STRUCTURAL STABILITY OF MAR-M-509 — A COBALT-BASE SUPERALLOY

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Abstract

The microstructure of Mar-M-509 alloy (0.6C - 21.5Cr - 10Ni - 7W - 3.5Ta - 0.2Ti - 0.5Zr - 0.1B - bal Co) was studied in the as-cast condition and, after prolonged exposure at elevated temperature, by optical microscopy, electron microscopy, X-ray diffraction, and electron-probe analysis. Tensile properties at room temperature were also determined after long-time exposure or creep at high temperature.

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INTRODUCTION

Mar-M-509 is a cast-cobalt superalloy developed by the Martin Metals Corporation for use at elevated temperatures.* The purpose of the present investigation was to determine the phases present in the alloy in the as-cast condition and, also, those forming after prolonged exposure at elevated temperature. The microstructures of the experimental alloys were studied by means of optical microscopy, thin-foil transmission electron microscopy and diffraction, X-ray diffraction of isolated particles, and electron-microprobe analysis. The effect of prolonged exposure at elevated temperature on the room-temperature mechanical properties of the alloy was also evaluated.

EXPERIMENTAL ALLOYS

The nominal composition of the Mar-M-509 is given in Table 1. The three alloys considered in this investigation were

Alloy A. Two plates of 100 x 40 x 7 mm^3 of Mar-M-509 alloy were made available to us by the Martin Metals Research Laboratories.

Alloy B. A melt of the alloy was prepared at CNRM in a vacuum induction furnace and cast in the form of bars of 50-mm diameter.

Alloy C. Melting stock of the alloy originating from Martin Metals was remelted in vacuum and precision cast in the form of tensile-test pieces.

In the subsequent sections the samples used will be referred to as Alloys A, B, and C, respectively.

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* H. L. Wheaton, Cobalt, No. 29, December 1965.

MICROSTRUCTURE IN THE AS-CAST CONDITION

The microstructure of the alloy in the as-cast condition as revealed with the light microscope is illustrated in Figure 1. Four different phases can be distinguished:

(1) The matrix (D1 in Figure 1a)

(2) A roughly etched phase or aggregate (A1 in Figure 1a). This phase was often observed near or within the eutectic (Phase 4).

(3) A bright-gray carbide that forms irregularly shaped aggregates (B1 and B or B' in Figures 1a and 1c, respectively.

(4) A eutectic-type mixture of carbide and matrix (C1 and C in Figure 1a and 1d, respectively).

Transmission-electron-microscopy examination of the alloys in the as-cast condition showed that the matrix was essentially fcc with stacking faults (Figure 2). Only MC-type carbides were identified by electron diffraction. Furthermore, X-ray diffraction of isolated particles unambigusously revealed the presence of MC and the probable presence of $M_{23}C_6$ carbides.

Further information on the nature and composition of the phases present was obtained by the analysis of the phases with the electron microprobe. Table 2 reproduces the compositions of the different phases of the three alloys investigated.

In spite of the different origins of the samples investigated, Table 2 shows that the different phases have basically the same composition, although variations are observed from one sample to the other or even within a single sample. The matrix is slightly enriched in chromium and nickel and slightly impoverished in tungsten. The content of tantalum, titanium, and zirconium in the matrix is appreciably lower than those in the nominal composition.

The irregularly shaped rod-type phase (B1, B, or B' phase) is highly rich in tantalum and corresponds, thus, to an Mc-type carbide. The latter also contains most of the titanium and zirconium present in the alloy, a fair quantity of tungsten, and minor quantities of the other addition elements.

The roughly etched globular phase (A1 type) is characterized by high chromium and tungsten contents. The precise identification of this phase is not as yet possible. Although X-ray or electron diffraction of extraction replicas does not contradict the presence of an M_6C-type carbide, the tungsten and chromium contents of this phase are in conflict with such an assumption.

The data obtained on the eutectic aggregate (C1 or C phase) show clearly that it consists of a high-chromium carbide and a cobalt-base solid solution, the composition of which is similar to that of the alloy matrix. The carbide phase in this eutectic is interpreted as an $M_{23}C_6$ carbide that has dissolved appreciable amounts of cobalt and tungsten.

The distribution of the different elements among the carbide phases was further assessed by means of electron-probe scanning images obtained, with the radiation corresponding to different elements. Figure 3 reproduces the images obtained on the region marked aa' and bb' in Figure 1c. These images confirm that the MC-type carbide is enriched in tantalum, zirconium, and titanium and that it is impoverished in chromium, cobalt, and nickel. Tungsten appears to be uniformly distributed between the matrix and the carbide.

MICROSTRUCTURES IN THE AGED CONDITION

Hardening Response

The hardening response of Mar-M-509 during aging at elevated temperature is shown in Table 3. The hardening is appreciable after only 10 hours at temperature. At 800 C a continual hardening is observed. At 900 C the hardness level remains constant after the initial increase, but decreases after 4,500 hours of exposure. At 950 C and 1100 C the hardness values indicate an overaging phenomenon or the solutioning of some of the initially present carbides.

