

The microstructure and crystallography of directionally solidified (Co, Ni)-Cr₂₃C₆ eutectic alloy

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The microstructure and morphology of directionally solidified samples of the pseudo-binary eutectic alloy CoNi–Cr₂₃C₆ have been characterized with respect to the growth rate and temperature gradient. Transmission electron microscopy studies show that, in spite of the irregularity of the microstructure, a simple and reproducible cube–cube orientation relationship exists between the phases, which can be explained in terms of the close atomic coincidence between the crystal lattices. The observed microstructures can readily be related to the crystallographic preferred growth directions of the alloy.

1. Introduction

Ternary and higher order alloy systems can give rise to mono- and multivariant eutectic reactions. Directional solidification of such systems permits the preparation of pseudo-binary composite materials in which there is the possibility of modifying the composition and volume fraction of the constituent phases. This is not the case for invariant binary eutectic alloys apart from the limited composition ranges which are obtained under extreme growth conditions [1].

Such reactions have been used as the basis of coupled cobalt and nickel eutectic alloys, i.e. “eutectic superalloys”. These alloys possess remarkable strength and creep resistance especially when directionally solidified. The pseudo-binary eutectic alloy, CoNi–Cr₂₃C₆, is one of these interesting systems. The composition of this eutectic alloy was estimated from the phase diagrams of the ternary systems Co–Cr–C [2] and Ni–Cr–C [4]. Fig. 1 shows the superposed, partial diagrams of these systems in the region relevant to the present alloy. The Co–Cr–C system comprises three ternary eutectic reactions: E_{T1} , E_{T2} and E_{T3} [5–8]. Along the eutectic troughs between the ternary eutectics, there exist monovariant eutectic

alloys exhibiting invariant reactions at the points of the eutectic trough which have a maximum temperature. These “saddle” points (S_1 , S_2) are pseudo-eutectic reactions between pseudo-binary eutectic cuts: $S_1 = \text{Co, Cr}(\gamma) + (\text{Cr, Co})_{23}\text{C}_6$ and $S_2 = \text{Co, Cr}(\gamma) + (\text{Cr, Co})_7\text{C}_3$.

The similarity between the Co–Cr–C and Ni–Cr–C systems suggested the likelihood of pseudo-eutectic reactions existing in the quaternary system. This hypothesis was confirmed by recent work, which demonstrated the possibilities of anisotropic, two-phase structures produced from ternary and higher order eutectic alloys [9]. The aim of this paper is the characterization of the microstructure of the pseudo-eutectic alloy, CoNi–Cr₂₃C₆, under directional solidification, and crystallographic description of the eutectic phases.

2. Experimental methods

The preparation of the Co–Cr–Ni–C pseudo-binary eutectic was carried out using the pure elements: Co (99.9%), Ni (99.97%), Cr (99.997%), C (spectrographic grade). The composition chosen was Co, 35.1; Cr, 48; Ni, 15 and C, 1.9 wt% (pseudo-eutectic alloy CoNi 15–Cr₂₃C₆).

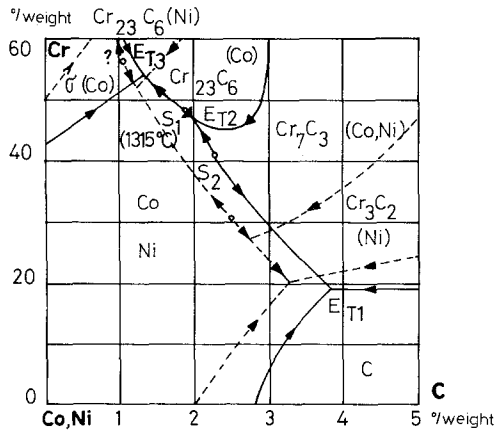


Figure 1 Ternary systems Co–Cr–C and Ni–Cr–C.

