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Summary Progress Report on

ELECTRON METALLOGRAPHIC INVESTIGATIONS OF HEAT-RESISTANT ALLOYS

to 15 August 1957

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SUMMARY

This report summarizes the general program of research which has been carried out to 15 August 1957 under Contract AF 33(616)-3250 to develop and apply electron metallographic techniques for studies of high-temperature alloys of the types used in jet aircraft construction. This research has been divided into two general phases: the first involving the development of improved techniques for adapting electron metallographic methods to the heat resistant alloys, and the second involving the application of these techniques to studies of particular alloys.

The work on the development of techniques has included: studies of methods of preparing extraction replicas for identification of carbides in the alloys, the construction and preliminary testing of a vacuum cathodic etching apparatus, and further work in developing an etchant which selectively attacks the columbium and titanium carbide and nitride phases.

The studies of particular alloys has included: studies of effects of vacuum versus air melting on microstructures of nickel-base alloys, investigation of the mechanism by which boron and zirconium influence the properties of nickel-base alloys, studies of the influence of cobalt and molybdenum on the microstructures of nickel-base alloys, correlations of hardness of commercial nickel-base alloys with their microstructures to determine the basic hardening mechanism, and identification of phases precipitating in the S816 cobalt-base alloy on aging and overheating during testing.

INTRODUCTION AND OBJECTIVES

Various recent metallurgical investigations indicate that the minor phases which precipitate in heat-resistant alloys during exposure to stresses and high temperatures have pronounced effects on the metallurgical properties of the alloys. To better understand and control the alloys' properties it is therefore desirable to have detailed information on their minor phases. The work under contract AF 33(616)-3250 has been undertaken to employ the highly sensitive techniques of electron diffraction and electron microscopy in 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.

Inasmuch as special reports, technical notes, or manuscripts for journal publication, have been submitted in lieu of progress reports for the past three quarters, this report is designed to give a general description of the overall program of research which has been carried out under Contract AF 33(616)-3250 for the past three quarters. To do this, the various research problems that have been worked on are described in relation to the overall objective of the project, the methods used are indicated, and the general nature of the results obtained to date are described. Detailed descriptions of methods, observations, and research data are not given, however, in order to preserve clarity and brevity of presentation.

RESEARCH WORK UNDERTAKEN

As indicated above the work on Contract AF 33(616)-3250 during the period covered by this report has been divided into two general categories: (1) the development of techniques for use in applying electron diffraction and electron microscopic methods to the heat-resistant alloys, and (2) application of these techniques to studies of the minor phases of particular alloy systems.

Development of Electron Metallographic Techniques

The work on developing techniques for electron metallography has included further study and refinement of the selective etching technique for identifying columbium and titanium carbides and nitrides. This procedure involves electrolytic etching in a solution of 1 part of concentrated nitric acid to 3 parts of concentrated hydrofluoric acid, and has been found to attack particles of the above phases preferentially to carbides such as $M_{23}C_6$ and M_6C. This permits identification of the titanium and columbium phases by observation of etched surfaces by optical or electron microscopy. This method has been used in examinations of "overheated" specimens of S816 alloy to determine the distribution of carbide phases. It has also been found that substitution of fuming nitric acid for the "concentrated" acid eliminates the necessity for electrolysis. With this modification, the reagent has been used to dissolve columbium and titanium carbides and nitrides from extracted residues, thus simplifying the patterns making identification of other carbides easier.

A vacuum cathodic etching apparatus has also been constructed and preliminary testing has been completed. This apparatus is of a simplified design which was developed at the General Electric Laboratories by J. B. Newkirk. Several unusual difficulties developed in the power supply and vacuum system, and slowed the progress somewhat, but very favorable preliminary results have recently been obtained on brass samples which are used as a reference for comparison with Newkirk's published results. The method is now being tested on the 16-25-6 alloy, whose minor phases and structure are already quite well known. It is hoped that this technique will prove useful in electron diffraction work by eliminating corrosion products and similar contaminations which frequently form on surfaces during the etching procedures in solutions.

