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

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The electron microscopic studies of these specimens were carried out on the electron microscope of the School of Public Health of the University of Michigan, through the courtesy and cooperation of Professor Thomas Francis, Chairman of the Department of Epidemiology, and Dr. R. E. Hartmann of the Virology Laboratories.

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SUMMARY

Electron microscopic studies have been made of the microstructures of solution-treated and aged specimens of Waspalloy and Udimet alloys. Only a few large precipitate particles are observed in the solution-treated specimens. Aging treatments of a few hours at temperatures of 1500°F are sufficient to produce heavy precipitation of very fine particles within the matrix grains of these alloys. Evidence based on selective etching characteristics of the particles indicates that this precipitate is the intermetallic γ' phase. It has been estimated that with long periods of aging this phase constitutes approximately 20 and 30% of the volumes of the Waspalloy and Udimet alloys, respectively. The microstructures of these alloys are compared with previous observations on the microstructure of Inconel-X alloy.

OBJECTIVE

Recent metallurgical investigations have shown that the minor phases which precipitate in the heat-resistant alloys under conditions of stress and high temperature have a pronounced influence on the mechanical properties of the alloys. The present investigation was undertaken to apply the sensitive methods of electron diffraction and electron microscopy to the study of these minor phases. The specific objectives of this project include the development of procedures for applying these methods to the complex heat-resistant alloys, and the use of these procedures to study the development of minor phases in alloys typical of those currently used in the manufacture of jet aircraft engines.

I. INTRODUCTION

The general procedures for studying the minor phases of alloy systems by electron diffraction and electron microscopy have been described by Heidenreich and his associates.[1,2] Briefly, the minor phases of the alloys are identified by their electron-diffraction patterns, and the size, shape, and distribution of the minor-phase particles are determined by electron microscopy. These studies are carried out on surfaces of specimens of the alloys which are prepared by polishing and etching treatments chosen to expose the minor-phase particles in relief with respect to the matrix phase. The electron-diffraction patterns are obtained by directing an electron beam across the surfaces at a grazing angle so that it strikes the protruding minor-phase particles. The patterns thus obtained are analogous to patterns obtained from fine powders by x-ray diffraction and are interpreted similarly. The electron microscopic examinations of the surfaces are made through the use of replica techniques. In the present work the simple and rapid collodion replica method has been employed. This method has been described in detail in the literature[3] and in previous reports on this project.[4,5]

Previous work on this project has included studies of various polishing and etching procedures for use in preparing the heat-resistant alloys for the electron metallographic studies. In addition, extensive studies have been made of the development of minor phases in 16-25-6 and Inconel-X alloys with aging at 1200°, 1400°, and 1600°F. The results of these studies have been described in detail in a recent technical report.[4] The work carried out during the period of this report has been concerned primarily with the microstructures of the titanium-aluminum-hardened nickel-chromium alloys, Waspalloy and Udimet.

