cases substantially empty). These sites tend to be occupied by elements at and to the right of Mn, and the atoms would be somewhat negative by electron transfer. In the other coordinations the *d* degeneracy is removed, and *d*, *s*, and *p* orbitals might be expected to hybridize to form directed bonds in the 6-coordinated ligand directions. These sites tend to be occupied by elements at and to the left of Cr and Mo (Kasper & Waterstrat, 1956), with Mo replacing Cr in the higher coordinations because of larger size; these atoms would then be somewhat positive by electron transfer. These considerations will be discussed more in detail elsewhere (Shoemaker, 1960).

Some preliminary single-crystal exploration was done by Dr Clara B. Shoemaker; reference to her photographs materially aided in the establishment of the monocrystallinity of the crystal fragment which we used. Mr Paul Metzger assisted with the refinement of the lattice constants with powder data.

We wish to thank Prof. Paul A. Beck of the University of Illinois for supplying us with *R* phase specimens and for much helpful assistance and discussion. We gratefully acknowledge the use of the IBM 704 at the MIT Computation Center, and wish to thank Prof. Vladimir Vand of Pennsylvania State University for Programming and operating suggestions. We are also happy to acknowledge the financial support of the Office of Ordnance Research.

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X-Ray Diffraction Studies of the δ Phase, Mo–Ni*

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Single-crystal X-ray diffraction studies of the δ phase, Mo–Ni (61·1 weight percent Mo) have shown that it is at least pseudotetragonal, with $a_0 = 9\cdot108$, $c_0 = 8\cdot852$ Å, and extinctions suggesting space group D_4^6–$P4_22_12$. There are, however, a few cases of differing intensity between (*hkl*) and (*khl*), indicating a reduction of the true Laue symmetry to D_{2h}; the true space group is perhaps $P2_12_12$ or $P2_12_12_1$. The (0*kl*) and (*h*0*l*) weighted reciprocal lattice nets closely resemble the (*hk*0) net of the σ phase. All attempts to determine the structure in detail were unsuccessful.

Introduction

In connection with work in these laboratories on the crystal structures of the *P* phase, Mo–Ni–Cr (Shoemaker, Shoemaker & Wilson, 1957) and the *R* phase Mo–Co–Cr (Komura, Sly & Shoemaker, 1960), we undertook to investigate the crystal structure of the δ phase, Mo–Ni, discovered by Ellinger (1942). This phase appeared to be closely related to the σ phase (Bergman & Shoemaker, 1954) and to the *P* phase, as was demonstrated clearly in the work of Beck and coworkers (Rideout *et al.*, 1951) who found σ, *P*, and δ phase regions arranged in a roughly linear row on the Mo-Ni-Cr phase diagram at 1200 °C. The δ phase in the Mo–Ni system exists at the approximate atomic ratio 1:1, in the range 61 to 63 weight percent molybdenum.

Experimental

A specimen of this alloy, annealed at 1200 °C., was kindly supplied by Prof. Paul A. Beck of the Univer-

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Table 1. *X-ray powder photographic data for* δ-MoNi