Optical Microscopy

Figures 4 to 7 reproduce the microstructures of the alloy after aging for varying times at 800, 900, 950, and 1100 C, respectively. In the initial as-cast structure (Figure 1), the matrix appears essentially free of any precipitation. After aging at high temperature, an abundant precipitation is observed, particularly near the eutectic and globular initial precipitates. The morphology of the latter changes appreciably as the time of aging increases at 950 C and 1100 C. At this latter temperature, the primary carbides become coarser and go into solution progressively.

X-Ray Diffraction

Specimens of the as-cast alloy and specimens aged for 1000 hours at temperature were subjected to electrolytic extraction and the isolated particles were analyzed by Debye-Scherrer X-ray diffraction. The results of this investigation are reproduced schematically in Figure 8. As mentioned previously, the reticular distances and their relative intensities measured for the as-cast specimen correspond well to MC lattice and partially to that of $M_{23}C_6$. The specimens aged at 800, 900, and 950 C show both the MC- and the $M_{23}C_6$-type carbides. Finally the specimen aged at 1100 C for 1000 hours shows only the presence of the MC carbide. No evidence was found for the precipitation of an M_6C-type carbide.

Thin-Foil Transmission Microscopy

A better understanding of the precipitation phenomenon was obtained by thin-foil transmission-microscopy examination of specimens aged under several conditions. For this purpose, samples of Alloy A aged for various periods of time in the range of 800 to 1200 C were used.

Figures 9 to 11 show the evolution of the microstructure during aging at 800 C. After 100 hours of treatment (Figure 9), fine TaC carbides appear on the 111 planes and exhibit a parallel orientation with the fcc structure of the matrix. These partially coherent TaC particles have dimensions of the order of 100 to 250 A. The structure contains some coarse $M_{23}C_6$ particles and also fine TaC carbides without definite orientations (Figure 9b).

After 250 hours of aging at the same temperature, TaC carbides appear on the $\{111\}$ planes, which often exhibit stacking faults (Figure 10a). These partially coherent particles have dimensions of the order of 125 to 300 A and give rise to stresses in the surrounding matrix (Figure 10a); the measurements are made of carbides located on $\{111\}$ planes inclined to the plane of the thin foil (Figure 10 c and 10d). Simultaneously, partially coherent $M_{23}C_6$ particles grow preferentially on the $\{111\}$ planes and have dimensions of the order of 200 to 500 A (Figure 10b).

After aging at 800 C for 500 hours, TaC and $M_{23}C_6$ particles located on $\{111\}$ planes have dimensions between 125-450 A and 375-1500 A, respectively, (Figure 11).

After 1000 hours of aging at the same temperature partially coherent and noncoherent TaC particles were again apparent, and only isolated coarse $M_{23}C_6$ carbides were observed.

The same microstructure prevails during aging at 900 C: fine MC partially coherent carbides (Figure 12a) and relatively coarse $M_{23}C_6$ with interfacial dislocations were observed (Figure 12b). No substantial change in the nature or the morphology of the precipitated particles was observed up to 1000 hours of exposure at 900 C.

The same microstructures appear during aging at 1000 C, but the precipitate's size has increased. Figure 13 shows a dense dispersion of $M_{23}C_6$ carbides in a specimen aged for 100 hours at 1000 C. After 500 hours of treatment at this temperature, TaC particles have reached dimensions between 300 and 1000 A (Figure 14). Essentially the same microstructures were observed after 1000 hours at 1000 C.

At 1100 C, the precipitation reactions within the matrix are much less intense than at the lower temperatures. Figure 15 shows a coarse $M_{23}C_6$ particle after 100 hours of treatment and also typical TaC particles after a treatment of 250 hours. These coarse particles originate from the initial condition.

At 1200 C, all carbides go into solution except the MC's which, however, coalesce.

For the treatments described, it appears that increasing heat-treatment time or temperature stabilizes the fcc allotropic form of cobalt after cooling to room temperature. In fact a substantial amount of the hcp form was observed only after the 100-hour treatments at 900 or 1000 C. All other treatments yielded essentially the fcc allotropic form. The relative stabilization of the hcp phase after the treatments indicated above is probably due to the enhanced precipitation reactions during these treatments.

Effect on Room-Temperature Mechanical Properties

Tensile-test specimens of Alloy C were subjected to long-time exposure at elevated temperature and then tensile tested at room temperature. Table 4 shows that for the treatments considered at 800, 900, and 950 C the 0.2 percent yield strength increases, whereas elongation is lower than in the as-cast condition. Increasing the aging time at 900 or 950 C from 1000 hours to 4500 hours results in a decrease of the room-temperature mechanical strength. This observation, in agreement with the metallographic observation, shows an overaging effect.

Aging Under Stress

Creep specimens of Alloy C were tested for 500 and 1000 hours at 800 C under a stress of 20 kg/mm^2, and for 500 and 1000 hours at 950 C under a stress of 8 kg/mm^2 in order to assess the effect of the stress condition on the microstructure and on the room-temperature mechanical properties. The comparison of the microstructures in the threaded section of the specimen to that in the gage length (Figure 16) indicates that the stress condition enhances the precipitation rate. Thin-foil transmission-microscopy examinations showed that the nature of the precipitating carbides MC and $M_{23}C_6$ is not altered. The size, however, of the precipitating carbides is larger and the proportion of randomly oriented MC carbides increases in the gage length subjected to stress. As shown from a few data available (Table 4) the effect of strain aging on the room-temperature mechanical properties also reveals the enhancing influence of the stress condition on the precipitation rate.

