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ELECTRON METALLOGRAPHIC INVESTIGATIONS OF THE MINOR PHASES OF HEAT-RESISTANT ALLOYS

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SUMMARY

The progress of the experimental work on Contract No. AF 33(616)-3250 during the first quarter of the contract year is described. This work includes: (1) studies of etching reagents for preparing S816 alloy specimens for electron metallographic examinations, (2) studies of the microstructures of three commercial nickel-base alloys, M-252, Waspalloy, and Udimet, to determine the distribution of the age-hardening γ' precipitate phase, (3) studies of the microstructure of an experimental alloy containing higher percentages of Ti and Al than the above commercial alloys, and (4) electron microscopic studies of a low-strength heat of a nickel-base alloy having an unusual banded structure.

OBJECTIVE

Various recent metallurgical investigations indicate that the minor phases which precipitate in the heat-resistant alloys during exposure to stresses and high temperatures have a pronounced effect on the metallurgical properties of the alloys. To understand and control better the properties of these alloys it is therefore desirable to have more detailed information on their minor phases. This project has been undertaken in order to employ the highly sensitive techniques of electron diffraction and electron microscopy in identifying the minor phases and in studying their distribution within the alloys, with the overall objective of obtaining such information.

The work of this project falls into two general phases. The first is concerned with the development of various experimental procedures necessary for adapting the techniques of electron diffraction and electron microscopy to the study of the complex heat-resistant alloys. This involves principally the development of polishing, etching, and rinsing procedures for use in preparing surfaces of the various alloys for examination by the electron methods. The general problems associated with this phase of the work have been discussed in WADC Technical Report 54-589 which was prepared under a previous contract. The second phase of the work is concerned with applying these special experimental procedures to studies of typical alloys used in the manufacture of components of jet aircraft engines and similar high-temperature applications. Here close cooperation is maintained with Professor J. W. Freeman and his group in the Department of Chemical and Metallurgical Engineering who are doing metallurgical research in these alloys, and particular attention is given to attempting to correlate variations in the high-temperature properties of the alloys with the variations observed in their minor phases.

INTRODUCTION

This report covers the experimental work which has been carried out on the project during the first quarter of the contract year. This work has included further experimentation to develop etching techniques for preparing S816 alloy for electron studies; diffraction studies of the minor phases of the S816 alloy; examinations of the microstructures of aged specimens of Waspalloy, Udimet, and M-252 nickel-base alloys; electron microscopic examination of a nickel-base alloy having low strength associated with a peculiar "banded" structure; and preliminary studies of the microstructure of special nickel-base alloys containing high percentages of Ti and Al. The first two of these topics represent continuations of studies which were started under a previous contract (No. AF 33(616)-23), while the latter studies are preliminary investigations undertaken to expand the overall scope of the project. The results obtained in these various areas will be described briefly in the following sections.

EXPERIMENTAL METHODS

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] and some of the special procedures which have been developed for applying these methods to the heat-resistant alloys have been described in a previous Air Force Technical Report.[3] Briefly, the minor phases are identified by electron diffraction patterns obtained by directing the electron beam across surfaces of the alloy specimens which are etched by special techniques so that the minor phases protrude slightly above the matrix metal. Because of the low penetrating power of the electron beam, these patterns arise almost entirely from the protruding minor-phase particles. These patterns are analogous to patterns obtained from fine crystalline powders by x-ray diffraction methods and are interpreted similarly. The size, shape, and distribution of the minor phases are determined by electron microscopic studies which are usually made on the same surfaces used for the diffraction studies. These electron microscopic studies are made through the use of palladium-shadowed collodion replicas. The preparation of these replicas and the interpretation of the resulting micrographs have been described previously.[3]