Considerable effort has also been directed to developing etching procedures for preparing extraction replicas of carbides in grain boundaries of the heat resistant alloys so that they can be studied by selected-area electron diffraction methods. Applications to polished and etched surfaces have not been successful so far, apparently because of the general resistances of the alloys to chemical attack and because the carbide particles are quite large in most cases and are difficult to free. Some success has recently been obtained by preparing extraction replicas of fractured surfaces where the carbides are well exposed by the fracture and do not penetrate to such great depths below the surface. If perfected, these techniques would be of great value, for many recent observations on the metallurgical properties of the alloys indicate that their long-time rupture properties are to a large measure grain-boundary controlled.

Studies of Minor Phases in Alloys

The studies of alloy systems have been carried out in conjunction with the program of research on metallurgical properties of heat-resistant alloys conducted by Professor J. W. Freeman. In large part these studies have been devoted to the nickel-base alloys, and particular emphasis has been placed on attempting to relate the metallurgical properties of the alloys to their microstructures. In the course of the work to date several different structural effects have been investigated, including: the effects of vacuum versus air melting, the influence of additions of trace amounts of boron and zirconium, and the roles of the various other elements which are present in larger amounts.

Interest in the methods of melting arose from the fact that general experience indicated that the nickel-base alloys generally had much better high-temperature properties when vacuum melted than when air-melted. This difference was attributed to differences in carbon, oxygen, and nitrogen contents in various ways. In cooperation with Professor Freeman's group, who prepared and tested the alloys, studies were made of microstructures of various heats of an alloy of substantially the composition of Udimet-500 (55%Ni, 20%Cr, 15%Co, 4%Mo, 3%Ti, 3%Al, 2%Fe, with varying amounts of C, N, and O). No significant differences in properties or structure were found which correlated with nitrogen, oxygen, or carbon content. Consequently, other effects were looked for, and Mr. Decker and Mr. Rowe of Professor Freeman's group, discovered a correlation between boron content and rupture strength, and ascertained that boron was being picked up by the molten metal from the crucible materials used in the vacuum furnaces. They have subsequently established that the addition of a few thousandths of a percent of boron or zirconium is sufficient to produce marked increases in the creep and rupture strengths of these alloys.

Recently, therefore, a major effort has been directed to determining the manner in which these very small amounts of boron and zirconium produce such large changes in properties. Electron microscope studies show very little difference in microstructures of heats containing boron and those that do not, when the heats are subjected to simple aging treatments. When aged under stress, however, the characteristics of the grain boundary precipitates differ for the two types of heats, and an unusual acicular precipitate is observed within the grains of the boron heats. From analyses of stressed samples it has also been shown that the overall strength of the alloys correlates with the strength of the grain boundaries as indicated by the concentration of micro cracks. Attempts are therefore being made to unequivocally identify the acicular precipitates in the grains of the boron-containing heats, and to look for differences in the grain boundary precipitates in the boron-containing and boron-free heats.

All available methods of analyses are being used in this work, including x-ray diffraction studies of phases separated from the alloy by dissolving the matrix chemically or electrolytically, reflection electron diffraction examinations of etched surfaces, and selected area electron diffraction studies on precipitate particles separated from the matrix by extraction replicas. The x-ray diffraction results obtained to date have not been of much help. The patterns usually obtained provide satisfactory identification of titanium carbide, and in some few cases also titanium nitride. In most cases diffraction lines of additional materials are present which are too weak, too diffuse, and too numerous to permit good identifications. In some few cases there is good agreement between some of these lines and some of those expected for the $M_{23}C_6$-type carbide. In most cases however there is also agreement with some of the lines expected for the M_6C and Cr_7C_3 phases. Because of the overlap of these patterns it is not possible to decide whether only combinations of these phases, or these plus some other phase is present. The reflection electron diffraction studies yield essentially the same results, though there is hope that by application of some selective etching techniques the patterns can be simplified and analyses obtained in stages. The most promising method, however, appears to be the selected-area electron diffraction method.

