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The Structure of the σ Phase in Vanadium-Nickel Alloys

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The σ phase in the system vanadium–nickel has been investigated by single-crystal and powder-photograph methods. The unit cell is tetragonal with $a = 8{\cdot}966$ and $c = 4{\cdot}641$ Å for an alloy containing 60 atomic% vanadium. Structure factors obtained from Cu oscillation photographs and Cu and Cr powder photographs are compared with those calculated from the atomic positions given by Tucker for β-uranium and Kasper, Decker & Belanger for the cobalt–chromium σ phase. The Cr oscillation photographs suggest there may be a tendency towards ordering of the atomic positions in which the layers are occupied alternately by one kind of atom or the other. Powder photographs have been used to obtain accurate d values for the principal σ phase lines of the σ phases formed in the first long period and, except for slight variations in axial ratio, these phases appear to be completely isomorphous.

Introduction

Preliminary accounts of the structure of σ phase alloys have recently been published by several workers. The symmetry and unit cell of the iron–chromium σ phase were determined by Bergman & Shoemaker (1951) and cobalt–chromium crystals have been investigated by Dickens, Douglas & Taylor (1951) and by Kasper, Decker & Belanger (1951). All these workers found the structure to be tetragonal, with axial ratio c/a of about 0·5 and 30 atoms in the unit cell. The systematic absences limit the space group to $P4/mnm$, $P4nm$ or $P\bar{4}n2$. Laue photographs along the c axis show pseudo hexagonal symmetry, and the structure is closely related to one in which the atomic positions are in close-packed layers perpendicular to the c axis. Dickens *et al.* noticed a strong similarity between the σ structures and the structure of β-uranium, a preliminary account of this having recently been published by Tucker (1951).

Tucker considered that his intensity data for general (hkl) reflections eliminated the most symmetrical space group, $P4/mnm$, and he proposed a structure having space group $P4nm$. Dickens *et al.* found reasonably good agreement with intensities calculated from this structure and visually estimated intensities for the first 30 lines of the iron–chromium σ phase powder pattern. This structure is, however, not yet established and Kasper and his co-workers found rough agreement of calculated and experimental intensities up to the Cr $K\alpha$ wavelength limit for a structure with the centrosymmetrical space group $P4/mnm$. This space group is also considered more probable by Bergman & Shoemaker who obtained Weissenberg photographs up to the Cu $K\alpha$ limit ($l = 5$) and $2kl$ photographs up to the Mo $K\alpha$ limit ($l = 12$). They found that after correcting for normal decline the structure factors for reflections with given h and k were always the same for l odd and l a multiple of $4n$ or $4n+2$, this being the condition for all atoms to be confined to planes normal to the c axis and separated by distances $\frac{1}{4}c$. These workers believe that Tucker's data can also be reconciled with this structure, if allowance is made for the large absorption in uranium.

The above investigations all suffer from the restriction that the difference in scattering powers of the two kinds of atom present is very small and it is not therefore possible to distinguish the positions of the atoms of one kind from those of the other. The wide range of compositions and differing atomic percentages at which σ phases are found make it certain that they are not definite intermetallic compounds, but the great stability of the phases in some cases suggests there may be a tendency towards superlattice formation in which some sites are occupied preferentially by one kind of atom. Of the known σ phases the most suitable for detecting an ordered arrangement is that occuring in iron–molybdenum alloys, but as this phase is stable only at high temperatures the experimental difficulties in obtaining single crystals are very great. A considerable difference in X-ray scattering powers is also found in nickel–vanadium alloys if chromium radiation is used, whereas with copper radiation the scattering powers of nickel and vanadium are almost identical. Unpublished work at Oxford shows that in the system vanadium–nickel the σ phase extends from 55 to > 70 atomic% vanadium and is stable up to the solidus. The conditions are thus favourable for obtaining single crystals.

Single-crystal experiments

An alloy containing 60 atomic% vanadium had a relatively coarse structure after annealing just below the solidus, and X-ray examination of fragments crushed in an agate mortar showed that several of these were single crystals. The crystal selected was of irregular shape and plate-like form; the two larger dimensions were greater than $\frac{1}{2}$ mm. so that there were considerable absorption errors in the observed intensities, but the crystal had the advantage of needing relatively short exposures. Laue and rotation photographs established that the lattice is tetragonal with

$$a = 8{\cdot}97, \quad c = 4{\cdot}64 \text{ Å}.$$

There are 30 atoms in the unit cell and the Laue symmetry is D_{4h} in agreement with the other workers.

