Although it is not the purpose here to consider the analysis of the interdiffusion process by this X-ray technique (this will be published elsewhere) it is of interest to note briefly some of the more striking conclusions from the results presented. First it is seen from Figs. 4 and 5 that although significant interdiffusion has already occurred in 5 min., after 36,000 min. the homogenization is far from complete. Secondly, Ni diffuses into Cu much more rapidly than Cu into Ni; after 5 min. no pure Cu remains although there is considerable pure Ni.

Summary

The broadening of a diffraction line from an inhomogeneous binary solid solution has been quantitatively analyzed to yield the composition distribution, $N(x)$, defined as the number of unit cells of composition x. The analysis hinges on the minimization of diffraction-line instrumental broadening. Stokes's Fourier method of instrumental-effect minimization has been reviewed. An alternative method has also been described; it is shown that by choosing a high angle reflection and mathematically eliminating the $K\alpha_2$ component the instrumental effect can be made negligible in cases of moderate dependence of lattice parameter on composition.

The analysis has been applied to mixed Cu–Ni powders (36 at.% Cu) interdiffused at 780 °C. The results have been presented in the form of diagrams of x versus

$$\int_0^x N(x)\,dx \Big/ \int_0^1 N(x)\,dx$$

which have been shown to be analogous to the description of interdiffusion by the usual concentration-penetration curve. The average compositions of the resulting inhomogeneous solid solutions have been determined by the X-ray analysis to $\pm 1{\cdot}5\%$.

The method of analysis by $K\alpha_2$ elimination has been compared with Stokes's Fourier method with the conclusion that the former, in the example considered, was more reliable and about ten times more rapid.

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The Crystal Structure of $PuNi_4$*

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The structure of $PuNi_4$ has been determined by single crystal X-ray methods. The unit cell is monoclinic, space group $C2/m$ with

$$a = 4{\cdot}87,\ b = 8{\cdot}46,\ c = 10{\cdot}27\ \text{Å},\ \beta = 100°.$$

There are six formula units per unit cell. Two of the six Pu atoms have a coordination essentially identical to that of the Pu in $PuNi_5$. The other Pu atoms have a coordination somewhat similar to the Pu in $PuNi_5$. The $PuNi_4$ structure can be obtained by removing the Ni atoms at $z = \frac{1}{2}$ from every third unit cell of $PuNi_5$ and by slightly shifting the remaining atoms.

Introduction

There are six binary compounds in the Pu–Ni system (Wensch & Whyte, 1951). The structures of $PuNi_2$, $PuNi_5$ and Pu_2Ni_{17} have been reported by Coffinberry & Ellinger (1956). The structure of PuNi has been reported by Cromer & Roof (1959) and that of $PuNi_3$ by Cromer & Olsen (1959). The structure of $PuNi_4$, the remaining compound of the series, is the subject of the present report.

Experimental

An alloy containing 78·5 at.% Ni was prepared by melting the components in vacuum and then annealing the resulting ingot at 1240 °C. for 10 hr.

* Work done under the auspices of the U.S. Atomic Energy Commission.

Table 1. *Final least-squares parameters for* $PuNi_4$

Atom	x	y	z	B (Å^2)
Pu_1	0	0	0	$1{\cdot}59 \pm 0{\cdot}13$
Pu_2	$0{\cdot}1263 \pm 0{\cdot}0010$	0	$0{\cdot}3552 \pm 0{\cdot}0004$	$1{\cdot}67 \pm 0{\cdot}10$
Ni_1	0	$0{\cdot}3331 \pm 0{\cdot}0011$	0	$1{\cdot}99 \pm 0{\cdot}31$
Ni_2	$0{\cdot}5712 \pm 0{\cdot}0028$	0	$0{\cdot}1987 \pm 0{\cdot}0013$	$1{\cdot}50 \pm 0{\cdot}28$
Ni_3	$0{\cdot}3199 \pm 0{\cdot}0019$	$0{\cdot}2507 \pm 0{\cdot}0009$	$0{\cdot}1993 \pm 0{\cdot}0007$	$1{\cdot}70 \pm 0{\cdot}18$
Ni_4	$0{\cdot}1422 \pm 0{\cdot}0020$	$0{\cdot}3300 \pm 0{\cdot}0007$	$0{\cdot}4066 \pm 0{\cdot}0009$	$2{\cdot}11 \pm 0{\cdot}23$

