tures are composed of the same Zr_4Al_3 and Cr_3Si building blocks, they can intergrow easily and the match between these domains is therefore generally good.

The authors would like to thank Drs Y. D. Lin and J. W. Steeds of Bristol University for providing unpublished structural information of a new phase identical to our F phase. Throughout this work we have enjoyed many stimulating discussions with Professor H. Q. Ye of our laboratory.

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Identification of a Hitherto Unreported Frank–Kasper Phase

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Abstract

A previously unreported intermetallic phase has been discovered in a commercial superalloy. The phase was generally found in a highly faulted state. Small regular regions have been investigated by convergent-beam electron diffraction to give a space group of $P6/mmm$ and cell constants $a_0 = 12{\cdot}6 \pm 0{\cdot}1$ and $c_0 = 4{\cdot}6 \pm 0{\cdot}05$ Å. The diffracted intensities and some preliminary high-resolution micrographs indicate that the phase is one of those proposed by Frank & Kasper [*Acta Cryst.* (1959), **12**, 483-499], but not previously observed. Parallel work in China on another alloy has identified an apparently similar phase, named F phase, a description adopted here.

Introduction

Many intermetallic compounds, particularly those formed by transition metals, can be classified as having tetrahedrally close-packed structures containing interpenetrating polyhedra with coordination numbers 12, 14, 15 or 16 (Frank & Kasper 1958, 1959; Shoemaker & Shoemaker, 1969). Frank & Kasper showed that most of these compounds are layer-structured and that whole families of structures, including some hypothetical ones, could be generated by stacking similar layers in different ways and by introducing tessellation faults. The structure of these compounds generally consists of two primary layers at $z = 0$ and $\frac{1}{2}$ formed by tessellations of triangles and either hexagons or pentagons. Two identical secondary layers, at $z = \frac{1}{4}$ and $\frac{3}{4}$, centre the hexagonal or pentagonal antiprisms formed by the superposition of the primary layers.

We report here the space group of an intermetallic phase with a structure apparently agreeing with one predicted by Frank & Kasper (1959) in which the primary layers consist of a tessellation of hexagons and triangles, while the secondary layers consist of a $3^6 + 3^2\,434\,(1:6)$ net (for notation, see Pearson, 1972). The new phase has been named F in honour of the work of Frank & Kasper at the suggestion of Professor Kuo, who has, with Dr Li, simultaneously and independently identified the phase using high-resolution electron microscopy (Li & Kuo, 1986).

Experimental

The new phase was found in a Ni-based powder-metallurgical superalloy with the following composition (in wt%): Cr 10·0, Co 15·0, W 6·0, Mo 3·0, Ti 4·0, Al 4·0, Nb 1·7, Hf 0·7, Fe < 1·0, Mn < 0·15, Si < 0·2, Zr 0·05, C 0·04, B 0·002, Ni balance (these values were obtained from the suppliers: Rolls Royce Ltd, Filton, England.)

After hot isostatic pressing at 1443 K, the alloy was forged at 1423 K, solution treated at 1450 K for 4 h and aged at 1033 K for 16 h. Carbon-extraction replicas were prepared from gauge sections of samples which had been either creep tested at 953 K

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and 710 MN m^{-2} or stress ruptured at 1003 K and 750 MN m^{-2}. Samples were first etched in Kalling's etch (Modin & Modin, 1973) and, after coating with carbon, the replicas were released electrolytically in 10% HCl in methanol at 3 V at room temperature. The replicas were examined in either a Philips EM 430 electron microscope using a 200 Å probe for convergent-beam electron diffraction (CBED) and energy-dispersive X-ray analysis (EDXA) or a Philips EM 400 electron microscope equipped with a Link 860 energy-dispersive X-ray analysis system. High-resolution microscopy was performed on the Philips EM 430.

Results and discussion

The composition of the *F* phase was determined from energy-dispersive X-ray spectroscopy (Fig. 1) to be (in at %): Cr 41, Co 20, Ni 12, Mo 16, W 11.

