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DEVELOPMENT OF PROCEDURES FOR THE  
IDENTIFICATION OF MINOR PHASES IN

HEAT-RESISTANT ALLOYS BY

ELECTRON DIFFRACTION

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DEVELOPMENT OF PROCEDURES FOR THE IDENTIFICATION OF  
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INTRODUCTION

At the present time one of the principal factors preventing the manufacture of more efficient and more powerful jet aircraft engines is the lack of suitable materials for use in the construction of their high-temperature components. The development of improved heat-resistant alloys has therefore become one of the most important metallurgical problems of the day.

A number of recent investigations<sup>1,2,3</sup> have shown that the properties of these alloys are determined to a large extent by the precipitates, or minor phases, which form in them. Although these materials generally represent less than a tenth of a percent of the total of the alloys, they influence not only the ductility, hardness, creep resistance, and rupture strength of the alloys but also their resistance to corrosion and oxidation. It is evident, therefore, that the study of the minor phases is of the greatest importance for a thorough understanding of the properties of the alloys currently available and also for developing the metallurgical principles necessary for the design of improved alloys.

This project was undertaken to study the applicability of electron diffraction methods to the identification of the minor phases of heat-resistant alloys of the type currently used in jet aircraft engines. The use of electron diffraction for studying the minor phases of alloy systems was first proposed by Heidenreich, Sturkey, and Woods<sup>4,5</sup> and was effectively applied by them to magnesium, aluminum, and copper alloys and to plain carbon steel<sup>4,5,6,7</sup>. Their success with the method suggested that it could be profitably used on heat-resistant alloys to provide information which cannot be readily obtained by other currently available methods.

In the electron diffraction method, alloy specimens are prepared by selective etching treatments chosen to attack the matrix phases preferentially and leave the minor phase particles protruding in relief from the etched surfaces. A monoenergetic beam of electrons is then passed across the etched surfaces at a grazing angle. Under these circumstances the electrons

strike the protruding minor-phase particles and produce characteristic diffraction patterns from them. Because the electron beam has a very limited penetration, these patterns arise mainly from the minor-phase particles, with little contribution from the underlying matrix phase. Furthermore, the strong scattering power of materials for electrons (about  $10^6$  times that for x-rays) makes it possible to obtain good patterns from very small quantities of minor phases. The electron diffraction patterns are analogous to the familiar x-ray diffraction "powder" patterns and are used to identify the minor phases by comparison with x-ray diffraction powder data for known materials. These data are available from various x-ray diffraction investigations of metallurgical materials and from the file of x-ray data compiled by the American Society for Testing Materials. Finally, the etched surfaces are examined by optical and electron microscopy to correlate the electron diffraction results with the microstructures of the specimens.

This method offers several advantages over the currently-used x-ray method, which consists of chemically or electrolytically digesting the alloy specimen to concentrate the minor phases in the residues of the digestion process, and then examining the residues by x-ray diffraction to identify the minor phases. First, because of the high sensitivity of electron diffraction, it is possible to detect and identify minor phases in a suitably etched sample when they represent no more than a few hundredths of a percent of the total sample. This is of importance, since phases present in such small amounts may be missed entirely by the x-ray method even though favorable digestion procedures are used. Second, the polishing and etching procedures once established, are faster and less laborious than the digestion procedures and permit a larger number of samples to be studied and a larger number of duplicate runs to be made in a given time. Third, smaller samples can be used and only small parts of these are destroyed, thus permitting the method to be used where only limited quantities of the alloys are available. Fourth, by choosing suitably mild etching and polishing treatments it is often possible to reveal phases which might be destroyed in the more severe digestion process. Fifth, when used in conjunction with electron microscopic studies, it is possible to determine with some certainty when all the minor phases in a given alloy have been detected. From electron microscopic examination of the etched surfaces the relief of the minor-phase particles can be determined. If essentially all the particles are protruding properly it is reasonable to assume that all the minor phases present have contributed to the electron diffraction pattern and are therefore subject to identification. In addition, the electron micrographs provide detailed information about the shape, size, and distribution of the minor-phase particles, and can also be used to evaluate the effectiveness of various polishing and etching procedures.

The principal disadvantage of the electron diffraction method arises from the difficulties that may be encountered in obtaining proper surface preparations. Due to the complex compositions of the heat-resistant alloys



and their general resistance to chemical attack, the selection of suitable polishing and etching procedures may be a difficult matter. However, similar difficulties are encountered in selecting digestion processes for the x-ray method and since electron microscopic examinations can be used to guide the selection of polishing and etching procedures, the electron diffraction method has an overall advantage. It is appropriate to point out here that in both the x-ray and electron diffraction methods the identification of the minor phases is accomplished by comparing the diffraction patterns with data previously obtained from x-ray diffraction studies of known materials. New phases, previously unobserved, can usually be characterized with regard to crystallographic cell size and type, but their chemical compositions cannot be determined from the diffraction data alone; for this purpose chemical spectrographic, or x-ray fluorescence analyses must be used.

There are two principal objectives of this project. The first is to develop procedures for adapting the electron diffraction method to the study of heat-resistant alloys. The second is to use the electron diffraction method to study the influence of factors such as compositional variations and thermal and mechanical treatments on the development of minor phases in some alloys typical of those currently used in the manufacture of jet engines. The alloys chosen for this purpose include 16-25-6, low-carbon N-155, S816, and Inconel-X. Close cooperation is maintained with Dr. J. W. Freeman and his associates in the Department of Chemical and Metallurgical Engineering of this University, who are carrying on an extensive study of the metallurgical properties of these alloys at high temperatures. In this way a correlation of the electron diffraction results and the metallurgical results can be obtained.

