SHORT COMMUNICATIONS

Crystal Structures of Silicon Nitride

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Leslie, Carrol and Fisher[1] separated silicon nitride from nitrided silicon steel and, by studying the X-ray and the electron diffractions of the nitride, proposed an orthorhombic cell for Si_3N_4. More recently Turkdogan and Ignatowiez[2] reported that non-metallic inclusions extracted from the nitrided Iron-Silicon alloys are identical with one of the two silicon nitrides synthesized.

It has been established[2-5] that when silicon is nitrided at high temperatures varying from 1200 to 1400°C, a mixture of two phases (α and β) of nitrides is formed. Vassiliou and Wilde[3] mentioned that these two phases were regarded as orthorhombic (α) and hexagonal (β), respectively. But Popper and Ruddlesden[4] reported that one of them (β) can be indexed as rhombohedral, while both of the two phases were claimed to be hexagonal by Hardie and Jack[6]. More recently Forgeng and Decker[5] have come to the same view as Hardie and Jack's. The spacings, however, calculated by the various investigators are in good agreement with one another, notwithstanding that they differ in opinions on these two phases. Thus, it may not yet be concluded that the behavior of silicon nitride in steel is unequivocally solved.

The present authors prepared silicon nitrides in the following way and made a study on their X-ray and electron diffractions, using an electron microscope also at the same time. As it was difficult to obtain the appropriately large single crystal of silicon nitride for X-ray diffraction, the N-pattern obtained with a selected area electron diffraction was used for a study of the crystal structure of this material, in the place of the precession diagram in the X-ray diffraction study. This paper is to present a brief report of the results obtained.

The samples of silicon nitrides were prepared by heating the powdered elementary silicon in a current of ammonia* in the temperature range 1200° to 1500°C. Caution, however, was paid: at every several hours' interval the reaction product was taken out, ground into particles of about 150 mesh in size, and then submitted to the repeated reactions.

The final product is composed of the two specimens; the major part is grayish white powder, and the other of less quantity white mould growing on the former. When the mould-form product is ground, it changes into grayish white powder similar to that of the major part. It is to be noted that there is no distinguishable difference between these two specimens, as far as the X-ray diffraction spectra obtained with a diffractometer are concerned. This leads the present authors to a suggestion that both of these two specimens can be regarded as a mixture of α and β silicon nitride and others, as described below.

Table I shows the results from our studies of the X-ray diffraction (on both two specimens) and the selected area electron diffraction (on the material shown in Fig. 1). The spacings are in good agreement with those given by other investigators. One of the substances, which is more frequently found in the mould-form portion, is in the form of the flat needle as shown in Fig. 1. Its pattern of the selected area electron diffraction in the form of rectangle-shaped N-pattern is illustrated in Fig. 2. It is regarded that this pattern corresponds to the reciprocal lattice of $(11\bar{2}0)$ plane of hexagonal α-silicon nitride

1) W. C. Leslie, K. G. Carroll and R. M. Fisher, *Trans. Am. Inst. Mining Met. Engrs.*, **194**, 204 (1952).
2) E. T. Turkdogan and S. Ignatowiez, *J. Iron and Steel Inst.*, **185**, 200 (1957).
3) B. Vassiliou and F. G. Wilde, *Nature*, **179**, 435 (1957).
4) P. Popper and S. N. Ruddlesden, ibid., **179**, 1129 (1957).
5) W. D. Forgeng and B. F. Debker, *Trans. Am. Inst. Mining Met. Engrs.*, **212**, 343 (1958).
6) D. Hardie and K. H. Jack, *Nature*, **180**, 332 (1957).

* Purification of ammonia was made following the method of A. Farkas and H. W. Melville: "Experimental methods in Gas Reactions", Macmillan, London (1939), p. 162. Flow rate was regulated as 250 cc./min./3.14 cm^2.