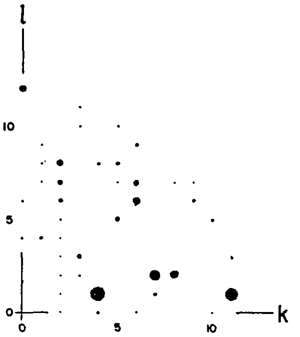
hkℓ	$\frac{mF^2}{100}$	$\frac{1}{d_{calc}}$	i^*_{obs}	$\frac{1}{d_{obs}}$
202	8	.3151	—	
221	7	.3305	—	
212	9	.3336	—	
310	6	.3472	—	
103	7	.3562	—	
311	12	.3651	—	
113	66	.3728	w	.3748
320	22	.3959	vf	.3997
302	9	.3994	—	
321	35	.4116	m	.4142
312	97	.4142		
213	13	.4185		
400	10	.4392	vf	.4388
410	11	.4527	s	.4537
401	290	.4535		
322	78	.4558		
104	9	.4650	—	
411	145	.4666	m	.4675
303	41	.4726	vf	.4743
114	286	.4778	mw	.4801
331	11	.4793		
313	528	.4852	vs	.4875
420	198	.4910	mw	.4916
421	229	.5039	ms	.5042
412	22	.5060		
214	15	.5143	—	
332	119	.5177	w	.5183
323	44	.5211	—	
422	62	.5405	vw	.5410
430	27	.5490	vf	.5503
413	11	.5655	—	
314	38	.5698	f	.5712
511	14	.5711		
324	12	.6007	—	
441	11	.6313	vf	.6310
225	15	.6446	vf	.6468
531	12	.6501	—	
442	20	.6609	vf	.6619
532	26	.6789	vf	.6789
523	10	.6815	—	
325	20	.6897	vf	.6919
621	11	.7035	—	
612	13	.7051	—	
434	14	.7110	—	
504	12	.7110		
541	28	.7121	vf	.7142
206	40	.7125		
514	70	.7195	vf	.7214
216	18	.7209		
415	26	.7239	vw	.7246
533	83	.7244		
335	20	.7321	—	
630	28	.7365	vf	.7345
542	74	.7385	f	.7386
524	48	.7442	w	.7457
631	37	.7452		
226	120	.7456		
425	56	.7484	w	.7484
613	14	.7489		
632	37	.7704	vf	.7709
701	18	.7768	—	
543	19	.7805	—	
534	185	.7836	m	.7841
711	18	.7846	—	
326	24	.7849	—	
505	31	.7877	vf	.7900
640	46	.7918	—	
515	136	.7953	vw	.7963
720	16	.7993	w	.8007
641	109	.7998		
702	133	.8011		
614	16	.8064	—	
721	50	.8073	m	.8083
552	29	.8086		
712	166	.8086		
633	19	.8108	—	
525	36	.8177	vf	.8180
207	35	.8207		
642	22	.8234	—	
217	15	.8280	—	
624	11	.8285	—	
722	18	.8307	—	
544	11	.8357	—	
426	39	.8370	vf	.8385
731	42	.8348	vf	.8450
553	18	.8471	—	
227	104	.8496	w	.8517
535	14	.8538	—	
615	19	.8747	vf	.8755
741	30	.8924	vf	.8913
811	13	.8924		
625	58	.8951	f	.8970
714	13	.8983	—	
545	13	.9018	—	
802	78	.9070	f	.9068
821	69	.9124	vw	.9140
742	12	.9136		
812	106	.9136		
724	20	.9182	—	
635	58	.9282	w	.9324
208	42	.9300		
427	73	.9308		
822	26	.9332	—	
218	13	.9365	—	
830	11	.9381	—	
831	97	.9449	w	.9462
606	61	.9452		
743	39	.9479		
734	18	.9505	f	.9527
751	20	.9512		
616	82	.9516		
228	29	.9556	—	
626	25	.9704	—	
752	23	.9712	f	.9724
645	37	.9726		
546	52	.9765	f	.9787
725	18	.9788		
814	18	.9878	f	.9887
841	80	.9885		
833	25	.9974	vf	.9975
753	65	1.0035	f	1.0039
735	25	1.0091	vf	1.0061 ?
418	29	1.0108	—	
824	15	1.0119	—	
760	47	1.0123	f	1.0111
761	24	1.0186	vf	1.0185
921	16	1.0186		
912	10	1.0196	—	
119	35	1.0285	f	1.0310
428	31	1.0285		
607	19	1.0292		
556	10	1.0306		
843	16	1.0389	vf	1.0368
209	35	1.0401	—	
754	15	1.0470	vf	1.0489
726	10	1.0480		
627	23	1.0524	vf	1.0542
508	10	1.0574	—	
518	27	1.0631	vf	1.0602
932	18	1.0658	—	
763	15	1.0675	vf	1.0666
923	13	1.0675		
319	31	1.0743	—	
528	26	1.0800	vf	1.0791

* s = strong, m = medium, w = weak, f = faint, v = very

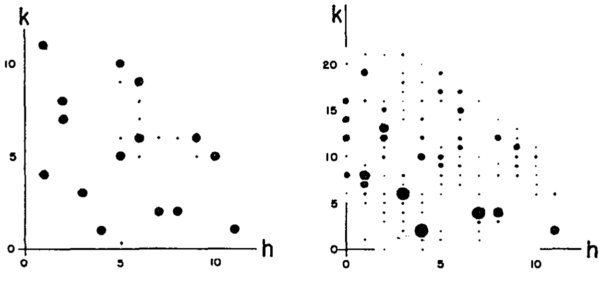
sity of Illinois. As with the other phases mentioned the material was microcrystalline, and it was necessary to pulverize the material and examine many small fragments by Laue photography to find a single crystal. The monocrystalline fragments finally used were about 0·1 mm. in size. With Laue, Weissenberg, and precession photographs the Laue symmetry and lattice constants were obtained. The lattice constants were later refined with powder data (Table 1) by the method used by Shoemaker, Shoemaker & Wilson (1957), giving $a_0 = 9{\cdot}108 \pm 0{\cdot}005$, $c_0 = 8{\cdot}852 \pm 0{\cdot}005$ Å. The $mF^2/100$ values given in Table 1 were calculated from single crystal observed intensities. Planes too weak to contribute significantly are omitted.