II. RESULTS

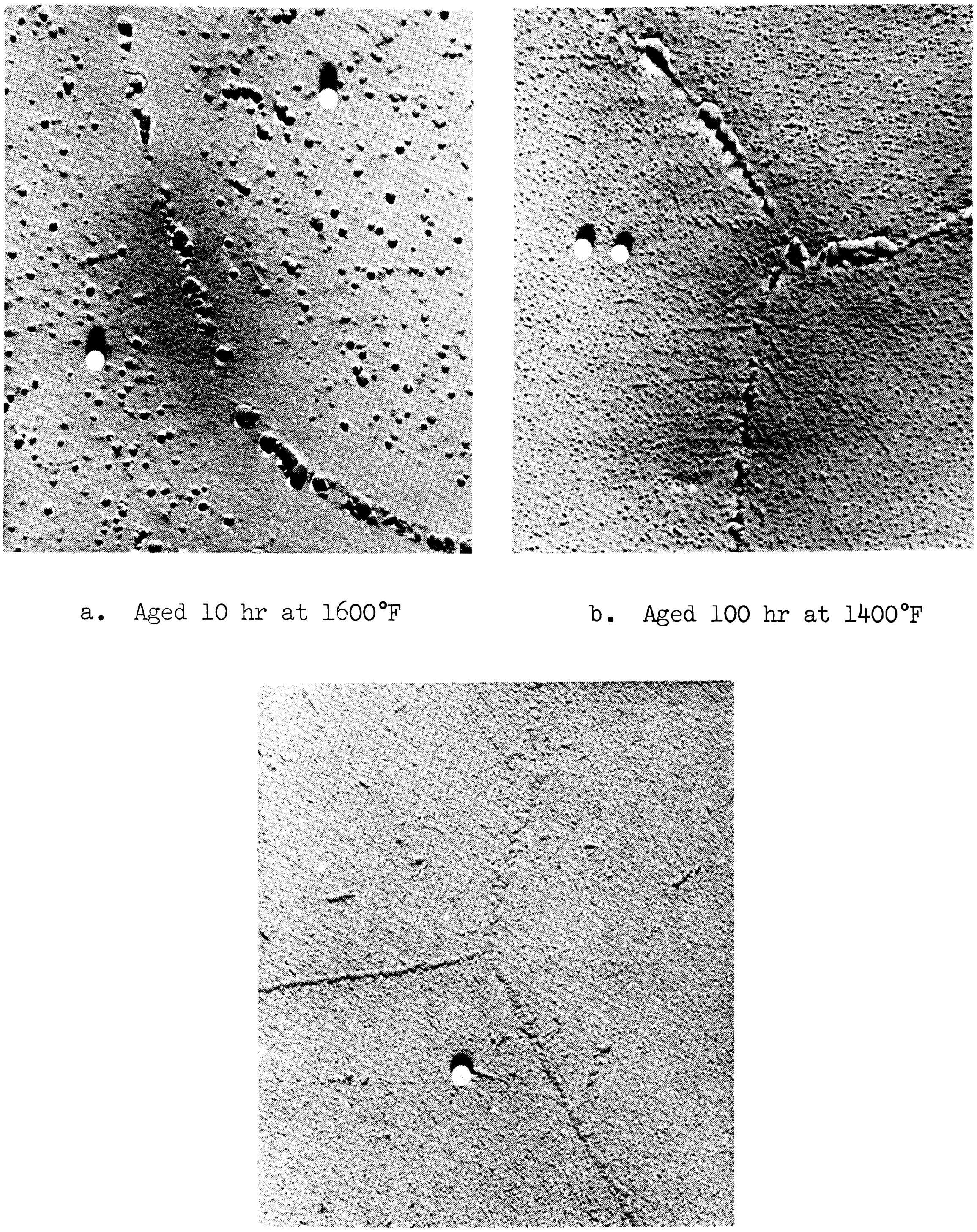
Interest in the Waspalloy and Udimet alloys arises from the results of previous studies of Inconel-X alloy which showed that the strengthening and hardening of this alloy during aging results from the precipitation of a fine dispersion of particles of the intermetallic γ' phase within the matrix grains.[4,6] Electron micrographs showing the γ' particles in specimens of Inconel-X alloy aged 10 hr at 1600°F, 100 hr at 1400°F, and 1000 hr at 1200°F are reproduced in Figure 1. The Waspalloy and Udimet alloys are similar to the Inconel-X alloy in that they are nickel-chromium base alloys containing titanium and aluminum as hardening agents; however, they are generally superior to Inconel-X in strength and creep resistance at high temperatures. The compositions of these alloys are compared with Inconel-X in Table I. The variations in the amounts of titanium and aluminum among these alloys may be particularly significant since these elements are involved in the formation of the intermetallic γ' phase, which was found to be important in determining the properties of the Inconel-X alloy. Studies of these alloys combined with the previous studies of Inconel-X alloy may provide indications of the relationships between the metallurgical properties, the microstructures, and the compositions of these alloys, and may lead to a more fundamental understanding of the age-hardening phenomena in the titanium-aluminum-hardened nickel-chromium alloys as a group.

