SIX MONTH PROGRESS REPORT

on

MODIFIED EUTECTIC ALLOYS
FOR HIGH TEMPERATURE SERVICE

to

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INTRODUCTION

A study of the modification of high temperature eutectic structures of superalloys has been undertaken to improve both their stress rupture and room temperature tensile properties. It is the aim of the research to improve these properties by changing the normal plate, rod or needle-like eutectic structure, with its planes of brittleness, to a modified, finer, more dispersed morphology. In general, a more finely dispersed structure provides increased strength by reducing the mean interparticle distance through the matrix, and improved ductility without loss of strength by changing the shape of these dispersed particles from their plate-like or elongated dimensions to a more rounded or equiaxed type.

Modification of eutectic structures in superalloys is also of interest because of several possible advantages over the types of cast superalloys now employed. Most of these present superalloys depend on precipitation hardening for strengthening mechanisms. The strengthening phases of precipitation hardening systems are taken into solution well below the melting point of the alloy whereas the phases of eutectic alloys can exist up to the melting point. The melting point is high for many eutectic compositions of superalloys, as high or higher than one of the primary metals. Eutectic alloys are also appreciably more castable than solid solution types. The narrow liquidus-solidus solidification temperature range of eutectics produces: better fluidity; longer feeding distances of risers; reduced susceptibility to hot tearing and a reduced tendency towards dispersed or microshrinkage.

During the first year of this research program, an investigation of seven high-temperature eutectics with melting points greater than 2400°F was completed. The eutectics studied included: Co-10Al, Co-42Cr, Co-37Mo, Co-45W, Ni-37Ta, Ni-45W. These structures were modified by small additions of Mg, Ca, Y, Ce, La, Ti, Zr, B, Al and C. On the basis of microstructure, four different eutectics, Co-10Al, Ni-37Ta, Co-45W, and Ni-45W, were chosen for mechanical property determination. One of the unmodified eutectics of each composition plus at least one modification of each eutectic were cast and tested.

The results of stress rupture tests in air at 1800°F and room temperature tensile tests of the four different eutectics indicated that modification was capable of producing substantial improvements in properties. Small additions of B, C, and Ti increased the time to rupture of the eutectics up to 23 times and increased room temperature ductility from less than 1 percent to as high as 7.5 percent. The microstructures were altered in several significant ways to provide these improved properties.

PROCEDURE

Based on the results obtained during the first year of this investigation, two alloy systems, nickel-tungsten and cobalt-tungsten, were chosen for further study. These systems were selected since these provided the best properties and response to modification. It is the purpose of this continued investigation to utilize the principles of modification to obtain improvements in the properties of superalloys over those currently attained with cast Ni-W and Co-W base alloys. The investigation includes alloys of hypo- and hyper-eutectic compositions when the properties of these offer advantages over eutectics. The mechanism of modification and effective limits of modifying additions are also being studied.

Two series of test bar clusters for each of the alloy systems studied were cast. Stress-rupture specimens from these clusters were tested in air at 1800°F. Four compositions were chosen from each system (Ni-W and Co-W) so that one solid solution alloy (-35W), one hypo-eutectic alloy (-40W), one eutectic alloy (-45W), and one hyper-eutectic alloy (-50W) were included. The Ni-45W and Co-45W is the eutectic in each system. One series of tests for each composition was unmodified; another series was modified by a single addition that resulted in a composition of 0.7% Zr, 0.5 to 0.7% Ti, .2%C and .1%B. This relatively large and complex mixture of alloying elements was chosen to insure considerable modification.

In addition to the stress rupture tests, the microstructure of each alloy was examined. Metallographic tests were taken from the gage section of the untested stress rupture bars. The test location was at half radius in each bar.

RESULTS AND DISCUSSION

Composition

The type of melting furnace utilized influenced the chemical composition of the melts appreciably compared to prior work. A 960 cycle, high frequency vacuum induction furnace was employed for melting all the superalloys in this six month period. This melting furnace was lower in frequency than the 9,600 cycle furnace employed during the first year of this grant. A change in the recovery of the alloying element resulted from the different furnaces, the pick-up of zirconium from the crucible was altered, and the gas content of the melt was influenced. The recovery of tungsten was higher but the loss of oxidizable additions increased. The lower frequency decreased both the melting time and temperatures required for solution of the tungsten and lowered the zirconium pick-up from the crucible. The microstructures were changed appreciably by this difference in composition compared to the results from first year of the program. This different structure influenced the stress-rupture properties appreciably. The analyses of the heats from which the stress rupture bars were cast are listed in Table I. Attention is called to the variation in alloys including the difference in nitrogen content.