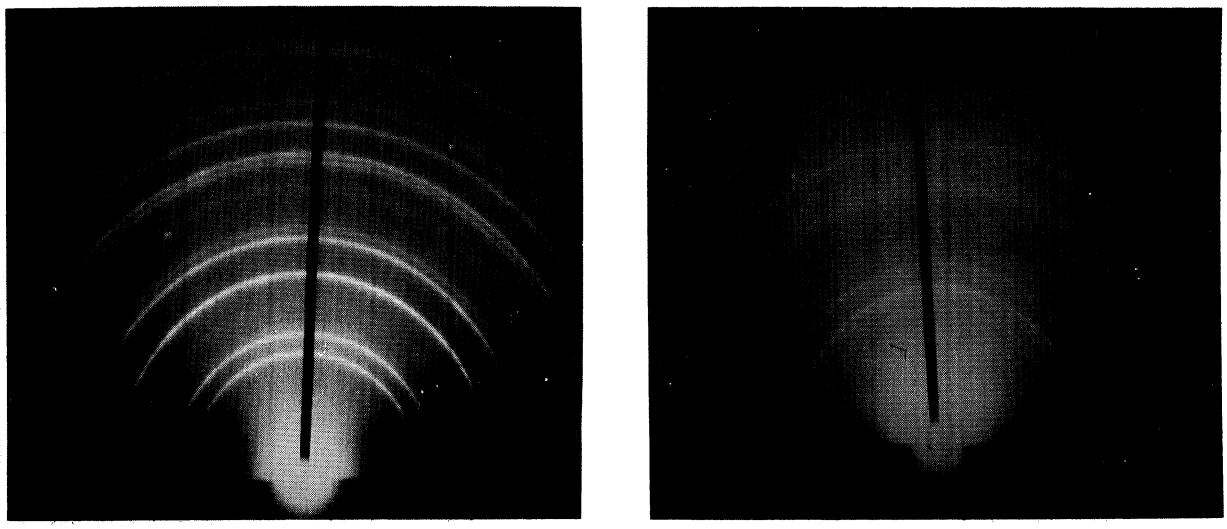
DEVELOPMENT AND APPLICATION OF A SELECTIVE ETCHANT FOR THE CARBIDES AND NITRIDES OF Cb AND Ti IN STUDIES OF S816 ALLOY

Considerable experimentation has been required in developing polishing and etching procedures for preparing the S816 alloy for electron diffraction studies. Recently reasonable success has been obtained by electrolytically polishing the alloy in a solution of 10 parts perchloric acid (70%) to 90 parts glacial acetic acid. This leaves a yellow deposit on the surface of the specimens, but this is usually soluble in the strongly acidic etching solutions and does not interfere. Satisfactory etching without staining has been attained electrolytically in a solution consisting of 12 parts phosphoric acid (85%), 47 parts sulfuric acid (96%), and 41 parts nitric acid (70%). This solution is commonly referred to as "Etching Reagent G."

The electron diffraction patterns obtained from surfaces prepared in this way showed only diffraction rings corresponding to CbC and the alloy matrix phase. In these patterns the CbC rings were very strong and distinct, while the matrix rings were usually weak by comparison. A typical pattern is reproduced in Fig. 1a and the corresponding diffraction data are given in Table I.

Consideration of the microstructure and composition of the alloy suggested that minor phases other than the CbC probably were present, particularly in specimens aged for long periods at 1600°F. Electron micrographs showed that these specimens usually contained a number of very large spheroidal particles, which were thought to be the CbC particles, and additional smaller particles which were considered to be another phase. This is illustrated by the electron micrograph of Fig. 2. It was concluded that the smaller particles probably were masked from the electron beam in the diffraction experiments by the large CbC particles and therefore were not contributing to the diffraction patterns. A procedure therefore was desired which would preferentially remove the large CbC particles without removing the smaller particles of the other phase.

Fortunately it was found that electrolytic etching in a solution consisting of 1 part nitric acid (70%) to 3 parts hydrofluoric acid (48%) would accomplish this. This solution is referred to as "Etching Reagent R." Its action on the large precipitate particles of the S816 alloy is illustrated by the electron micrographs of Fig. 3. Electron diffraction patterns obtained from surfaces etched with this reagent show only weak CbC rings, but contain additional rings which correspond to an $M_{23}C_6$ carbide. One of these patterns is reproduced in Fig. 1b, and the corresponding diffraction data are listed in Table I. At present the $M_{23}C_6$ lines are rather weak, but some mod-



a. Etched with Reagent G.

b. Etched with Reagent R.

Fig. 1. Electron diffraction patterns from a specimen of S816 alloy, aged 1 hour at 1600°F.