TABLE 1

COMPOSITIONS OF INCONEL-X, WASPALLOY, AND UDIMET ALLOYS
(Weight Percent)

Element	Inconel-X	Waspalloy	Udimet
Ni	73.4	56.5	55.4
Cr	14.6	19.5	19.5
Co	----	13.4	14.8
Fe	6.9	2.9	----
Mo	----	2.8	3.8
Cb	1.0	----	----
Ti	2.3	2.2	2.8
Al	0.67	1.1	2.9
Mn	0.51	0.88	0.17
Si	0.39	0.62	0.50
C	0.05	0.09	0.08

To date, only preliminary studies of the Waspalloy and Udimet alloys have been completed; however, these have led to the development of procedures suitable for preparing these alloys for examination by electron diffraction



a. Aged 10 hr at 1600°F

b. Aged 100 hr at 1400°F

c. Aged 1000 hr at 1200°F

Figure 1. Electron micrographs showing matrix precipitation in aged specimens of Inconel-X alloy (12,000 X).

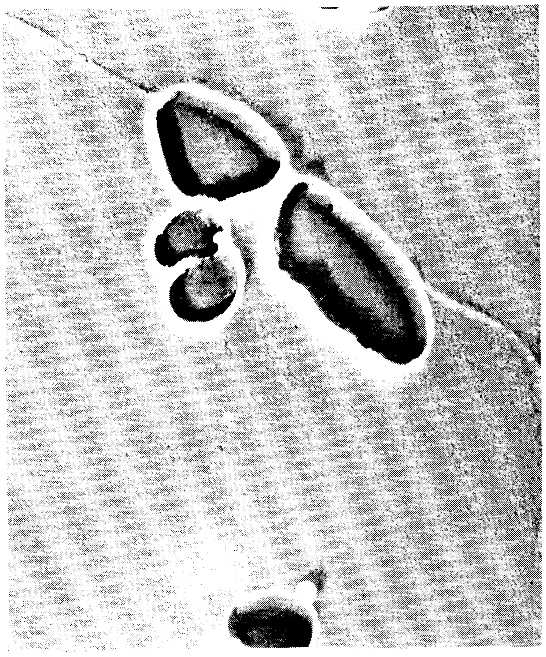
and electron microscopy, and have provided considerable information on their general microstructural characteristics. It has been found that these alloys can be electrolytically polished with a solution consisting of one part perchloric acid (72%) to nine parts glacial acetic acid, using the apparatus and techniques described previously.[4] For specimens about 1/2 x 1/2 x 1 inch in size, electrolysis at currents of the order of 3-6 amp for periods of 30-90 sec is required to produce a satisfactory polish on specimens previously rough polished with 3/0 metallographic emery paper. Satisfactory etching of these alloys has been obtained with two different reagents having the following compositions: (1) 10 ml glycerol, 5 ml hydrofluoric acid (48%), and 85 ml ethyl alcohol (95%), and (2) 7 ml phosphoric acid (85%), 28 ml sulfuric acid (96%), and 24 ml nitric acid (40%). The latter of these reagents produces staining of some specimens of these alloys and is therefore generally less satisfactory than the former for the electron diffraction studies.

Solution treatment of the Waspalloy and Udimet alloys at 2150°F for 2-4 hr and subsequent quenching in water or ice brine leaves only a few large precipitate particles as shown in the electron micrographs of Figures 2 and 5. These resemble the particles observed in the solution-treated Inconel-X alloy and, as was the case in the Inconel-X, are probably particles of carbides or nitrides such as TiN, TiC, M_6C and $M_{23}C_6$. Electron diffraction and x-ray diffraction studies are being carried out to provide definite identifications of these particles.