Microstructure

The structure of the unmodified and modified superalloys is illustrated in Figures 1 through 4. Figures 1 and 2 show the structure for the Ni-35W, Ni-40W, Ni-45W and Ni-50W. Figures 3 and 4 illustrate the microstructure for Co-35W, Co-40W, Co-45W and Co-50W. The structures were electrolytically etched; the Ni-W with oxilic acid and the Co-W alloys with 6% hydrochloric acid. All of the photomicrographs in Figures 1-4 are shown at 100X.

The structures of the superalloys investigated were modified markedly by the combination of additions, except for the Co-50W. The lamellar types of eutectic structures were replaced for the most part by a globular carbide with only minor amounts of fine eutectic dispersed along the grain boundaries. The modified structures generally appear more columnar in form and usually contain dendrites that are clearly outlined by carbides and small eutectic islands.

The unmodified alloy of the Co-35W composition contained a Widmanstatten precipitate of Co_3W in the grain boundaries; the Ni-35W alloy, however, had a large grain equiaxed structure without grain boundary precipitates. Modification changed both alloys to a columnar structure with islands of carbides and eutectic dispersed discontinuously along the grain boundaries. The unmodified Co-40W and Ni-40W alloys had an equiaxed structure with a thin layer of eutectic at the grain boundary. This thin eutectic layer was modified to more columnar type structure with globular carbides and small islands of fine eutectic. The distribution of the carbides and eutectic was noticeably finer for the cobalt than nickel alloys for both 35 and 40W.

The unmodified Co-45 was almost totally eutectic, while the Ni-45W had considerable primary nickel despite of the fact that the equilibrium diagram indicates that both are eutectic compositions. Modification of the Co-45W results in thick platelets of the intermetallic W_6CO_7 or μ phase as well as globular carbides. The modified Ni-45W contained no primary tungsten but a considerable amount of carbides both in massive globular form and as more angular"chinese script". Modification completely eliminated lamellar eutectic that occurred in these unmodified eutectic alloys.

The unmodified structures and the influence of modification of the Ni-50W and Co-50W differed appreciably. The Ni-50W unmodified structure contained both primary nickel and rounded or star-shaped primary tungsten with some areas of fine eutectic.

Modification replaced the eutectic with coarse angular carbides. The amounts of primary nickel were increased and primary tungsten decreased by this modification. The unmodified Co-50W had a large grained lamellar eutectic structure of alternate platelets of μ phase and primary cobalt. Modification coarsened this lamellar structure markedly without appearing to alter the phases.

Stress-Rupture Properties

The stress-rupture properties of the alloys tested to date are presented in Table II. Figure 5 shows the stress rupture curves for the Ni-W alloys and Figure 6 for the Co-W. In general, modification of the structure resulted in a ten fold or higher increase in time to fracture and considerable improvement in ductility at 1800°F. The modified Co-W alloys provided the largest increase in properties and the longest times to fracture of the alloys studied. Modification of Co-45W alloy increased the time to fracture at 1800°F from 0.9 hr. to 180 hrs. at an initial stress of 15,000 psi. The elongation increased from 1 to 20%. The stress-rupture properties of the Co-35W were increased from 6-7 hr. life at 15,000 psi for the unmodified alloy to 52 hr. at 15,000 psi in the modified condition; the ductility was also improved from 3 to over 50%.

The unmodified Co-45W and Co-50W were brittle and with life to fracture of only 2-6 hr. at 10,000 psi. The modified Co-50W was so brittle that a sound casting could not be obtained. The modified Co-45W has not been stress-rupture tested as yet.

The Ni-W alloys tended to be brittle in the unmodified condition and had life-to-fracture of only 1-4 hrs.at 15,000 psi. Modification increased both the life-to-fracture and the ductility of these alloys. The modified Ni-35W alloy increased in life from less than 1 hr. to 15.8 hr. at 15,000 psi. The unmodified alloy failed transgranularly with nil ductility; the modified alloy failed in a ductile manner with elongations of approximately 40%. The time to fracture at 15,000 for the Ni-40W alloy was increased from 1 hr. to 9 hrs. by modification. The ductility increased from less than 1% to about 32%. Limited test results on the Ni-45W indicate that modification will result in improving the properties more than for the Ni-40W but less than the Ni-50W. The Ni-50W alloy had the best properties for this series both unmodified and modified. Modification increased the time to fracture from 4 to 40 hrs. at 15,000 psi and its ductility from less than 1 to about 10%.

The results of the stress rupture tests obtained in the previous years work are shown in Figures 5 and 6 for comparison.

Generally the results of the unmodified Co-W and Ni-W alloys were substantially poorer than those of similar compositions cast previously. This difference is thought to result from the different compositions and melting procedures utilized because of the variation in the melting furnaces described previously. The differences in structure and properties are currently under study.