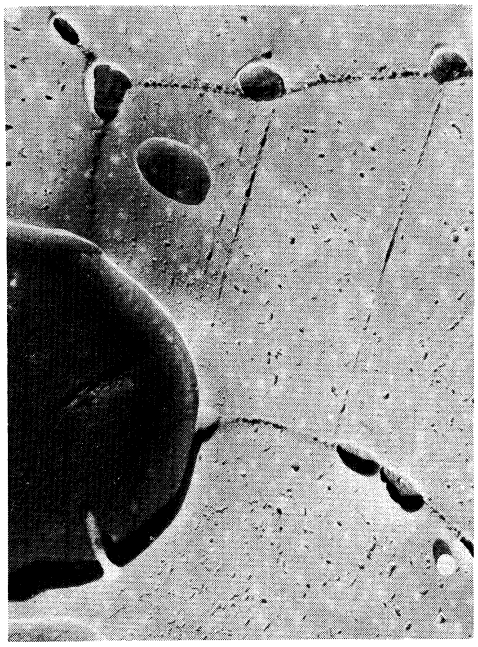
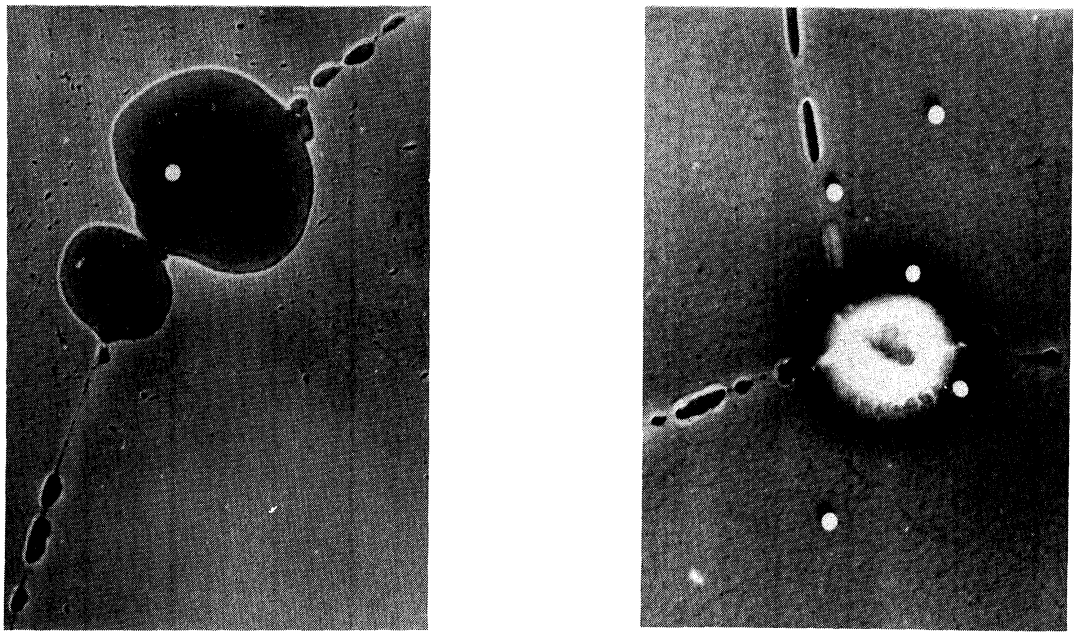


Fig. 2. Electron micrograph showing the minor phases of a specimen of S816 alloy, aged 200 hours at 1600°F. X10,000.

TABLE I. ELECTRON DIFFRACTION DATA OBTAINED FROM A SPECIMEN OF S816 ALLOY, AGED 1 HOUR AT 1600°F, AFTER DIFFERENT ETCHING TREATMENTS

Electron Diffraction Patterns				Standard Diffraction Data					
Etched with G		Etched with R		$M_{23}C_6$		CbC		Matrix	
d	I	d	I	d	I	d	I	d	I
		5.8	vvw	5.3	vw				
		4.6	vvw						
		4.2	vvw						
		3.8	w	3.8	vw				
		3.52	w						
		3.24	vw	3.21	vw				
		3.06	wm	3.07	vw				
		2.81	wm						
		2.60	vw	2.66	w				
2.56	s					2.56	s		
		2.44	vvw	2.43	vw				
		2.40	ms	2.38	s				
2.20	s	2.22	vvw			2.20	s		
		2.19	ms	2.17	s				
2.08	w	2.06	s	2.04	s			2.07	s
		1.89	m	1.88	m				
		1.85	vw						
1.81	w	1.79	ms	1.79	s			1.79	s
		1.68	wm	1.68	w				
		1.62	w	1.62	w				
1.56	s					1.56	ms		
		1.54	vvw	1.53	vvw				
		1.48	vw	1.49	vw				
		1.38	vw	1.38	vw				
1.34	m	1.34	vw	1.33	w	1.34	m		
1.28	wm	1.29	vw	1.30	wm	1.28	wm		
		1.27	w					1.27	s
		1.26	w	1.26	ms				
1.11	w					1.11	wm		
1.09	w	1.08	m					1.08	s



a. Etched with Reagent G.

b. Etched with Reagent R.

