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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 electron diffraction method has been applied to the study of Alcoa M-276 Sintered Aluminum Product and  $\gamma$ - $\text{Al}_2\text{O}_3$  has been identified as the principal minor phase in this material. A special etching procedure using HCl and  $\text{Cl}_2$  gasses was developed for this work to minimize the oxidation of the aluminum during preparation.

A number of polishing and etching treatments have been investigated for suitability in preparation of Inconel-X alloy for the electron diffraction studies. Polishing methods which appear to be satisfactory have been found; however, difficulty has been encountered in etching this alloy due to the formation of reaction products on the samples during the etching process.

Data have been obtained which indicate a variation of about 1 per cent in the unit cell size of the  $\text{M}_6\text{C}$  phase of the 16-25-6 alloy, depending on the temperature of the aging treatment.

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INTRODUCTION

This project has as its objectives the development of procedures for the identification of the minor phases of heat-resistant alloys by the electron diffraction method, and the application of this method to the study of the influences of thermal and mechanical treatments on the minor phases of some alloys typical of those currently used in jet aircraft engines.

The experimental procedures employed have been discussed in detail in a previous report<sup>1</sup> and therefore will be described only briefly here. The alloy samples are prepared by electrolytic polishing, followed by special etching and rinsing treatments. The etching treatments are chosen to attack selectively the matrix phase, leaving the minor phase particles protruding in relief from the surrounding matrix metal. The selection of etching reagents and conditions is of prime importance in determining the effectiveness of the electron diffraction method and constitutes one of the principal problems in adapting the method to the heat-resistant alloys. The rinsing serves to remove etching reagents and products from the samples and to leave the etched surfaces clean and dry for the diffraction studies. Electron diffraction patterns, which are analogous to X-ray powder diffraction patterns and serve to identify the minor phases, are obtained from the protruding minor-phase particles by passing the electron beam across the etched surfaces at a grazing angle and recording the diffracted electrons photographically. Finally, the etched surfaces are studied by optical and electron microscopy to correlate the microstructures with the diffraction results.

Previously, studies were made of the effects of heat treatments for periods up to 1000 hours at temperatures of 1200°, 1400°, and 1600°F on the minor phases of 16-25-6 alloy. Additional preliminary studies were made on S816 and N-155 alloys. These results were described in the summary report for the past contract year<sup>1</sup> which also contained a discussion of the factors involved in the preparation of alloy samples for the diffraction work.

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This report covers the period of 15 January to 15 April 1953. The work carried out during this period includes (1) an identification of the oxide phase of a sintered aluminum product, (2) preliminary work to develop polishing and etching procedures for Inconel-X alloy, and (3) a study of the lattice parameters of the  $M_6C$  phase in 16-25-6 alloy.

The Inconel-X alloy was supplied by Dr. J. W. Freeman and his associates in the Department of Chemical and Metallurgical Engineering of this University. The electron micrographs for this report were taken with the electron microscope in the School of Public Health of this University through the cooperation of Dr. Thomas Francis and Miss Hilda Kurtz. Most of the polishing and etching studies of the Inconel-X alloy were carried out by Mr. J. A. Amy.

### RESULTS AND CONCLUSIONS

#### Sintered Aluminum Product

This work was undertaken at the request of Professor N. J. Grant of the Massachusetts Institute of Technology and with the concurrence of Mr. J. B. Johnson, Chief of Metallurgy Research Branch, Aeronautical Research Laboratory (WCRRL), Wright Air Development Center. X-ray diffraction studies carried out at M. I. T. on residues after extraction of SAP with dilute hydrochloric acid solutions indicated that a secondary oxide phase was present; however there was some question concerning possible effects of the extraction procedures on the form of the oxide. The electron diffraction studies were requested to provide an independent identification of the phase by a method not involving extraction techniques.