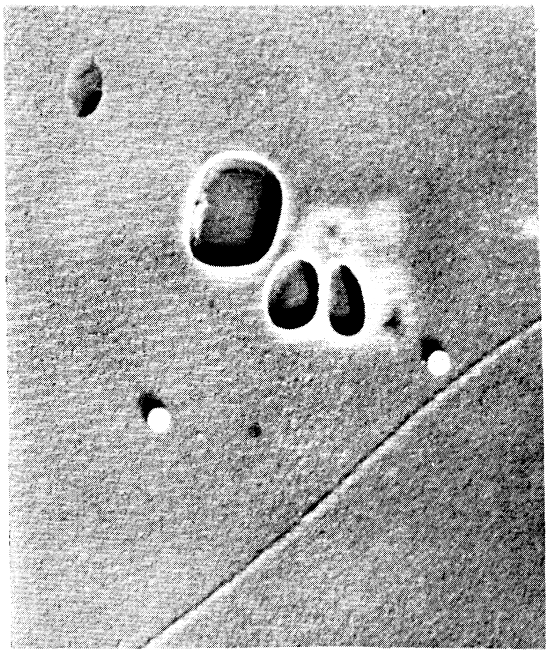
The most interesting microstructural feature of these alloys is the extensive matrix precipitate which develops when they are subjected to aging treatments at high temperatures. The numerous particles of this precipitate are clearly evident in the electron micrographs of Figures 3, 4, and 5. These particles are generally rounded or spheroidal in shape and appear to be randomly distributed within the matrix grains. Their diameters and their separation in the matrix grains are usually of the order of 1000Å.

Only short aging treatments are required to produce the extensive matrix precipitation in the Udimet alloy shown in the micrographs of Figures 3 and 4. The micrographs of Figures 3a and 3b were taken from specimens which were solution treated, water quenched, and then aged at 1500°F for periods of 12 and 24 hours, respectively. The micrograph of Figure 4a was taken from a bar of the alloy which was allowed to air cool after solution treatment at 2150°F. Subsequent aging of this bar for 500 hr at 1400°F produced very little change in the size, shape, or distribution of the precipitate as shown by Figure 4b. A rough lineal analysis of this latter micrograph indicates that the precipitate phase comprises more than 30% of the volume of the alloy.

Figure 5b shows the extensive matrix precipitation which takes place in the Waspalloy upon aging the alloy for 500 hr at 1400°F, following solution treatment at 2150°F and water quenching. A rough lineal analysis of this