DISCUSSION

The Mar-M-509 alloy exhibits in the as-cast condition a complex microstructure consisting of four "phases". These are a cobalt-base matrix, a dendritic (Ta, Ti, Zr) C carbide, a matrix-$M_{23}C_6$ eutectic, and an unidentified phase of approximately the following formula: 3.5Co, 0.5Ni, 3.5Cr, 0.5W. The identification of this phase as a M_6C carbide would require the chromium atoms to be equally distributed between A and B atoms in a A_4B_2C carbide. Lack of other convincing X-ray or electron-diffraction data do not allow confirmation of the validity of this or other assumptions. The phase could, in fact, be an intermetallic compound or a fine $M_{23}C_6$-matrix eutectic in which the matrix has a high tungsten content. In view of the high chromium content in this phase the hypothesis of a fine M_6C-matrix eutectic is not probable.

Exposure of the alloy at elevated temperature results in the precipitation of fine semicoherent $M_{23}C_6$ and MC carbides on $\{111\}$ planes of the fcc matrix. The application of stress enhances the precipitation reaction and favors the loss of coherency of the precipitated particles. The precipitation reactions are active up to 1100 C. Only after prolonged exposure at this temperature does $M_{23}C_6$ go into solution and the MC carbides coalesce extensively. At 1200 C only coalesced MC carbides are present.

ACKNOWLEDGMENT

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TABLE 1. CHEMICAL COMPOSITION OF ALLOYS INVESTIGATED

Alloy No.	C	Mn	Cr	Ni	W	Ti	Ta	Zr	B	Co
Nominal	0.6	0.1 max	21.5	10	7	0.2	3.5	0.5	0.1 max	Bal
B	0.58	-	21.3	9.9	7.5	0.08	2.88	0.45	-	Bal
C	0.63	-	23.8	9.9	7.2	0.19	3.6	0.52	0.01	Bal

TABLE 2. PHASE COMPOSITION IN ALLOY MAR-M-509

		Component, percent								Total,
Phases	Alloy	Cr	Co	Ni	W	Ta	Ti	Zr	C, est.	percent
Matrix	A	23.8	57.5	11.0	6.7	0.89	0.08	0.14	-	100.1
	B	21.0	62.0	11.4	5.8	1.1	0.07	0.1	-	101.4
	C	26.1	56.6	11.3	6.7	1.3	0.02	0.06	-	102.0
Rods	A	0.77	1.05	0.18	2.2	70.2	4.2	9.8	7.0	95.4
	A	2.0	1.4	0.24	5.8	68.7	3.9	10.6	7.0	99.5
	B	7.7	17.1	3.2	5.5	53.6	2.7	8.5	7	105.3
	C	1.5	2.3	0.4	3.5	65.0	3.3	11.5	7	94.5
Globular phase	A	45.3	33.6	4.8	14.2	1.5	0.09	0.34	2.0	101.8
	B	42.6	35.9	4.7	13.1	1.2	0.07	0.16	2.0	99.5
	C	50.5	22.6	2.7	14.3	1.7	0.03	0.3	3.0	95.2
Eutectic	A(a)	17.9	54.8	10.0	8.25	0.5	-	0.14	-	101.4
	B(b)	65.3	16.3	1.7	9.1	1.0	0.07	0.1	5.0	97.4
	C(a)	28.8	54.5	10.3	7.7	0.68	-	0.15	-	102.0

(a) Matrix of the eutectic

(b) Carbide of the eutectic.