The crystal was then mounted with an a axis vertical and 15° oscillation photographs were taken in a 6 cm. diameter camera using unfiltered Cu radiation, and Cr $K\alpha$ radiation filtered through 0·001 inch vanadium foil. The photographs with each radiation covered a total range of 99° with 3° overlaps, and the exposure times varied from 4 hr. for the Cu to 12 hr. for the Cr photographs. Rotation about an a axis instead of the more usual c axis ensured that each reflexion with both h and $k \leq 4$ was recorded at least twice (as (hkl) and (khl)), thus giving a check on observed intensities, and also that systematic absences ($0kl$ with $k+l$ odd) were all zero-layer-line reflexions. If ordering exists it is possible that the n glide plane is destroyed in the ordered structure

Table 1. *Calculated and observed structure factors*

F_1 based on structure of Tucker (1951).
F_2 based on structure of Kasper *et al.* (1951).

	$l = 0$			$l = 1$			$l = 2$		
h k	$\lvert F_1\rvert$	$\lvert F_2\rvert$	$\lvert F_o\rvert$	$\lvert F_1\rvert$	$\lvert F_2\rvert$	$\lvert F_o\rvert$	$\lvert F_1\rvert$	$\lvert F_2\rvert$	$\lvert F_o\rvert$
0 0	—	—	—	0	0	0	223	231	243
1 0	0	0	0	29	5	18	0	0	0
1 1	6	21	0	1	46	0	56	41	77
2 0	21	19	0	0	0	0	148	186	126
2 1	4	10	0	32	9	0	163	139	160
2 2	1	51	0	19	48	0	115	112	113
3 0	0	0	0	16	13	0	0	0	0
3 1	32	12	16	46	38	42	55	66	100
3 2	10	23	0	23	1	< 19	33	59	66
3 3	229	208	199	213	201	219	54	38	0
4 0	15	44	0	0	0	0	18	28	50
4 1	234	250	193	200	204	176	24	14	42
4 2	24	27	20	67	12	< 22	11	72	24
4 3	18	26	< 23	45	32	61	30	88	73
4 4	26	34	0	28	31	0	11	48	0
5 0	0	0	0	17	62	30	0	0	0
5 1	42	3	46	54	41	44	56	51	35
5 2	5	34	0	4	15	< 23	80	30	82
5 3	2	8	0	6	4	0	145	142	184
5 4	32	6	0	38	24	30	93	30	105
6 0	1	33	39	0	0	0	172	87	210
6 1	8	73	0	22	51	0	71	97	129
6 2	36	14	0	48	18	82	51	57	99
6 3	7	59	0	17	33	< 28	39	73	44
6 4	7	12	0	51	38	< 40	26	5	< 40
7 0	0	0	0	32	47	64	0	0	0
7 1	28	21	0	17	17	0	24	20	0
7 2	201	138	138	91	123	118	65	73	82
7 3	3	46	0	26	6	< 30	19	54	65
7 4	1	15	0	15	22	0	137	94	237
8 0	2	3	0	0	0	0	124	124	171
8 1	17	54	0	20	21	0	54	36	0
8 2	175	164	165	67	117	78	65	50	72
8 3	34	15	0	22	65	0	15	38	0
8 4	7	20	0	25	38	0	36	18	0
9 0	0	0	0	34	35	< 30	0	0	0
9 1	7	17	0	21	37	30	33	25	40
9 2	41	4	42	64	41	60	36	85	73
9 3	1	55	0	12	41	0	99	15	27
9 4	6	98	0	15	28	0	78	35	127
10 0	7	105	< 28	0	0	0	52	33	93
10 1	50	23	49	58	12	52	67	23	124
10 2	25	32	0	9	5	36	42	75	69
10 3	4	37	0	24	2	0	29	37	0
11 0	0	0	0	28	16	0	0	0	0
11 1	104	99	104	72	64	29	—	—	—
11 2	22	32	0	35	18	0	—	—	—

Table 1 (*cont.*).