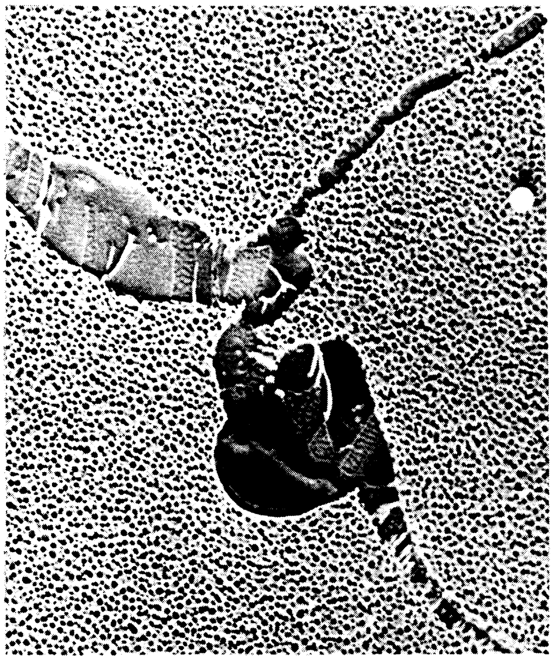


a. Ice-brine quenched

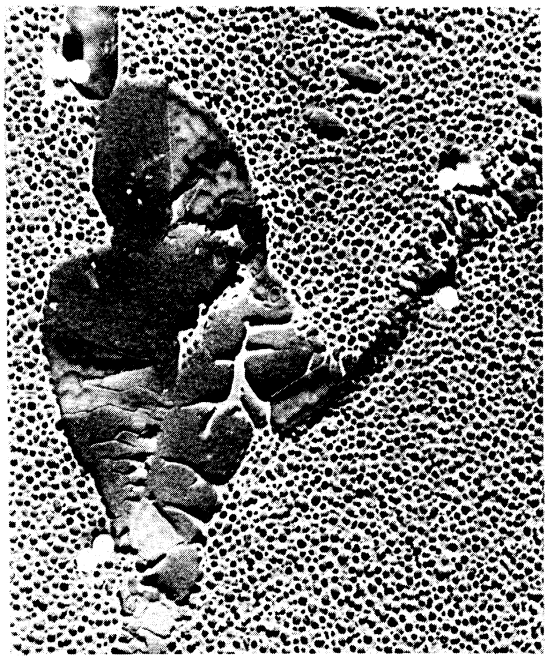


b. Water quenched

Figure 2. Microstructure of Udimet alloy after solution treatment at 2150°F and quenching as indicated (12,000 X).

