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DEVELOPMENT OF PROCEDURES FOR THE IDENTIFICATION OF  
MINOR PHASES IN HEAT-RESISTANT ALLOYS BY ELECTRON DIFFRACTION

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### SUMMARY

The work during the period covered by this report has been devoted primarily to 16-25-6 and S816 alloys.

Studies have been made to develop polishing and etching procedures for use in preparing samples of each of these alloys for study by electron diffraction methods.

Electron diffraction patterns have been obtained from minor phase materials in samples of 16-25-6 alloy aged for periods of 1 to 1000 hours at temperatures of 1400 and 1600°F. These results indicate that the development of the minor phases in this alloy proceeds in two stages: (a) the formation of an  $M_{23}C_6$  phase during the first few hours of aging, and (b) the transformation of this phase to an MC phase as aging progresses. A more detailed investigation of this process is now being conducted.

Preliminary electron diffraction results have identified a CbC-CbN phase in several differently aged samples of S816 alloy. In addition, indications of an  $M_{23}C_6$  phase in this alloy have been obtained.

DEVELOPMENT OF PROCEDURES FOR THE IDENTIFICATION OF  
MINOR PHASES IN HEAT-RESISTANT ALLOYS BY ELECTRON DIFFRACTION

INTRODUCTION

The purpose of this investigation is to develop experimental procedures for adapting the electron diffraction method for use in detecting and identifying the minor phases of heat-resistant alloys and to apply this method to the study of the influence of mechanical working and high-temperature aging on the development of minor phases in some typical alloys.

In studying the minor phases of alloys by the electron diffraction method, alloy samples are electrolytically polished and then etched, using reagents and conditions which preferentially attack the matrix of the alloys so that the minor phase particles are left protruding slightly from the etched surfaces. Electron diffraction patterns of the minor phase particles are then obtained from these surfaces by the reflection method and serve as the basis for identifying the minor phases of the alloys. It is also possible to study the etched surfaces by optical and electron microscopy to correlate the diffraction results with the distribution of the minor phase particles. The advantages of this method and the details of the experimental procedures involved have been described in an earlier report.<sup>1</sup>

Four alloys metallurgically typical of those currently used for the construction of high-temperature components of jet propulsion systems, have been chosen for study. These include (a) low-carbon N-155, (b) 16-25-6, (c) S-816 and (d) Inconel-X alloys. The high-temperature metallurgical properties of each of these alloys have been investigated extensively by Dr. J. W. Freeman and his associates in the Department of Chemical and Metallurgical Engineering of the University of Michigan. Close cooperation is maintained with these workers so that a correlation of the electron diffraction and the metallurgical studies can be made.

This is the second progress report on this project and covers the work for the period of 15 April to 15 July, 1952.

EXPERIMENTAL RESULTS

The work carried out during the period of this report has been directed primarily toward completing the studies of the influence of high-temperature aging on the development of the minor phases of 16-25-6 alloy. In addition, however, a considerable amount of progress has been made on the preliminary work to find suitable polishing and etching reagents for use in preparing samples of the S816 alloy for electron diffraction studies

16-25-6 Alloy

A number of preliminary experiments were carried out to find suitable electrolytic solutions for use in polishing samples of this alloy. It was found, in general, that solutions based on perchloric acid polish more rapidly and with less trouble due to gas evolution and pitting than do solutions based on sulfuric and phosphoric acids. The best-appearing surface was produced by a solution of 900 ml of glacial acetic acid and 100 ml of perchloric acid (70%) when used with current densities of about 10 amperes per square inch. This solution does not appear to be satisfactory for use in preparing samples for electron diffraction studies, however, because of a tendency to dislodge the precipitate particles from the surfaces of the samples. A solution (A) consisting of 700 ml ethyl alcohol (95%), 200 ml perchloric acid (70%) and 100 ml glycerine also polished the alloy well and rapidly with current densities of about 4 amperes per square inch. Examination of the polished surfaces by electron microscopy shows that the minor phase particles are not dislodged by this solution. Most of the phosphoric-sulfuric acid solutions produced films of insoluble reaction products on the surfaces of the samples and were not considered satisfactory for use. An exception was found in the case of a solution (B) consisting of 100 grams of  $\text{CrO}_3$  dissolved in 120 ml of water, 600 ml of concentrated phosphoric acid, and 150 ml of concentrated sulfuric acid. When used at temperatures of 70-80°C and with current densities of about 1 ampere per square inch, this solution gives a combination of polishing and etching, so that good diffraction patterns are obtained from surfaces polished with it. It acts slowly, however, and tends to pit the surfaces severely when used for prolonged periods. With current densities of about 0.1 ampere per square inch this solution is also a very good etching medium.