SUMMARY

Modification has been shown to exert a beneficial influence on nickel and cobalt alloys containing 35,40, and 45% tungsten. This modification was also successful in producing beneficial results with the Ni-50W alloy, but failed to do so for the Co-50W alloy. Modification generally replaced the lamellar eutectic structure with a mixture of primary dendrites, more or less finely divided globular carbides and small islands of finely divided eutectic. The modified structures produced about a ten-fold increase in time-to-fracture at 15,000 psi initial stress at 1800°F in air. The ductility at 1800°F was also markedly improved by this modification.

The properties of the Co-W alloys are better than those obtained with the first years work. However, the Ni-W alloys have not obtained the same time-to-fracture at 1800°F in air under initial stress of 15,000 psi that was previously reported. The lower properties in the current investigation are believed to result from compositional and structural variations that are presently under study.

TABLE I - CHEMICAL ANALYSES

ELEMENTS DETERMINED

Alloy	Co	Ni	Ti	Zr	C	B	O	N
Ni-35W Unmod.		64.04		0.010				
Ni-35W Mod.		65.7	0.56	0.79	0.25	0.09	0.0027	0.0010
Ni-40W Unmod.		60.01						
Ni-45W Unmod.		55.93		0.009				
Ni-50W Unmod.		49.73						
Ni-50W Mod.		49.3	0.54	0.72	0.20	0.10		
Co-35W Unmod.	65.77			<0.005				
Co-35W Mod.	65.0		0.74	0.72	0.22	0.10	0.0022	0.0017
Co-40W Unmod.	60.75			<0.005				
Co-45W Unmod.	55.45			<0.005				
Co-50W Unmod.	50.45			<0.005				
Previous Years Work								
Co-45W Unmod.	55.46			0.065			0.0024	0.0052
Co-45W 0.2C	58.20			0.13	0.18			
Ni-45W Unmod.		54.98		0.050			0.0022	0.0044
Ni-45W+.1 ea. T. Zr B.C.		59.50	0.15	0.017	0.11	0.18		

TABLE II RESULTS OF STRESS RUPTURE TESTS IN AIR AT 1800°F.

Cluster Number	Alloy	Initial Stress, Psi	Time to Fracture, Hours	Elongation Percent
Ni-W Series:				
514	Ni-35W-Unmod.	15,000	0.9-1.4	Nil
643	Ni-35W-Mod.(a)	15,000	15.8	47.1
		20,000	0.9	44.1
524	Ni-40W-Unmod.	15,000	0.8-1.4	<1
645	Ni-40W-Mod.(a)	15,000	8.2-9.1	24
		20,000	2.6	32.4
558	Ni-45W-Unmod.	15,000	1.5-4.0	<1
650	Ni-45W-Mod.(a)	20,000	4.6	7.4
530	Ni-50W-Unmod.	15,000	4.0-4.7	<1
644	Ni-50W-Mod.(a)	15,000	38.9-40.4	13.2
		20,000	9.7-12.6	7.7-11.8
Co-W Series				
534	Co-35W-Unmod.	10,000	41.1-81.7	~4
		15,000	6.3-6.7	~7
646	Co-35W-Mod.(b)	15,000	52.2	50
		20,000	20.2-44.3	26-38
		25,000	5.3	27.8
559	Co-40W-Unmod.	10,000	3.2-3.5	<1
		15,000	0.9	<1
647	Co-40W-Mod.(b)	15,000	78.7	11.8
		20,000	28.2-32.0	20.4
		25,000	12.2	17.6

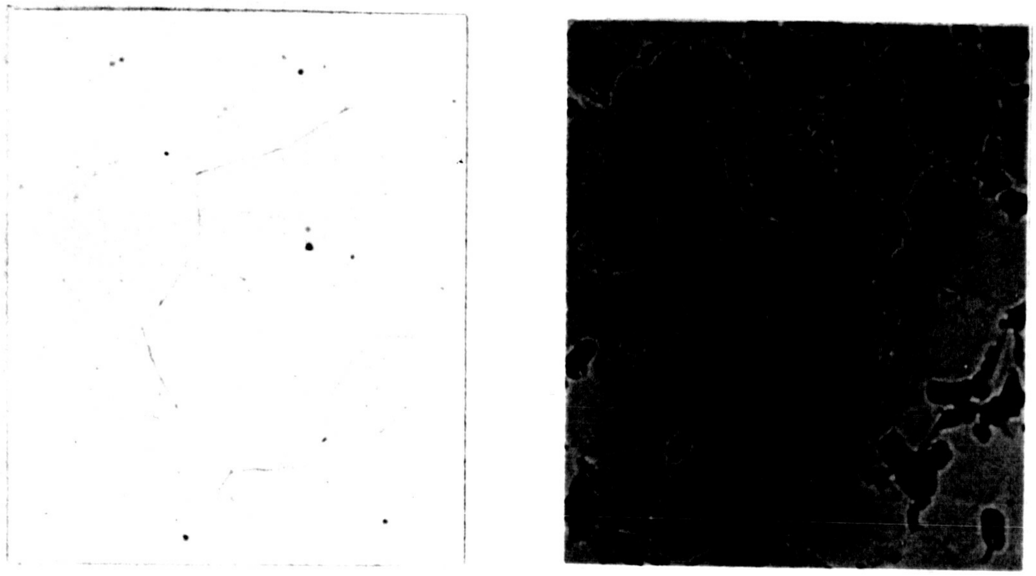
a) Additions Resulted in approximate composition of: 0.7Zr, 0.5Ti, 0.2C, 0.1B

b) Additions Resulted in Approximate composition of: 0.7Zr, 0.7Ti, 0.2C, 0.1B.