This report summarizes the work completed on this project during the first contract year, from 15 January 1952 to 15 January 1953. During this period an extensive investigation has been made of the influence of high-temperature aging on the minor phases of 16-25-6 alloy and preliminary studies have been made of S816 and low-carbon N-155 alloys. In addition, a considerable amount of information has been obtained on the techniques of preparing heat-resistance alloy samples for the electron diffraction studies. This report is devoted principally to the discussion of these techniques because sample preparation is the most important and the most difficult part of the adaptation of the electron diffraction method to the heat-resistant alloys and also because this material has not been organized and presented previously. The results of the studies of the S816, N-155, and 16-25-6 alloys will be described only briefly, inasmuch as they have been presented in detail in the preceding quarterly reports.

PREPARATION OF HEAT-RESISTANT ALLOY SAMPLES  
FOR ELECTRON DIFFRACTION

The general techniques of electron diffraction are well known;<sup>11</sup> therefore, the problem of adapting this method to the study of the minor phases of heat-resistant alloys is largely one of finding suitable methods of sample preparation. It is necessary that the surfaces from which the electron diffraction patterns are obtained be reasonably flat, with the minor-phase particles protruding in relief above the matrix phase. The surfaces must also be scrupulously clean. Due to the high sensitivity and low penetrating power of the electrons, traces of foreign crystalline materials may give rise to diffraction patterns which would confuse the identification of the minor phases, while contamination by fingerprints or thin grease films may obscure the diffraction patterns altogether.

There are three steps in the preparation of alloy samples: first, a polishing operation to produce flat, smooth surfaces suitable for subsequent electron diffraction and electron microscopic examination; second, the etching of the surfaces to leave the minor-phase particles protruding from the matrix phase so that they can be detected by electron diffraction; and third, rinsing of the samples to remove all traces of reagents and reaction products from the etching treatment and to leave the surfaces clean, dry, and grease-free.

### Polishing

Two general methods are available for polishing metal surfaces: the usual metallographic method and the electrolytic method. In this work, the metallographic method is not preferred because it produces distortion, fragmentation, and working of the surface metal which may alter the structure or destroy some of the minor phases at the surface and lead to erroneous results. This is an important consideration in the case of the complex heat-resistant alloys, where some of the minor phases may be intermetallic compounds. In the electrolytic polishing method, the alloy sample is used as the anode in an electrolytic cell. With a proper choice of electrolytes and conditions, the electrolysis removes metal most rapidly from the peaks of the asperities of the surface, the overall result being a leveling and polishing action. Surfaces polished in this manner are completely free of distorted or worked metal and are well suited for both electron diffraction and electron microscope studies.

Electrolytes and conditions have been developed for electrolytically polishing a variety of metals.<sup>12,13,14,15,16</sup> The electrolytes commonly recommended for stainless steels and similar alloys fall into two classes; those requiring low current densities and those which operate at high current densities. The first group generally includes aqueous solutions of inorganic acids such as phosphoric, sulfuric, or chromic acids, while the second group usually contains perchloric acid and an organic solvent. From the work with the N-155, 16-25-6, S816, and Inconel-X alloys it appears that the perchloric acid solutions are more satisfactory than the phosphoric-sulfuric acid solutions for polishing heat-resistant alloys, since they polish more rapidly and have little tendency to pit or etch the surfaces. It is important to note, however, that these solutions are potentially dangerous due to the explosive character of perchloric acid when in contact with hot organic materials. Precautions for their use have been described by Jacquet.<sup>17</sup>

TABLE I

## COMPOSITIONS OF ELECTROLYTIC POLISHING SOLUTIONS

Solution	Composition*
A	70% ethyl alcohol 20% perchloric acid 10% glycerine
B	80% ethyl alcohol 20% perchloric acid
C	80% ethyl alcohol 5% perchloric acid, 15% water
D	90% glacial acetic acid 10% perchloric acid

\* Compositions are given in % by volume. 95% ethyl alcohol and 68-72% perchloric acid were used in all cases.

The compositions of several of the solutions which have been used successfully with heat-resistant alloys are given in Table I. The optimum current densities were found to vary for the different alloys and also with the heat treatment of the individual samples, but generally they do not exceed 10 amperes per square inch. Solutions were kept below 30°C at all times and gentle stirring was used to reduce localized heating during electrolysis. Best results were obtained when the surfaces to be polished were held horizontal, facing upward, and directly beneath the cathode.

This prevents the bubbles which form on the cathode from coming in contact with the surfaces and results in more uniform polish. The sample support and the cathode were both of platinum to prevent contamination of the solutions. It also appears best to reserve separate lots of solutions for different alloys and to replace the solutions frequently.

The character of the surfaces produced by electrolytic polishing is shown by the electron micrographs in Fig. 1\*. These micrographs were taken from a sample of 16-25-6 alloy (aged 10 hours at 1600°F) after polishing in each of the solutions listed in Table I. It will be noted that the surface produced in each case is smooth on a submicroscopic scale and is free of distorted or worked metal and that the true structure of the sample is revealed. Solutions A, B, and C also leave the minor-phase particles in considerable relief, so that relatively little etching is required to finish preparing the sample for electron diffraction. Solution D, on the other hand, removes particles from the surface, and while this solution produces a smoother, brighter polish than the others it is less satisfactory for the electron diffraction studies.