Using these observations, the following procedure was devised, which has proved very successful in preparing samples of this alloy for electron diffraction studies: The samples are first abraded with metallographic emery paper through 3/0 grade and then electrolyzed in solution A at current densities of about 3 amperes per square inch until all traces

of the emery scratches are removed. Following this they are electrolyzed at 0.7-0.9 amperes per square inch in solution B for about 1 minute. This usually improved the appearance of the surfaces considerably and also outlines the minor phase particles more clearly. The current is then reduced to 0.1-0.2 amperes per square inch and the samples are etched for 10 to 30 seconds. There is some variation in the optimum current density and time required for each of these operations, depending on the individual samples. When the samples are removed from solution B they are rinsed immediately in running tap water, then in freshly distilled water, and finally, several times with a 50-50 mixture of methanol and acetone. They are then allowed to drain and air-dry, after which the diffraction patterns are taken.

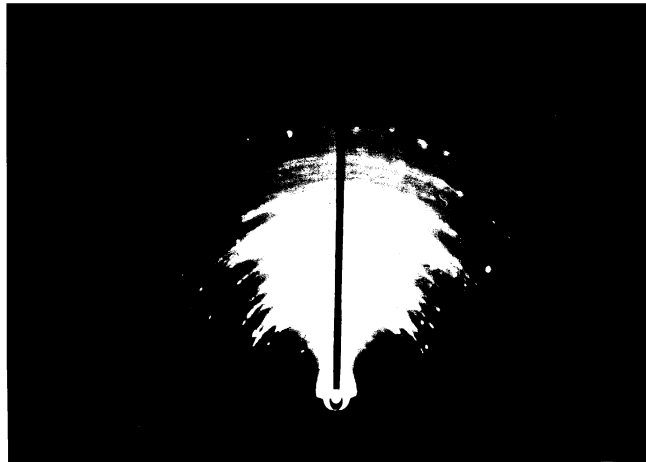
Five different samples of the alloy have been studied using the above method of surface preparation. These samples represent a variety of heat treatments as shown in Table I. Very good diffraction patterns of minor phase materials have been obtained from each of these samples with the exception of sample 2-A. In this case only patterns of the matrix phase have been obtained, and these patterns are generally obtained only after prolonged etching.

TABLE I

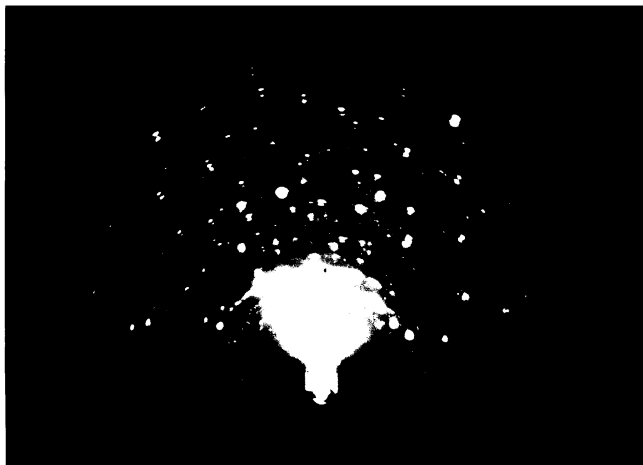
## HEAT TREATMENT OF 16-25-6 ALLOY SAMPLES

<u>Sample</u>	<u>Heat Treatment</u>
2-A	Solution treated for 2 hrs at 2050°F; water quenched.
2-B	Solution treated for 2 hrs at 2050°F; water quenched; aged 1 hr at 1400°F; air cooled.
2-C	Solution treated for 2 hrs at 2050°F; water quenched; aged 1000 hrs at 1400°F; air cooled.
2-D	Solution treated for 2 hrs at 2050°F; water quenched; aged for 10 hrs at 1600°F; air cooled.
2-E	Solution treated for 2 hrs at 2050°F; water quenched; aged 500 hrs at 1600°F; air cooled.

