoms of aluminium and chromium must first rearrange themselves in an icosahedral structure, and then these icosahedrons have to move to the lattice points of the

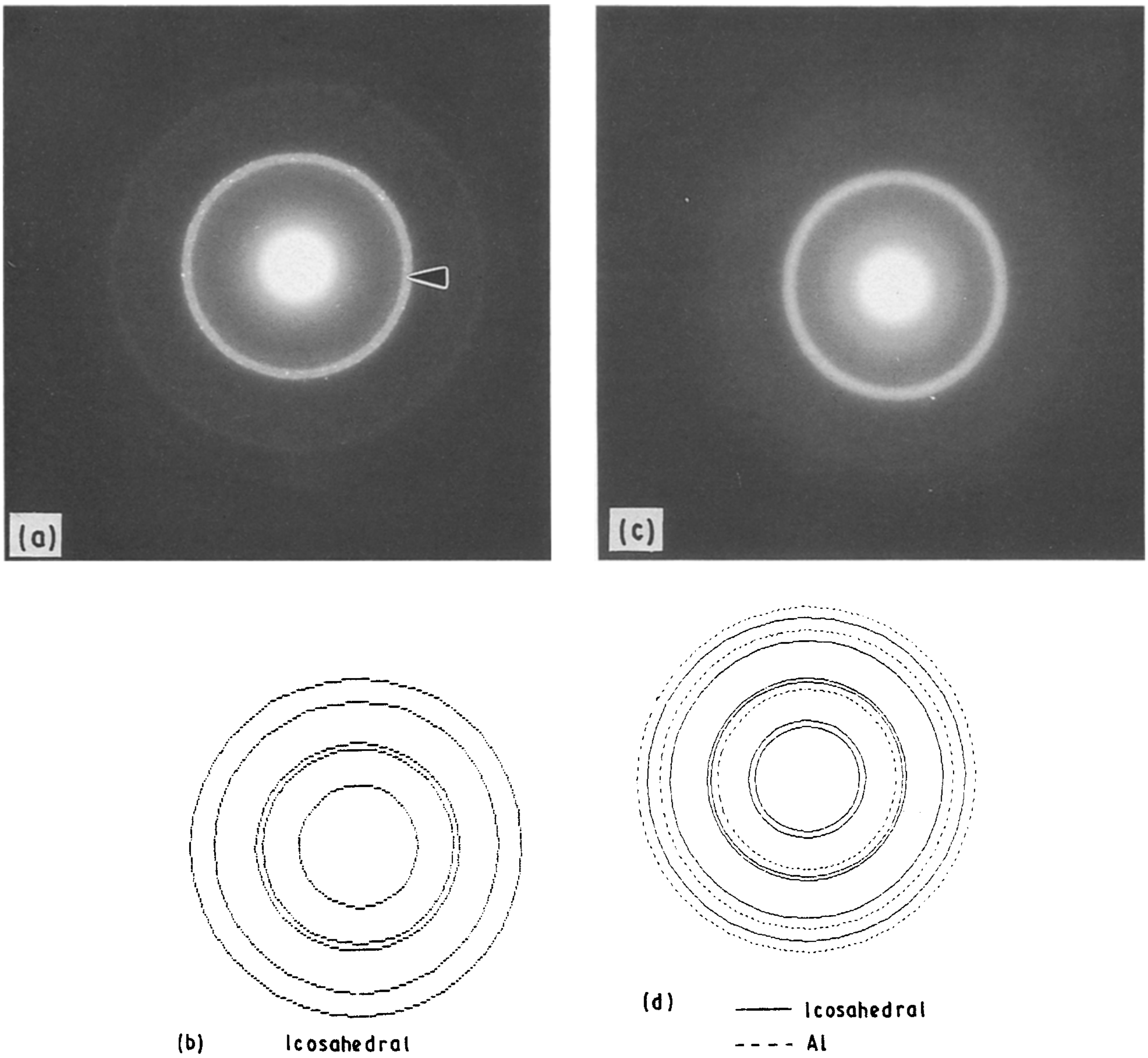

Figure 2 Structure of the flat-on samples after annealing at 400 °C for 1 h. (a) Electron diffraction pattern taken from the samples with the thinner layers: icosahedral phase. (b) Schematic diagram of (a). (c) Electron diffraction pattern taken from the sample with the thickest layers: icosahedral and aluminium. (d) Schematic diagram of (c).