The chief difficulty encountered in electrolytically polishing the heat-resistant alloys involves the formation of films of reaction products on the samples during electrolysis. These films are usually loosely adherent and dark brown or black in color and very insoluble. Attempts to dissolve them, using reagents such as dilute hydrofluoric, hydrochloric, nitric, sulfuric, phosphoric, and acetic acids and sodium and ammonium hydroxides, have been generally unsuccessful. The formation of these films depends not only on the polishing solutions but also on the alloys. Of the alloys studied to date, 16-25-6 is by far the easiest to polish. As indicated above, satisfactory results are obtained on this alloy with all the solutions listed in Table I and several phosphoric-sulfuric acid solutions may also be used. In contrast, S816 alloy is very difficult to polish. Twenty different solutions were tried with this alloy and only four were found which do not produce insoluble reaction products. The most satisfactory of these is solution D of Table I. This solution produces a yellow granular deposit on the samples, but this is soluble in dilute hydrochloric acid and does not form if a small amount of the acid is added to the polishing solution. The N-155 and Inconel-X alloys are more difficult than 16-25-6 but less difficult than S816 to polish. There is also some indication that the phosphoric-sulfuric acid polishing solutions produce reaction products more readily than the perchloric acid solutions.

In addition, the polishing characteristics of samples of a given alloy vary markedly depending on the heat treatments they have received.

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\* The preparation and interpretation of the micrographs is discussed in the appendix.

Generally, samples aged for short periods polish slowly, but take on a smooth, bright finish. Samples aged for long periods (e.g., 500-1000 hours) at high temperatures polish more rapidly but often have a fine matte appearance and, unless the current density is carefully adjusted, may be easily pitted or etched. These samples are also more likely to become covered with films than those aged for short periods. In some cases it may prove advantageous to use different polishing solutions for different aged samples.

### Etching

The etching of the samples is undoubtedly the most important step in preparing them for the electron diffraction studies. An ideal etching treatment is one which leaves all the particles of all the minor phases of the alloy protruding in relief from the matrix and which does not stain or oxidize the surfaces of the samples. In addition, the etching agents should not permit the redeposition of dissolved metal nor the formation of insoluble reaction products on the samples. When electron microscope studies are to be made in conjunction with the electron diffraction studies, the surfaces of the samples should not be unduly pitted or roughened; otherwise the electron microscope replicas may be badly distorted or torn or may not separate easily from the samples.

These requirements are much more stringent than those placed on etchants for the preparation of alloy samples for ordinary metallographic examination. For metallographic studies the principal requirement is the enhancement of optical contrast between the various phases. Since the examination of the samples is only by optical microscopy, there is no concern about the relief of the minor phases relative to the alloy matrix nor about the presence of traces of contaminants of the samples; staining and oxidation of the samples are therefore acceptable techniques. Furthermore, due to the low resolving power of the light microscope, the etching need not be effective on as fine a scale as for the electron microscope.

As a consequence of these differences, etching techniques which are highly satisfactory for metallographic purposes are often not at all suited for use in conjunction with the electron diffraction and electron microscope studies. This is illustrated by the micrographs in Figs. 2 and 3 for the case of two commonly used electrolytic etchants for stainless steels: 10% oxalic acid and 10% potassium ferricyanide.<sup>18</sup> Fig. 2a is an electron micrograph of a sample of 16-25-6 alloy etched for 30 seconds at a current density of about 0.25 ampere per square inch in the oxalic acid solution. Although these etching conditions are relatively mild all the minor-phase particles have been attacked and etched out of the matrix, producing a surface which is highly unsatisfactory for electron diffraction studies of the minor phases. Furthermore, it is not useful in revealing the structure of the alloy for electron microscopy because of the extensive pitting. On the other hand,

Fig. 2b, which is an optical micrograph of the same sample, shows that this etch is entirely satisfactory for the usual metallographic studies. Figures 3a and 3b are respectively electron and optical micrographs of the same sample etched for 30 seconds at 0.25 ampere per square inch in the ferricyanide solution. Again the etching action is unsatisfactory for electron diffraction and electron microscopic studies but satisfactory for metallographic purposes. In this case not only are the minor-phase particles etched out of the matrix, but contaminating reaction products are formed on the surface. Particles of these products adhere to the replica as it is stripped from the sample and since they are "opaque" to electrons appear as white areas in the electron micrograph. The alloy sample used in making the micrographs of Figs. 2 and 3 is the same as was used for Fig. 1. Prior to etching, the sample was polished with solution A of Table I. The appearance of the polished surface is shown in Fig. 1a.

Unfortunately there is no 'a priori' method for determining the suitability of an etchant for the electron diffraction studies. Various reagents for both immersion and electrolytic etching of stainless steels have been developed for metallographic applications<sup>18,19</sup> and it is usually most convenient to try these first even though many prove unsatisfactory. In addition, it has been found that phosphoric-sulfuric acid electrolytic polishing solutions can be satisfactory for electrolytic etching of heat-resistant alloys with current densities somewhat lower than those used for polishing. The action under these conditions is a combination of polishing and etching so that pitting and grain-boundary attack are often less severe than for many of the more conventional etchants. One solution which has worked well with the 16-25-6 alloy consists of 10 gm of  $\text{CrO}_3$  dissolved in 60 ml of concentrated phosphoric acid, 15 ml concentrated sulfuric acid, and 12 ml of water. For best results this solution must be used hot with current densities up to 1 ampere per square inch. Whether the etching is done by the electrolytic or the immersion method, careful adjustment must be made of factors such as the composition and the temperature of the solutions, the time of etching, and, for the electrolytic method, the current density, in order to obtain best results. The importance of these factors in etching 16-25-6 alloy electrolytically in phosphoric acid solutions is illustrated by the electron micrographs of Fig. 4. Figure 4a shows that a very satisfactory etch is obtained with an 85% (by volume) solution of concentrated phosphoric acid at room temperature using a current density of 0.2 ampere per square inch for a period of 30 seconds. If the current density is doubled, a severe attack at the grain boundaries and around the minor-phase particles results, as shown in Fig. 4b; however, by raising the temperature of the solution to about  $70^\circ\text{C}$  satisfactory etching action can be obtained with current densities up to 0.7 ampere per square inch, as shown in Fig. 4c. If the solution is diluted to 75%, etching at 0.2 ampere per square inch for 30 seconds again produces unsatisfactory results, as shown in Fig. 4d. The sample used in these experiments was aged for 1000 hours at  $1400^\circ\text{F}$ , and was electropolished in solution A of Table I prior to etching.