A sample of Alcoa sintered aluminum product M-276 was furnished in the "as-received" condition by Professor Grant. This material is reported to contain 15 to 17 per cent oxide and to have been manufactured from oxidized aluminum powder, cold pressed at 30,000 psi, hot pressed at 600°C and 30,000 psi, and extruded at 600°C.

For the electron diffraction studies, the SAP was electrolytically polished in a solution recommended by Mr. Eric Gregory of M.I.T., consisting of 1/3 perchloric acid (72%) and 2/3 acetic anhydride. A number of other electrolytic polishing reagents commonly recommended for aluminum were found unsatisfactory due to the formation of oxide films and reaction products on the SAP. These solutions include:

- (1) 70 ml ethyl alcohol, 20 ml perchloric acid, 10 ml glycerine
- (2) 80 ml ethyl alcohol, 20 ml perchloric acid

- (3) 80 ml ethyl alcohol, 5 ml perchloric acid, 15 ml water
- (4) 90 ml glacial acetic acid, 10 ml perchloric acid
- (5) 60 ml phosphoric acid, 15 ml sulfuric acid, 12 ml water, 10 g  $\text{CrO}_3$
- (6) 85 ml phosphoric acid, 15 ml water
- (7) 10 g  $\text{Na}_2\text{CO}_3$ , 5 g  $\text{Na}_3\text{PO}_4$ , 80 ml water
- (8) 25 ml sulfuric acid, 75 ml phosphoric acid
- (9) 10-25 ml water, 80-75 ml acetone; saturated with  $\text{NaNO}_3$
- (10) 100 ml sulfuric acid, 200 ml glycerine
- (11) 25 ml water, 75 ml phosphoric acid, 30 g oxalic acid, 15 g boric acid, 0.1 g litharge.

The phosphoric, sulfuric, and perchloric acids in these solutions were the common "concentrated" reagents having compositions of 85, 95, and 72 per cent respectively. The unsatisfactory character of these solutions is evident from the photograph of Figure 1, which shows samples of SAP polished with the perchloric acid-acetic anhydride solution and with solutions 1 and 6 above. The coloration of the samples polished in solutions 1 and 6 is due to the heavy deposits of reactions products. The nature of these products was not determined.

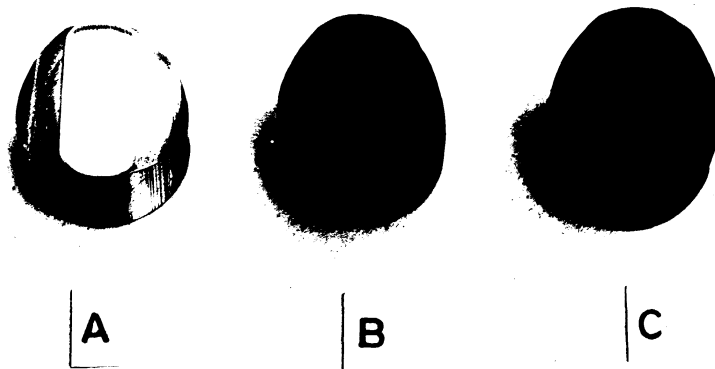


Figure 1. Samples of SAP Showing Reaction Products Formed by Electropolishing.

- a. Polished in perchloric acid-acetic anhydride solution
- b. Polished in solution 1.
- c. Polished in solution 6.