The phase was found commonly at boundaries between γ and $\gamma+\gamma'$ grains and there is evidence to suggest that the precipitation of the *F* phase was enhanced by the presence of applied stress. The precipitates formed were generally sheet-like with their largest dimensions ranging from ~500 Å to ~1 μm and with thicknesses up to a few hundreds of Å. Fig. 2 shows a typical selected-area diffraction pattern for the *F* phase. The pattern shows only approximate sixfold symmetry and close inspection reveals that the spots are often broadened and sometimes streaked and that their locations deviated from those dictated by sixfold symmetry. The incommensurate nature of the diffraction pattern is associated with the presence of extensive faults within the *F*-phase precipitates. In order to determine unambiguously the point group and space group of the *F* phase by symmetry analysis of the CBED patterns, it is necessary to ensure that the patterns arise from unfaulted regions. However, the size of the unfaulted domains was quite small, generally comparable or smaller than the probe size. In some cases, structural irregularities extended down to the unit-cell level. Nevertheless, the CBED patterns obtained could be indexed in terms of a hexagonal *P* lattice with $c_0=4{\cdot}6$ and $a_0=12{\cdot}6$ Å. Patterns for the [0001] and [10$\bar{1}$0] zone axes (Figs. 3 and 4) show whole-pattern symmetries of 6 *mm* and 2 *mm* respectively. Small deviations from the precise symmetries could be detected by careful inspection and are probably due to the convergent probe covering more than one fault-free domain. By referring these results to the tables in Buxton, Eades, Steeds & Rackham (1976), it follows that the crystal has a point group of 6/*mmm*. The salient points are summarized in Table 1. The lattice, deduced from the diffraction pattern, is primitive and therefore the possible space groups are *P*6/*mmm*, *P*6/*mcc*, *P*6$_3$/*mcm* or *P*6$_3$/*mmc*. Since neither the [0001] nor the [10$\bar{1}$0] patterns show absent reflections or their equivalent (dynamic absences) in the case of strong dynamical diffraction (Steeds & Vincent, 1983), it is concluded that the space group of the *F* phase is *P*6/*mmm*.

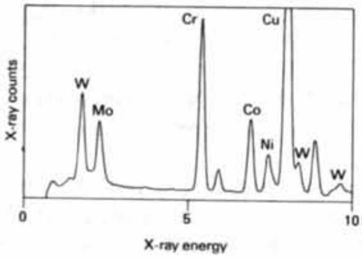

Fig. 1. Energy-dispersive X-ray spectrum for the *F* phase. The Cu peaks are due to the support grid. (1 eV ≡ $1{\cdot}6\times10^{-19}$J.)

Table 1. *Deduction of the 6/ mmm point group for the F phase from CBED pattern symmetries (summarized from Buxton et al.,* 1976)

Axis	Pattern symmetry	Possible diffraction groups	Possible point groups
[0001]	6*mm*	6*mm* 6*mm*1$_R$	6*mm* 6/*mmm*
[10$\bar{1}$0]	2*mm*	2*mm* 2*mm*1$_R$	$\bar{6}$*m*2 6/*mmm*

Although no σ-phase particles have been found in the present alloy, similarities between the [0001]$_F$ pattern (Fig. 3) and the [001]$_\sigma$ pattern (The Bristol Group, 1984) obtained in other alloys are apparent. There is a ring of strong reflections at ~0·24 Å^{-1}, indexed as {12$\bar{3}$0} in Fig. 3, which resembles the ring

Fig. 2. Selected-area electron diffraction pattern of the *F* phase; [0001] axis.

of {200} and {210} reflections in the corresponding σ-phase pattern. A second ring of strong reflections at $\sim 0{\cdot}46$ Å^{-1} indexed {50$\bar{5}$0} and {33$\bar{6}$0} is similar to the second strong ring in the 6 [001] pattern composed of {410} and {330} reflections. Another possible similarity exists with the [0001] diffraction pattern of the $9a_0$–$2H$ superstructure in ordered Au–29% Cd alloys (Hirabayashi, Yamaguchi, Hiraga, Ino, Sato & Toth, 1970). However, the space group in this case is $P6_3/mcm$ as compared with the $P6/mmm$ in the F phase and this major difference led us to eliminate the possibility.