The action of the etching reagents may vary considerably on different alloys, so that an etch that works well with one alloy may not be satisfactory for another. This is particularly true with regard to the formation of films of insoluble reaction products. The difficulties in this respect are the same as were described in connection with polishing. In general, it appears better to look for etches which do not produce the films rather than to try to find means of dissolving them. Optimum etching conditions also depend on the prior treatment of the individual samples and must be adjusted accordingly; usually, the longer or more strenuous the mechanical or heat treatment to which the samples have been subjected, the more easily they etch and the more likely they are to produce films.

### Rinsing

Proper rinsing of the alloy samples following the etching treatment is of the utmost importance. This step serves to remove the etching reagents from the samples and to leave the surface clean and dry for electron diffraction examination. In some cases, special rinses may be used to prevent oxidation of the samples or to dissolve reaction products formed during the etching process.<sup>4</sup>

In this work with heat-resistant alloys, satisfactory results have been obtained by first rinsing the samples with running tap water, then with distilled water, and finally with a 50-50 mixture of acetone and methanol. The samples are drained on a clean cloth or filtered paper, allowed to dry in air, and then transferred immediately to the electron diffraction instrument. Due to the inert character of the heat-resistant alloys, aqueous rinses can be used without danger of oxidizing the samples. This makes the rinsing processes considerably simpler than those needed for more active alloys.<sup>4</sup> In most cases where reaction products have been formed in etching, it has not been possible to find reagents which will satisfactorily dissolve them; the principal effort has therefore been devoted to developing etches which do not produce such products rather than to searching at great length for rinses to dissolve them.

Precautions must be taken at all times to prevent the contamination of the samples by grease and similar materials. The methanol and acetone used in the final rinsing steps must be redistilled; even reagent-grade solvents contain sufficient dissolved grease to leave undesirable films on the surfaces. The distilling apparatus should be all glass and should be cleaned in chromic acid prior to use and any ground-glass joints should not be lubricated. Frequently, laboratory distilled-water lines are contaminated with cements used on the joints, so that it is best to redistill the distilled water. Tap water drawn from an old and much used line is usually grease-free; otherwise distilled water should be used in place of the tap water in

the first step. All glassware for containing the solvents and rinsing solutions should be glass-stoppered, and should be cleaned in chromic acid prior to use. If electrolytic polishing is used the samples will usually be cleaned by the electrolysis and it is desirable to proceed immediately with the etching and rinsing without drying the samples. The samples should be handled only with clean tweezers or similar instruments, which can be degreased by treating them with benzene in a Soxhlet extractor.

APPLICATION OF THE ELECTRON DIFFRACTION METHOD  
TO THE STUDY OF THE MINOR PHASES OF HEAT-RESISTANT ALLOYS

The application of the electron diffraction method to the identification of minor phases of heat-resistant alloys has included an extensive study of the influence of high-temperature aging on the development of carbides in 16-25-6 alloy and preliminary studies of S816 and low-carbon N-155 alloys. The results of these studies will be described briefly in the following sections.

16-25-6 Alloy

Samples of this alloy aged at three different temperatures, 1200°F, 1400°F, and 1600°F, for periods up to 1000 hours have been studied. For aging periods of a few hours at each of these temperatures, the principal minor phase identified is a carbide of the  $M_{23}C_6$ -type; however, traces of an  $M_6C$  carbide have also been detected. For long periods of aging (500-1000 hours) the  $M_6C$  carbide becomes the principal minor phase and only traces of the  $M_{23}C_6$  carbide are detected. The results for each of the samples studied are indicated in Table II.

The  $M_{23}C_6$  and  $M_6C$  carbides both have crystal structures based on face-centered cubic lattices with unit cell edges of 10.6Å and 10.9Å respectively. The interplanar spacings and relative intensities of the electron diffraction patterns of each of these materials are given in Table III. A typical pattern of the  $M_6C$  carbide is reproduced in Fig. 5a; the  $M_{23}C_6$  patterns are similar in appearance although differing both in scale factor and in the relative intensities of some of the rings. All the alloy specimens have yielded electron diffraction patterns which are clear, intense, and of excellent quality. It will be noted in Table III that rings recorded include virtually all the possible reflections for a face-centered cubic structure out to the 800 line. These data are much more complete than those usually reported from x-ray studies,<sup>27,28,29</sup> particularly for lines of large  $d_{hkl}$  values.