The electron diffraction pattern obtained from sample 2-B is reproduced in Fig. 1a. The clarity and resolution of this pattern is excellent. The calculated interplanar spacings ( $d_{hkl}$  values) and observed relative intensities (I) are listed in Table II with the corresponding data



a.  $M_{23}C_6$  Pattern from Sample 2-B



b.  $M_6C$  Pattern from Samples 2-C, 2-D and 2-E

Fig. 1. Electron Diffraction Patterns  
from 16-25-6 Alloy

TABLE II

## COMPARISON OF THE ELECTRON DIFFRACTION PATTERN

FROM 16-25-6 ALLOY SAMPLE 2-B WITH THE  $M_{23}C_6$  PATTERN

Electron Diffraction Pattern		$M_{23}C_6$ Pattern, (FCC, $a_0 = 10.63 \text{ \AA}$ )		
$d_{hkl}$	I	hkl	$d_{hkl}$	I
61.1 <sup>o</sup>	W	111	6.13 <sup>o</sup>	
5.4	W	200	5.32	
3.8	W	220	3.76	
3.2	W	311	3.21	VW
3.1	VW	222	3.07	VW
2.68	VW	400	2.66	W
2.48	M	331	2.43	VW
2.39	ME	420	2.38	S
2.18	S	422	2.17	S
2.06	S	511	2.04	VS
1.89	M	440	1.88	M
1.80	M	531	1.79	M
1.77	M	600	1.77	W
1.67	WM	620	1.68	W
1.61	WM	533	1.62	VW
		622	1.60	VW
1.54	VVVW	444	1.53	VVW
		711	1.49	VW
1.48	VVW	640	1.48	VW
1.43	M	642	1.42	W
1.38	VVVW	731	1.38	VW
1.32	VVW	800	1.33	W
		733	1.30	
1.29	W	644	1.29	WM
1.25	WM	822	1.26	MS
1.23	W	555	1.23	VW
		622	1.22	VW
1.19	W	840	1.18	
1.17	W	911	1.17	
		842	1.16	
		644	1.14	



TABLE III

## COMPARISON OF THE ELECTRON DIFFRACTION PATTERN

FROM 16-25-6 ALLOY SAMPLES 2-C, 2-D AND 2-E WITH THE  $M_6C$  PATTERN

Electron Diffraction Pattern		$M_{23}C_6$ Pattern, (FCC, $a_0 = 10.97 \text{ \AA}$ )		
d h k l	I	h k l	d h k l I	
6.4 $\text{\AA}$	W	111	6.30 $\text{\AA}$	
		200	5.48	
3.9	W	220	3.88	
3.3	W	311	3.31	
3.2	W	222	3.16	
2.8	W	400	2.74	M
2.5	M	331	2.51	M
2.38 *	W			
		420	2.45	
2.26	S	422	2.24	S
2.19 *	VW			
2.12	S	511	2.11	VS
2.03 *	VW			
1.94	W	420	1.94	M
		531	1.85	
1.84	VW	600	1.83	W
1.73	VW	620	1.73	
1.66	M	533	1.67	
		622	1.65	
		444	1.58	
1.54	M	711	1.54	W
		640	1.52	
1.47	VW	642	1.46	
1.43	WM	731	1.43	WM
		800	1.37	
		733	1.34	
1.33	WM	644	1.33	
1.29	S	822	1.29	MS
		555	1.27	
1.26	W	622	1.26	
		840	1.22	
1.20	M	911	1.20	

\* These correspond to the three strongest reflections of the  $M_{23}C_6$  Pattern.

for the pattern of the  $M_{23}C_6$  type carbide. The agreement between the two patterns is very good and indicates that the principal minor phase material of this sample is an  $M_{23}C_6$  carbide.

A different diffraction pattern was obtained from samples 2-C, 2-D, and 2-E. This pattern is reproduced in Fig 1b, and the  $d_{hkl}$  values and relative intensities of its rings are listed in Table III. As shown in this table, this pattern agrees very well with the  $M_6C$  carbide pattern, except for three very weak rings which appear to belong to the  $M_{23}C_6$  pattern. It therefore appears that the principal minor phase material in these three samples is an  $M_6C$  carbide and that only traces of the  $M_{23}C_6$  carbide are present.

#### Preliminary Studies of S816 Alloy

This alloy has proved to be extremely difficult to work with due to the fact that most of the solutions commonly used for electrolytic polishing and etching produce films of insoluble reaction products on the surfaces of samples of this alloy. The following polishing solutions have been tried and found unsatisfactory for this reason.