The Laue symmetry at first appeared to be D_{4h}, but significant intensity differences were found for a small number of weak and medium reflections (most noticeably at small Bragg angles, but present also at larger angles) indicating a reduction of symmetry to D_{2h}. In nearly all of our subsequent work these deviations were neglected, and averages of (hkl) and (khl) intensities were employed where necessary. No deviation from tetragonal symmetry was observable in the axial lengths. The intensity deviations do not appear to be due to absorption; two different crystal fragments gave similar results.

The percentage of molybdenum was found by analysis to be $61{\cdot}1 \pm 0{\cdot}3$ weight percent. The density was found to be $9{\cdot}71 \pm 0{\cdot}01$ g.cm.$^{-3}$ with a pycnometer. These figures lead to $55{\cdot}8 \pm 0{\cdot}2$ atoms per unit cell. This strongly indicates 56, but low values found for the *P* and *R* phases (presumably due to slag inclusions) suggest that 57 or 58 are also possible.



δ-MoNi (0kl)



σ-FeCr (hk0) P-MoNiCr (hk0)

Fig. 1. Weighted reciprocal lattice nets of δ, σ, and *P* phases. Relative intensities are indicated qualitatively by the sizes of the dots.

The lattice is primitive. All odd (*h*00), (0*k*0), and (00*l*) reflections are absent. (Of the (00*l*) reflections only (004), (006), and (0,0,12) were observed within the copper limit.) These results suggest the space group (assuming the tetragonal system)

$$D_4^6\text{-}P4_22_12\ .$$

Strong indications of a close structural relationship between the δ and *P* phases were shown, not only by the lattice constants, but also by the fact that the (0*kl*) and (*h*0*l*) weighted reciprocal nets strongly resemble the (*hk*0) net of the sigma phase. This is shown in Fig. 1. The (*hk*0) net looks very different; its strongest plane is (420).

Three-dimensional Patterson functions were calculated with three-dimensional Cu $K\alpha$ Weissenberg data. A function calculated on the IBM 704 (program written by W. G. Sly) with orthorhombic intensity deviations taken into account differed only in very minor respects from one calculated earlier on X-RAC with coefficients conforming to tetragonal symmetry. Characteristic features of the Patterson function include: (1) very strong peaks at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, \frac{1}{2}, 0{\cdot}15)$, with magnitude close to half that of the origin peak; (2) absence of peaks along $(x, x, 0; x+\frac{1}{2})$ and of any but weak peaks along $(x, 0, 0)$, implying absence of vertical mirror planes, in agreement with the above provisional space group; (3) strong peaks belonging to superimposed slightly distorted hexagonal nets (as in the σ phase), the net planes being tipped about 15° from the vertical positions occupied by (100) and (010).

All attempts to elucidate the structure in detail have been unsuccessful. These include use of the Patterson superposition (vector convergence) method to locate some atoms provisionally, computations of electron-density functions in three dimensions to find more atoms, and attempted least-squares refinement of trial structures. Many attempts to build up a reasonable trial structure out of known coordination polyhedra have also failed. These failures suggest that the assumed space group is not correct, and perhaps also that the observed deviations from tetragonal symmetry need to be taken seriously.

If the true structure represents a small orthorhombic deviation from an 'ideal' tetragonal $P4_22_12$ structure, the true space group could be the subgroup $P2_12_12$. However, if the deviations are in the atomic positions (rather than in occupancy by various atomic species in various sites), one would expect deviations in intensity between (*hkl*) and (*khl*) to increase with scattering angle. Perhaps the structure deviates not slightly but considerably from tetragonal symmetry (having perhaps space group $P2_12_12_1$), but is intimately and interpenetratingly twinned.

Work on this problem has been stopped for the present.

We wish to thank Prof. Paul A. Beck of the University of Illinois for supplying us with specimens and for helpful suggestions. We are indebted to Dr William G. Sly for programming and computational assistance with the IBM 704 calculations, and Prof. Ray Pepinsky of Pennsylvania State University for his cooperation in regard to the use of X-RAC. Analytical and density determinations were made by Mr Frank C. Wilson, and powder-data calculations by Mr A. D. Pearson.

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