TABLE II  
MINOR PHASES IDENTIFIED IN 16-25-6 ALLOY SAMPLES\*

Time of Aging (hrs)	Aging Temperature		
	1200°F	1400°F	1600°F
1		M <sub>23</sub> C <sub>6</sub>	M <sub>23</sub> C <sub>6</sub> **
10	M <sub>23</sub> C <sub>6</sub> **	M <sub>23</sub> C <sub>6</sub> **	M <sub>6</sub> C***
100	M <sub>23</sub> C <sub>6</sub> **		
500			M <sub>6</sub> C***
1000	M <sub>6</sub> C***	M <sub>6</sub> C***	

\* All samples were solution-treated at 2050°F for 2 hours before aging  
 \*\* Small amounts of M<sub>6</sub>C also present  
 \*\*\* Small amounts of M<sub>23</sub>C<sub>6</sub> also present

TABLE III  
INTERPLANAR SPACINGS AND RELATIVE INTENSITIES FOR ELECTRON DIFFRACTION PATTERNS OF M<sub>23</sub>C<sub>6</sub> AND M<sub>6</sub>C CARBIDES

M <sub>23</sub> C <sub>6</sub> Carbide		hkl	M <sub>6</sub> C Carbide	
d <sub>hkl</sub>	I		d <sub>hkl</sub>	I
6.2Å	VW	111	6.3Å	W
5.4	VW	200	5.4	W
3.7	W	220	3.8	W
3.2	W	311	3.2	W
3.1	W	222	3.1	VW
		400	2.7	VW
2.46	M	331	2.49	W
2.38	MS	420	2.40	VW
2.16	S	422	2.22	S
2.05	S	511	2.10	VS
1.88	M	440	1.92	M
1.79	S	531		
		600	1.82	M
1.68	WM	620	1.72	W
1.62	W	533		
1.59	W	622	1.63	W
		444	1.56	VW
1.48	W	711	1.52	W
1.42	W	642	1.45	VW
1.38	W	731	1.41	W
1.33	VW	800	1.36	VW

The electron diffraction results indicate that the development of minor phases of 16-25-6 alloy at high temperatures proceeds in two more or less distinct stages. The first of these takes place during the first few hours of aging and involves the formation of the  $M_{23}C_6$  carbide. The second occurs with longer periods of aging and consists of a transformation of the  $M_{23}C_6$  carbide to the  $M_6C$  carbide. The alternative possibility that the  $M_{23}C_6$  persists and that the  $M_6C$  forms in addition to it is not supported by the electron diffraction data. It also appears that the period required for the transformation to take place decreases as the aging temperature is increased. Thus, at 1200°F the  $M_{23}C_6$  carbide persists as the principal minor phase for the first 100 hours of aging, while at 1600°F it is replaced by the  $M_6C$  carbide after only 10 hours. Reference to Table II will illustrate these points.

These electron diffraction results can be correlated with variations which have been observed in the properties of the alloy as a result of aging treatments. As an illustration, the variations in the lattice parameter of the matrix phase of the alloy may be considered. For the solution-treated alloy the matrix lattice parameter is about 3.600Å. During the first hour of aging at 1400°F the lattice parameter decreases to 3.596Å and then remains at this value until after about 10 hours when it decreases again and finally reaches a constant value of about 3.587Å between 100 and 1000 hours of aging. At 1200°F the decrease to 3.596Å is observed during the first hour but the parameter remains at this value for about 100 hours. Data beyond this point are not available for this temperature. At 1600°F the decrease is more or less gradual and a value 3.587Å is reached after about 100 hours. These relationships are indicated in Fig. 6. The data cited here were obtained in the course of an investigation of the metallurgical properties of this alloy which was sponsored by the National Advisory Committee for Aeronautics and carried out under the direction of Dr. J. W. Freeman of the Department of Chemical and Metallurgical Engineering of this University

In terms of the electron diffraction results, the decrease in lattice parameter of the matrix phase which occurs during the first hour of aging may be accounted for by the formation of the  $M_{23}C_6$  carbides in the first stage of the development of the minor phases. This type of carbide frequently contains molybdenum as one of the constituent metals. Since the atoms of this element are somewhat larger than the atoms of iron, chromium, and nickel\* which form the bulk of the matrix phase, the transfer of molybdenum atoms from the matrix to the carbide would be expected to decrease the lattice parameter of the matrix phase. The further decrease in lattice parameter after 10 hours of aging at 1400°F can be accounted for by further removal

\* The diameters of the atoms of these metals are: Fe, 2.48; Cr, 2.49; Ni, Mo, 2.72Å. The composition of the alloy is given in Table IV.

of molybdenum from the matrix in the transformation from  $M_{23}C_6$  to  $M_6C$  carbide. The fact that there is no similar decrease in lattice parameter for 100 hours of aging at  $1200^\circ F$  is consistent with the persistence of the  $M_{23}C_6$  carbide as the principal minor phase over this period. However, the lattice parameter would be expected to decrease between 100 and 1000 hours at this temperature, since the carbide transformation takes place during this period. The more rapid decrease in the lattice parameter at  $1600^\circ F$  is due to the accelerated transformation of the  $M_{23}C_6$  to  $M_6C$  at this higher temperature.

In addition to these electron diffraction studies, extensive electron microscope studies have been made of the structure of this alloy. A fuller description and discussion of this work will be published in a technical journal.