TABLE 3. HARDENING RESPONSE (HV50) OF MAR-M-509 (ALLOY C) AFTER AGING

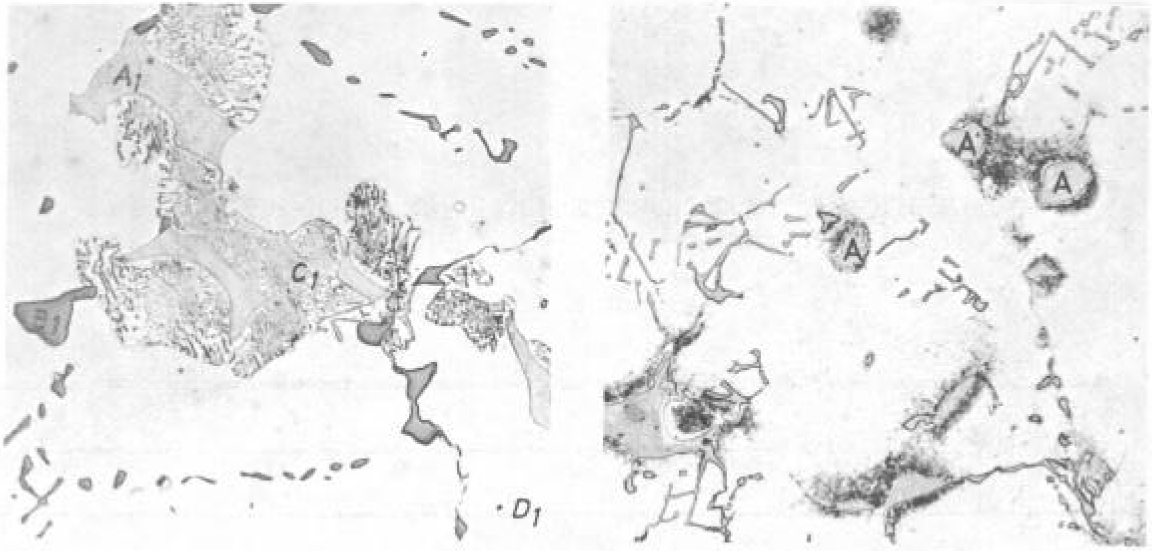
As-cast hardness: 330 HV50

Aging Temperature, C	Aging Time, hours 10	100	500	1000	4500
800	357	371	371	386	402
900	371	365	371	371	350
950	371	357	371	343	343
1100	343	315	343	307	295

TABLE 4. EFFECT OF PROLONGED AGING ON ROOM-TEMPERATURE MECHANICAL PROPERTIES OF MAR-M-509

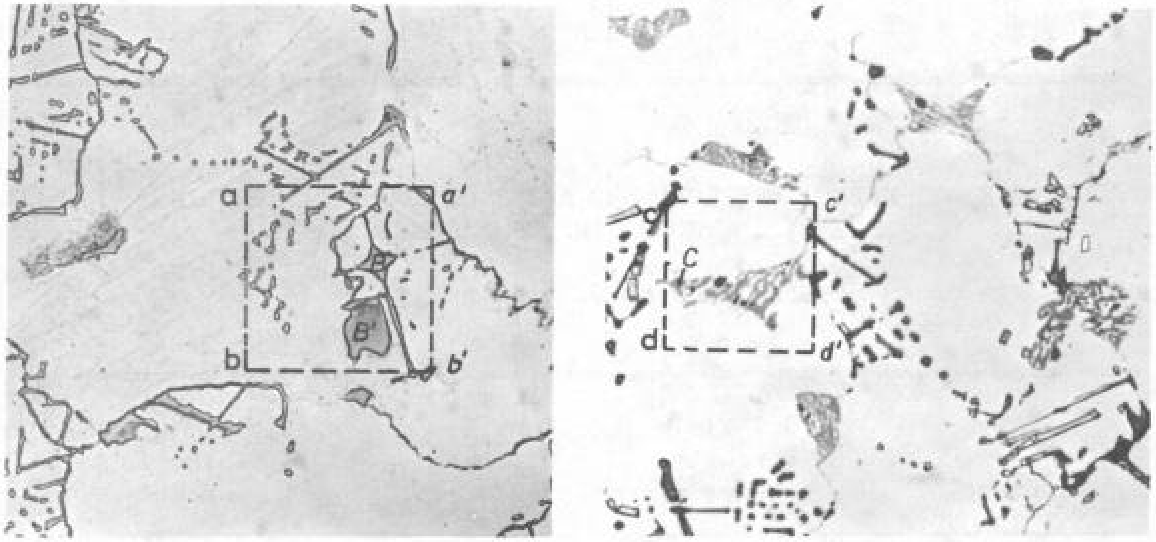
Strain Rate: 0.005 min^{-1}

Heat Treatment	0.2 Yield Strength, kg/mm^2	Ultimate Tensile Strength, kg/mm^2	Elongation, percent
As cast	53.1	79.0	3.4
800 C/1000 hr/water	72.3	89.9	1.2
800 C/500 hr/20 kg/mm^2	81.0	93.4	0.8
900 C/1000 hr/20 kg/mm^2	78.3	90.0	0.8
900 C/1000 hr/water	64.6	65.9 ?	0.6
900 C/4500 hr/water	62.9	80.3	1.1
950 C/1000 hr/water	61.7	77.8	1.4
950 C/4500 hr/water	54.6	72.2	1.6
950/500 hr/8 kg/mm^2	68.0	80.8	1.2



a) Alloy A

b) Alloy B



c) Alloy B

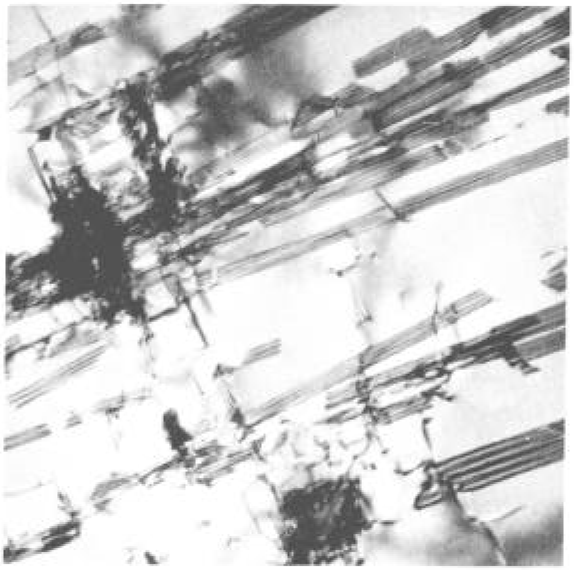
d) Alloy B

Figure 1. Microstructure of Alloy Mar-M-509 in the as Cast Condition. Magnification x 500.