$h\ k$	$l = 3$			$l = 4$			$l = 5$		
	$\|F_1\|$	$\|F_2\|$	$\|F_o\|$	$\|F_1\|$	$\|F_2\|$	$\|F_o\|$	$\|F_1\|$	$\|F_2\|$	$\|F_o\|$
0 0	0	0	0	253	322	323	0	0	0
1 0	3	3	30	0	0	0	13	2	0
1 1	23	29	25	28	13	0	44	68	0
2 0	0	0	0	71	10	0	0	0	0
2 1	61	6	33	51	5	$<$ 29	61	3	0
2 2	32	33	$<$ 26	41	28	0	22	25	28
3 0	23	9	0	0	0	0	38	6	59
3 1	39	28	67	53	7	30	36	20	61
3 2	29	1	$<$ 27	11	13	0	28	1	$<$ 27
3 3	145	148	270	101	129	126	96	114	171
4 0	0	0	0	38	26	0	0	0	0
4 1	136	156	124	130	151	170	74	115	176
4 2	49	9	65	29	18	35	24	7	27
4 3	25	26	88	35	17	$<$ 30	15	19	70
4 4	21	25	0	14	25	0	—	—	—
5 0	20	50	30	0	0	0	17	37	60
5 1	54	33	85	23	2	47	48	25	55
5 2	10	18	$<$ 31	62	23	0	17	14	$<$ 23
5 3	9	4	0	74	6	0	—	—	—
5 4	51	22	40	31	25	83	—	—	—
6 0	0	0	0	23	24	0	—	—	—
6 1	40	46	0	27	52	0	—	—	—
6 2	41	15	82	57	11	60	—	—	—
6 3	36	29	0	45	43	0	—	—	—
6 4	21	33	$<$ 40	36	9	0	—	—	—
7 0	40	40	67	0	0	0	—	—	—
7 1	19	47	0	5	15	0	—	—	—
7 2	62	106	79	122	108	254	—	—	—
7 3	28	5	56	13	34	0	—	—	—
7 4	33	6	46	—	—	—	—	—	—
8 0	0	0	0	56	2	0	—	—	—
8 1	30	5	53	30	41	0	—	—	—
8 2	56	98	109	98	121	174	—	—	—
8 3	12	62	0	—	—	—	—	—	—
8 4	24	35	0	—	—	—	—	—	—
9 0	46	31	37	—	—	—	—	—	—
9 1	20	70	0	—	—	—	—	—	—
9 2	45	40	0	—	—	—	—	—	—
9 3	30	35	0	—	—	—	—	—	—

and the Cr photographs were taken in order to search for reflexions which were characteristic absences on the Cu photographs. Three films in series were exposed together for the oscillation photographs in order to provide a reasonable range of intensities. The intensities of the reflections on the photographs taken with Cu radiation were determined by visual comparison with standard exposures made with a sectored disc. These intensities were used to obtain structure factors up to the Cu $K\alpha$ limit, but as no correction was made for the absorption in the crystal these structure factors were only very approximate.

Powder photographs

Debye–Scherrer powder photographs of the vanadium-nickel σ phase were taken in a 19 cm. diameter camera using both Cr $K\alpha$ and Cu $K\alpha$ filtered radiation. The films were used to obtain accurate lattice parameters for various alloys in the σ phase region of the diagram, and in view of the absorption error in the single-crystal photographs referred to above some intensity measurements were also made on powder photographs, where the absorption factor sould be calculated reasonably accurately. The σ-phase powder pattern shows characteristic groups of moderately strong lines, and the intensities of the lines in the first two groups for Cr $K\alpha$ and Cu $K\alpha$ photographs of the 60 atomic% vanadium film were measured with a photometer.

Many workers have published lists of d values for one or other of the σ phases and there has been some discussion of the considerable divergencies in the reported patterns. Our experience has been that some of the published data are unreliable and a number of powder photographs of σ phases were taken with filtered Cr radiation to clear up this position. The positions of the main lines of the σ phase were measured as accurately as possible on all these photographs and corresponding sets of d values were calculated for each alloy system.

Results and discussion

Table 1 shows the calculated structure factors for the structure proposed by Tucker (F_1) and that proposed by Kasper *et al.* (F_2) together with the structure factors (F_o) calculated from the intensities on the Cu oscillation photographs, and placed on the same scale as F_1 and F_2 by trial and error. The values are such that $\Sigma|F_1|$, $\Sigma|F_2|$ and $\Sigma|F_o|$ are all approximately equal, the values of these three quantities being 9208, 9194 and 9233 respectively. The intensities were corrected for velocity factor and Lorentz polarization factors, but owing to the absorption error a factor of two in the observed structure factor is not necessarily significant. The intensity scale used is such that the minimum structure factor measurable is about 30, the exact value for a particular line depending on the angular factors.