TABLE VI

TYPICAL ALLOY CONSUMPTIONS  
(Percent by weight)

Element	16-25-6	N-155	S816
Fe	50%	32%	3%
Cr	16	20	20
Co		20	44
Ni	25	20	20
Mo	6	2	4
Mn	1.5	2	1
W		2	4
Cb		1.2	4
C	0.1	0.2	0.4
N	0.1	0.2	
P	0.02	trace	trace
S	0.07	trace	trace
Si	0.7	trace	trace

N-155 and S816 Alloys

The work with these alloys has not been as extensive as with the 16-25-6 alloy; however, some interesting preliminary results have been obtained. Both these alloys contain columbium (see Table IV), which combines readily with carbon and nitrogen to form carbides, nitrides, and carbonitrides. CbC and CbN have been identified as minor phases in the S816 and the N-155 alloys, respectively, by x-ray diffraction methods,<sup>27</sup> and these phases have also been identified here by electron diffraction. One of the CbC patterns

obtained from the S816 alloy is reproduced in Fig. 5b. The strong rings in this pattern are the CbC rings, while the weaker rings were produced by the matrix phase. Due to the similarity in the crystallographic structures of the CbC and CbN, the patterns from the N-155 alloy are similar in appearance to Fig. 5b.

Patterns have also been obtained from each of these alloys which contain a number of rings in addition to those of CbC, CbN, and the matrix and which are tentatively considered to indicate the presence of  $M_{23}C_6$  carbide in these alloys. Typical patterns are reproduced in Figs. 5c and 5d. If this identification is substantiated by further work, it will be of considerable interest since this carbide has not been previously detected in these alloys.

#### DISCUSSION

The results which have been obtained from the studies of 16-25-6, N-155, and S816 alloys indicate that the electron diffraction method is well suited for the study of the minor phases of heat-resistant alloys. This method can provide information which is not readily obtained by other methods of minor-phase investigation and is well adapted to the study of relatively large numbers of samples of a given alloy. The electron diffraction results are particularly useful when correlated with metallurgical, x-ray diffraction, and electron microscopic studies of the same samples.

The electron diffraction method can be applied to the study of any alloy system for which suitable methods of sample preparation can be developed. Unfortunately a considerable amount of experimentation is required in developing satisfactory polishing and etching procedures for heat-resistant alloys. This is due not only to the inert character of the alloys and the rather stringent requirements placed on the polishing and etching processes, but also to the general lack of information on the action of various polishing and etching agents on these alloys. However, the evaluation and selection of polishing and etching reagents can be greatly facilitated by the use of the electron microscope.

In continuing this work, it is planned to carry out investigations of the influence of high-temperature aging on the development of minor phases in S816 and N-155 alloys which will be similar in extent to the study just completed on 16-25-6 alloy. Some of the preliminary work to select polishing and etching reagents for these alloys has already been completed. It would also be interesting and useful to extend the work to include some of the newer type of alloys containing larger amounts of titanium and molybdenum.

In connection with the development of polishing and etching procedures for this work, some experimental evidence has been obtained to suggest that various complexing agents may be effective in preventing the formation of films of reaction products on the samples. This would be of interest not only for electron diffraction applications but also in preparing samples for optical and electron microscope studies. This matter will be investigated as time permits.

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## APPENDIX



## PREPARATION AND INTERPRETATION OF ELECTRON MICROGRAPHS

The electron micrographs of the polished and etched surfaces were obtained through the use of shadow-cast, negative collodion replicas.<sup>5,20</sup> Collodion replicas were adopted for this work because they are simple and rapid to prepare and the micrographs obtained from them are relatively straight-forward to interpret. Because of the importance of the electron microscope studies, the preparation of the replicas and the interpretation of the micrographs will be discussed in some detail.

A collodion replica is formed by placing a small drop of a dilute collodion solution (USP collodion solution diluted with 7-10 parts of amyl acetate) on the surface and allowing it to evaporate to dryness. This leaves a very thin film of collodion which conforms in minute detail to the feature of the surface. The side of the film which was in contact with the surface reproduces the features of the surface in negative relief; that is, indentations on the surface become protrusions on the replica and vice versa. Separation of the film from the sample may be accomplished in several ways,<sup>20, 21,22</sup> but the "dry-stripping" method was adopted here because of its simplicity. A wire gauze disc of the type used for mounting specimens in the electron microscope is placed on top of the film and Scotch tape is pressed firmly over and around the disc. By carefully lifting the Scotch tape, the film can be stripped from the surface and a portion of it will be stretched across the gauze disc. The disc, carrying this portion of the film, is then separated from the tape by creasing the tape beneath the disc and lifting the disc off with a pair of tweezers.

There are several techniques which help considerably in this process. If the side of the gauze disc which is to be in contact with the film is first pressed onto Scotch tape, adhesive from the tape will remain on the wires of the gauze. The collodion film then adheres more tightly to the gauze and is less likely to be torn or wrinkled in the stripping process. Breathing heavily on the sample immediately before applying the Scotch tape to the sample condenses moisture on the surface which penetrates the film and helps separate it from the metal. In applying the Scotch tape it is essential to press it gently, but firmly, to the surface around the edges of the gauze. This also serves to reduce wrinkling and tearing of the film. The separation of the gauze from the tape after stripping is made easier if a disc of thin paper, smaller in diameter than the gauze disc, is placed on top of the gauze disc before the tape is applied to the sample. (An alternative procedure is to place the paper disc on the tape, then lay the gauze over it, and then apply the tape and gauze to the surface.)

The contrast of the replica is increased and the relief of the surface features is defined by "shadow-casting" the replica prior to taking the micrographs. The shadow-casting technique consists of evaporating a thin

film of a heavy metal, such as gold, palladium, or uranium, onto the replica at a low angle from a hot tungsten filament.<sup>20,23,24</sup> The thickness of the metal film varies over the replica in a manner related to the contour of its surface. When the electron beam is passed through the replica in making micrographs, the electrons pass most readily through the shaded areas where there is the least metal and the corresponding regions on the photographic plates appear most dense. Other areas produce variations in density depending on the thickness of metal through which the electrons pass. "Opaque" objects appear white in the micrographs, while shaded areas of the replica appear as shadows. The overall appearance of the micrographs is similar to an aerial photograph of a landscape taken with the sun near the horizon.