Two different etching techniques were employed: (1) immersion in an aqueous solution of 10 ml hydrochloric acid (35%), 10 ml of hydrofluoric acid (48%), and 80 ml of water, and (2) exposure to a mixture of HCl and Cl<sub>2</sub> gases at 200°C. After the immersion etching treatments the samples were rinsed with distilled water and then with distilled, grease-free acetone and placed immediately in the diffraction instrument. The gaseous etching procedure was developed to avoid exposure of the samples to water, thereby minimizing the surface oxidation during etching. This process was carried out in a pyrex tube 1-1/2 inches in diameter and 8 inches long, closed with an ungreased, ground-glass joint and heated by an external winding of nichrome wire. Five 8-mm tubes were connected to this main tube. Three of these led respectively to tanks of chlorine, hydrogen chloride and argon gases; the fourth connected through a stopcock to a bubbling column filled with a strong sodium hydroxide solution; the fifth passed through a stopcock to a vacuum pump. In use, the system was freed of oxygen by alternate evacuation and flushing with argon, after which the temperature was raised to 200°C and a slow stream of HCl and Cl<sub>2</sub> gases, in approximately equal amounts, was passed over the sample. The escaping gases were trapped in the sodium hydroxide solution. A treatment of approximately 5 minutes under these conditions produced satisfactory etching. The product of the etching is AlCl<sub>3</sub> which is volatile at 200°C and is removed from the sample in the gas stream. At the end of the etching treatment, the system was flushed with argon and then evacuated and maintained at 200°C for 5 to 10 minutes to insure complete removal of the AlCl<sub>3</sub>. The sample was then cooled to room temperature in argon and transferred directly to the diffraction instrument with minimum exposure to air.

Samples were examined by electron diffraction after electropolishing, and after subsequent etching by each of the methods described above. Diffraction patterns were obtained in all cases, the patterns from the etched surfaces being considerably better than those from the surfaces which were only electropolished. In general, the patterns had a rather heavy background and the diffraction rings were somewhat broad and poorly resolved. This is probably due to electrostatic charging of the nonconducting oxide phase by the electron beam. A typical pattern is reproduced in Figure 2, and the calculated interplanar spacings and observed intensities are compared with corresponding data for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in Table I. The electron diffraction patterns include all of the reflections of strong and medium intensity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the range of the data. The fact that the weak  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reflections are not observed in the electron diffraction pattern can reasonably be attributed to the high background of the patterns.

To preclude the possibility that the electron diffraction patterns were produced by materials formed from the aluminum during the polishing and etching procedures, a sample of 3S-grade aluminum was examined by electron diffraction after preparation by each of the methods used on the SAP samples. The principal diffraction pattern obtained was of aluminum, and in no case was the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pattern obtained.



TABLE I

COMPARISON OF THE ELECTRON DIFFRACTION PATTERN FROM SINTERED  
ALUMINUM PRODUCT WITH THE PATTERN FOR  $\gamma\text{-Al}_2\text{O}_3$

SAP Pattern		$\gamma\text{-Al}_2\text{O}_3$ Pattern	
$d_{hkl}$	I *	$d_{hkl}$	I*
		5.59 Å	W
4.6 Å	VW	4.59	W
		3.54	W
2.80	W	2.80	M
		2.65	VW
		2.50	VW
2.39	S	2.38	S
		2.28	W
		2.20	VW
2.13	W	2.12	WM
1.98	MS	1.98	M $\bar{S}$
		1.92	VW
		1.87	VW
		1.73	VW
		1.69	VW
		1.65	VW
		1.61	W
		1.55	VW
1.52	W	1.52	M
		1.47	VW
		1.44	VW
1.39	S	1.40	S

\* S = Strong, M = Medium, W = Weak, V = Very



Figure 2. Electron Diffraction Pattern from Sintered Aluminum Product

From these results it is concluded that the principal secondary phase of the SAP is  $\gamma$ - $\text{Al}_2\text{O}_3$ . The agreement between the electron diffraction patterns and the  $\gamma$ - $\text{Al}_2\text{O}_3$  pattern is good, even though the electron diffraction patterns are of rather poor quality. There are no indications of other secondary phases; this may not be highly significant, however, since the charging effects due to the  $\gamma$ - $\text{Al}_2\text{O}_3$  would make it extremely difficult to obtain patterns from small amounts of other materials.