TABLE II (cont) STRESS-RUPTURE RESULTS

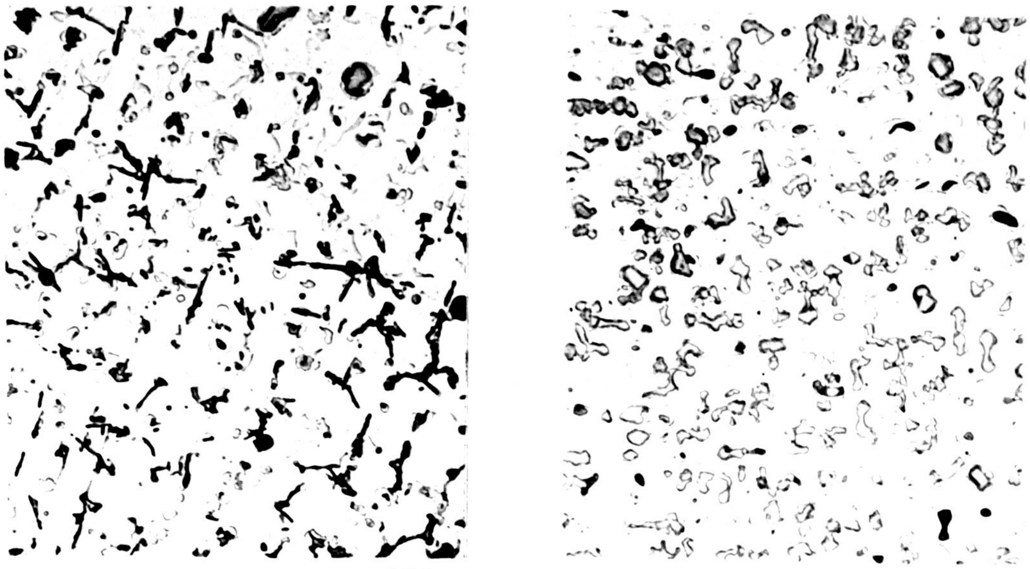
Cluster Number	Alloy	Initial Stress, psi	Time to Fracture, Hours	Elongation Percent
540 648	Co-45-W-Unmod. Co-45W-Mod.(b)	10,000	1.0-1.7	1
539	Co-50W-Mod.(b)	10,000	3.5-7.3	1

(b) Additions Resulted in Approximate composition of: 0.7Zr, 0.7Ti, 0.2C, 0.1B.



100X 100X

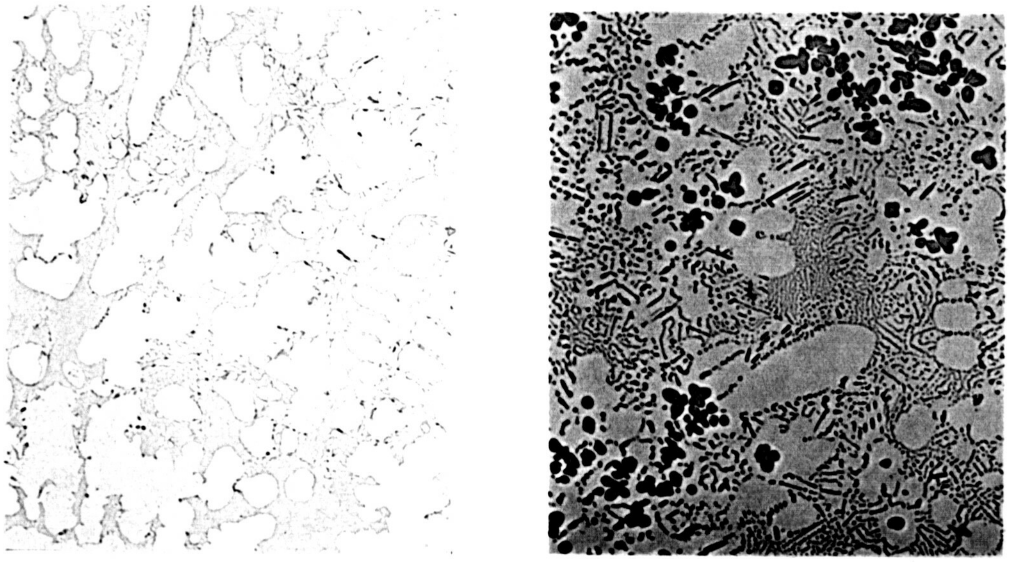
a) Ni-35W, unmodified b) Ni-40W, unmodified