With one or two exceptions the agreement between F_1 and F_o shown in Table 1 is quite satisfactory, but the agreement between F_2 and F_o is not very good. This is shown particularly by reflexions (103), (115), (213), (305), (423), (510), (514), (542), (610), (733), (743), (813), (831), (913), (920), (940), (942), (10,0,0), (10,1,2), and (10,2,1), in all of which the divergence is very large. It seems clear from these data that the atomic parameters given by Tucker are more nearly correct than those proposed by Kasper *et al.* This does not rule out the possibility of the σ phase having space group *P*4/*mnm*, but if this is so it seems improbable that the atomic layers are spaced exactly $\frac{1}{4}c$ apart as suggested by Bergman & Shoemaker.

The principal discrepancy between F_1 and F_o lies in the reflexions (103), (204), (215), (534), (600) and (10,2,1). These differences may, however, reasonably be attributed to the experimental inaccuracy combined with the fact that the structure is only approximate and the atomic parameters have yet to be refined. The comparism of F_1 and F_2 with F_o may also be expressed by an agreement factor. The usual factor $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ is not very reliable if F_o is subject to absorption errors, as may be seen by considering a hypothetical case with $F_o=30$, $F_1=70$ and $F_2=3$. The agreement between F_o and F_1 is better than that between F_o and F_2 but the contribution to R_1 is considerably greater than that to R_2. The value of R is also considerably increased by the lines for which F_c is < 30 and F_o is 0, which do not in fact represent a real disagreement. The values of R_1 and R_2 calculated from Table 1 are 0·53 and 0·65 respectively, and, though both factors are large, R_1 is certainly better than R_2.

Table 2 gives the observed structure factors calculated for the most important powder photograph lines after correction for absorption, Lorentz polarization factors etc., and the agreement between F_1 and F_o (Cu) is fairly good in all cases. Structure factors for the (330) and (532) reflexions could not be obtained from the Cu film owing to the presence of weak extra reflexions. The (413) (602) and (333) (612) reflexions were not fully resolved in the Cu films so for these lines (and for the three coincident lines) a composite structure factor was calculated, as shown in the table. The values of the agreement factors R_1 and R_2 calculated for the lines listed in Table 2 are 0·10 and 0·17 respectively.

Table 2. *Calculated and observed structure factors*

hkl	$\lvert F_1\rvert$	$\lvert F_2\rvert$	$\lvert F_o\rvert$(Cu)	$\lvert F_o\rvert$(Cr)
002	223	231	230	254
410	234	250	234	234
330	229	208	—	221
202	148	186	170	140
212	163	139	158	130
411	200	204	193	163
331	213	201	205	188
222	115	112	109	97
312	55	66	72	—
431, 501	66*	77*	67*	—
511	54	41	58	—
532	145	142	—	82
710, 550	161*	243*	128*	137*
413	136 } 258*	156 } 238*	234*	90 } 154*
602	172	87		86
333	145 } 177*	148 } 202*	159*	94 } 123*
612	71	97		54
720	201	138	155	113
711, 551	125*	101*	113*	85*
622	51	57	46	37
542	93	30	60	32
721	91	123	95	86
004	253	323	237	—

* These values are $\sqrt{(2F_A^2+F_B^2)}$, where F_A and F_B are the structure factors of two overlapping or coincident reflexions.

The composition of the alloy (60 atomic % vanadium) did not correspond to a simple atomic ratio, and hence a completely ordered structure would be impossible, but an attempt was made to detect any long-range order present by comparison of the Cr and Cu films. On several of the Cr oscillation photographs a weak reflexion apparently corresponding to the (001) reflexion was observed. The reflexion was partially obscured by the Laue streak of the strong (002) reflection, but the spot shape was consistent with the other reflections. The observation was repeated several times with different operating conditions and the reflexion could also be seen on the complete rotation photograph. On two films a reflexion corresponding to the (003) reflexion was observed, but here the spot shape was not satisfactory and attempts to repeat the observations were unsuccessful. A faint reflexion corresponding to (061) was observed on several films taken over the appropriate oscillation range and on one occasion a spot was indexed as (201) on the second layer line, but this was so faint as to be barely visible. Unfortunately no Weissenberg camera was available, so it was not possible to prove that the spots were

Table 3. *Calculated and observed structure factors for ordered structure*

hkl	F_1'	F_o
001	90	< 30
003	57	$\leqslant 30$
203	37	0
601	36	< 5
201	21	$\leqslant 5$?