H-72204

H-72204

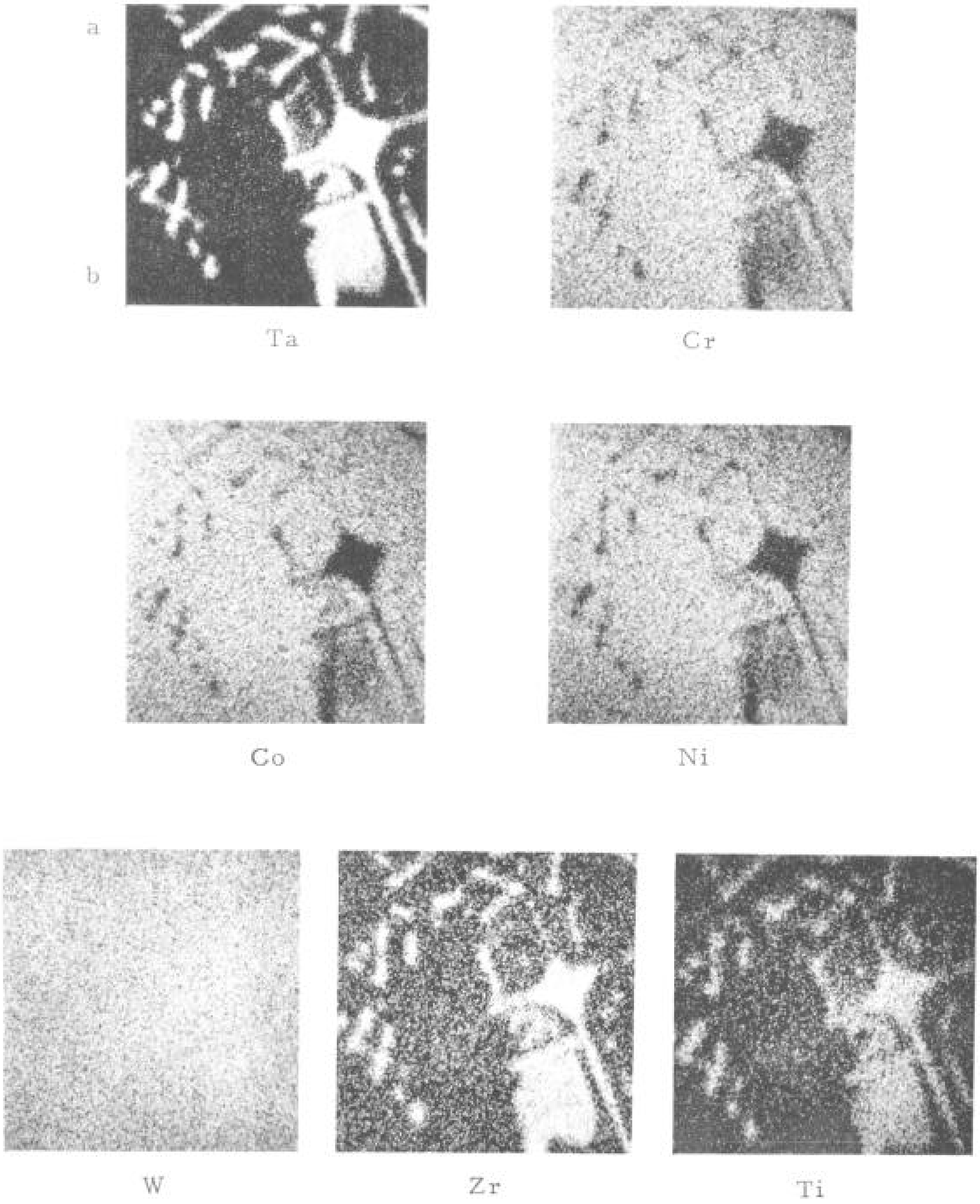
H-72205



x 40,000

Figure 2. Thin Foil Transmission Electron Micrograph of Alloy (A) in the As-Cast Condition.