The σ-like similarity, however, led us to re-examine the paper of Frank & Kasper (1959). They describe the σ phase as kagomé tiled, with tiling units containing four hexagons, and point out that other larger kagomé tiling units exist, incuding a large hexagonal unit containing seven smaller hexagons. This structure has 52 atoms per unit cell and consists of a $3636+6^23^2+6^3$ (6:3:1) net (the hexagonal kagomé tile) at $z=0$, a $3636+6^23^2+6^3$ (1:1:1) net at $z=\frac{1}{2}$ and two 3^6+3^2434 (1:6) nets at $z=\frac{1}{4}$ and $\frac{3}{4}$. In deducing this hypothetical structure, Frank & Kasper started with a primary layer of kagomé tiles with seven hexagons each (at $z=0$). For the next primary layer (at $z=\frac{1}{2}$) Frank & Kasper placed atoms above the centres of triangles and above the centres of edges that are shared by hexagons. Although the second primary layer produced by such a procedure also consisted of tiles of kagomé nets, distortions of the hexagons and triangles were evident. However, the distortions were reduced, consistent with the space group of the structure, by introducing additional small displacements along mirror lines in the structure. The idealized atom coordinates derived from the above description of nets and assuming tessellation of perfect hexagons and triangles are given in Table 2. This hypothetical case is consistent with our cell dimensions and space group and seems a very strong candidate for the structure of the newly discovered phase. Multislice calculations were therefore performed on the basis of this assumption and generated diffraction patterns closely resembling our experimental results. Further work is in hand to identify the sites occupied by the different atoms in the structure but there seems little doubt that the phase has been correctly identified. Parallel work by Li & Kuo (1986) has revealed an apparently identical phase of quite different composition, and its structure has been deduced by high-resolution electron microscopy as the hexagonal tiled kagomé phase of Frank & Kasper. Our high-resolution results (Fig. 5) are in close accord with theirs. This image, generated close to the Scherzer defocus, from a thin region ~ 100 Å thick, is believed to record the structure of the phase accurately. The close resemblance to the image (Fig. 4) of Li & Kuo (1986) is evidence that we have indeed studied related phases. The similarity of the [0001] projection of the F phase to that of the [001] σ phase, for which many computer-generated high-resolution image simulations have been performed, allows us to be confident that the bright spots represent the hexagonal regions of comparatively low electron density in the phase (see Fig. 16 of Frank & Kasper, 1959). The hexagonal regions cluster in sevens to form hexagonal tiles constituting the new phase.

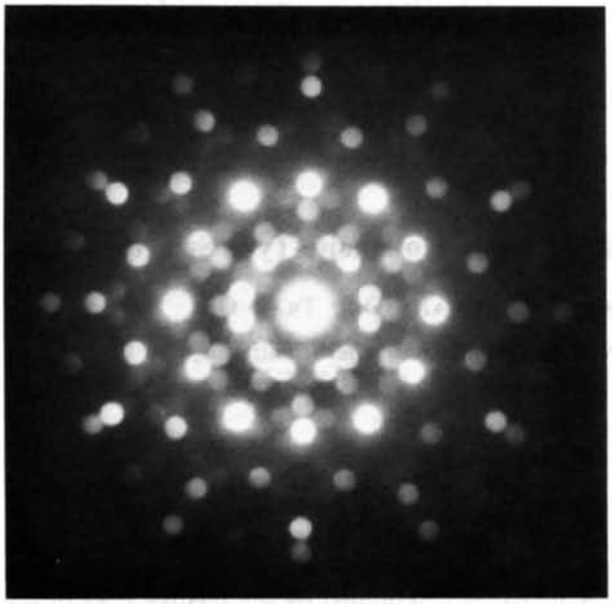

Fig. 3. Convergent-beam electron diffraction pattern of the F phase; [0001] axis. Whole pattern symmetry is close to 6 mm.

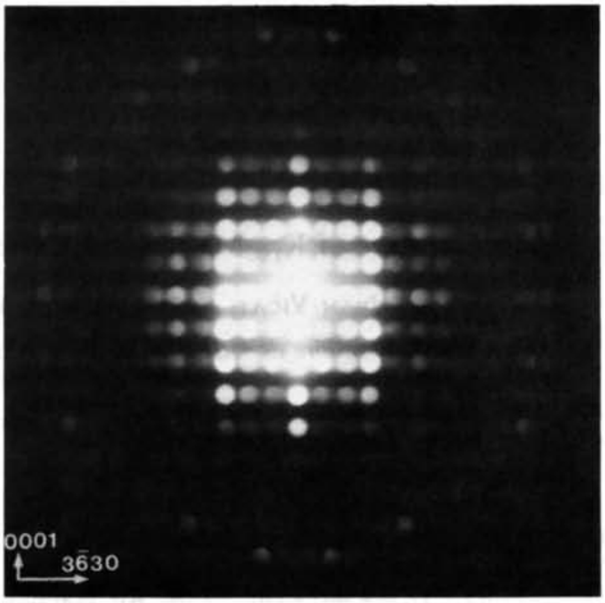

Fig. 4. [10$\bar{1}$0] axis of the F phase. Whole pattern symmetry is 2 mm.

Examination of Fig. 5 clearly reveals hexagonal arrays of seven white spots, although irregularities exist because of the faulting (such as indicated by the arrows) which occurs on a very fine scale.

We conclude that the atomic arrangement in the *F* phase is that of a hypothetical structure proposed by Frank & Kasper (1959) and can be thought of as composed of hexagonal kagomé tiles. Diffraction pattern intensities and high-resolution images are consistent with expectations from the proposed structure.

