Technical Note

Formation of Sigma Phase in the Mn-Mo System

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THE existence of σ phase in the Mn-Mo system was discovered in this laboratory several years ago,[1] but neither the conditions of its formation nor its composition were known, and preliminary attempts to reproduce the phase were unsuccessful. We wish now to specify the information appropriate to σ phase formation on the basis of experiments performed since that time.

The starting materials were in every case electrolytic manganese and high purity molybdenum. Two methods of preparation were employed: 1—arc-melting varying combinations of the elements in an inert atmosphere and subsequent heat treating, and 2—sintering compressed mixtures of finely divided powders of the elements. In the latter method, the powders were first passed through 200 mesh screen and then compressed into cylinders of 3/8 in. diameter and ½ in. length, which were sintered at elevated temperatures in an atmosphere of dry hydrogen. For some samples, the sintering temperature was 1200°C (for 1 hr), and these were then heat-

Table I. Results Obtained from Samples Produced by Sintering Compressed Mixtures

Sample	Treatment	Wt Pct Mn	Wt Pct Mo	At. Pct Mn	X-Ray Pattern
1	Sintered 1125°C 3 hr	53.0	46.7	66.5	σ + some α-Mn
2	Sintered 1125°C 3 hr	49.8	49.6	63.7	σ + trace α-Mn†
3	Sintered 1125°C 3 hr	43.4	56.5	57.3	σ + some Mo
4	Sintered 1125°C 3 hr	33.1	66.8	46.4	σ + some Mo
5	Sintered 1200°C 1 hr + 1125°C 24 hr	80*	20*	87.5*	α-Mn + trace σ
6	Sintered 1200°C 1 hr + 1125°C 24 hr	90*	10*	94.0*	α-Mn

* Nominal starting composition.
† Only evidence for α-Mn is one very weak line.

treated at lower temperatures for times up to 24 hr. Eventually it was found, for the proper composition, that essentially pure σ phase could be produced by sintering at 1125°C for 3 hr. Quenching to room temperature was effected by means of a stream of cold, dry hydrogen in a water-cooled chamber.

The arc-melting procedure was found to be unsatisfactory after an investigation of many samples at different compositions and temperatures. Large quantities of manganese were vaporized during melting and none of the products were homogeneous or contained extended regions of pure σ phase. Nonetheless, these experiments established that no σ formation occurs in the Mn-Mo system below 1115°C, and indicated, at least roughly, the composition range of interest for further exploration.

The more definite results obtained from samples produced by the second method are given in Table I.

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Table II. X-ray Powder Pattern for Mn-Mo Sigma (64 Atomic Pct Mn). Crystal system, tetragonal $a_0 = 9.10$, $c_0 = 4.74$Å. Cr Kα radiation.

Mn-Mo σ			Fe-Mo σ[3]	
hkl	*d*	*I**	*d*	*I**
311	2.463	m	2.46	w
002	2.368	m	2.35	mw
410	2.205	s	2.21	s
330	2.144	ms	2.13	m
202	2.097	ms	2.08	m
212	2.045	s	2.04	ms
411	2.000	vs	1.99	s
331	1.952	s	1.93	m
222	1.907	mw	1.90	w
312	1.829	mw+	1.82	w
431, 501	1.697	vvw		
511	1.672	vvw		
432	1.444	mw	1.44	vw
611, 512	1.426	mw	1.43	mw
313	1.385	vw		
621, 522	1.377	ms	1.37	m
541	1.362	vvw		
532, 631	1.304	s	1.30	ms
413, 550, 710	1.286	vs		
602	1.279	m		
333	1.272	ms	1.28	s
612	1.267	m		
701, 720	1.253	s		
551, 711	1.244	m	1.246	mw
622	1.232	mw		
542, 641	1.221	mw	1.220	m
721	1.211	ms		
433, 503	1.195	vvw	1.205	w
004	1.187	s	1.177	m

* w, weak; mw, medium weak; vw, very weak; vvw, very, very weak; m, medium; ms, medium strong; s, strong; vs, very strong.

A portion of sample 2 heated for 16 hr at 1000°C in a Vycor tube transformed to molybdenum plus unidentified phases of complex X-ray pattern.

From these few results it appears that the region of σ phase is quite narrow in composition. It is of interest that the composition is such as to make for difficulties in correlating this structure on an electron atom basis with other σ structures of iron, cobalt, and nickel. In that respect Mn-Mo shows the same anomaly as Mn-Cr and Mn-V systems.[2] A second feature is that in common with the two other known molybdenum σ's (Fe-Mo and Co-Mo), Mn-Mo σ exists only at elevated temperatures.

The X-ray powder pattern of the pure σ phase of Mn-Mo is given in Table II. It agrees well with the patterns established for other σ structures, especially with that for Fe-Mo σ as given by Goldschmidt.[3] An attempt is being made to establish whether an ordering of the respective atoms occurs and such information will be reported in a future publication.

Acknowledgment

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References

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[3] H. J. Goldschmidt: *Research* (1949) **2**, p. 343.