H-72205



Ta Cr

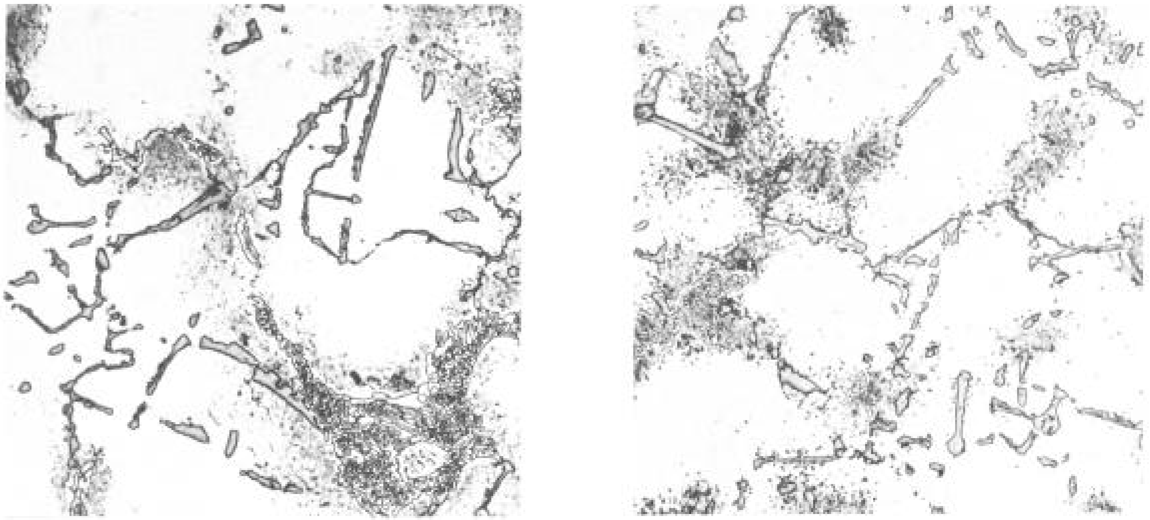
Co Ni

W Zr Ti

Figure 3. Electron Probe Scanning Images for Various Alloying Elements in as Cast Mar-M-509 (Alloy B). Regions aa' bb' in Figure 1.c.