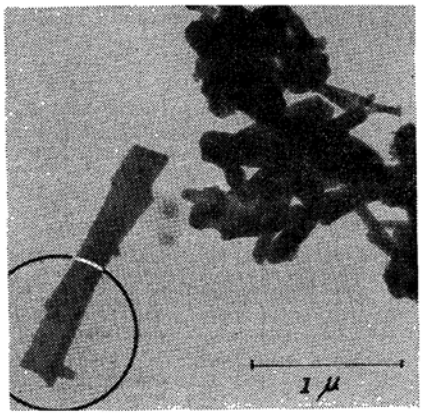

Fig. 1. Electron Micrograph of α-silicon nitride.

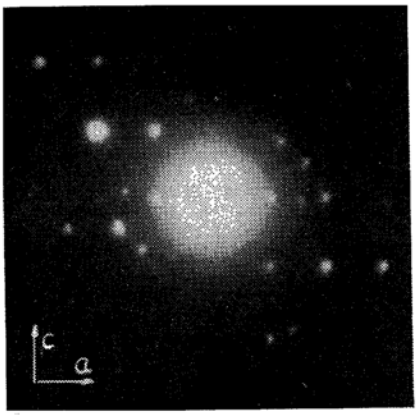

Fig. 2. Electron diffraction pattern of nitride, pertinent to the portion as enclosed by the circle in Fig. 1.

TABLE I

X-RAY DATA FOR THE SILICON NITRIDE

Electron diffraction	Diffractometer		α-Si_3N_4		β-Si_3N_4		Forgeng, Decker[5] Si_2ON	
d Obsd.	*d* Obsd.	Int.	*hkl*	*d* Calcd.	*hkl*	*d* Calcd.	*hkl*	*d*
6.68 Å	6.67 Å	13	100	6.74 Å				
	6.63	9			100	6.58 Å		
5.76			001	5.64				
	5.15	9						
	4.64	9					110	4.69 Å
	4.46	13					020	4.44
4.29	4.32	100	101	4.33				
	3.89	36	110	3.88				
	3.82	13			110	3.80		
	3.47	13						
3.34	3.37	36	200	3.37			111	3.38
	3.30	27			200	3.29		
2.84	2.89	82	201	2.89				
2.78	2.82	9	002	2.82				
	2.67	32			101	2.73	200	2.75_3
2.58	2.60	77	102	2.60				
	2.54	73	210	2.54				
	2.49	23			210	2.49		
	2.43	9					002	2.42_9
	2.39	13					201	2.39_4
	2.32	45	211	2.32	111	2.31	131	2.30_1
	2.28	9	112	2.28				
2.21	2.24	4	300	2.25			040	2.22_5
	2.18	9			201	2.19		
2.12	2.16	27	202	2.16			112	2.15_1
	2.13	5					022	2.12_9
2.05	2.08	32	301	2.08			221	2.10_7
			220	1.94				
					220	1.90		
	1.88_7	10	212	1.88_8	211	1.89_3		
1.87			003	1.88_0				
	1.86_7	13	310	1.86_5				
	1.80_8	9	103	1.81_3			202	1.81_9
	1.76_8	9	311	1.77_0			310	1.79_7
1.72	1.75_4	9	302	1.75_4	301	1.75_3	132	1.77_9

mentioned by the other investigators[5,6]. And it can not be indexed according to Leslie's[1] orthorhombic lattice.

In view of the above, the crystal structure of α-silicon nitride is regarded more likely as hexagonal. The selected area electron diffraction could not be applied to β-silicon nitride; however, considering the structure of β silicon nitride as hexagonal, as mentioned by the other investigators[5,6], the X-ray diffraction data shown in Table I can be explained as resulting from the mixture of α and β nitrides.

The parameters of these hexagonal cells of α and β silicon nitrides which are yielded from the X-ray diffraction data are as follows:

α-silicon nitride $a_0=7.76\pm0.05$ Å

$c_0=5.64\pm0.006$ Å $\quad c/a=0.727$

β-silicon nitride $a_0=7.59\pm0.06$ Å

$c_0=2.92\pm0.008$ Å $\quad c/a=0.385$

There are some discrepancies between the observed values for spacings obtained with the diffractometer and the calculated values. One of such discrepancies is also found in Leslie's data[1]. These discrepant spacings coincide with those of silicon oxynitride determined by Forgeng and Decker[5] as shown in Table I.

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