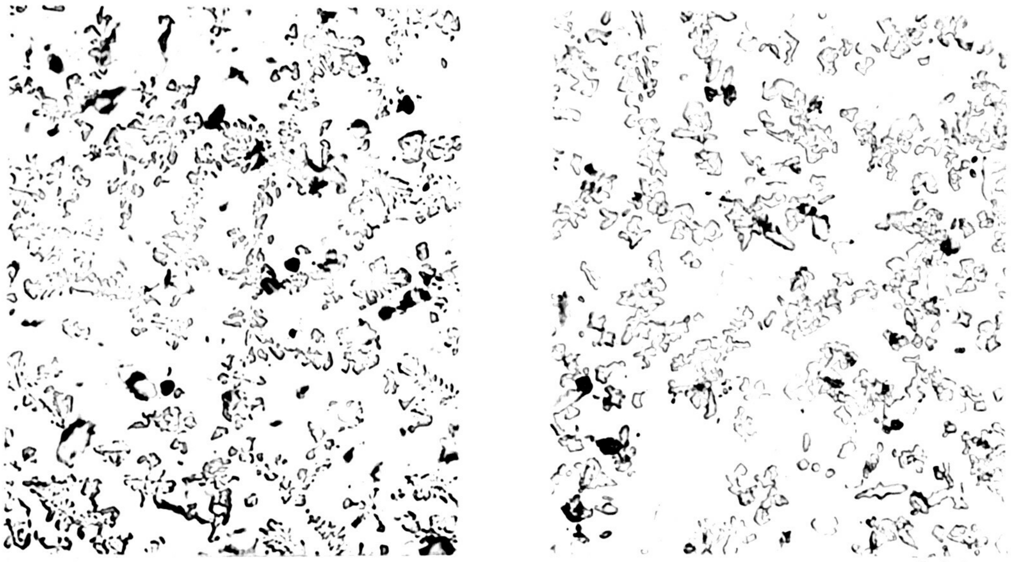
100X 100X

c) Ni-35W, modified d) Ni-40W, modified

Figure 1. Nickel-Tungsten Alloys, from gage section of untested, cast stress-rupture specimen.