The amount of Ni in the alloy was purposely held to somewhat below 80 at.%, the theoretical composition of $PuNi_4$, in order to ensure that the primary phase would be $PuNi_4$. Metallographic examination showed that the specimen consisted almost entirely of coarse grained $PuNi_4$. However, because of the very soft, graphite-like texture of $PuNi_4$, it was impossible to separate crystals of good quality from the aggregate. After X-ray examination of a number of fragments, one single crystal of poor but usable quality was obtained. Precession photographs were taken of this crystal with Mo radiation ($\lambda = 0{\cdot}7107$ Å) and the unit cell was found to be monoclinic with

$$a = 4{\cdot}87 \pm 0{\cdot}01,\ b = 8{\cdot}46 \pm 0{\cdot}02,\ c = 10{\cdot}27 \pm 0{\cdot}02 \text{ Å},$$
$$\beta = 100 \pm 0{\cdot}1°.$$

The systematic extinctions were consistent with space groups $C2$, Cm or $C2/m$. No measured density was obtained. The unit-cell volume, however, was consistent with six formula units per unit cell and the calculated density is therefore 11·3 g.cm.$^{-3}$. The structure determination itself is the best evidence for the identity of the compound.

The best crystal was an irregular fragment having the approximate dimensions $0{\cdot}20 \times 0{\cdot}03 \times 0{\cdot}04$ mm. and its longest dimension nearly coincident with the b axis. For intensity data this crystal was rotated about the b axis and a series of timed exposures was made on a precession camera for each of the zones $hk0$, $0kl$, hkh and $hk\bar{h}$. Mo $K\alpha$ radiation was used. The intensities were estimated visually and the four sets of data were placed on approximately the same scale by comparing the common $0k0$ reflections. Lp corrections were applied (Waser, 1951) but absorption errors were ignored.

Determination of the trial structure

$PuNi_3$ had been found to have a structure related to both $PuNi_2$ and $PuNi_5$ (Cromer & Olsen, 1959; Cromer & Larson, 1959). It seemed reasonable to expect, therefore, that $PuNi_4$ would also be structurally related to $PuNi_5$. Further, Ellinger (1959) had observed that the powder pattern of $PuNi_4$ was very similar to that of $PuNi_5$. It was also noted that the a and b unit-cell dimensions of $PuNi_4$ are nearly the same as the a and b dimensions of the orthohexagonal cell of $PuNi_5$. The assumption was initially made that the space group is $C2/m$, and because a satisfactory structure was found in this space group the other two space groups were not considered.

The $0kl$ data were used to calculate a Patterson projection. The most prominent vectors indicated that there were linear groups of three Pu atoms, as in $PuNi_3$, and that the central Pu atom was surrounded by Ni atoms as in $PuNi_5$. Two Pu_1 atoms were placed in $2a$ (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0) and four Pu_2 atoms in $4i$ (x, 0, z; etc.) with $z_{Pu_2} \approx 0{\cdot}35$. In order to provide a reasonable interatomic distance between the Pu atoms at x, 0, z and $\bar{x}$, 0, $\bar{z}$, x_{Pu_2} must be $\approx 0{\cdot}13$. Pu_1 could be surrounded by Ni atoms as in $PuNi_5$ by placing four Ni_1 atoms in $4g$ (0, y, 0; etc.) with $y_{Ni_1} \approx \frac{1}{3}$, four Ni_2 atoms in $4i$ with $x_{Ni_2} \approx 0{\cdot}57$ and $z_{Ni_2} \approx 0{\cdot}20$ and eight Ni_3 in the general position with $x_{Ni_3} \approx \frac{1}{3}$, $y_{Ni_3} \approx \frac{1}{4}$ and $z_{Ni_3} \approx 0{\cdot}20$. Sixteen of the 24 Ni atoms were thus accounted for. It was consistent with the

Table 2. *Observed and calculated structure factors for* $PuNi_4$

If $F_o = 0$, the reflection was obscured by the beam trap. If $F_o < 0$, the reflection was unobserved and the minus sign should be interpreted as 'less than'