The alloys were made by melting the elements together, under argon, in alumina crucibles. Unidirectional solidification was carried out by withdrawing the alloy contained in alumina tubes, vertically downwards from a Bridgman furnace. The temperature gradient, measured in the furnace at the melting temperature of the alloy, was 75°C cm^{-1} .

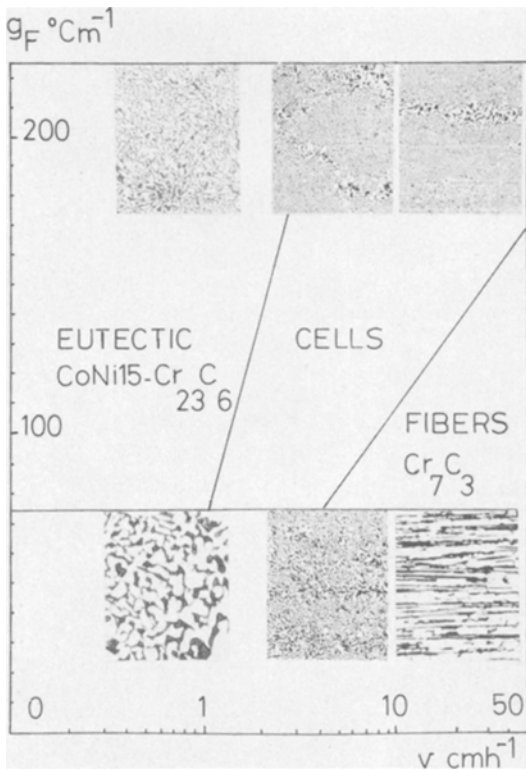


Figure 2 Changes in the microstructure of CoNi 15–Cr₂₃C₆ eutectic as a function of the growth rate, v , and the temperature gradient, g_F .

The microstructure was polished using normal metallographic techniques and etched with an alcoholic solution of potassium ferricyanide. Thin films were prepared by a double jet electrolytic thinning technique using a solution based on perchloric acid. They were studied by transmission electron microscopy using a Philips EM 300 microscope.

The geometric characteristics of the carbides: volume fraction, V_c , average width, λ_c and intercarbide distance, λ , were determined using a Quantimet 720 image analyser, by a progressive image erosion technique [10].

3. Microstructure

Variation in the growth rate produces a change in the microstructure of the eutectic. Three distinct domains of characteristic microstructure were identified within the range of 0.06 cm h^{-1} to 24 cm h^{-1} ($g_F = 75^\circ\text{C cm}^{-1}$, Fig. 2).

(a) For growth rates less than 2.4 cm h^{-1} , one observes CoNi 15–Cr₂₃C₆ eutectic having a regular distribution of carbides.

(b) For growth rates between 2.4 cm h^{-1} and 12 cm h^{-1} , the interface is cellular.

(c) For growth rates greater than 12 cm h^{-1} , a new structure is observed, comprising well-oriented fibres of Cr₇C₃ carbide in a ductile matrix of CoNi.

The same microstructures were obtained when using additional cooling during solidification ($g_F = 225^\circ\text{C cm}^{-1}$) but were displaced to higher growth rates. This behaviour is similar to that observed in other eutectics e.g. Al–Si [11]. In this study, we analyse crystallographically only the complex-regular carbide microstructure. The crystallographic structure of the Cr₂₃C₆ carbide is of cubic

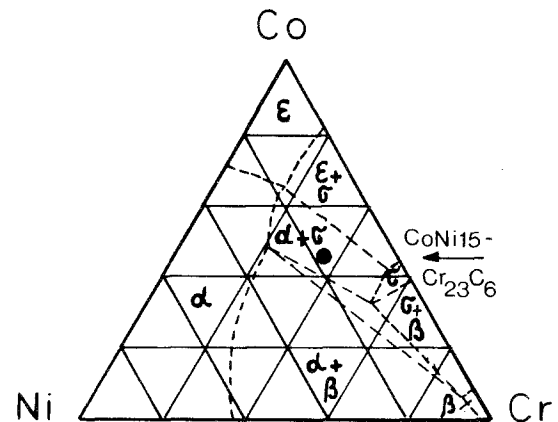


Figure 3 Phase diagram of Co–Cr–Ni system at 20°C .