- (1) 700 ml ethyl alcohol (95%), 200 ml perchloric acid 100 ml glycerine.
- (2) 800 ml ethyl alcohol (95%), 200 ml perchloric acid.
- (3) 800 ml ethyl alcohol (95%), 50 ml perchloric acid, 150 ml water.
- (4) 600 ml phosphoric acid, 300 ml glacial acetic acid, 100 ml water.
- (5) 600 ml phosphoric acid, 200 ml sulfuric acid, 200 ml water.
- (6) 500 ml phosphoric acid, 500 ml water.
- (7) 250 ml sulfuric acid, 750 ml water.
- (8) 800 ml sulfuric acid, 200 ml water.
- (9) 750 ml phosphoric acid, 250 ml water.
- (10) 50 ml sulfuric acid, 200 ml glacial acetic acid, 750 ml water
- (11) 430 gm  $CrO_3$ , 570 ml water
- (12) 330 ml hydrochloric acid, 670 ml glycerine ethylene glycol, or ethyl alcohol
- (13) 600 ml phosphoric acid, 150 ml sulfuric acid, 120 ml water, 100 gm  $CrO_3$ .

The concentrations of the acids used in preparing these solutions are as follows: sulfuric, 96%; phosphoric, 85%; hydrochloric, 35%; acetic, 99%; perchloric, 70%. Solutions 6, 7, 8, and 9 produced the heaviest films, while solutions 12 and 13 produced only very slight traces of films.

The films precipitated in these solutions are generally loosely adhering and deep brown or black in color. They do not dissolve from the samples in dilute solutions of any of the following acids: hydrofluoric, hydrochloric, nitric, sulfuric, phosphoric, and acetic. Neither are they soluble in dilute sodium, potassium, or ammonium hydroxide solutions. There is some evidence that the precipitate is amorphous in character. On several occasions electron diffraction patterns were taken from alloy samples which were covered with heavy film. In each case the only diffraction rings obtained were those of CbC-CbN one of the known minor phases of this alloy.

An attempt was also made to obtain an x-ray diffraction pattern of the precipitate. In this case a sample was electrolyzed in solution 7 until a very heavy film was formed. This film was then carefully scraped from the sample and used for the x-ray analysis. Again the diffraction results show that the material comprising the film is amorphous, for only diffraction lines of the CbC-CbN phase were obtained. The CbC-CbN particles were undoubtedly left on the surface as the alloy was electrolyzed and were scraped off with the film.

The solution of 900 ml of glacial acetic acid and 100 ml of perchloric acid, which polishes the 16-25-6 alloy so well, also gives a very good-appearing polish with this alloy. Its use results in a yellow granular film on the surface of the alloy, but this is readily soluble in dilute hydrochloric acid. Four other solutions have been found to date which produce no detectable traces of precipitates on samples polished in them. These include the following:

- (14) 10 to 25 per cent by volume of glacial acetic acid, with the remainder of solution 12.
- (15) 300 ml nitric acid (70%), 700 ml methyl alcohol.
- (16) 560 ml phosphoric acid (85%), 230 ml sulfuric acid (96%), 210 ml nitric acid (70%).
- (17) 250 ml sulfuric acid (96%), 750 ml water, 1800 gm citric acid.

These solutions act rather slowly and they pit the surfaces badly if current densities greater than about 1 ampere per square inch are used. They generally have a combined polishing and etching action

and if currents of about 0.1 ampere per square inch are used they are effective etchants.

Difficulties have also been encountered in finding suitable electrolytes for use in electrolytically etching the samples of this alloy. All the solutions recommended for this purpose by Watkins<sup>2</sup> have been tried and found to be unsatisfactory. Some chemical etching agents are now under investigation.