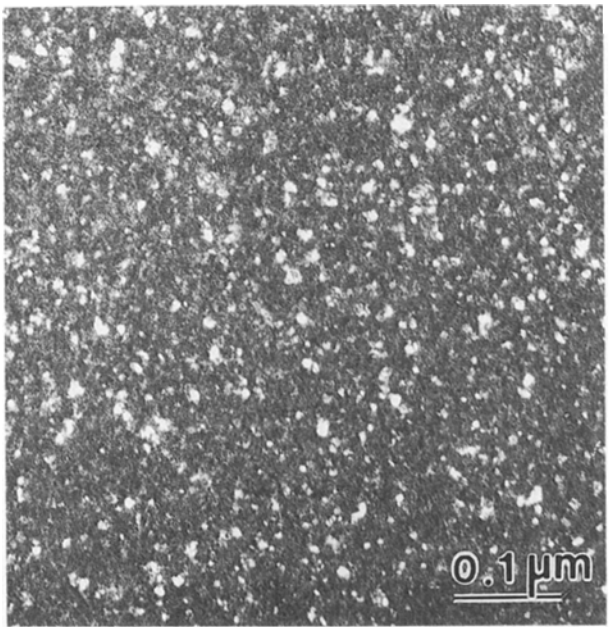

Figure 3 Dark-field image taken from the strongest doublet marked in Fig. 2a: small grains of the icosahedral phase.

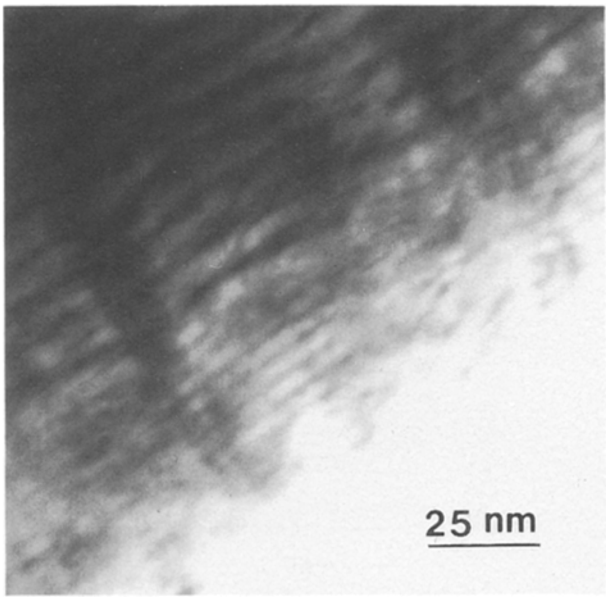

Figure 4 Cross-section image of the alternating layers before heat treatment.