Fig. 3. Electron micrographs from a specimen of S816 alloy, aged 1 hour at 1600°F, showing the selective etching attack on the CbC particles produced by Etching Reagent R. X8000.

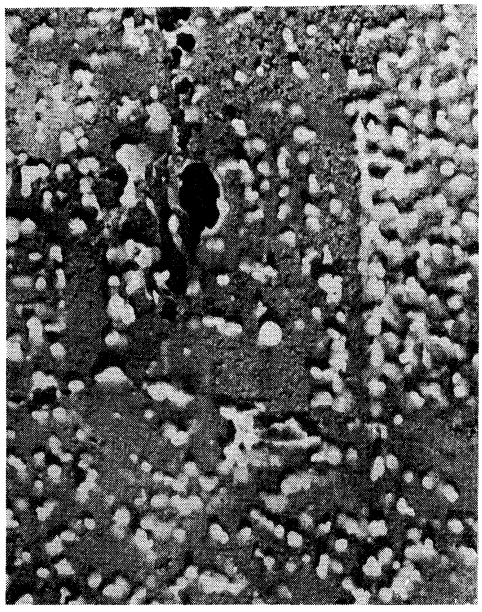


Fig. 4. Electron micrograph of a specimen of Inconel-X alloy, aged 1000 hours at 1400°F, showing the action of Etching Reagent R. X12,000.

ification of the reagent, or additional etching with another reagent, may improve this.

Apart from the importance of this reagent for electron diffraction studies, it may prove to be a very valuable and useful reagent for distinguishing among different phases by electron microscopy. This is illustrated very well by the micrographs of Fig. 3, which indicate that the large spheroidal particles are the CbC phase while the smaller particles in the grains and grain boundaries are a different phase. Another example is given by the micrograph of Fig. 4, which shows that the grain-boundary precipitates of the Inconel-X alloy are not attacked by this reagent. This indicates that they are not CbC particles and is consistent with the conclusion that they are the $M_{23}C_6$ carbide which was reached on the basis of other considerations.[3]

From chemical considerations it appears that the reagent should dissolve both the carbides and nitrides of columbium and also those of titanium, so that it is probably not a highly selective etchant. Nonetheless, the results shown here indicate that it may be very useful in distinguishing these phases from the complex carbides by electron microscopy, and that it may be used to advantage in eliminating interference of these phases in electron diffraction studies.

MICROSTRUCTURES OF M-252, WASPALLOY, AND UDIMET ALLOYS

Previous electron microscope studies[3] of aged specimens of Inconel-X alloy had revealed microstructural details which were well beyond the limits of resolution of light microscopy and provided a correlation of variations in the size and distribution of minor-phase particles with variations in the metallurgical properties of the alloy. To provide information of a wider scope concerning the microstructures of the nickel-base alloys, electron microscopic studies are being made of selected aged specimens of M-252, Waspalloy, and Udimet alloys. These are commercial alloys which have been developed recently and differ in composition from the Inconel-X alloy, particularly in that they generally contain larger quantities of the precipitation-hardening elements titanium and aluminum, as shown in Table II.

To date, specimens of each alloy prepared as follows have been examined: (1) solution-treated 4 hours at 1975°F, ice-brine quenched; (2) solution-treated 4 hours at 1975°F, air-cooled; (3) solution-treated 4 hours at 1975°F, ice-brine quenched, aged 10 hours at 1400°F, and (4) solution-treated 4 hours at 1975°F, ice-brine quenched, aged 100 hours at 1400°F. The general character of the age-hardening precipitate observed to develop with aging is similar to that previously described for the Waspalloy and Udimet alloys.[4] In general this precipitate is not observed in the solution-treated, ice-