Some problems have been encountered in preparing the extraction replicas, as described above. Also it has been difficult to standardize the electron microscope well enough to calculate "d" values with sufficient accuracy to permit the different phases to be distinguished. As indicated above, the problems in preparing the extraction replicas have been partially solved by working with fractured surfaces. It appears that the standardization problems have recently been overcome by evaporating aluminum on to the replicas and using it as an internal standard. Very recently an unequivocal identification of

$M_{23}C_6$ has been achieved in this way, and the work is now being pursued to attempt identification of other phases.

In conjunction with these studies of the effects of minor constituents on the properties of the nickel-base alloys, some consideration has been given to the role of elements present in major amounts, particularly molybdenum and cobalt. For this purpose a series of special alloys of compositions given in Table I have been used, and studies have been made of effects of various solution and aging treatments on the microstructures, particularly in regard to the development of the γ' phase.

Table I. Compositions of Special Alloys
(weight percent)

Alloy	Ni	Cr	Ti	Al	Co	Mo
1093	70	24	3	3		
1094	58	21	3	3	15	
1128	67	24	3	3	-	3.5

The effectiveness of solution treatments of 4 hours at 1800°F, 4 hours at 1975°F, and 1 hour at 2150°F have been investigated. The first of these appeared to act more as a high-temperature aging treatment for all alloys, producing large agglomerated γ' particles and massive grain boundary precipitates. Similar results were obtained with the second treatment for alloys 1093 and 1128, but in alloy 1094 the γ' phase was dissolved. The solution treatment at 2150°F was effective in dissolving the γ' and virtually all carbides in all three alloys.

Aging for 10 hours at 1400°F after the 1975°F solution treatment resulted in the precipitation of additional γ' particles in the 1093 and 1128 alloys. These were very small in size and formed in a fine dispersion in the areas of the matrix between the larger particles which remained from the solution treatment. No detectable γ' particles were produced in the 1094 alloy, however. Aging 4 hours at 1600°F after the 2150°F solution treatment produced fine dispersion of γ' particles in all three alloys. Both aging treatments caused the amount of grain boundary precipitates to increase in all alloys, and the form of these precipitates varied among the different alloys.

These results show that elements such as cobalt and molybdenum have different effects on the microstructures of the nickel-base alloys, and influence both the precipitation of the γ' phase and the carbides at the grain boundaries. One particular conclusion is that cobalt in amounts of 15 percent markedly increases the solubility of titanium and aluminum, thus decreasing the rate of precipitation of the γ' phase. In this connection it is interesting to note that Udimet-500 alloy, which contains basically 55%Ni, 20%Cr, 3%Ti, 3%Al, 15%Co, and 4%Mo, behaves very much like alloy 1094 in regard to solution treatment, but more like alloy 1128 in aging characteristics. It is proposed to continue studies of this kind, for they may well lead to a better understanding of the differences in behavior of various commercial alloys. It is presently believed that if boron and zirconium contents are carefully controlled, property variations due to other elements can be investigated.

Studies have also been made of the age-hardening phenomenon in the nickel-base alloys to attempt to determine the relative contributions of coherency, solution, and dispersion effects. By comparison of the hardness with the development of the γ' precipitate in Inconel-X, Waspalloy, M-252, and Udimet alloys during aging at 1400°F and 1600°F, it has been concluded that the age hardening arises primarily from coherency stresses between the matrix and the γ' particles. Because of the unusual relationships between the precipitate and matrix phase (i.e. nearly the same crystal structure and unit cell size), it appears that these coherency strains increase as the particles grow during aging and are retained for unexpectedly long periods and for exceptionally large particle sizes. It also appears that the volume percent of the γ' phase depends on the sum of the amounts of titanium and aluminum, for usual alloy compositions, and is not markedly influenced by molybdenum content. Lineal analyses of electron micrographs also show that the volume percent of γ' is greater than expected for compositions of Ni_3Al or $Ni_3(Al,Ti)$, indicating that elements other than titanium and aluminum combine with nickel in forming this phase. These results emphasize further the importance of obtaining information on effects of composition in properties and microstructures in the nickel-base alloys.