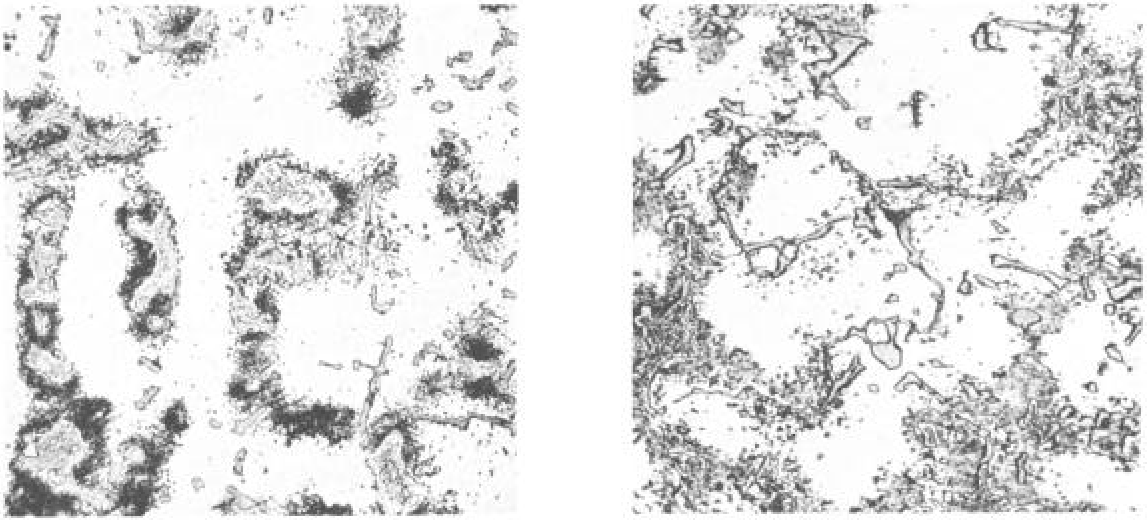
H-72206

H-72206



a) 10 Hours

b) 100 Hours

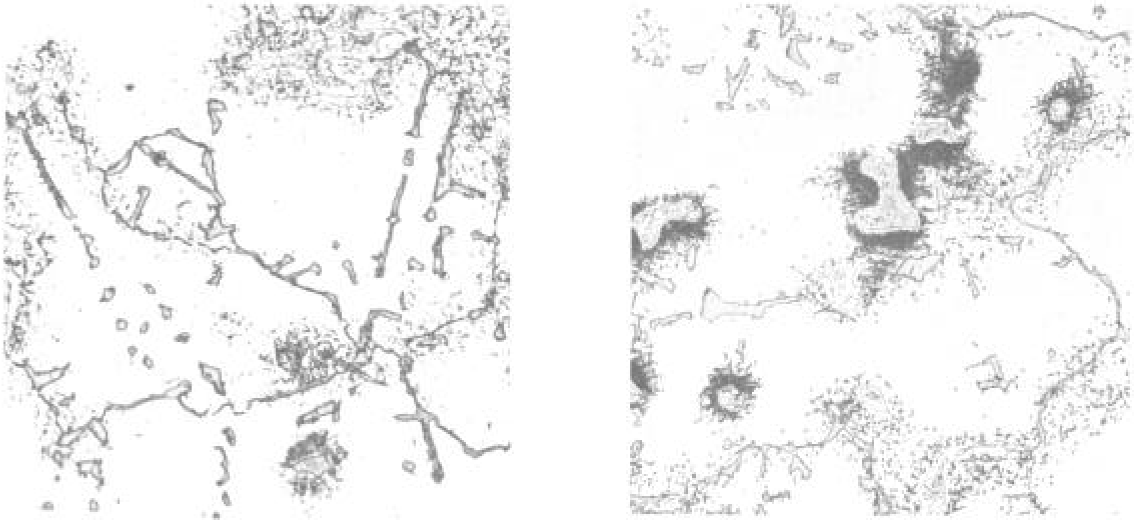


c) 500 Hours

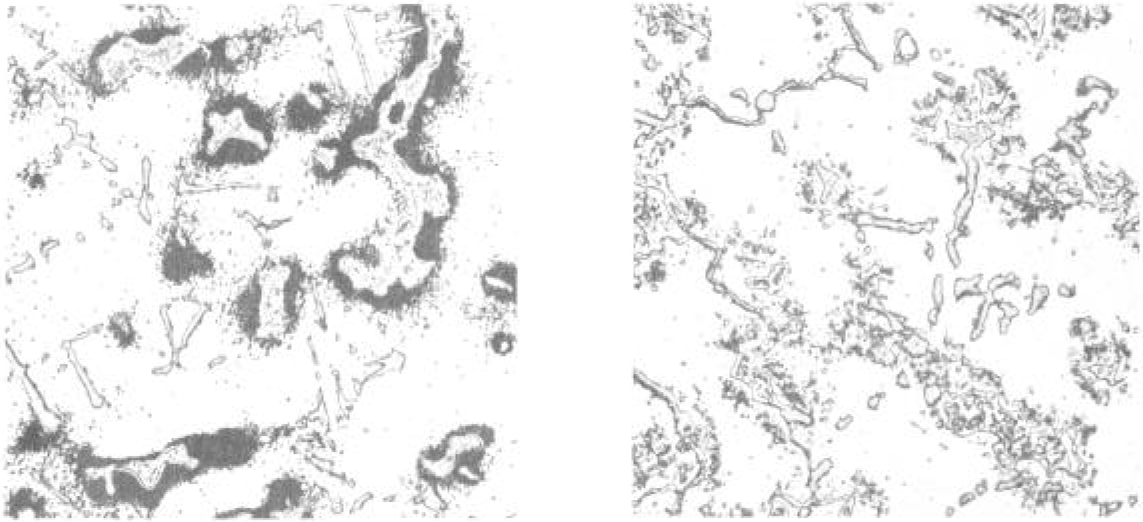
d) 1000 Hours

Figure 4. Microstructures of Mar-M-509 (Alloy C) After Aging for Indicated Times at 800°C. Magnification x 500.

H-72207



a) 10 Hours　　b) 100 Hours



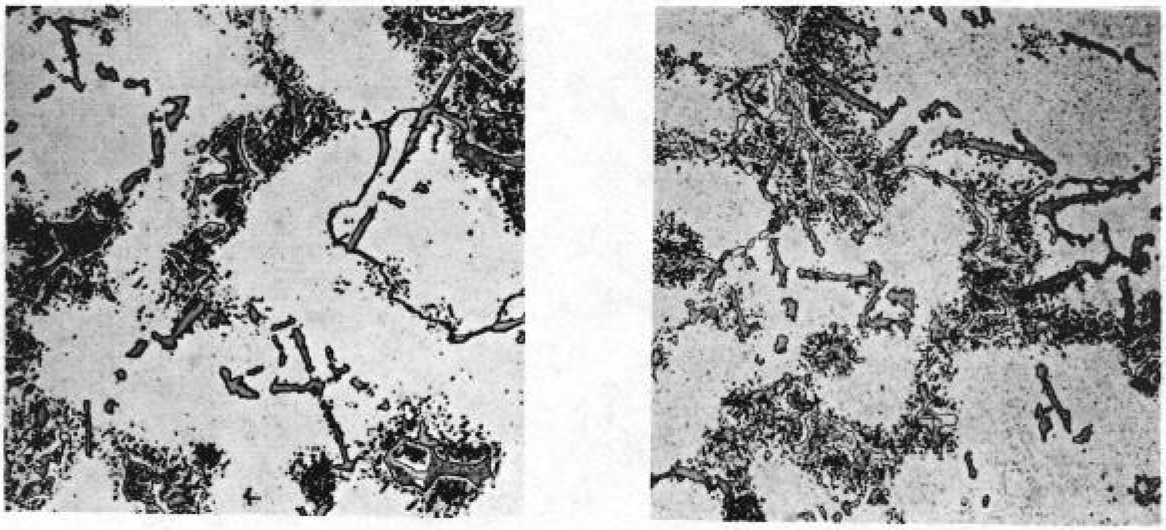
c) 500 Hours　　d) 1000 Hours

Figure 5. Microstructures of Mar-M-509 (Alloy C) After Aging for Indicated Times at 900°C. Magnification x 500.