Table 4. *Intensities and interplanar spacings for the main lines in powder photographs of σ phases*

	Cr–Mn	Cr–Fe	V–Mn	V–Fe	V–Co	V–Ni
Composition (atomic %)	Mn 75·5 % Cr 24·5 %	Fe 48·2 % Cr 51·8 %	Mn 75·7 % V 24·3 %	Fe 52 % V 48 %	Co 49·5 % V 50·5 %	Ni 45 % V 55 %
Radiation	Cr	Cr	Cr	Cr	Cr	Cr
Multiplication factor to make *d* values = CrMn	1	1·008	0·9935	0·9908	0·9984	0·9930
hkl						
002	*m* 2·291 Å	*m* 2·273 Å	*m* 2·307 Å	*m* 2·309 Å	*m* 2·297 Å	*m* 2·312 Å
410	*s* 2·146	*s* 2·126	*s* 2·161	*s* 2·167	*s* 2·140	*s* 2·161
330	*ms* 2·085	*m* 2·067	*ms* 2·101	*ms* 2·106	*ms* 2·091	*m* 2·099
202	*ms* 2·037	*mw* 2·019	*ms* 2·049	*m* 2·051	*m* 2·040	*m* 2·052
212	*s* 1·981	*s* 1·968	*s* 1·997	*s* 1·999	*ms* 1·988	*s* 2·000
411	*s* 1·943	*vs* 1·928	*s* 1·958	*s* 1·962	*s* 1·949	*s* 1·959
331	*s* 1·898	*ms* 1·884	*ms* 1·912	*ms* 1·916	*ms* 1·903	*s* 1·914
222	*mw* 1·847	*mw* 1·834	*mw* 1·862	*mw* 1·864	*mw* 1·860	*mw* 1·865
312	*mw* 1·772	*m* 1·760	*mw* 1·786	*mw* 1·789	*mw* 1·778	*mw* 1·789
322	*vw* 1·677	*vw* 1·661	*w* 1·692	*w* 1·688	*w* 1·679	*w* 1·689
431, 501	*vw* 1·652	*vw* 1·639	*w* 1·663	*w* 1·667	*w* 1·655	*w* 1·664
511	*vw* 1·625	*vw* 1·610	*w* 1·636	*w* 1·640	*w* 1·628	*w* 1·636
522	*m* 1·338	*mw* 1·328	*vw* 1·346	*vw* 1·348	*vw* 1·341	*vw* 1·347
532	*s* 1·267	*ms* 1·257	*s* 1·275	*s* 1·279	*s* 1·271	*s* 1·277
550, 710	*m* 1·254	*mw* 1·243	*m* 1·262	*mw* 1·265	*m* 1·256	*m* 1·262
413	*s* 1·2461	*s* 1·236	*s* 1·2540	*s* 1·256	*s* 1·2573	*s* 1·2564
602	*m* 1·2419	*m* 1·232	*m* 1·2498	—	*m* 1·2440	*ms* 1·2512
333	*ms* 1·2347	*m* 1·227	*s* 1·2418	*s* 1·244	*s* 1·2364	*s* 1·2442
612	*m* 1·2299	*m* 1·219	*m* 1·2388	—	*s* 1·2321	*ms* 1·2392
720	*s* 1·2179	*s* 1·207	*s* 1·2255	*s* 1·2287	*s* 1·2194	*s* 1·2257
551, 711	*s* 1·2089	*ms* 1·199	*s* 1·2171	*s* 1·2202	*s* 1·2109	*s* 1·2175
622	*m* 1·1958	*m* 1·186	*m* 1·2045	*mw* 1·206	*m* 1·198	*m* 1·2047
542	*m* 1·1863	*m* 1·175	*m* 1·1929	*w* 1·195	*m* 1·187	*m* 1·1939
721	*s* 1·1767	*s* 1·167	*s* 1·1844	*s* 1·1874	*s* 1·1786	*s* 1·1850
004	—	—	*s* 1·153	*ms* 1·155	—	*s* 1·1575

The *d* values in this table are uncorrected for absorption and eccentricity errors.

genuine σ phase reflections and not due to contaminating wavelengths. Many longer exposures were made using 5°, 10° or 15° oscillations in order to strengthen the reflections and also to look for others of the $(0kl)$, $k+l$ odd, spots, but these were all unsuccessful as the background and Laue streaks became very dense and effects from other radiations began to appear.