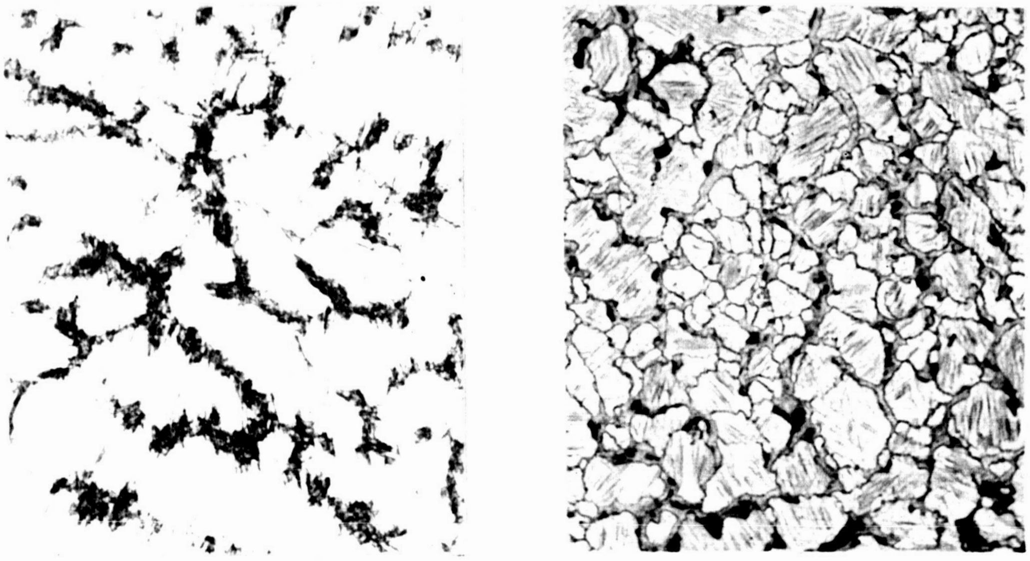


a) Ni-45W, unmodified b) Ni-50W, unmodified

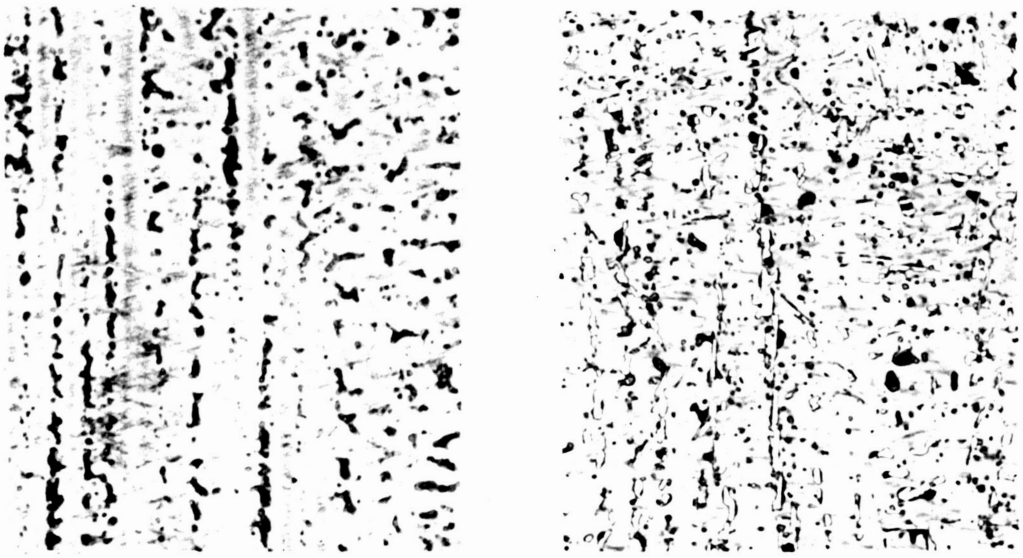


c) Ni-45W, modified d) Ni-50W, modified

Figure 2. Nickel-Tungsten Alloys, from gage section of untested cast stress-rupture specimen.