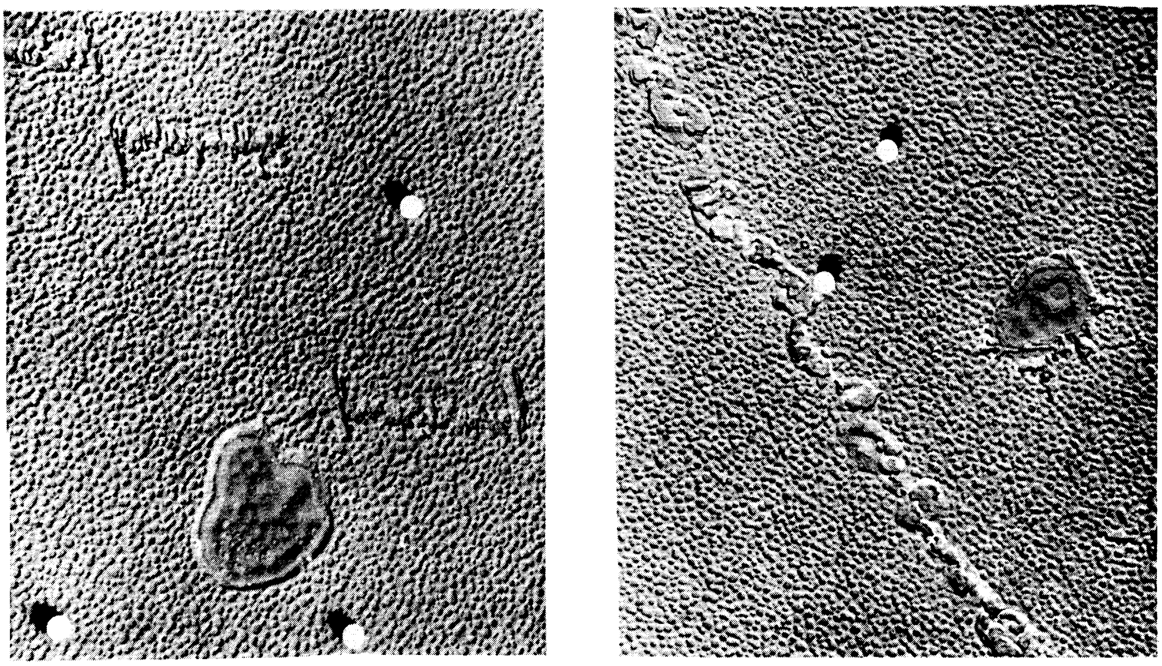


a. Aged 12 hr



b. Aged 24 hr

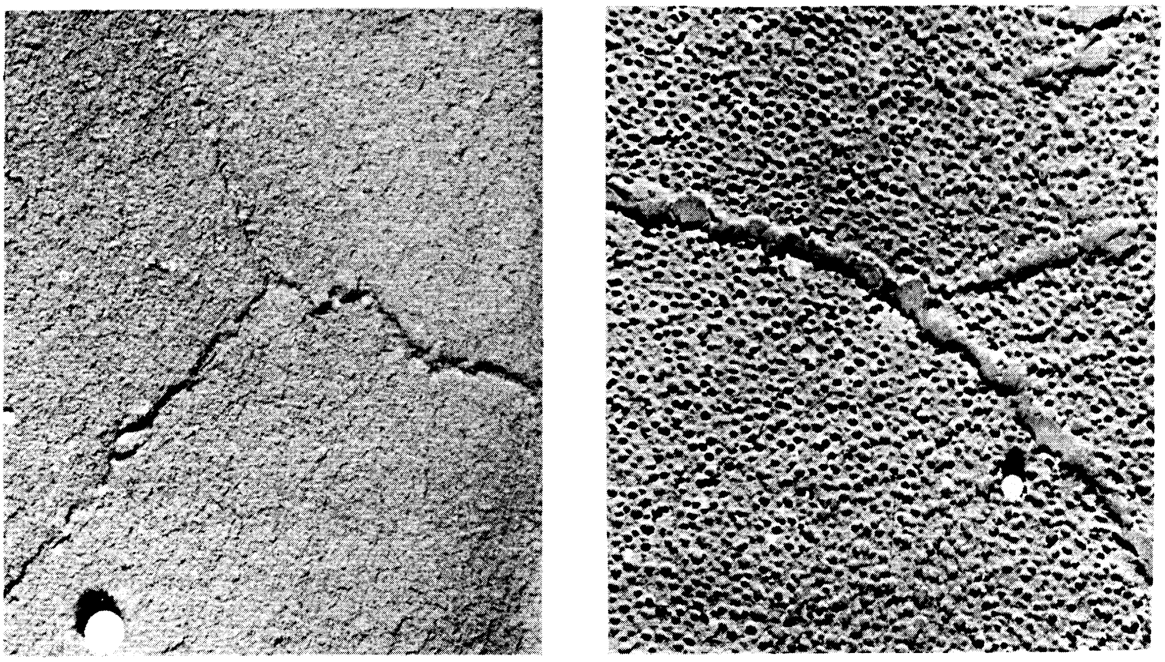
Figure 3. Microstructure of solution-treated Udimet alloy, water quenched and aged at 1500°F (12,000 X).



a. Unaged

b. Aged 500 hr at 1400°F

Figure 4. Microstructure of Udimet alloy, air cooled from solution treatment at 2150°F and aged as indicated (12,000 X).



a. Unaged (20,000 X)

b. Aged 500 hr at 1400°F (12,000 X)

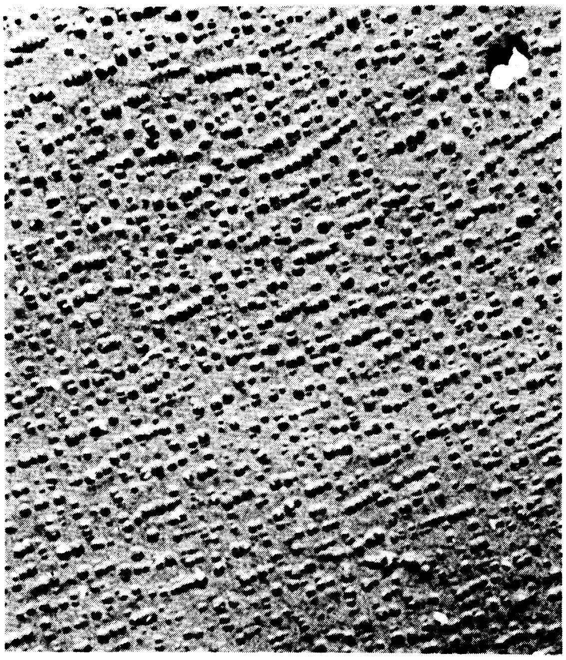
Figure 5. Microstructure of Waspalloy alloy, solution-treated at 2150°F, water quenched and aged as indicated.

micrograph indicates that the matrix precipitate constitutes about 20% of the volume of the alloy. The effects of short aging treatments and of air cooling after solution treatment, on the development of the matrix precipitate have not yet been determined for this alloy.