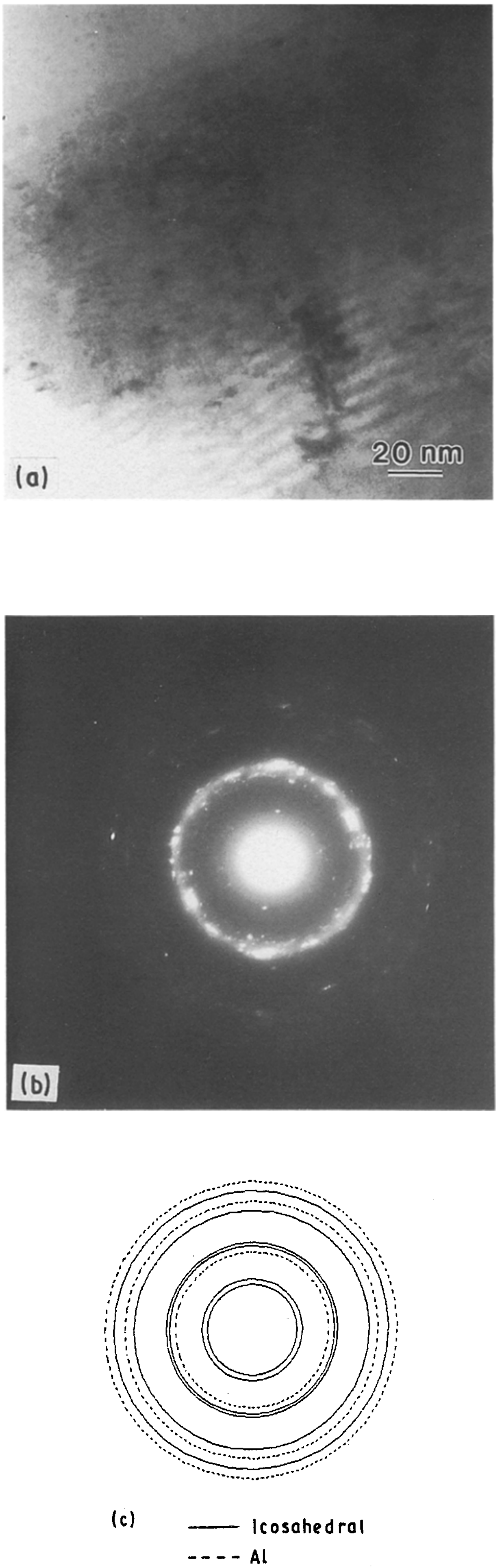

Figure 5 (a) Cross-section image of the layers after annealing at 300 °C for 1 h. (b) Electron diffraction pattern of (a). (c) Schematic diagram of (b).

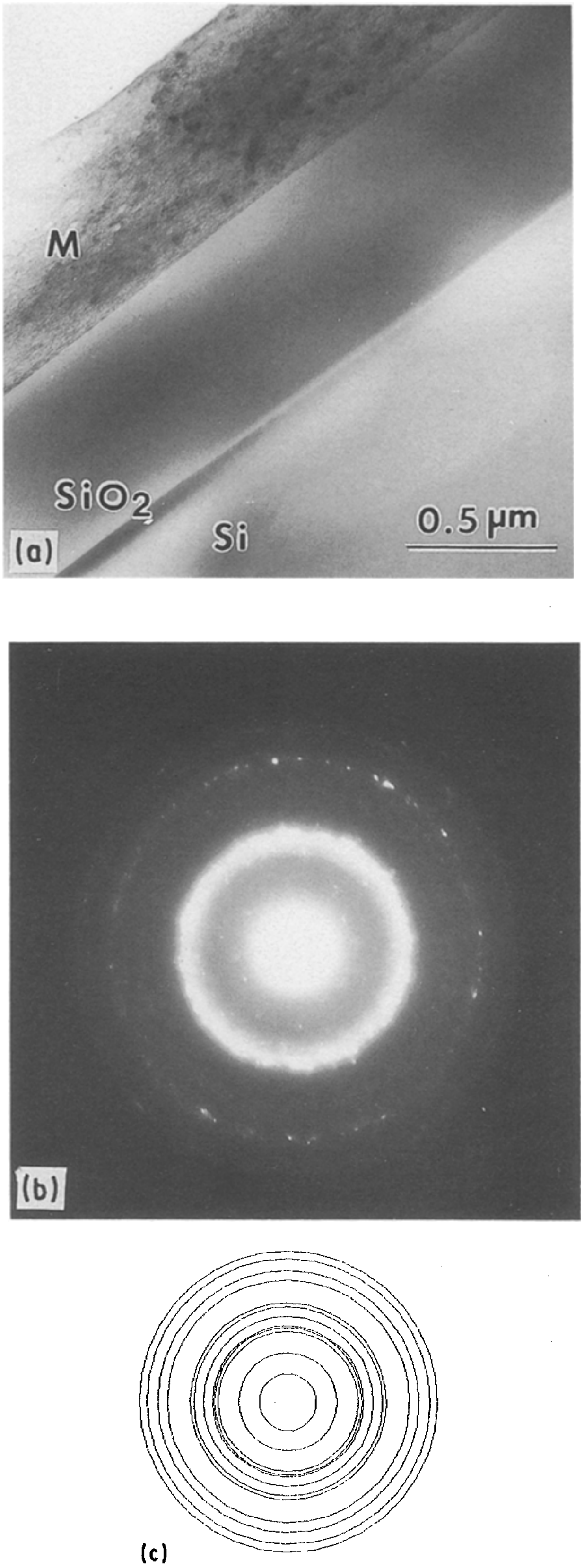

Figure 6 (a) Cross-section image of the layers after annealing at 480 °C for 1 h. (b) Electron diffraction pattern of (a). (c) Schematic diagram of (b).

monoclinic structure. On the other hand, in order to form the icosahedral phase, the icosahedrons have to be arranged in a long-range orientational order but without long-range translational order.