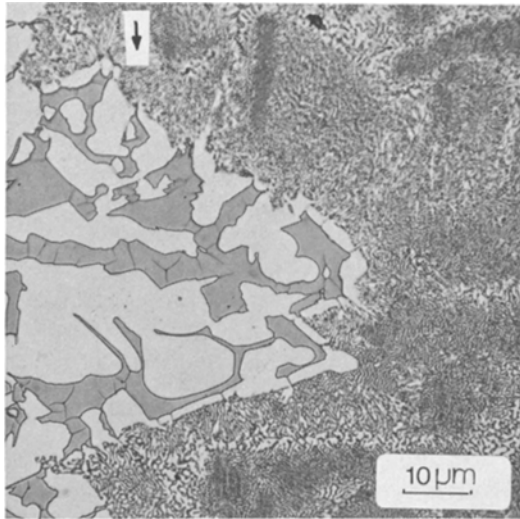


Figure 4 Interface quenched during directional solidification of CoNi 15–Cr₂₃C₆ eutectic.

type (D8₄) and corresponds to the approximate composition: Cr_{19.8}Co_{2.5}Ni_{0.7}C₆ determined by electron microprobe analysis. The composition of the ductile phase is Co, 45; Cr, 35 and Ni, 20 wt%. According to the ternary phase diagram Co–Ni–Cr [12] (Fig. 3) the ductile phase formed is a solid solution, $\alpha = \text{Ni, Co, Cr (fcc)}$ with eventually a precipitation of a phase, σ ; Co, Cr or of a phase, ϵ ; Co, Cr (hcp).

The mode of growth of the phases of the CoNi 15–Cr₂₃C₆ eutectic could be studied by quenching the interface. Fig. 4 shows a section perpendicular to the quenched interface. The irregular growth gives rise to an angular skeleton of carbide surrounded by a ductile Co–Ni–Cr phase. Such a

microstructure is to be expected in a eutectic of the faceted/non-faceted type where the anisotropy of the interface attachment kinetics of the faceted phase prevent fully cooperative growth [13]. A well-known typical example of this class of eutectic is Al–Si [11].

The morphology of the carbides can be regarded as an irregular arrangement of frequently branched plates which form an interconnected and multidirectional network throughout the microstructure. This is illustrated in the longitudinal and transverse sections of Fig. 5. The structure occasionally shows local areas of high regularity (Fig. 6). It has been suggested [13, 14] that this “complex-regular” structure, often observed in faceted/non-faceted eutectics, occurs when the alloy is too rich in the faceted component. The exact nature of the Co–Ni–Cr phase depends on the growth conditions.

The relation between the intercarbide spacing, λ , and the growth rate, v , is shown in Fig. 7. The relationship can be described by the law:

$$\lambda^{3.1}v = \text{constant}. \quad (1)$$

This value of the exponent of 3.1 differs from the value of 2 that is normally observed in regular lamellar or rod-like eutectic systems. This is not unreasonable since the theories of eutectic growth which predict the $\lambda^2 \cdot v = \text{constant}$ relationship, strictly only apply to non-faceted eutectic combinations [15, 16].

As Toloui and Hellawell have shown [17], the interphase spacings in faceted/non-faceted alloys (such as Al–Si) are affected not only by the growth rate but also by the temperature gradient.