In addition to the work on the nickel-base alloys, some further studies have been made of the cobalt-base alloy designated as S816 (20%Cr, 20%Ni, 43%Co, 4%Mo, 4%W, 4%Cb, 3%Fe, 1.5%Mn, 0.38%C). These have been in part a continuation of previous work on this alloy to determine the effects of aging at 1200°, 1400°, and 1600°F on the development of minor phases, but have also included new studies of specimens subjected to periodic short overheating treatments (10 min at 2000°F, without load, every 6-8 hours) during rupture testing at 1500°F.

In the aging studies, Cb(C,N) and $M_{23}C_6$ have been identified in specimens aged at 1200° and 1400°F for periods up to 1000 hours, but at 1600°F the $M_{23}C_6$ is found only for short periods of aging (i.e. 100 hours and less). In addition, numerous very fine precipitate particles are observed to form within the matrix grains at 1600°F but not at the lower temperatures. This suggests that the $M_{23}C_6$ forms rapidly at 1600°F, but over a long period is not able to compete with the Cb(C,N), or perhaps the finely dispersed precipitate, for some element such as carbon, and thus dissolves. This is an unusual reaction, and is not well understood, partly because a good identification of the fine precipitate has not been possible by x-ray or reflection electron diffraction methods due to interference from the much larger amounts of the Cb(C,N) phase present. A somewhat similar, fine precipitate has been observed in the overheated specimens, but again identification has not been possible. At present attempts are being made to employ extraction replica techniques to isolate this precipitate from the alloy and to identify it by selected area electron diffraction methods.

DISCUSSION AND PROPOSALS FOR FUTURE WORK

The research program described above has been designed to investigate the relations between the properties and microstructures of heat-resistant alloys on as fundamental a level as possible. This work has been greatly enhanced by cooperation with Professor Freeman's group which has wide experience in the metallurgical processing and testing of these alloys. Particular emphasis has been placed on the work with the nickel-base alloys because of the present technological importance of these alloys. As a result of the recent findings regarding the importance of traces of boron and zirconium in producing major changes in the strengths of these alloys, it is considered that the cooperative program is in a position to make large contributions to the fundamental understanding of the factors controlling their properties.

In continuing the work on Contract AF 33(616)-3250 it is therefore proposed to give particular attention to determining the mechanism by which boron and zirconium affect the properties of the nickel-base alloys. The work which is in progress to identify the precipitates in the boron-containing alloys will be continued, and comparisons will be made with phases identified in alloys free of boron for similar conditions of aging and testing. Results obtained will be correlated with mechanical properties observed by the members of Professor Freeman's group.

It is also proposed to extend the studies of the roles of the major alloying constituents such as cobalt and molybdenum to include correlations of properties such as hardness, rupture strength, and creep strength, with microstructures and minor phases. The amounts of alloys 1093, 1094, and 1128 presently available are insufficient for a program of this scope, in addition, the boron and zirconium contents vary among these alloys. Therefore it is considered desirable to prepare new heats with controlled boron and zirconium content before the work is resumed. Arrangements are now being made to carry out the melting, rolling, and aging in cooperation with Professor Freeman's group, and it is hoped that these operations can be completed within the next few weeks so that the microstructural studies can be resumed shortly. The creep and rupture testing would also be carried out on a cooperative basis, but may be somewhat delayed because the necessary equipment is in use on other work.

In conjunction with the above studies, the work to develop improved methods for electron metallography will be continued. Particular interest is presently attached to the vacuum cathodic etching technique because of the possibility that it will reduce problems of surface contamination. In addition it is proposed to continue the studies of the aged and "overheated" S816 alloy specimens to whatever extent possible, though this will, to a considerable extent, depend on the development of improved methods of specimen preparation.

In addition to the above work which is already in progress, there are several new topics which appear interesting and important and which it is proposed to undertake if time and personnel are available. One of these involves the use of x-ray line-broadening in analysis of coherency strains in the nickel-base alloys, to provide further information on the hardening mechanisms and on the relationship of creep strength and hardness to microstructure. Another would involve electron microscopic examinations of very thin foils of these alloys, whereby it would be possible to observe individual dislocations, and to study the distribution of strains around the γ' particles and their interactions with moving dislocations.

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