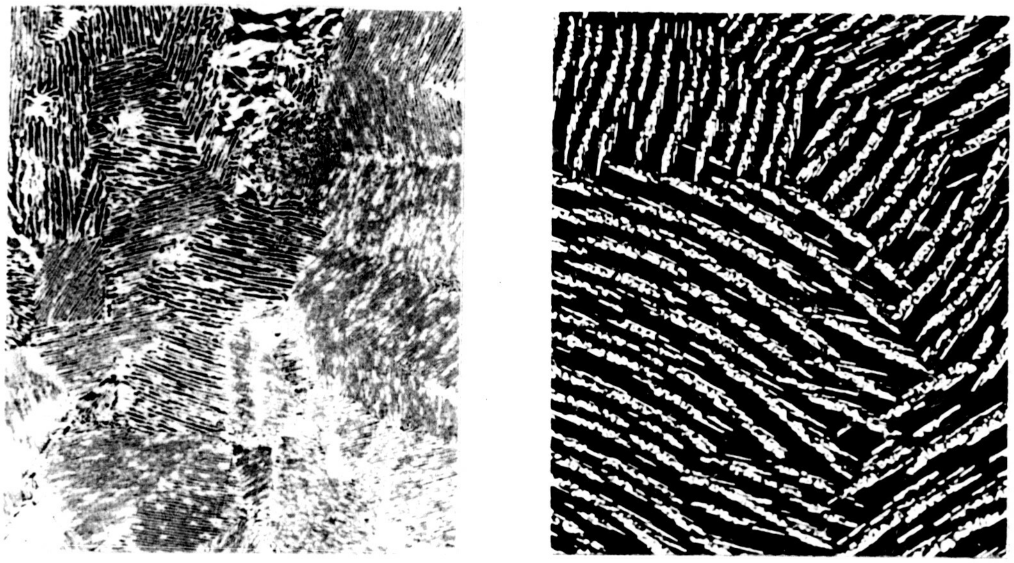


a) Co-35W, unmodified　　b) Co-40W, unmodified



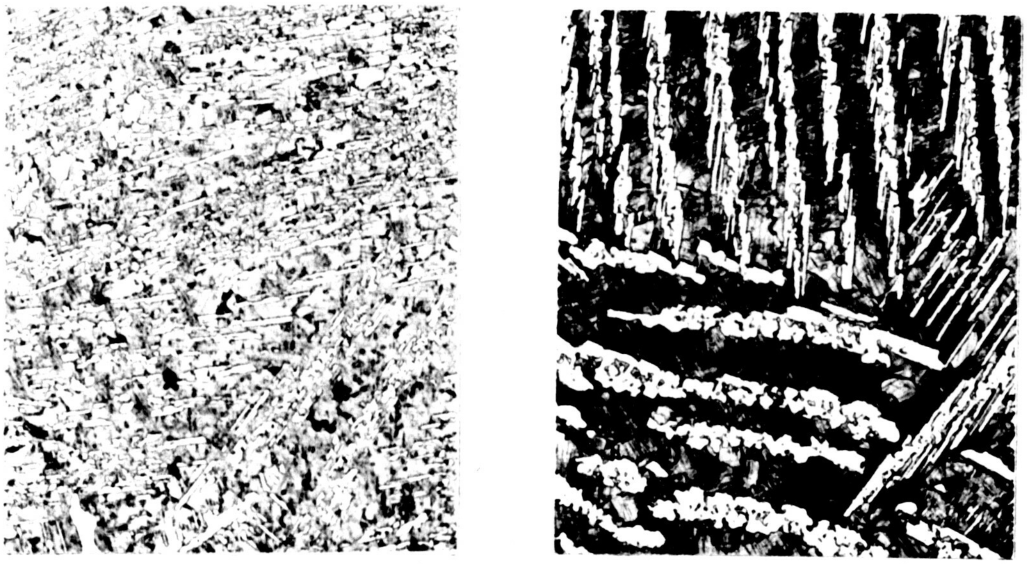
c) Co-35W, modified　　d) Co-40W, unmodified

Figure 3. Cobalt-Tungsten Alloys, from gage section of untested, cast stress-rupture specimen.



100X 100X

a) Co-45W, unmodified b) Co-50W, unmodified



100X 100X

c) Co-45W, modified d) Co-50W, modified

Figure 4. Cobalt-Tungsten Alloys, from gage section of untested, cast stress-rupture specimen.

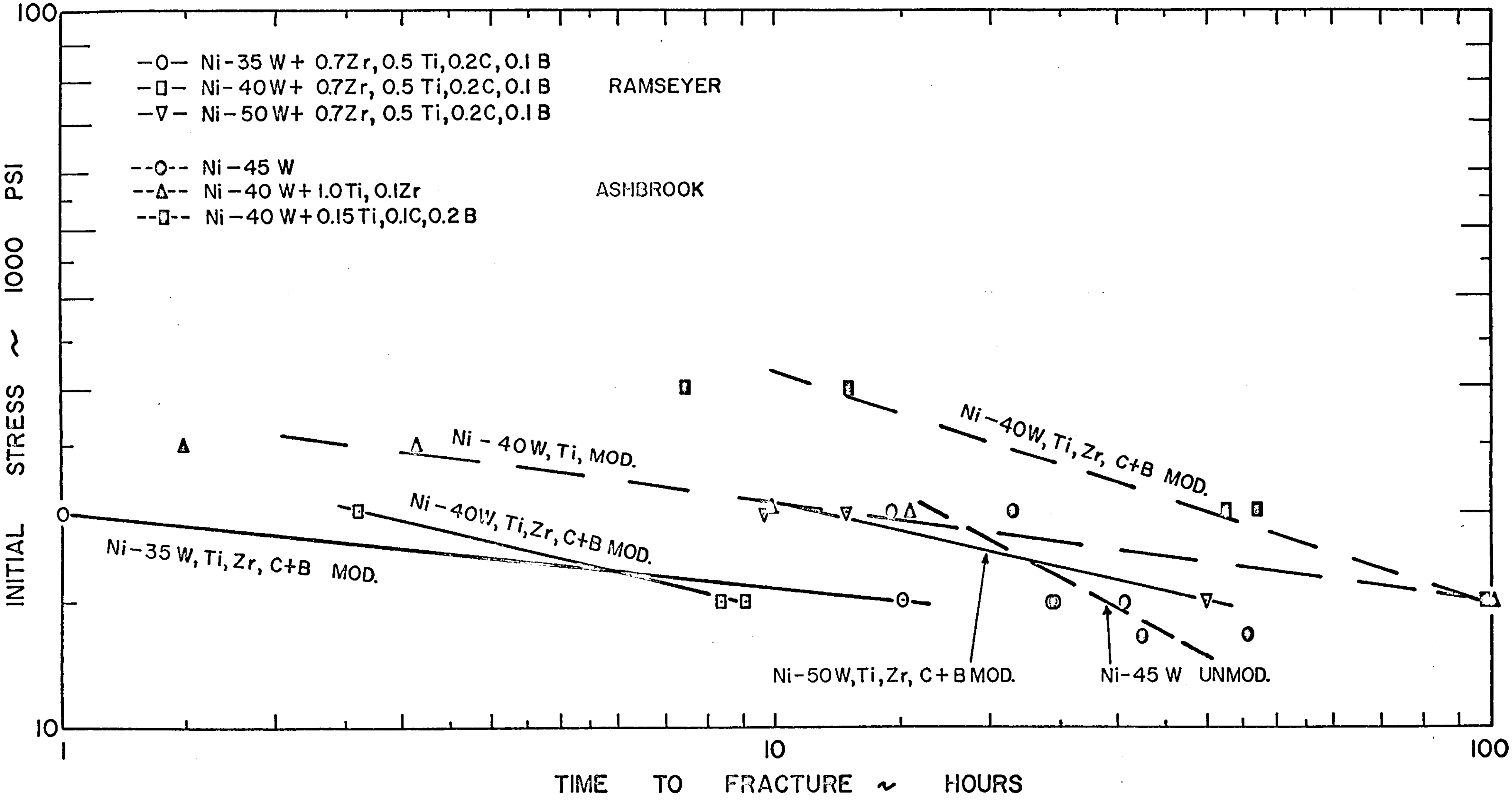


FIG. 5 : STRESS - RUPTURE TESTING OF SEVERAL NICKEL - TUNGSTEN ALLOYS (TESTED AT 1800°F IN AIR).