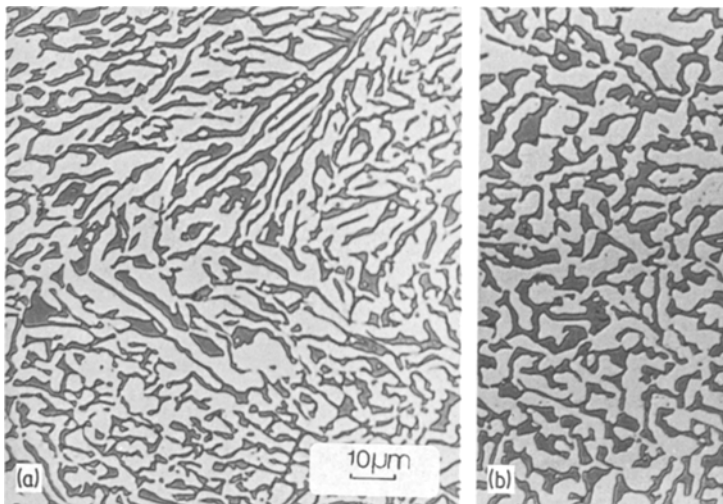


Figure 5 Oriented pseudo-binary eutectic CoNi–Cr₂₃C₆, $v = 2.4 \text{ cm h}^{-1}$, $g_T = 75^\circ \text{ C cm}^{-1}$, (a) longitudinal section, (b) transverse section.

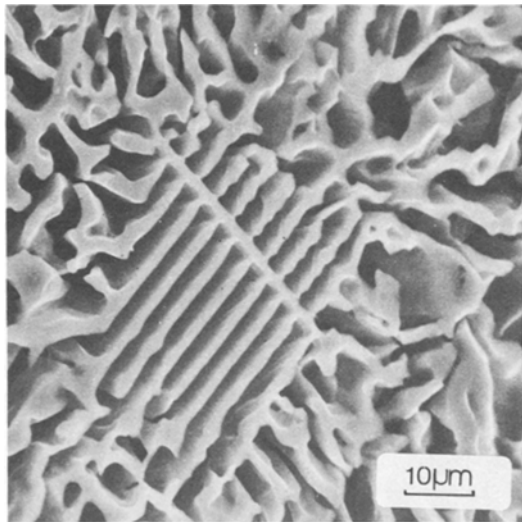


Figure 6 Complex-regular structure of Cr_{23}C_6 .

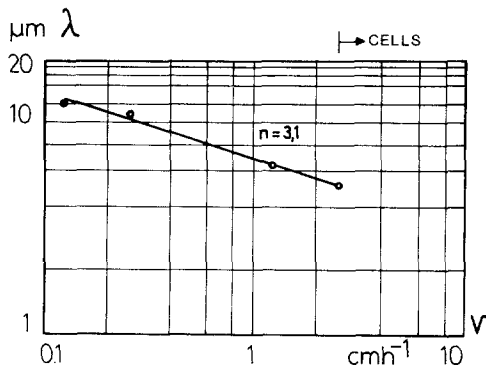


Figure 7 Variation of the intercarbide spacing, λ as a function of the growth rate, v . Pseudo-binary eutectic $\text{CoNi}_{15}\text{-Cr}_{23}\text{C}_6$.

This is probably due to an increased branching frequency of the faceted phase with increased G [13]. In the present study, it is possible that there was a systematic decrease in the temperature gradient in the sample with increasing growth velocity.

4. Crystallographic aspects

In spite of the apparent irregularity of the eutectic microstructure, transmission electron microscopy reveals that a specific and reproducible orientation relationship exists between the carbide and the $\text{Co}(\text{Ni})$ matrix phase. The micrographs of Figs. 8a and b are sections from thin foils cut parallel to and transverse to the growth axis respectively. In both cases, the superposed selected area diffrac-

tion patterns show that the phases are mutually aligned in a simple cube-cube configuration such that:

$$\begin{aligned} (100) \text{Co}(\text{Ni}) \parallel (100) \text{Cr}_{23}\text{C}_6 \\ [010] \text{Co}(\text{Ni}) \parallel [010] \text{Cr}_{23}\text{C}_6 \end{aligned}$$

In Fig. 8b, the plane of the foil is normal to the electron beam and from the symmetry of the diffraction pattern, it is evident that the common growth direction of both phases lies parallel to $\langle 111 \rangle$. This growth texture was found to be the preferred one in most of the samples that we examined. From these micrographs, it is also apparent that the interfaces between the phases, which seem so random on a macroscopic scale, are not wholly irrational. In the electron micrograph, the boundaries are often seen to consist of a number of straight segments or steps which give an overall faceted outline. From trace analysis, it is found that the individual facets usually correspond to the common $\{111\}$ planes of the two phases.