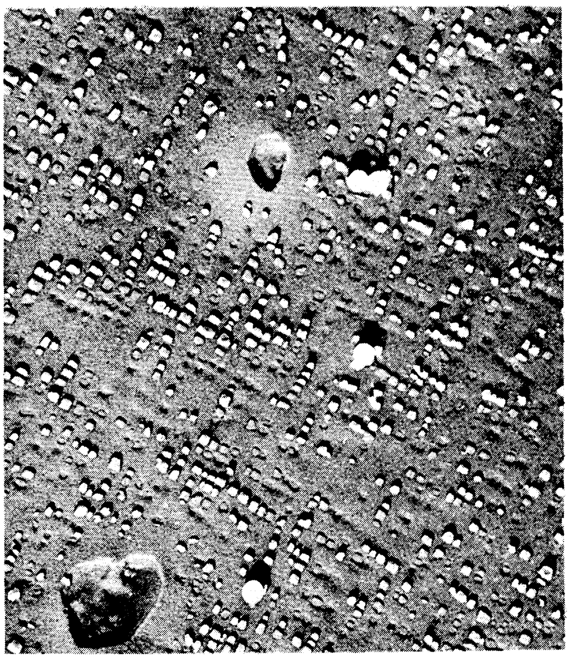
Electron microscopic evidence has been obtained indicating that the matrix precipitate in these alloys is the γ' phase, which also formed the matrix precipitate in Inconel-X alloy. This is derived from the similarity in the response of the matrix precipitate of the Waspalloy and Udimet alloys to that of the matrix precipitate of Inconel-X when etched with the reagent of Taylor and Floyd.[7] In the studies of the Inconel-X alloy it was observed that this etching reagent produced a preferential attack on the particles of the γ' phase. The character of the attack is shown in the electron micrographs of Figure 6 for a specimen of the Inconel-X alloy aged 1000 hr at 1400°F. Micrograph 6a was taken from the specimens after electrolytic polishing in the acetic-acid—perchloric-acid solution and etching in the HF-glycerol-alcohol solution described above. The particles of the γ' phase shown in this micrograph are in relief with respect to the surrounding matrix metal. Micrograph 6b was taken from the same specimen after a subsequent etching treatment for 1 sec at 0.2 amp in the reagent of Taylor and Floyd (5% hydrofluoric acid, 10% glycerol, 85% water). This micrograph shows clearly the preferential action of this reagent, which dissolves the γ' phase, leaving pits in the surface at the positions formerly occupied by the γ' particles. The response of Waspalloy and Udimet to similar etching treatments is shown by the micrographs of Figure 7. As in the Inconel-X alloy, the particles of the matrix precipitate are dissolved, leaving pits in the surfaces in their place. As mentioned above, this is considered to be a good indication that the matrix precipitate in these alloys is also the intermetallic γ' phase. In Figure 7b it will be noted that the preferential etching extends to portions of the heavy deposits at the grain boundaries, indicating that portions of these deposits are also of the γ' phase. From their structure (see Figure 3), it appears that these deposits grow during aging from the coalescence of the γ' particles in the grains near the grain boundaries. In some instances they appear to surround the carbide particles originally present in the boundaries.