H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c	H	K	L	F_o	F_c
0	2	0	264	207	0	2	0	198	207	0	2	0	245	207	0	2	0	201	207
0	4	0	523	480	0	4	0	515	480	0	4	0	530	480	0	4	0	482	480
0	6	0	370	363	0	6	0	386	363	0	6	0	400	363	0	6	0	339	363
0	8	0	246	240	0	8	0	219	240	0	8	0	272	240	0	8	0	234	240
0	10	0	96	86	0	10	0	83	86	0	10	0	87	86	0	10	0	97	86
0	0	1	0	-7	1	1	0	155	170	1	1	1	96	-94	1	1	-1	82	82
0	2	1	37	-59	1	3	0	392	409	1	3	1	188	-186	1	3	-1	152	167
0	4	1	74	57	1	5	0	112	112	1	5	1	47	-51	1	5	-1	60	57
0	6	1	77	-65	1	7	0	85	96	1	7	1	52	-59	1	7	-1	53	46
0	8	1	50	38	1	9	0	145	155	1	9	1	64	-64	1	9	-1	73	63
0	10	1	-42	-15	1	11	0	50	44	1	11	1	29	-20	1	11	-1	31	25
0	0	2	-18	15	2	0	0	114	117	2	0	2	629	643	2	0	-2	143	-168
0	2	2	75	62	2	2	0	211	233	2	2	2	26	36	2	2	-2	72	-74
0	4	2	197	-166	2	4	0	34	40	2	4	2	245	274	2	4	-2	58	-62
0	6	2	182	167	2	6	0	167	182	2	6	2	197	199	2	6	-2	104	-106
0	8	2	84	-85	2	8	0	32	28	2	8	2	142	147	2	8	-2	35	-26
0	10	2	-41	25	2	10	0	72	74	2	10	2	55	33	2	10	-2	46	-35
0	0	3	303	307	3	1	0	42	-38	3	1	3	78	-98	3	1	-3	-24	21
0	2	3	392	383	3	3	0	86	-86	3	3	3	86	-103	3	3	-3	133	114
0	4	3	101	101	3	5	0	31	-22	3	5	3	53	-66	3	5	-3	29	16
0	6	3	337	331	3	7	0	37	-24	3	7	3	51	-61	3	7	-3	30	15
0	8	3	71	60	3	9	0	53	-37	3	9	3	46	-43	3	9	-3	65	53
0	10	3	129	123	4	0	0	123	-130	4	0	4	353	375	4	0	-4	156	149
0	0	4	72	-59	4	2	0	42	-46	4	2	4	87	125	4	2	-4	149	142
0	2	4	95	-95	4	4	0	73	-73	4	4	4	193	234	4	4	-4	30	19
0	4	4	-37	-16	4	6	0	67	-64	4	6	4	120	155	4	6	-4	216	193
0	6	4	96	-85	4	8	0	39	-39	4	8	4	138	145	4	8	-4	-28	10
0	8	4	-43	1	5	1	0	-28	-5	5	1	5	35	-27	5	1	-5	119	104
0	10	4	45	-36	5	3	0	-28	14	5	3	5	-34	7	5	3	-5	112	101
0	0	5	517	573	5	5	0	-28	-2						5	5	-5	101	86
0	2	5	-33	-20	5	7	0	-22	-4						5	7	-5	82	67
0	4	5	210	216	6	0	0	115	102						6	0	-6	28	-20
0	6	5	173	167	6	2	0	31	-34						6	2	-6	-23	0
0	8	5	125	114	6	4	0	47	36										
0	10	5	-37	12															
0	0	6	238	255															
0	2	6	205	238															
0	4	6	242	258															
0	6	6	117	115															
0	8	6	151	159															
0	10	6	82	79															
0	0	7	105	-106															
0	2	7	99	-97															
0	4	7	214	-213															
0	6	7	-43	33															
0	8	7	126	-129															
0	10	7	51	-30															
0	0	8	102	91															
0	2	8	155	171															
0	4	8	-43	24															
0	6	8	163	160															
0	8	8	-41	18															
0	0	9	129	143															
0	2	9	93	99															
0	4	9	108	120															
0	6	9	72	70															
0	8	9	82	79															
0	0	10	145	137															
0	2	10	114	-123															
0	4	10	-45	10															
0	6	10	-43	-1															
0	8	10	-27	1															
0	0	11	137	144															
0	2	11	116	135															
0	4	11	162	151															
0	6	11	74	77															
0	0	12	-44	33															
0	2	12	-45	28															
0	4	12	42	-35															
0	6	12	75	75															
0	0	13	56	-59															
0	2	13	-45	-6															
0	4	13	76	-65															
0	0	14	108	111															
0	2	14	65	84															

Patterson projection and packing considerations to place the remaining eight Ni atoms in the general position with $x_{Ni_4} \approx 0{\cdot}14$, $y_{Ni_4} \approx \frac{1}{3}$ and $z_{Ni_4} \approx 0{\cdot}40$. Structure factors calculated from this trial structure were in reasonable agreement with the observed structure factors.

It might be of interest to note that for solving this and other structure problems we have found it convenient to use a computer for generating and sorting interatomic vectors. In this way trial structures can be quickly rejected or accepted for further study.