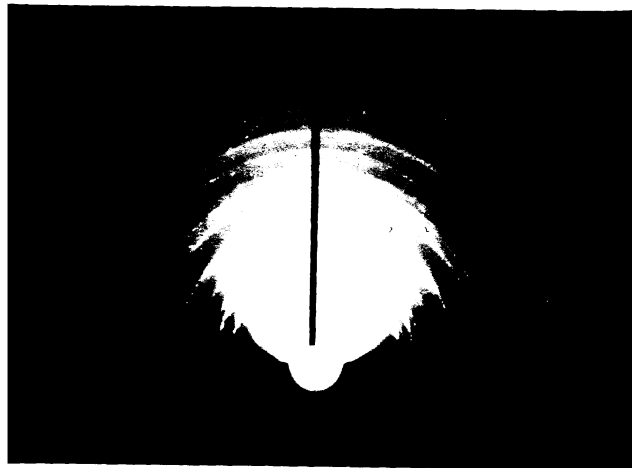
The combined polishing and etching action of solutions 14-17 has proved useful, however, and has made it possible to obtain electron diffraction patterns of minor phase materials from each of the samples of the alloy listed in Table IV. To prepare the samples for the diffraction studies, they were first abraded with successively finer grades of metallographic emery paper through 3/0 grade, and were then electrolyzed in the acetic acid, perchloric acid solution until all the emery scratches were removed. Following this they were rinsed with running tap water, then with distilled water, and finally with a 50-50 mixture of methanol and acetone. After rinsing, the samples were allowed to drain and air-dry, and the diffraction patterns were then taken.

Very good electron diffraction patterns of a minor phase which is either CbC or CbN have been obtained from each of the samples when prepared in this way. A typical pattern is reproduced in Fig. 2a, and the calculated interplanar spacings and estimated relative intensities of the rings of this pattern are compared with those of CbC and CbN<sup>3</sup> in Table V. It is not possible to distinguish between CbC and CbN from their electron diffraction patterns because they have the same crystal structure and their unit cells are nearly the same size.

Several times a pattern has been obtained from sample 3-B in which there are a number of different rings in addition to those produced by the CbC-CbN phase. The interplanar spacings and relative intensities for this pattern are listed in Table VI; it appears that some of the stronger rings are produced by the austenitic matrix phase of the alloy. The remaining strong rings are CbC-CbN rings. All the weaker rings of the pattern correspond to rings of the  $M_{23}C_6$  pattern (see Table II). Two of the strong  $M_{23}C_6$  rings, those corresponding to spacings of 2.18 and 2.04 Å, lie close to strong rings of austenite and CbC-CbN and are not resolved in the patterns obtained here. The other samples of the alloy are now being studied to see if similar patterns can be obtained from them.



a. Pattern of CbC or CbN



b. Pattern of CbC or CbN Matrix, and  
Possibly  $M_{23}C_6$  Phase

Fig. 2. Electron Diffraction Patterns from  
S816 Alloy

DISCUSSION

Considerable progress has been made in the study of the 16-25-6 alloy. Methods of sample preparation have been devised which have proved to be successful when applied to samples subjected to a wide range of high-temperature-aging treatments. The electron diffraction results from samples aged for periods from 1 to 1000 hours show a definite influence of the aging time on the nature of the minor phases present in the alloy. These results are summarized below:

<u>Sample</u>	<u>Aging Treatment</u>	<u>Minor Phases Identified</u>
2-A	Unaged	None
2-B	1 Hr at 1400°F	$M_{23}C_6$
2-C	10 Hr at 1600°F	$M_6C^*$
2-D	500 Hr at 1600°F	$M_6C^*$
2-E	1000 Hr at 1400°F	$M_6C^*$

The fact that no minor phases have been identified in the unaged samples is not conclusive evidence that none is present, for this sample is extremely resistant to attack and it is possible that the particles have not been properly revealed for obtaining electron diffraction patterns of them. It is noteworthy, however, that optical micrographs of this sample do not show any minor phase particles. All the rings in the electron diffraction patterns from sample 2-B appear to have been produced by an  $M_{23}C_6$  type carbide. The very clear, intense character of those rings strongly suggests that this is the principal minor phase present in this sample. Likewise, diffraction patterns indicate that the principal minor phase material in the samples which have been aged for longer periods is an  $M_6C$  type carbide. In these patterns there are only a few very weak rings, which may have been produced by the  $M_{23}C_6$  phase. It is therefore concluded that only very small quantities of this material are present in these samples.

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\*Traces of  $M_{23}C_6$  are also present.

From these results it is reasonable to propose that the development of the minor phases in this alloy, when aged at temperatures of about 1400°F - 1600°F, proceeds in two stages, as follows: first, the formation of an  $M_{23}C_6$  carbide during the first few hours of aging, and, second, the transformation of this phase to a carbide of the  $M_6C$  type as the aging continues. The alternative possibility that, in the second stage, the  $M_{23}C_6$  persists and that  $M_6C$  is formed in addition to it is not supported by the diffraction data presently available. If this were the case the  $M_{23}C_6$  rings in the patterns from samples 2-C, 2-D, and 2-E would be expected to be very much stronger than they are.