The carbide phase shows little contrast and is mostly featureless, but the metallic phase can be seen to contain numerous stacking faults that, in the micrograph, display characteristic fringe contrast effects. Seen in more detail (Fig. 9), the geometrical arrangement of the faults is compatible with their lying on a variety of intersecting $\{111\}$ planes.

The symmetrical epitaxy between the phases can be traced to the fact that the lattice parameter of the $\text{Co}(\text{Ni})$ phase (fcc , $a = 3.52$ to 3.56 \AA) is almost exactly one third that of the unit cell of the carbide phase (complex cubic, $a = 10.6 \text{ \AA}$). In the diffraction patterns of Fig. 8, this is apparent in the precise overlapping of the spots at intervals of every three reciprocal units. This size relationship allows very good matching between the two lattices in the cube-cube orientation, especially across a $\{111\}$ interface plane. The structure of Cr_{23}C_6 [18] is such that the $\{111\}$ planes consist of layers of chromium atoms, in an alternating hexagonal array, between puckered layers of mixed chromium and carbon atoms. As illustrated in Fig. 10, this arrangement gives a high degree of atomic coincidence across the $\{111\}$ habit plane between the chromium atoms in the carbide and the $\text{Co}(\text{Ni})$ atoms of the matrix. This feature would undoubtedly be associated with a substantial lowering of the interfacial energy between the two phases.

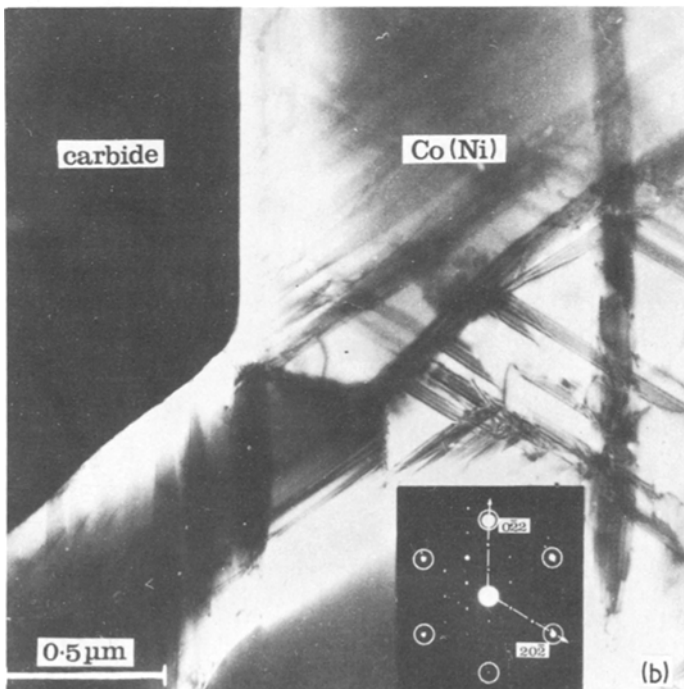
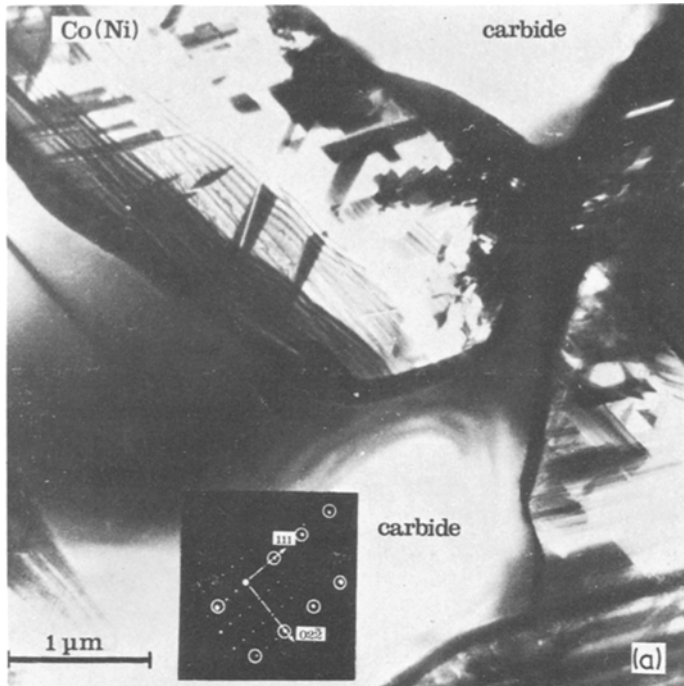