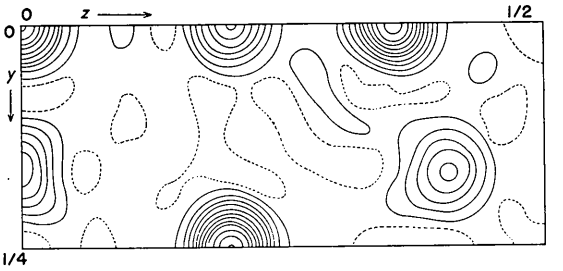

Fig. 1. Fourier projection of $PuNi_4$ down the a axis. The zero contour is dashed. The contour interval is 10 e.Å^{-2} around the Ni atoms and 20 e.Å^{-2} about the Pu atoms.

Refinement of the structure

The above trial structure provided starting parameters for a least-squares refinement which was carried out with the aid of an IBM–704 computer. Included as parameters were eleven atomic positions, six isotropic temperature factors and four scale factors, one for each zone. The Thomas–Fermi form factor of Pu was used after subtracting 10 electrons as an approximate correction for anomalous dispersion. The Viervoll & Øgrim (1949) form factor was used for Ni. All reflections were weighted equally. The final posi-

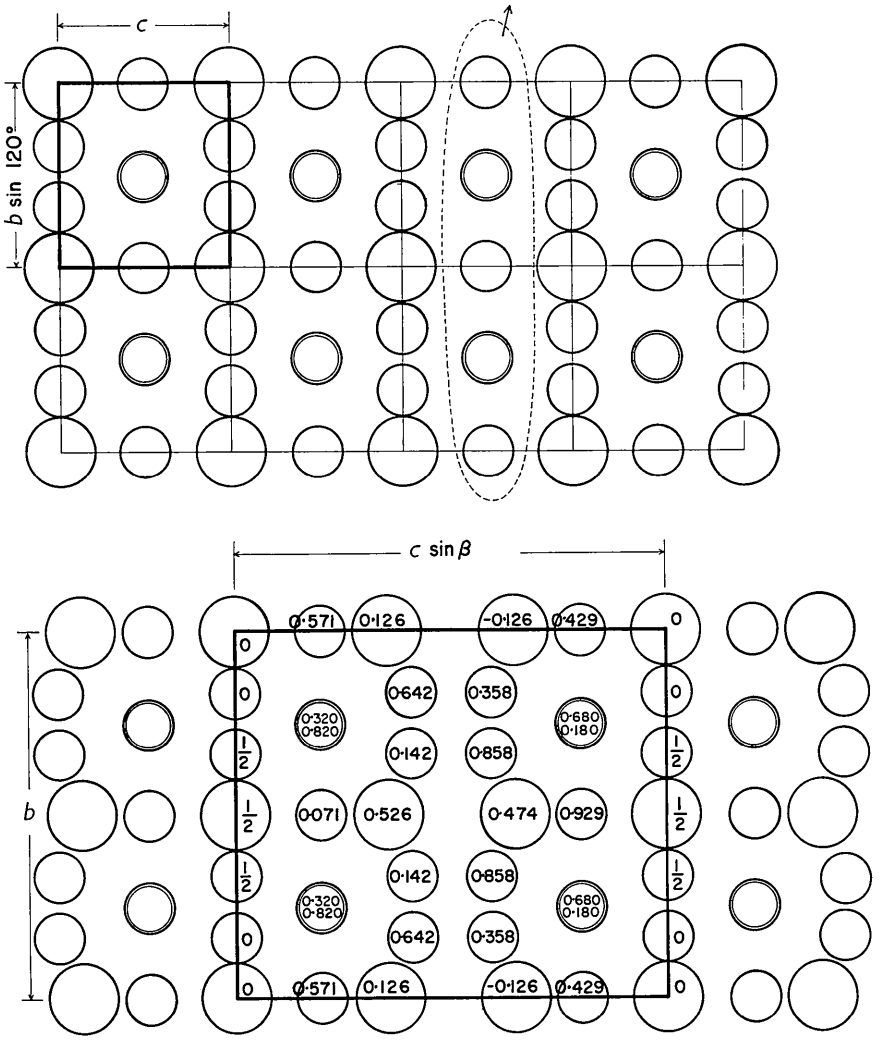

Fig. 2. (*a*) Several unit cells of $PuNi_5$. The large circles are Pu atoms and the small circles are Ni atoms. (*b*) The $PuNi_4$ structure in projection down [100]. The x coordinates of the atoms are given inside the circles.

tion and thermal parameters are listed in Table 1 and the observed and calculated structure factors, for which $R=8{\cdot}4\%$, are listed in Table 2. The standard deviations were estimated in the usual way by inverting the matrix of coefficients in the least-squares normal equations.