It is important to note that features which protrude from the replica produce external shadows. Since the replica is a negative reproduction of the original surface, these features correspond to indentations in the metal. On the other hand, features with internal shadows are indentations in the replica and correspond to protrusions from the original surface. To aid in interpreting the micrographs it is convenient to place polystyrene latex spheres<sup>25</sup> on the replica just prior to shadowing. These spheres are easily recognized and cast distinct shadows, which makes it possible to tell with certainty the direction from which the metal was evaporated in the shadow-casting process. In addition, they are of known size ( $2,580 \pm 30 \text{ \AA}$  in diameter) and serve as internal standards for determining the magnification of the micrographs:<sup>25,26</sup> the magnification is approximately equal to four times the diameter of the spheres (in mm) in the micrographs.



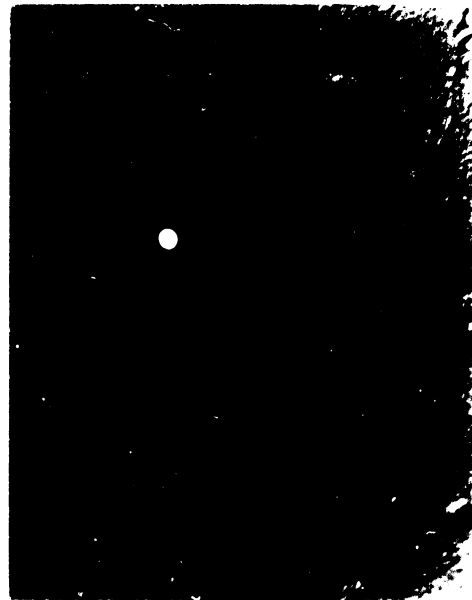
a. Polished in Solution A.



b. Polished in Solution B.



c. Polished in Solution C.



d. Polished in Solution D.

Fig. 1. Electron Micrographs of 16-25-6 Alloy Polished Electrolytically in Various Solutions of Table I. (X10,000).

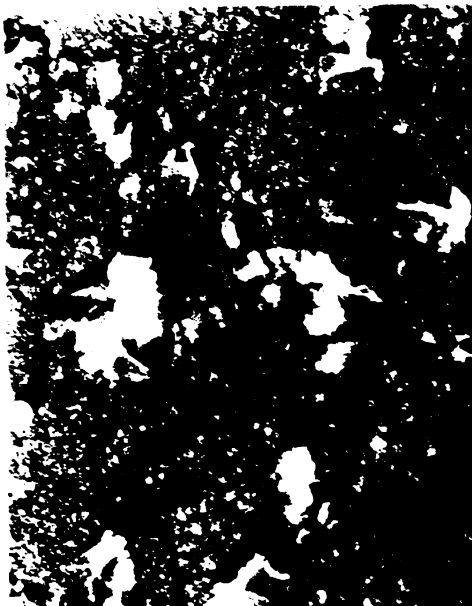


a. Electron Micrograph, X10,000.



b. Optical Micrograph, X1,000.

Fig. 2. Micrographs of Sample Etched in 10% Oxalic Acid.



a. Electron Micrograph, X10,000.



b. Optical Micrographs, X1,000.

Fig. 3. Micrographs of Sample Etched in 10% Potassium Ferricyanide.



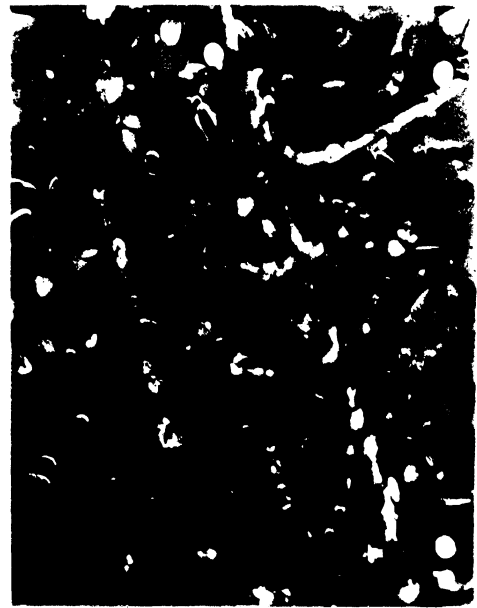
a. 85%  $H_3PO_4$ ; 30 secs, 0.2 amp,  
Room Temp.



b. 85%  $H_3PO_4$ ; 30 secs, 0.4 amp,  
Room Temp.



c. 85%  $H_3PO_4$ ; 30 secs, 0.7 amps,  
70°C.

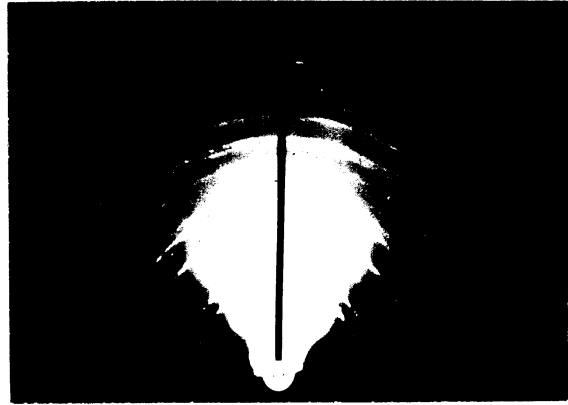


d. 75%  $H_3PO_4$ ; 30 secs, 0.2 amps,  
Room Temp.