This proposal is in qualitative agreement with results obtained in other studies of this alloy which have been carried out at this university under the sponsorship of the National Advisory Committee for Aeronautics. This work shows that when the alloy is aged at 1400°F there is an initial decrease in the size of the unit cell of the matrix phase during the first hour of aging. The cell size then remains approximately constant until after about 10 hours whereupon it again decreases and reaches a constant value after 100-1000 hours. When aged at 1600°F, the rate of decrease in cell size appears to be more or less uniform with some levelling off after 100-1000 hours.

In terms of the electron diffraction, the initial decrease of the unit cell size at 1400°F is associated with the formation of the  $M_{23}C_6$  carbide. Since this phase frequently contains molybdenum atoms in addition to chromium atoms, the removal of these large-radius atoms from the matrix would result in a decrease in the size of the matrix unit cell. It is also probable that the decrease in lattice parameter which occurs after about 10 hours of aging at 1400°F is associated with the transformation of the  $M_{23}C_6$  to the  $M_6C$  phase. Micrographic studies indicate no decrease in the quantity of minor phase materials present, and therefore such a transformation would also involve the removal of chromium and molybdenum atoms from the alloy matrix and would result in a decrease in the matrix cell size. The gradual decrease in cell size observed when the alloy is aged at 1600°F is possibly due to an accelerated transformation of  $M_{23}C_6$  to  $M_6C$  at this higher temperature.

In continuing the work of this alloy, particular interest will be attached to investigation more thoroughly the nature of the transition from the  $M_{23}C_6$  to the  $M_6C$  phase and the aging condition under which this transition takes place. This will require the study of a number of additional samples which have been aged for periods up to about 500 hours at temperatures ranging from 1200 to 1600°F. It will also be of interest to obtain electron and optical micrographs of the various samples. These should furnish information which will be useful in correlating the micro-

structures of the samples with the phases identified by the electron diffraction results and in determining the effectiveness of the polishing and etching procedures in revealing the minor phase particles for obtaining electron diffraction patterns from them.

In spite of the difficulties encountered in working with the S816 alloy, the results to date are encouraging. A minor phase, which is either CbC or CbN, has been identified in several samples of this alloy which have received different high-temperature-aging treatments. In addition, some evidence for the occurrence of an  $M_{23}C_6$  phase has been obtained from one of the samples. The fact that similar results have not been obtained with the other samples may be due to inadequacies in the polishing and etching procedures now in use. Further studies are in progress to improve these procedures. As this phase of the work progresses, additional samples of the alloy will be studied and the electron diffraction results will be supplemented by electron and optical microscopic studies.



TABLE IV

## TREATMENT OF S816 ALLOY SAMPLES

Sample	Heat Treatment
3-A	Solution treated for 1 hr at 2300°F; water quenched.
3-B	Solution treated for 1 hr at 2300°F; water quenched; aged 1000 hrs at 1400°F; air cooled.
3-C	Solution treated for 1 hr at 2300°F; water quenched; aged 1000 hrs at 1400°F; air cooled.
3-D	Solution treated for 1 hr at 2300°F; water quenched; aged 1000 hrs at 1600°F; air cooled.

TABLE V

## ELECTRON DIFFRACTION PATTERN OF Cbc-CbN PHASE OBTAINED FROM S816 ALLOY

E.D. Pattern		CbC Pattern		CbN Pattern	
$d_{hkl}$	I	$d_{hkl}$	I	$d_{hkl}$	I
2.54 Å	S	2.54	VS	2.52 Å	VS
2.18	S	2.20	S	2.18	S
1.55	MS	1.56	MS	1.55	MS
1.33	MS	1.33	MS	1.32	MS
1.26	W	1.27	MW	1.26	MW

TABLE VI

## ELECTRON DIFFRACTION PATTERN OBTAINED

FROM S816 ALLOY SAMPLE 3-B

E.D. Pattern		Austenite Pattern	
$d_{hkl}$	I	$d_{hkl}$	I
3.8	W		
3.2	VW		
2.53	S*		
2.37	W		
2.18	S*		
2.04	S	2.06	S
1.87	W		
1.79	M	1.79	S
1.68	VW		
1.62	W		
1.56	MS*		
1.49	VVW		
1.42	VVW		
1.38	VVW		
1.33	M*		
1.29	W		
1.26	WM*	1.26	MS
1.23	W		

\*These are undoubtedly CbC-CbN rings (see Table B).

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