DISCUSSION

The results described here indicate that a fine dispersion of particles of the intermetallic γ' phase forms in both the Waspalloy and Udimet alloys on aging at high temperatures. The density of the γ' particles in these alloys is generally much greater than was observed in the Inconel-X alloy and appears to be related to the combined titanium and aluminum content



a. Before etching



b. After etching

Figure 6. Electron micrographs from specimens of Inconel-X alloy aged 1000 hr at 1400°F, showing the effects of etching with the reagent of Taylor and Floyd (12,000 X).

a. Waspalloy

b. Udimet

Figure 7. Electron micrographs from aged specimens of Waspalloy and Udimet alloys etched with the reagent of Taylor and Floyd (12,000 X).

of the alloys, which amounts to about 5 and 9 atomic percent for the Waspalloy and Udimet alloys, respectively, as compared with about 4 atomic percent for the Inconel-X. The volume percentages of γ' in the Waspalloy and Udimet alloy specimens aged for long periods was estimated from rough lineal analyses of the micrographs of Figures 4b and 5b to be about 20 and 30%, respectively. Assuming a composition of $Ni_3(Ti,Al)$ for the γ' phase, these are about the maximum amounts possible for these alloys. The size and dispersion of the γ' particles in these alloys appears to be much less dependent on the aging treatment than was the case for the Inconel-X alloy. Thus, the difference in structure between the specimen of Udimet alloy which was solution treated and air cooled (see Figure 4a) and the specimen solution treated and aged 500 hr at 1400°F, is not as great as that between the specimen of Inconel-X aged 100 hr at 1400°F (see Figure 1b) and the specimen aged 1000 hr at 1400°F (Figure 6a). This greater structural stability of the Udimet alloy may be an important factor in regard to its superior high-temperature properties.

The present studies also suggest that electron microscopic methods may be among the most sensitive methods presently available for studying the microstructures of the nickel-base alloys. Since many microstructural features of these alloys are below the limits of optical resolution, the electron microscope provides considerably more information than can be obtained by the usual optical microscopic studies. Thus, the matrix precipitate particles in the micrographs of Waspalloy and Udimet alloys shown here do not exceed 2000Å in diameter, on the average, while particles less than 500Å in diameter are revealed in the micrographs of the Inconel-X alloy. Likewise, the selective etching procedures used here may provide a very useful means of identifying the intermetallic γ' phase in these alloys. This is often difficult to accomplish by x-ray and electron diffraction because the structure of the γ' phase is so similar to that of the matrix phases of these alloys. Furthermore, the γ' phase cannot be readily separated from the matrix by extraction techniques because of its metallic character, and it frequently occurs in quantities too small to be detected by direct diffraction studies on bulk specimens. The present indications are that when properly employed the selective etching procedures described here will reveal very small amounts of this phase. In addition, these procedures are most useful for distinguishing the particles of the γ' phase from those of the carbide phases in specimens having heavy overall precipitation.

In continuing the work on the Waspalloy and Udimet alloys it is planned to make a more systematic investigation of the effects of variations in the length and temperature of aging treatments on the size, shape, and distribution of the γ' particles and on the metallurgical properties of these alloys. Electron diffraction and x-ray diffraction studies are also planned to identify the carbide phase formed by the different aging treatments. In addition, some further investigations of the selective etching procedures for the identification of the γ' phase are in progress to determine their range of applicability and their overall reliability.

BIBLIOGRAPHY

1. Heidenreich, R. D., Sturkey, L., and Woods, H. W., J. Applied Physics, 17, 127 (1946).

2. Heidenreich, R. D., "Electron Diffraction and Electron Microscopy" in Modern Research Techniques in Physical Metallurgy, the American Society for Metals, Cleveland, 1953.

3. Fischer, R. B., Applied Electron Microscopy, Indiana University Press, Bloomington, 1953, p. 166.

4. Brockway, L. O. and Bigelow, W. C., WADC Technical Report 54-589, Aeronautical Research Laboratory (WCRRL), Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

5. Brockway, L. O. and Bigelow, W. C., Annual Summary Report 1952-1953, University of Michigan, Ann Arbor, Engineering Research Institute, Project 2020, October 1953.

6. Frey, D. N., Freeman, J. W., and White, A. E., Technical Note 2385, National Advisory Committee for Aeronautics, Washington, D.C., 1951.

7. Taylor, A., and Floyd, R. W., J. Inst. of Metals, 81, 25 (1952).