The principal questions which may be raised in connection with studies of the surfaces of reactive metals such as aluminum is the extent to which the preparative methods oxidize or otherwise alter the surfaces. In the present work, the control experiments with the 3S aluminum were carried out to check this point, and the results of these experiments indicate that the polishing and etching procedures used on the SAP do not produce the  $\gamma$ - $\text{Al}_2\text{O}_3$ . Heidenrich, Sturkey, and Woods<sup>2</sup> have shown that dilute hydrochloric acid solutions can be successfully used to etch pure aluminum and aluminum-copper alloys. In addition, previous experience at this laboratory has shown that the oxide films which form on aluminum surfaces upon exposure to air or water at room temperature are generally amorphous, and that crystalline oxides form only at higher temperatures. In the gaseous etching procedure, the HCl gas was introduced to remove any amorphous oxides and to prevent the formation of high-temperature crystalline oxides; the  $\text{Cl}_2$  gas is chiefly responsible for the etching of the aluminum. In view of the very high temperatures used in producing the SAP and the stability of the high-temperature oxides of aluminum, it is unlikely that conditions used in these studies would alter any oxide phase previously formed.

Polishing and Etching of Inconel-X Alloy

In preparation for an extended study of the minor phases of Inconel-X alloy, work has been undertaken to develop polishing and etching procedures for use in preparing samples of this alloy for electron diffraction examination.

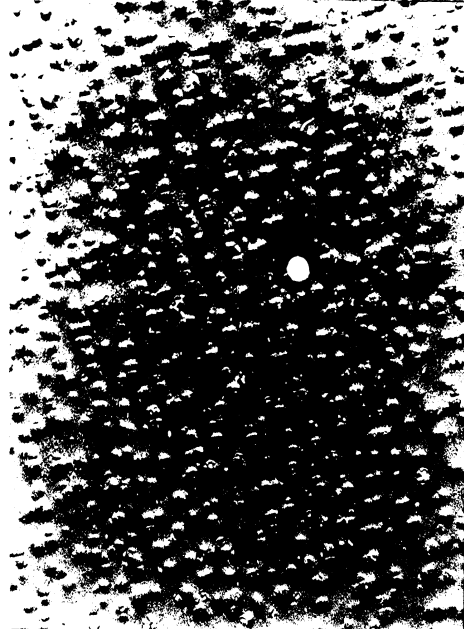
A variety of electrolytic polishing solutions were tried, including the following:

- (A) 70 ml ethyl alcohol, 20 ml perchloric acid, 10 ml glycerine
- (B) 80 ml ethyl alcohol, 20 ml perchloric acid
- (C) 80 ml ethyl alcohol, 15 ml perchloric acid, 5 ml water
- (D) 90 ml acetic acid, 10 ml perchloric acid
- (E) 60 ml phosphoric acid, 15 ml sulfuric acid, 12 ml water  
10 g CrO<sub>3</sub>
- (F) 32 ml phosphoric acid, 10 ml sulfuric acid, 10 ml water
- (G) 12 ml phosphoric acid, 47 ml sulfuric acid, 41 ml nitric acid
- (H) 66 ml sulfuric acid, 17 ml hydrofluoric acid, 17 ml  
hydrogen peroxide (3%)
- (I) 33 ml hydrochloric acid, 67 ml glycerine
- (J) 14 ml phosphoric acid, 36 ml nitric acid, 50 ml sulfuric acid
- (K) 30 ml phosphoric acid, 60 ml sulfuric acid, 10 ml water
- (L) 75 ml perchloric acid, 25 ml acetic acid
- (M) 33 ml perchloric acid, 67 ml acetic anhydride

The ethyl alcohol in these solutions was 95% grade; the acids were of the following concentrations: sulfuric, 96%; phosphoric, 85%; hydrochloric, 35%; acetic, 99%; perchloric, 72%; hydrofluoric, 48%; nitric 70%.