TABLE II. COMPOSITIONS OF NICKEL-BASE ALLOYS

Alloy	Composition in Weight Percent										
	Ni	Cr	Co	Fe	Mo	Ti	Al	Cb	Mn	Si	C
Inconel-X	73.4	14.6	----	6.90	----	2.33	0.67	1.04	0.51	0.39	0.05
Waspalloy	56.5	19.5	13.4	2.90	2.81	2.21	1.09	----	0.88	0.62	0.09
Udimet	55.4	19.5	14.8	----	3.80	2.79	2.94	----	0.17	0.50	0.08
Heat 1079	51.7	19.0	16.8	----	3.7	4.1	4.2	----	0.1	0.3	0.06

brine-quenched specimens, and in the solution-treated, air-cooled specimens the precipitation is extremely light. The overall amount in each case appears to depend on the amounts of titanium and aluminum in the alloys, and the hardness increases with the amount of the precipitate present.

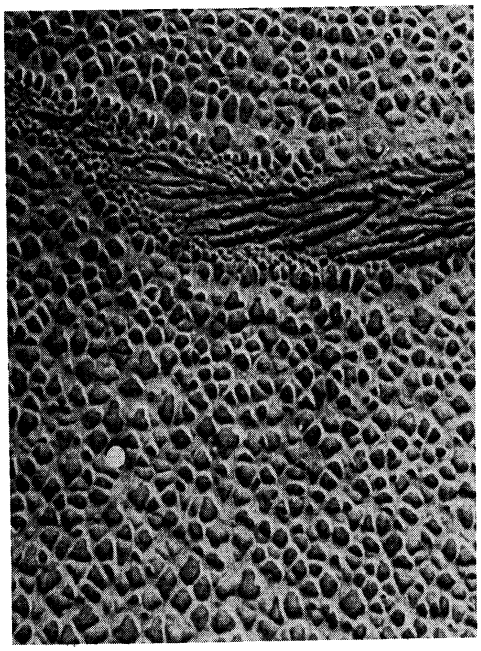
These studies are nearing completion and will be presented more fully in a separate report or paper for publication, in the near future.

MICROSTRUCTURE OF A NICKEL-BASE ALLOY CONTAINING 4 PERCENT TITANIUM AND ALUMINUM

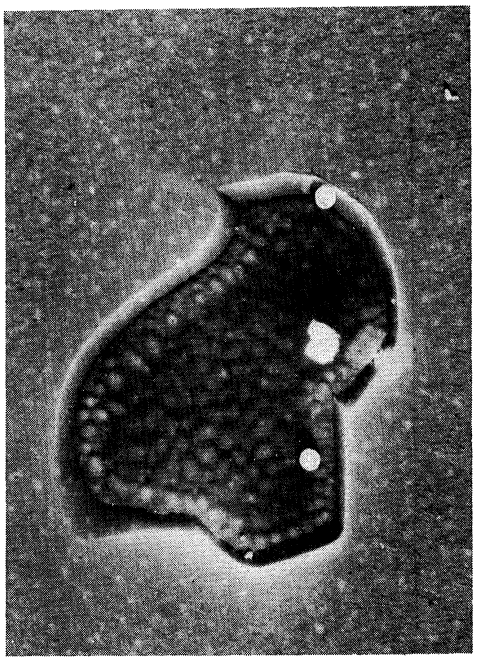
The studies of the M-252, Waspalloy, and Udimet alloys indicated a general increase in the quantity of the age-hardening precipitate in the nickel-base alloys with increasing titanium and aluminum content. An experimental heat of an alloy containing 4% of both Ti and Al, which was prepared by Dr. C. L. Corey in the Department of Chemical and Metallurgical Engineering, provided an opportunity to investigate the effects of Ti and Al contents greater than those in any of the above commercial alloys.

The composition of this experimental heat, designated as Heat 1079, is included in Table II. Specimens of this alloy as-cast, solution-treated 4 hours at 1975°F and ice-brine quenched, solution-treated 4 hours at 1975°F and air-cooled, and solution-treated 1 hour at 2150°F and ice-brine quenched, have been examined by electron microscopy to date to determine the form and distribution of precipitates.