An $0kl$ Fourier projection is shown in Fig. 1.

Discussion of the structure

The various interatomic distances in $PuNi_4$ are given in Table 3. The standard deviations of Pu–Pu, Pu–Ni and Ni–Ni distances are about 0·01, 0·02 and 0·03 Å, respectively. In Fig. 2(*b*) the structure of $PuNi_4$ is shown in projection parallel to the *a* axis. The $PuNi_4$ structure can be derived from the $PuNi_5$ structure but not by making substitutions and layer shifts of the type used to develop $PuNi_3$ and other similar structures (Cromer & Larson, 1959). Fig. 2(*a*) shows several unit cells of $PuNi_5$ ($CaCu_5$ structure type). In order to derive $PuNi_4$ from $PuNi_5$ the layer of atoms at $z=\frac{1}{2}$ in every third unit cell is removed, as indicated by the encircled atoms in Fig. 2(*a*). This operation changes the symmetry to $C2/m$ with a monoclinic β angle of 90°. The structure is then collapsed in order to fill up the vacated space. The Ni atoms in the layers next to the layer that was removed approach each other and move slightly out of the planes of the Pu atoms. A rotation of 10° about the *b* axis permits the exposed atoms to assume normal interatomic distances and produces the monoclinic β angle of 100°.

Table 3. *Interatomic distances in* $PuNi_4$

The number of neighbors of a given kind is in parentheses

Pu_1–Pu_2	3·59(2) Å	Pu_2–Pu_1	3·59(1) Å
–Ni_1	3·15(2)	–Pu_2	3·41(1)
–Ni_1	3·16(2)	–Ni_1	2·89(1)
–Ni_2	2·81(4)	–Ni_1	2·91(1)
–Ni_2	2·82(2)	–Ni_3	2·90(1)
–Ni_3	3·16(4)	–Ni_3	2·91(1)
–Ni_3	3·17(4)	–Ni_4	2·84(2)
		–Ni_4	2·86(2)
		–Ni_4	2·89(2)
		–Ni_4	2·89(2)
Ni_1–Pu_1	3·15(1) Å	Ni_2–Pu_1	2·81(2) Å
–Pu_1	3·16(1)	–Pu_1	2·82(1)
–Pu_2	2·89(1)	–Ni_1	2·45(2)
–Pu_2	2·91(1)	–Ni_2	2·81(2)
–Ni_2	2·45(2)	–Ni_2	2·82(1)
–Ni_3	2·43(2)	–Ni_3	2·45(2)
–Ni_3	2·45(2)	–Ni_3	2·46(2)
–Ni_4	2·55(2)		
Ni_3–Pu_1	3·16(1) Å	Ni_4–Pu_2	2·84(1) Å
–Pu_1	3·17(1)	–Pu_2	2·86(1)
–Pu_2	2·90(1)	–Pu_2	2·89(1)
–Pu_2	2·91(1)	–Pu_2	2·89(1)
–Ni_1	2·43(1)	–Ni_1	2·55(1)
–Ni_1	2·45(1)	–Ni_3	2·51(1)
–Ni_2	2·45(1)	–Ni_3	2·52(1)
–Ni_2	2·46(1)	–Ni_4	2·43(1)
–Ni_3	2·43(2)	–Ni_4	2·55(1)
–Ni_4	2·51(1)	–Ni_4	2·79(2)
–Ni_4	2·52(1)	–Ni_4	2·88(1)

Pu_1 has two Pu and 18 Ni neighbors in an arrangement essentially the same as the Pu in $PuNi_5$. Pu_2 has two Pu and 14 Ni neighbors. There are six Ni atoms approximately coplanar with Pu_2 and on one side there are six Ni atoms and one Pu atom. Thus far the coordination is about the same as it is in $PuNi_5$. However, on the other side of Pu_2 there are only three neighbors, one Pu atom and two Ni atoms, arranged in the form of a triangle. Thus the two Pu neighbors of Pu_2 form an angular rather than a linear group of three. Ni_1, Ni_3 and Ni_4 each have four Pu and eight Ni neighbors arranged in distorted icosohedrons. Ni_2 has three Pu and nine Ni neighbors in a coordination, similar to the twofold Ni in the $PuNi_5$ structure.

We are indebted to Mr V. O. Struebing for preparation of the alloy.

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