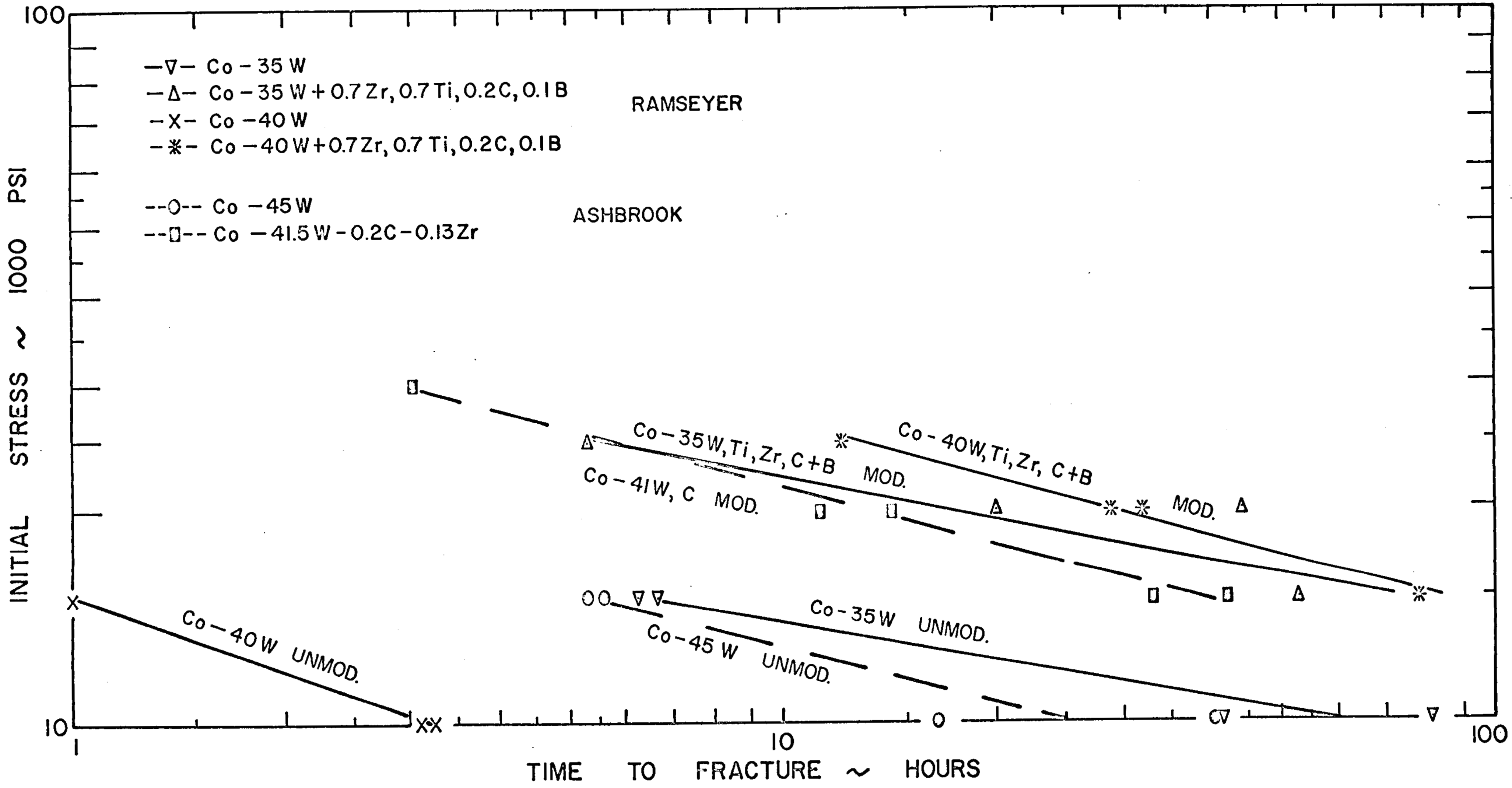


FIG. 6 : STRESS - RUPTURE TESTING OF SEVERAL COBALT - TUNGSTEN ALLOYS (TESTED AT 1800°F IN AIR).