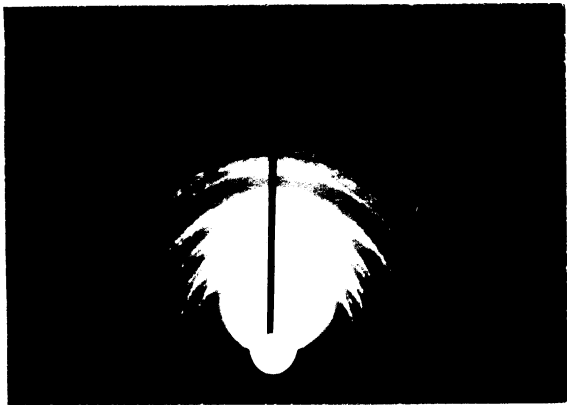
Fig. 4. Electron Micrographs (X10,000) Showing the Effect of Variation in Conditions on the Etching Action of Phosphoric Acid Solutions.



a.  $M_6C$  Pattern from 16-25-6 Alloy.



b. CbC Pattern from S816 Alloy.



c. Pattern of Cb(C-N) and Possibly  $M_{23}C_6$  from S816 Alloy.



d. Pattern of Cb(C-N) and Possibly  $M_{23}C_6$  from N-155 Alloy.

Fig. 5. Electron Diffraction Patterns of Minor Phases from Heat-Resistant Alloys.

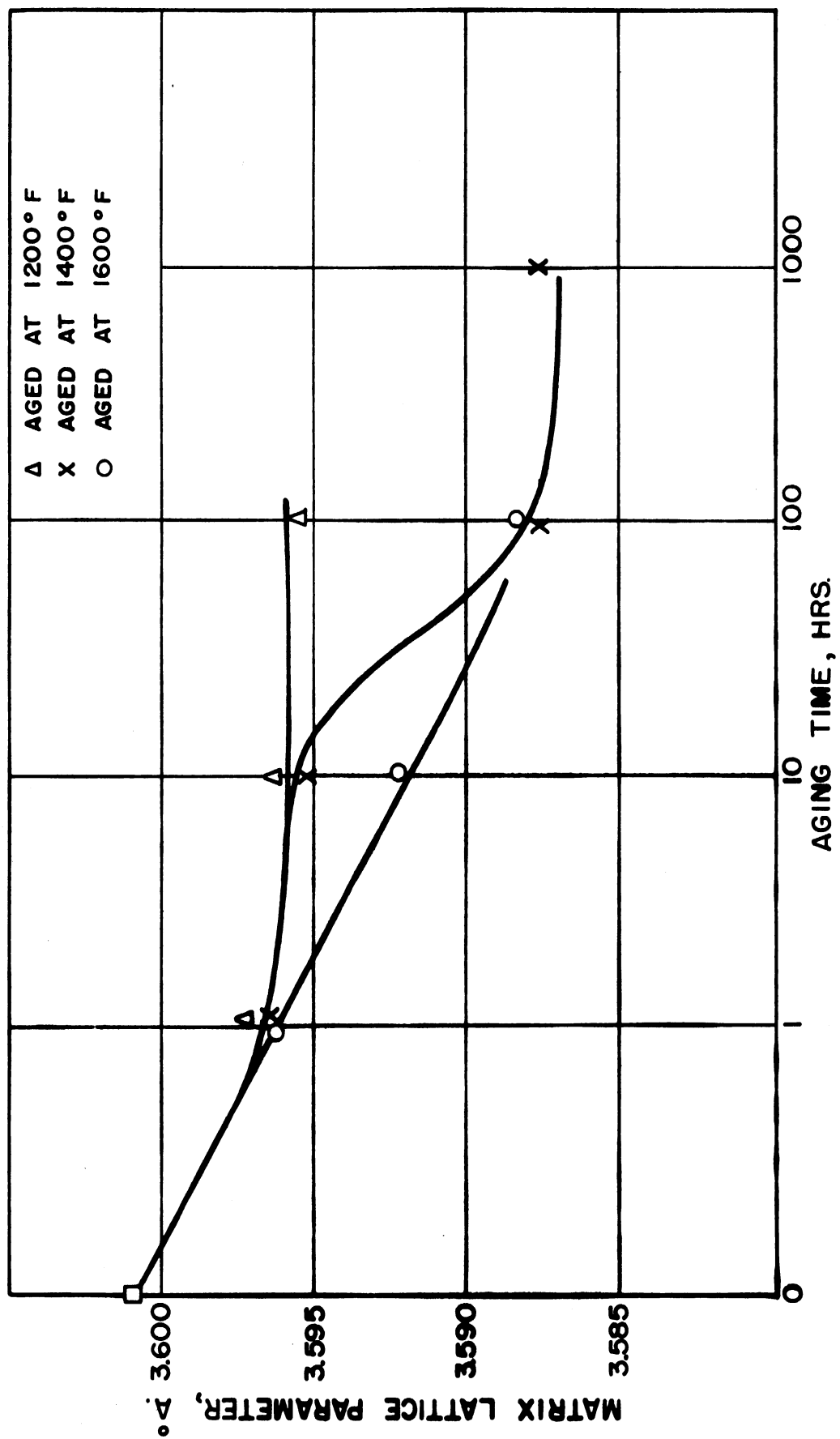


FIG. 6. INFLUENCE OF HIGH-TEMPERATURE AGING ON THE LATTICE PARAMETER OF THE MATRIX PHASE OF 16-25-6 ALLOY.

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