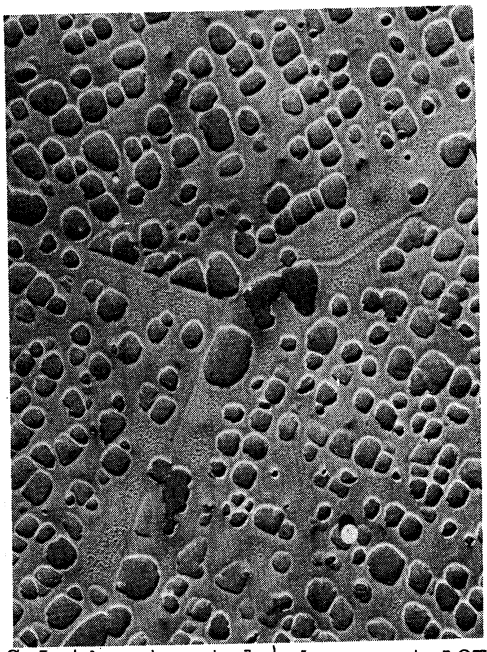
The microstructures and hardness values for these different specimens are shown in Fig. 5. This alloy characteristically contains much heavier precipitation than was observed in even the Udimet alloy, which contains the largest amounts of Ti and Al of any of the commercial alloys examined. Solution treatment at 1975°F or 2150°F followed by ice-brine quenching left



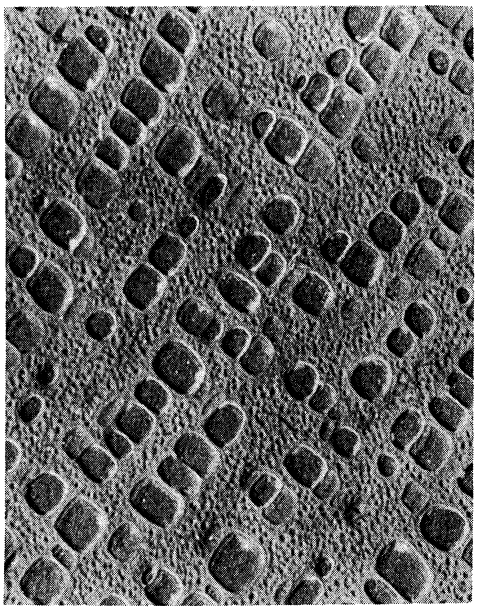
a. As cast. VHN 390.



b. Solution-treated 1 hour at 2150°F, ice-brine quenched. VHN 385.



c. Solution-treated 4 hours at 1975°F, ice-brine quenched. VHN 365.



d. Solution-treated 4 hours at 1975°F, as cast. VHN 380.

Fig. 5. Electron micrographs showing the microstructures of specimens of Heat 1079. X8000.

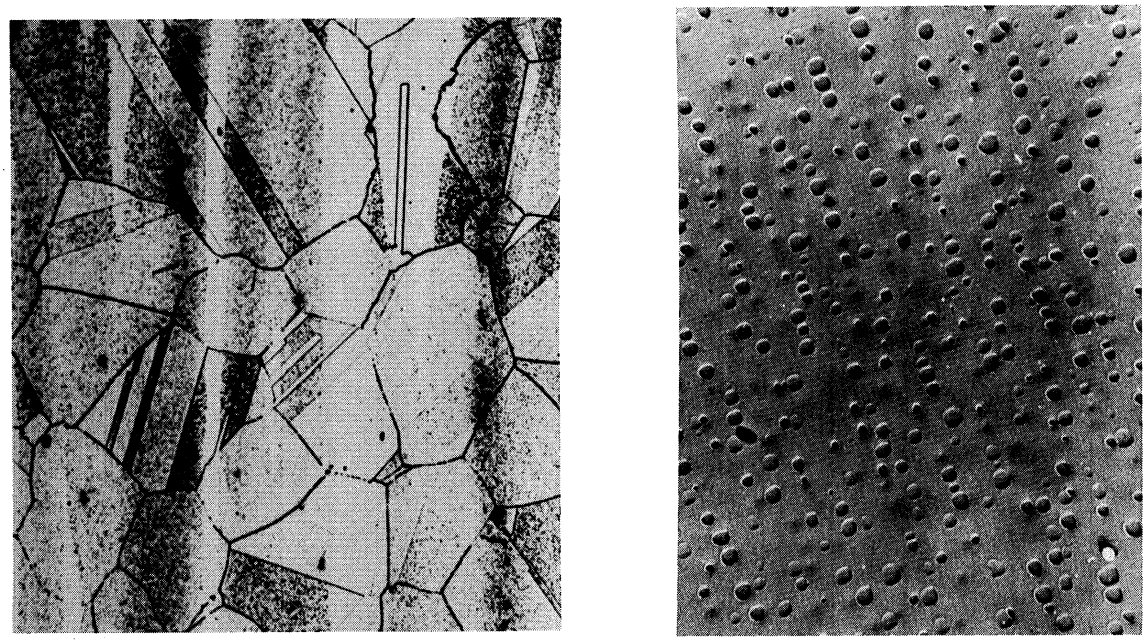
no detectable precipitate particles in the Udimet alloy. Air-cooling from the 1975°F solution treatment produced some precipitation, but the particles were of the order of 300 - 500Å in diameter. The hardness of Alloy 1079 is also considerably greater than that of Udimet alloy. For example, the Udimet specimen solution-treated at 1975°F and air-cooled had a Vickers Hardness Number of 359 (for 50-kg load) while the value for the corresponding specimen of Heat 1079 was 380.