Figure 8 Transmission electron micrographs of the directionally frozen eutectic alloy, (a) section parallel to the growth axis and (b) transverse. Superimposed selected area diffraction patterns (CoNi spots circled) show the sections to be in $(\bar{2}11)$ and (111) orientations respectively, with a simple cube-cube epitaxy between the two phases.

In the context of what has been said above, it is relevant to consider why the eutectic microstructure should be so irregular. To some extent, this must be due to the anisotropy in growth kinetics of the faceted phase, but it can probably also be related to certain obvious incompatibilities in the

crystallographic growth preferences. Many eutectic systems develop regular lamellar or rod-like microstructures. These are usually of non-faceted/non-faceted type, but regular eutectics having a faceted constituent also occur, e.g. Co-TaC, Ni-TaC (see for example Hogan *et al.* [19]). In regular eutec-

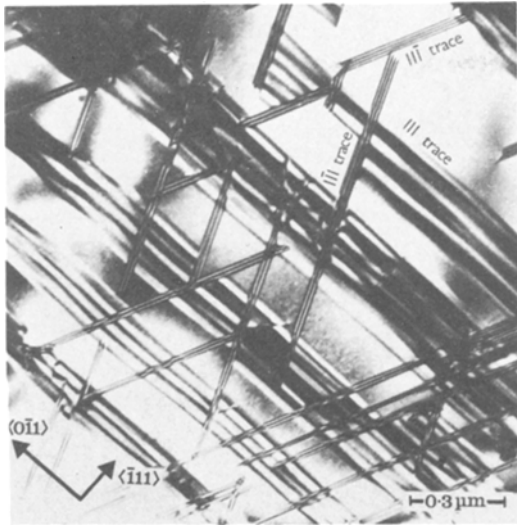


Figure 9 Detail of stacking faults in the CoNi matrix phase. The foil is in a $(2\ 1\ 1)$ orientation and the faults lie on intersecting $\{1\ 1\ 1\}$ planes. Transmission electron micrograph.

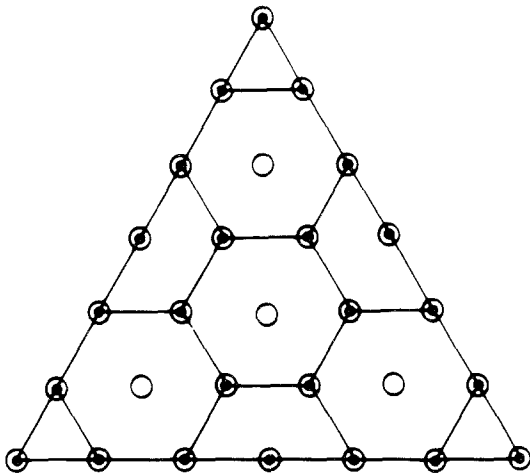


Figure 10 Diagram showing the close atomic coincidence across a $(1\ 1\ 1)$ interface plane between the chromium atoms in the carbide (●) and the CoNi atoms in the matrix (○).