The solutions based on perchloric acid are the most satisfactory; the others coat the samples with heavy films of reaction products. Of the perchloric acid solutions, D, L, and M act rapidly, produce clean, bright surfaces, and are the most convenient to use. Electron micrographs show that they leave the minor-phase particles in slight relief in surfaces so that only light etching treatments should be required to complete the preparation for electron diffraction identification of the minor phases. Micrographs of surfaces polished with solutions L and M are reproduced in Figure 3.

Considerable difficulty has been encountered in etching Inconel-X samples due to the chemical resistance of the alloy and also to the formation



a. Polished in Solution L

b. Polished in Solution M

Figure 3. Electron Micrographs of Electropolished Inconel-X

of films of reaction products on the samples. The following etching reagents, generally recommended <sup>3,4</sup> for stainless steels, have been tried:

(1) Immersion Etches:

- (a) 2 parts hydrofluoric acid, 1 part nitric acid, 2-4 parts glycerine
- (b) nitric acid (70%)
- (c) hydrochloric acid (35%)
- (d) 1 part nitric acid (70%), 1 part hydrochloric acid (35%)
- (e) 1 part nitric acid (70%), 2 parts hydrochloric acid (35%), 3 parts glycerine
- (f) fuming nitric acid

(2) Electrolytic Etches:

- (g) lactol: 50 ml lactic acid, 50 ml methyl alcohol, 5 ml hydrochloric acid
- (h) 10 g CrO<sub>3</sub>, 90 ml water
- (i) 10 g tartaric acid 90 ml water
- (j) 10 g oxalic acid, 90 ml water
- (k) 30 ml hydrochloric acid (35%), 70 ml glycerine

- (l) 45 g ferric chloride hexahydrate, 100 ml water
- (m) 85 ml phosphoric acid (85%), 15 ml water
- (n) 30 g citric acid, 45 g potassium iodide, water to make 90 ml

None of these reagents were satisfactory. With the exception of etches d and e, the immersion etches do not attack the alloy. Etches d and e, and all of the electrolytic etches, attack the alloy vigorously, but also produce stains or films of reaction products on the samples and are therefore considered undesirable for electron diffraction purposes. Figure 4 shows the extent of staining by etches e and h. In each case, only half of the sample was etched for comparison.



Figure 4. Samples of Inconel-X Alloy  
Etched with Reagents e and h.

Results which have been obtained in these preliminary studies indicate that satisfactory polishing of Inconel-X samples can be accomplished with one of the perchloric acid solutions. Unexpected difficulty has been encountered in the etching of this alloy; however, there are a number of etches which have not been tried as yet, and it is possible that some of these will prove satisfactory. In addition, it is possible that some of the polishing solutions can be used at low current densities or modified in composition to serve as etches. These possibilities are under investigation.

#### Lattice Parameters of $M_6C$ Phase in the 16-25-6 Alloy

The previous electron diffraction results from 16-25-6 alloy suggested a variation in the size of the unit cell of the  $M_6C$  carbide phase

depending on the temperature of aging. For the sample aged 1000 hours at 1200°F the value appeared to be about 10.9 Å, but for samples aged for a similar period at 1400°F and 1600°F it appeared to be more nearly 11.0 Å. Two series of experiments were carried out to investigate this further.

First, samples aged for 1000 hours at 1400°F and 1200°F were mounted side by side in the diffraction unit and comparison patterns were taken in which one half of the photographic plate was exposed to the pattern from one sample and the adjacent half to the pattern from the other. Very small differences in the radii of the diffraction rings of the two patterns can be detected by careful inspection along the line of their intersection on the photographic plate. Ten such comparison patterns were made and inspected: an enlargement of one of the patterns is shown in Figure 5. In all cases the rings from the sample aged at 1200°F were slightly larger in radius than those from the 1400°F sample. These results clearly indicate a smaller unit cell for the carbide in the 1200°F sample.