In order to explain the very small thickness of the layers needed for a full reaction, we will continue with the above model: Grushko and Shechtman derived an expression for the critical thickness of the intermediate layer [8]

$$H_c = \frac{D_{AB}}{R}\left[\frac{(C_1 - C_2)RL_c}{D_B \Delta C}\right] \quad (1)$$

where $R = r_A r_B/(r_A + r_B)$, r_A and r_B are the reaction constants at the A/AB and B/AB interfaces, respectively, D_{AB} is the diffusion constant of A in AB, $C_1 - C_2$ is the composition difference at AB layer, H_c is the critical thickness of AB, ΔC is the composition gradient at the AB/B interface, L_c is a critical diffusion distance needed to grow the crystal, and D_B is the self diffusion constant of B. From Equation 1, it can be seen that if D_{AB}, the diffusion constant of aluminium in the icosahedral layer, is very small, then the icosahedral layer (the AB layer) is very thin.

Very little is known about diffusion rates in the icosahedral phase. Diffusion in the icosahedral phase occurs by the motion of phasons and vacancies. Lubensky [13] claims that these diffusion constants have to be almost the same, and also similar to the vacancies diffusion constants of periodic phases composed of the same metals. Goldman *et al.* [14] show that some mobility of the phasons is seen only above 500 °C. Probably the low diffusion rates in the icosahedral phase can be explained if we look at the atomic structure based on the Mackay icosahedron [15, 16]. This structure is dense and chemically ordered, and it is known that in similar periodic structures, the diffusion is much slower compared to other simple structures, and requires a more complicated diffusion mechanism [17].

5. Conclusion

We conclude that the growth of the icosahedral phase is limited by the decrease in the atomic flux through the interface as the thickness of the icosahedral phase increases, as in amorphous phases [18, 19], but the low diffusivity in the icosahedral phase results in a very low critical thickness needed for its formation by solid-state diffusion of alternating thin layers. Consequently, only when the alternating layers are very thin (Al + Cr layer $\leqslant$ 5 nm), will the reaction between the aluminium and the chromium be completed and a single icosahedral phase be formed. When the alternating layers are thicker, the icosahedral phase will reach its maximal thickness before the elements react completely, and excess aluminium will always remain as a result of the transformation.

References

1. D. SHECHTMAN, I. BLECH, D. GRATIAS and J. W. CAHN, *Phys. Rev. Lett.* **53** (1984) 1951.
2. D. A. LILIENFELD, M. NASTASI, H. H. JOHNSON, D. G. AST and J. W. MAYER, *ibid.* **55** (1985) 1587.
3. D. M. FOLLSTAEDT and J. A. KNAPP, *J. Less-Common Metals* **140** (1988) 375.
4. *Idem., Phys. Rev. Lett.* **56** (1986) 1827.
5. D. A. LILIENFELD, M. NASTASI, H. H. JOHNSON, D. G. AST and J. W. MAYER, *J. Mater. Res.* **1**(2) (1986) 237.
6. K. G. KREIDER, F. S. BIANCANIELLO and M. J. KAUFMAN, *Scripta. Metall.* **21** (1987) 657.
7. D. A. PORTER and K. E. EASTERLING, "Phase Transformation in Metals and Alloys" (Van Nostrand Reinhold, 1981).
8. B. GRUSHKO and D. SHECHTMAN, *J. Appl. Phys.* **67** (1990) 2904.
9. W. B. PEARSON, "Handbook of Lattice Spacing and Structures of Metals and Alloys" (Pergamon Press, 1967).
10. M. J. COOPER, *Acta Crystallogr.* **13** (1960) 257.
11. L. A. BENDERSKY, R. S. ROTH, J. J. RAMON and D. SHECHTMAN, *Met. Trans.* submitted.
12. E. A. STERN, Y. MA, K. BAUER and C. E. BOULDIN, *J. Phys. Colloq.* **47** (1986) c3-371.
13. T. C. LUBENSKY, in "Introduction to Quasicrystals", edited by M. V. Jaric (Academic Press) p. 199.
14. A. J. GOLDMAN, J. E. SHIELD, C. A. GURYAM and P. W. STEPHENS, in "Proceedings of the Anniversary Adriatico Research Conference on Quasicrystals", edited by M. V. Jaric and S. Lundqvist (World Scientific) p. 60.
15. J. W. CAHN and D. GRATIAS, *J. Phys. Colloq.* **47** (1986) c3-415.
16. M. AUDIER and P. GUYOT, *ibid.* **47** (1986) c3-405.
17. L. N. LARIKOV, V. V. GEICHENKO and V. M. FAL'CHENKO. "Diffusion Processes in Ordered Alloys" (Amerind, New Delhi) translated.
18. W. L. JOHNSON, *Met. Sci. Engng* **97** (1988) 1.
19. K. SAMWER, H. SHRODER and K. PAMPUS, *ibid.* **97** (1988) 63

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