tics, the lamellae or rods tend to align themselves perpendicular to the solid–liquid interface, with the imposed growth direction lying parallel to, or close to, the lamellar plane or rod axis. Deviations from this arrangement (as in non directional solidification) generally result in a disruption and degeneration of the microstructure with a loss of preferred orientation between the phases [20, 21]. In the present case, where a $[1\ 1\ 1]$ growth texture and a preference for the formation of $\{\bar{1}\ 1\ 1\}$ interface planes exists, (a) the interface planes cannot

lie parallel to the growth axis but are inclined at some 20° to it, and, (b) three possible sets of such planes exist (corresponding to $(\bar{1}\ 1\ 1)$, $(1\ \bar{1}\ 1)$ and $(1\ 1\ \bar{1})$) in a symmetrical configuration about the growth axis. In the first instance, there will be a tendency for the phases to grow in an edgewise manner at the solid–liquid front (the results of this are evident in the longitudinal section of Fig. 3, for example) and in the second, they have the freedom to alternate in morphology between the multiplicity of low energy interface planes that are available. Under these circumstances it seems unlikely that, during directional freezing of this alloy, a stable profile with a closely coupled mode of growth between the phases could be maintained at the growth front. This would be necessary for the development of a regular microstructure. The result, in spite of the simple epitaxy between the phases, is the convoluted and irregular microstructure that is observed.

A rather exceptional situation occurs in the case of the “complex–regular” cells. As has been noted, these growth forms are probably stabilized only in alloys of hypereutectic composition. On a polished section, the geometrical arrangement of the spines and side plates in these web-like structures varies with the orientation at which the section is cut (namely Fig. 4). They usually show, however, a three-fold symmetry about a $[1\ 1\ 1]$ axis and from two-surface analysis it is apparent that they consist of alternating arrays of lamellae attached to spines, all of which lie parallel to intersecting $\{\bar{1}\ 1\ 1\}$ planes. The general arrangement, which is consistent with the orientation preferences detailed previously, is illustrated diagrammatically in Fig. 11. Similar complex–regular

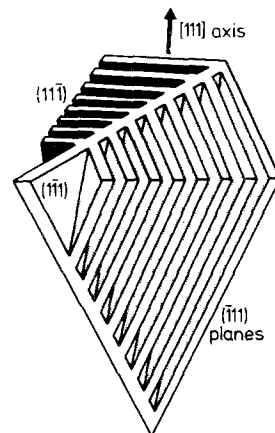


Figure 11 Diagram showing the $\{1\ 1\ 1\}$ geometry of a “complex–regular” cell.

structures have been observed in Al–Si and Al–Ge alloys [11, 22] and in the same way it has been shown that their overall morphologies can be correlated with the crystallographic arrangement of the constituent phases.

5. Conclusions

(1) Under conditions of directional solidification, the pseudo-binary eutectic alloy CoNi 15–Cr₂₃C₆ gives a highly irregular microstructure consisting of a branched and interconnected network of carbide in the metallic matrix. The interphase separation varies with growth rate as $\lambda^{3.1} v = \text{constant}$, a relationship which might be partly due to a dependence on the imposed temperature gradient.

(2) With increasing growth rate, three microstructural regimes are identified: (a) the irregular CoNi 15–Cr₂₃C₆ eutectic becoming (b) cellular and finally (c) transforming to fibrous CoNi–Cr₇C₆ eutectic. The transitions are displaced to higher rates with increasing temperature gradients.

(3) In spite of the irregularity of the eutectic CoNi 15–Cr₂₃C₆ microstructure, electron microscopy shows that a simple and reproducible cube–cube orientation relationship exists between the phases. There is a preference for a $\langle 111 \rangle$ growth texture and a tendency to the formation of $\{ \bar{1}11 \}$ interface planes.

(4) The orientation relationship between the phases can be associated with the close atomic coincidence that is possible between the two crystal lattices. The irregular nature of the microstructure is probably due, in some measure, to incompatibilities in the crystallographic alloy preferred directions growth. In hypereutectic alloys, the “complex–regular” cells that develop have a simple $\{111\}$ crystallographic geometry.

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