Figure 5. Comparison Diffraction Pattern of  $M_6C$  Carbides in Samples of 16-25-6 Alloy Aged at 1200° F and 1400° F

Second, an attempt was made to determine the difference between the values of the lattice parameters in the two samples. Ten different patterns were taken from each of the samples described above. Careful

measurements were made on the four strongest rings of these patterns and the corresponding  $d_{hkl}$  values were averaged and compared for the two samples. The results are summarized in Table II.

TABLE II  
COMPARISON OF AVERAGE  $d_{hkl}$  VALUES FOR  $M_6C$   
CARBIDE IN 16-25-6 ALLOY SAMPLES.

Sample	$d_{422}$	$d_{511}$	$d_{440}$	$d_{822}$
1200°F	2.23	2.10	1.93	1.28
1400°F	2.24	2.11	1.93	1.28

The differences in the average  $d_{hkl}$  values for the 422 and 511 rings listed in Table II are not considered as being particularly significant, principally because of the precision with which the electron diffraction patterns can be measured. The extremely short wavelength of the electrons (about 0.06 Å) results in very small diffraction angles and correspondingly small radii for the diffraction rings. Even with careful measurements, these radii cannot generally be determined with an accuracy better than 1 per cent, which places similar limits of error on the  $d_{hkl}$  values calculated from them. In the present case, therefore, the data show that the lattice parameters do not differ by more than this amount. This is consistent with estimates made from the comparison patterns. A more accurate determination of the cell sizes could be obtained from X-ray diffraction studies of carbides extracted from the samples.

#### DISCUSSION

The success of the studies of the Sintered Aluminum Product provides further evidence of the versatility and wide applicability of the electron diffraction method. A recent communication from Professor Grant reveals that the X-ray diffraction results obtained at his laboratory are in agreement with the results reported here.

The principal problem in the adaptation of the electron diffraction method to the study of the minor phases of the heat-resistant alloys continues to be the development of suitable procedures for polishing and etching the alloys. This is evident from the present work with Iconel-X alloy and also from previous work with S816 alloy.<sup>5</sup> Both of these alloys differ substantially from the 16-25-6 alloy in their polishing and etching characteristics. Most of the common etches and electrolytic polishing solutions produce films of insoluble reaction products on these alloys and therefore cannot be used

for the electron diffraction studies. This difficulty was encountered with only a few polishing and etching reagents with the 16-25-6 alloy. The fact that reaction products were formed on the Sintered Aluminum Product by many electrolytic polishing solutions suggests that the difficulty is not confined to heat-resistant alloys, but may be of general occurrence. The formation of such reaction products is not of great concern in the usual metallographic studies for which the polishing and etching reagents have been developed. These considerations indicate the need for the development of new etching and polishing procedures which would undoubtedly find applications in electron microscope studies as well as in electron diffraction work.

Electron diffraction results presented here suggest that the unit cell of the  $M_6C$  phase in 16-25-6 alloy aged for 1000 hours at 1200°F is about 1 per cent smaller than the unit cell of the same phase after a similar period of aging at 1400°F. While the data are not adequate to provide absolute values of the cell size showing this difference, a series of comparison patterns obtained on the same negatives give a qualitative indication of the difference in scale. It is interesting to note that a variation of this kind is consistent with the other observations on the carbides of this alloy. In the previous electron diffraction studies<sup>1</sup> it was observed that the  $M_{23}C_6$  carbide forms first in the aging process and then transforms to the  $M_6C$ . The transformation requires about 10 hours at 1400°F but more than 100 hours at 1200°F. X-ray diffraction studies show that this transformation is accompanied by a decrease in the unit cell of the matrix phase, indicating a transfer of large-radius atoms, probably chiefly of molybdenum, to the carbide in the process. It is evident that this transfer occurs more rapidly at the higher temperature, therefore it is not unreasonable to expect that, for equal periods of aging at 1200°F and 1400°F, the carbide formed at the higher temperature will be slightly richer in large-radius atoms and will therefore have a somewhat larger unit cell.



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