These results indicate, though without any certainty, that the atoms in the vanadium–nickel σ phase tend to take up special positions on the lattice, such that the *n* glide plane of symmetry disappears. For a 1 : 1 atom ratio a completely ordered structure of this kind could be formed if alternate layers (and sublayers) are composed entirely of one kind of atom. Table 3 shows calculated structure factors for Cr radiation of an ordered structure of this kind, derived from Tucker's structure by putting nickel atoms into the positions with $z = \sim 0, \frac{1}{4}$ and vanadium atoms into positions with $z = \sim \frac{1}{2}, \frac{3}{4}$. Only the superlattice reflections with the largest F_1 are included in the table. The space group of this ordered structure is *Cmm* but the indices in Table 3 are referred to the smaller unit cell of the disordered structure. It will be seen that the lines with the largest calculated F_1 include all the reflexions thought to have been observed, but the observed structure factors are much smaller and the alloy cannot be fully ordered.

Table 2 shows the observed structure factors calculated from the photometered Cr-radiation powder film, and there appear to be considerable differences between these values and F_o (Cu) for some lines. This was at first interpreted as evidence for the partially ordered structure, but calculation shows that complete ordering of a 50 atomic % alloy would result in only very slight alterations to the relative structure factors of the lines listed in Table 2. No explanation of the difference has been found, so that the experimental error in the photometering of the powder films may be greater than was expected.

Table 4 lists the *d* values and visually estimated intensities of the strongest lines in the powder patterns of the σ phases in Cr–Mn, Cr–Fe, V–Mn, V–Fe, V–Co and V–Ni alloys. The values for Cr–Fe are unpublished data kindly supplied to us by Dr A. M. B. Douglas. The *d* values are such that when multiplied by the factors shown in the table the correspondence is exact within the experimental error, when *l* is less than 4. The phases are thus completely isomorphous and the axial ratio is nearly the same in all cases. Lattice-spacing measurements on a series of Ni–V alloys show that in this system the axial ratio varies from *c.* 0·5187 at 55 atomic % vanadium to 0·5171 at 74 atomic % vanadium, and a similar variation presumably exists in all systems. The discrepancies in powder data noted by earlier workers were not found in the present work.

Conclusion

A full solution of the σ phase structure obviously requires very accurate intensity measurements with a small symmetrically shaped crystal to distinguish between the possible space groups and to refine the atomic parameters. In this paper the parameters proposed by Tucker for the β-uranium structure are shown to give reasonably good agreement between observed and calculated structure factors, and it is also suggested that in the Ni–V σ phase there may be a tendency for an ordering of the layer structure to take place. Accurate powder data show that a close correspondence of d values for the various σ phases is found when these are multiplied by appropriate factors, and the structures are therefore completely isomorphous.

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A Study of Cold-Worked Aluminium by an X-ray Micro-Beam Technique.

I. Measurement of Particle Volume and Misorientations

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When aluminium is cold-rolled, the original grains break up into smaller particles. X-ray micro-beam back reflexion photographs permit the determination of the mean particle size and misorientation, and of their variation with degree of deformation, time after rolling, and purity of specimen. It is found that for spectroscopically pure aluminium a limiting particle size of ~ 2 μ is reached after ~ 10 % reduction in thickness, and that the total range of misorientations of the particles in the original grain is several degrees, while the mean angle between neighbouring particles is estimated to be ~ 2°. The particle size decreases slightly with time after rolling; for impure aluminium, both the limiting particle size, and the mean angle between adjacent particles are smaller.

1. Introduction

In order to test theories of the strength of polycrystalline metals and to understand the processes of plastic deformation, the structure of the deformed metals must be determined (Bragg, 1948). Heavily deformed metals have been studied by X-ray line-broadening experiments, but the results are difficult to interpret since both small particle-size and strains can contribute to the broadening of the diffraction line. The principle of the present method is to use a micro-beam to reduce the volume of material illuminated to such an extent that spotty diffraction rings are obtained. The mean particle size can be determined from the number of spots on the rings; the shapes of the spots give information on the distortion of the particles. The micro-beam technique has been described elsewhere (Hirsch & Kellar, 1951; Kellar, Hirsch & Thorp, 1950). This paper describes the method for determining the particle volume from the 'spotty' rings, and gives the results obtained for cold-worked aluminium. The interpretation of the spot shapes and a discussion of the results will be presented in later papers.

Spectroscopically pure aluminium was chosen for the first experiments because this material shows small line-broadening even after heavy deformation, so that the particle size must be fairly large (~ 10^{-4} cm.) even in the heavily cold-worked state (Wood, 1939; Megaw & Stokes, 1945; Paterson, 1949; Hall, 1949). A heavily deformed specimen was used to test the

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* This paper describes work carried out in collaboration with the late J. N. Kellar and further work carried out after his death in July 1948.