One of the interesting microstructural features of Heat 1079 is the large square particles which appear in the specimens solution-treated at 1975°F. It appears that these form by agglomeration of the smaller, more numerous, angular particles of the as-cast specimen during solution treatment. The nature of these particles has not yet been determined, although it is considered possible that they are the η phase described by Taylor and Floyd. This phase is based on the NiAl phase of the nickel-aluminum system. The numerous smaller precipitate particles distributed between these large particles in the air-cooled specimen resemble the γ' particles observed in the commercial alloys in form and distribution, and are tentatively considered to be this phase. They are nearly as large in this specimen as in specimens of the commercial alloys aged for 10 hours at 1400°F. This undoubtedly is due to an increased rate of formation resulting from the higher amount of Ti and Al in Heat 1079. Some of these particles are even present in the 1079 specimen which was ice-brine quenched after solution treatment at 1975°F, though none are observed in the specimen solution-treated at 2150°F.

It would be considered of interest to make some observations on specimens of Heat 1079 which are aged after solution treatment, and also to attempt to identify the large precipitate particles. If possible, these studies will be made in the near future and reported with studies of the commercial alloys.

BANDED STRUCTURE OF NICKEL-BASE ALLOYS

Several experimental heats of nickel-base alloys which have recently been prepared in the Department of Chemical and Metallurgical Engineering have shown an unusual "banded" structure which appears to result in very low rupture strengths for the alloys. An example of this type of structure is shown by the optical micrograph of Fig. 6a taken from a specimen of experimental heat No. 1057 (Composition: 0.3% C, 3.0% Ti, 3.0% Al, 3.5% Mo, 19.5% Cr, 14.5% Co, 0.25% Si, balance Ni), which was solution-treated for 4 hours at 1975°F, water-quenched, and then aged 10 hours at 1400°F. This specimen ruptured upon loading in the rupture-test unit, whereas specimens of heats of similar composition which have normal structures, and which are



a. Optical micrograph, X100. b. Electron micrograph, X7500.

Fig. 6. Banded structure of nickel-base alloys.

solution-treated and aged under the same conditions, have rupture lives of about 100 hours at 1600°F and 25,000 psi.

The above specimen was examined by electron microscopy to determine the distribution of the age-hardening precipitate. The dark bands seen in the optical micrographs were found to be areas of the matrix which contained numerous precipitate particles, while the white bands were found to be devoid of precipitate particles. The particles in the dark bands were generally round in shape and averaged about 3000Å in diameter, as shown in the electron micrograph of Fig. 6b. These particles are similar in appearance to the γ' particles observed in specimens of Inconel-X alloy which were aged beyond their maximum strength at 1600°F.[3]

This distribution of precipitates is very greatly different from that found in normal, high-strength alloys of this general type prepared under comparable conditions. In these alloys the age-hardening precipitate particles usually average 500 - 1000Å in diameter and are uniformly distributed throughout all regions of the matrix grains.[4] The low strength of the banded heats therefore has been attributed to the lack of a proper, fine dispersion of the age-hardening precipitate throughout the matrix grains. The distribution of the precipitate in restricted bands was attributed to a non-uniform distribution of Ti and Al through the alloy as a result of two low melting, pouring, or solution-treating temperatures, or to strain-induced precipitation arising from rolling at temperatures which were too low.

Working on these postulates, it has since been possible to avoid producing heats showing the banded structures.

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