We would like to thank Dr R. Vincent for informative discussions and for implementing the multislice program, Professor K. H. Kuo for communication of unpublished work, Rolls Royce Ltd for provision of sample material and the Science and Engineering Research Council for financial support for one of us (YPL).

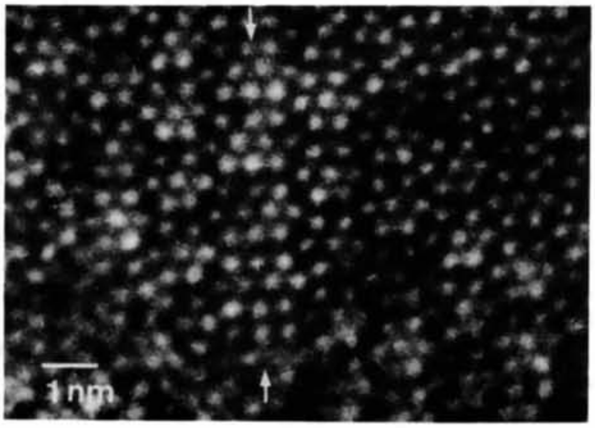

Fig. 5. [0001] high-resolution image of the *F* phase recorded at 300 kV showing bright spots arranged in a $3^6+3^2\,434$ (1:6) net. The two arrows indicate a fault line in the structure. (1 nm = 10 Å.)

Table 2. *Crystallographic data for the F phase, assuming tessellation of perfect hexagons and triangles*

Space group: $P6/mmm$
Lattice parameters: $a_0=12{\cdot}6$, $c_0=4{\cdot}6$ Å, $\gamma=120°$
Atoms per unit cell (Z): 52

Number	Wyckoff position	Coordinates			Value of variable
2	c	$\frac{1}{3},\frac{2}{3},0$	$\frac{2}{3},\frac{1}{3},0$		
2	e	$0,0,z$	$0,0,\bar{z}$		$z=\frac{1}{4}$
6	j	$x,0,0,$	$0,x,0$	$\bar{x},\bar{x},0$	$x=\frac{1}{3}$
		$\bar{x},0,0$	$0,\bar{x},0$	$x,x,0$	
6	k_1	$\{x,0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}\}$	$x_1=\frac{1}{3}$
6	k_2	$\{\bar{x},0,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	$x,x,\frac{1}{2}\}$	$x_2=\frac{2}{3}$
6	l_1	$\{x,2x,0$	$\overline{2x},\bar{x},0$	$x,\bar{x},0\}$	$x_1=\frac{1}{9}$
6	l_2	$\{\bar{x},\overline{2x},0$	$2x,x,0$	$\bar{x},x,0\}$	$x_2=\frac{4}{9}$
6	m	$x,2x,\frac{1}{2}$	$\overline{2x},\bar{x},\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	$x=\frac{2}{5}$
		$\bar{x},\overline{2x},\frac{1}{2}$	$\overline{2x},x,\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	
12	o	$x,2x,z$	$\overline{2x},\bar{x},z$	$x,\bar{x},z$	$x=\frac{2}{9}$
		$\bar{x},\overline{2x},z$	$2x,x,z$	$\bar{x},x,z$	$z=\frac{1}{4}$
		$x,2x,\bar{z}$	$\overline{2x},\bar{x},\bar{z}$	$x,\bar{x},\bar{z}$	
		$\bar{x},\overline{2x},\bar{z}$	$2x,x,\bar{z}$	$\bar{x},x,\bar{z}$	

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The Structure of $K_{1\cdot33}Mn_8O_{16}$ and Cation Ordering in Hollandite-Type Structures

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Abstract

Crystal data: $M_r=747{\cdot}5$, tetragonal, $I4/m$, $a=9{\cdot}866\,(3)$, $c=2{\cdot}872\,(1)$ Å, $V=279{\cdot}6\,(2)$ Å^3, $Z=8$ ($K_{0\cdot167}MnO_2$), $D_x=4{\cdot}442$ g cm^{-3}, λ(Ag $K\alpha$, graphite monochromator) $=0{\cdot}56005$ Å, $\mu=49{\cdot}9$ cm^{-1}, $F(000)=353{\cdot}5$, $T=295$ K, final $R=1{\cdot}9\%$ for 436 unique reflections. In this mixed-valence compound $K_xMn^{4+}_{8-x}Mn^{3+}_xO_{16}$ ($x=1{\cdot}33$) the channel cation position (K^+) is not at $00\frac{1}{2}$ but at $00z$ with $z=0{\cdot}375$. It is shown that the symmetry of hollandite-type structures ($A_xB_8O_{16}$) is determined by the relative sizes of the framework (B) and the channel (A) cations. Single-crystal rotation photographs around **c** show extra

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