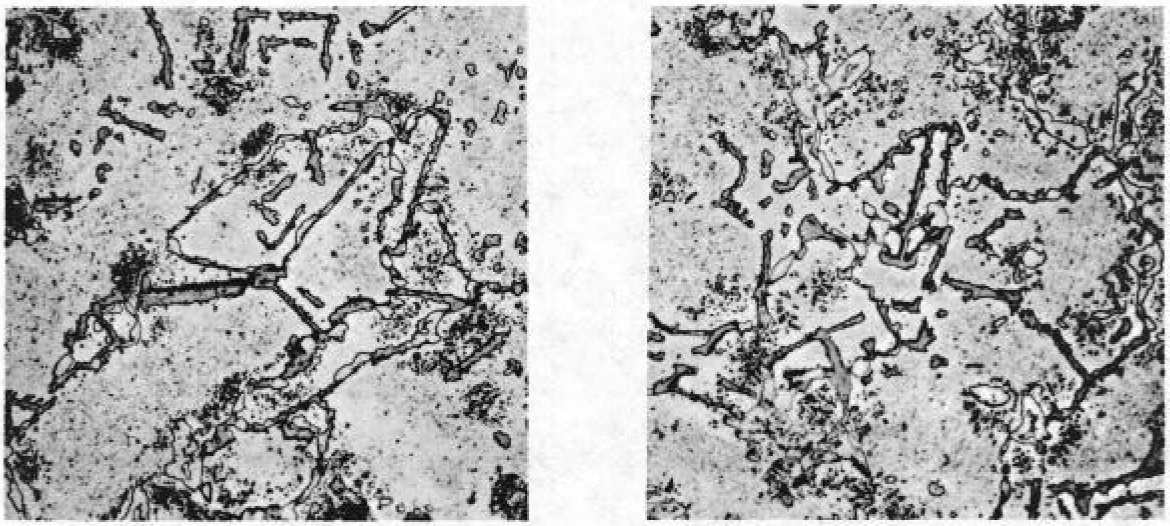
H-72208

H-72208

H-72209



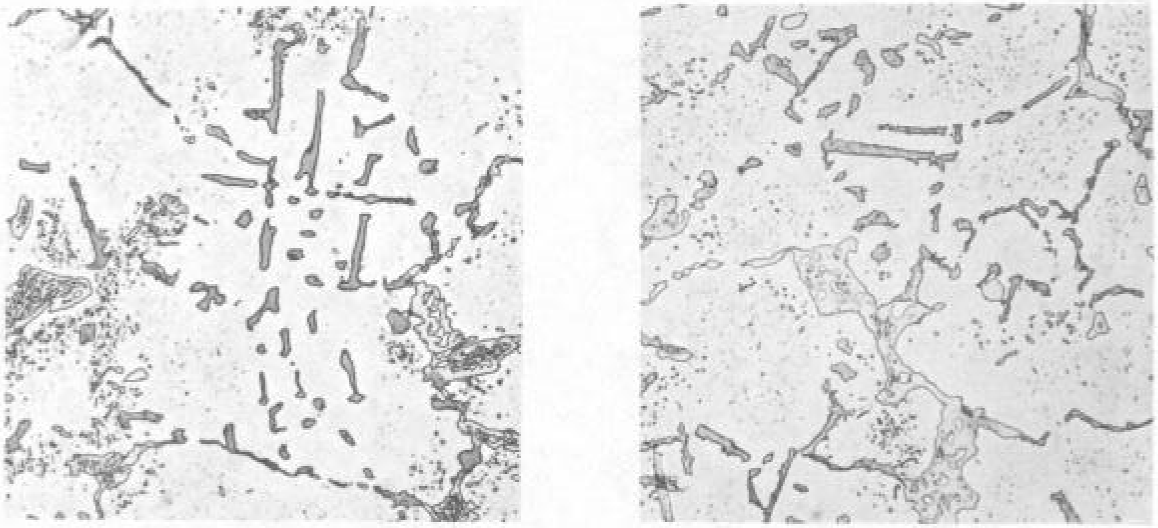
a) 10 Hours b) 100 Hours



c) 500 Hours d) 1000 Hours

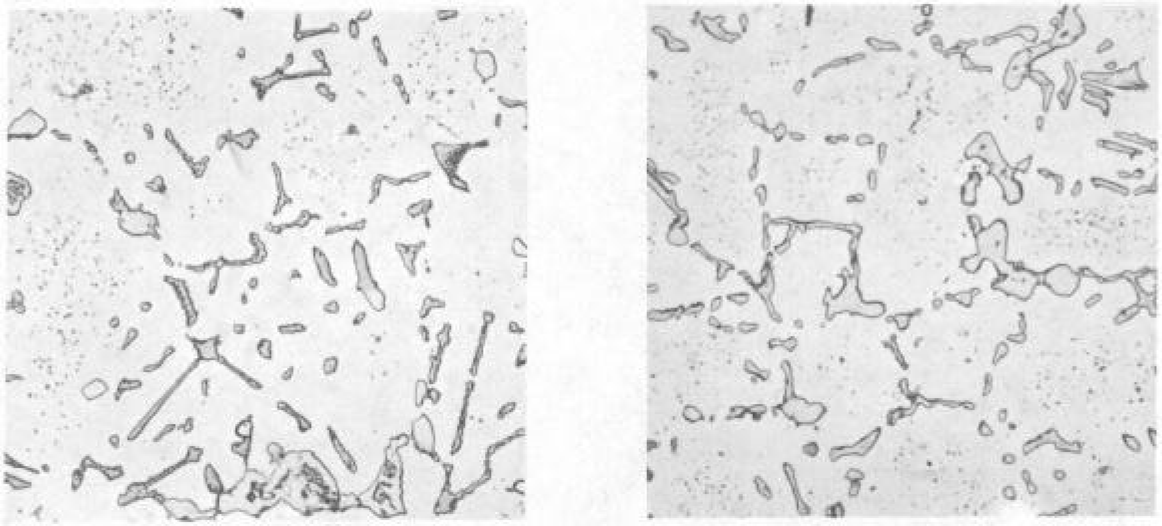
Figure 6. Microstructures of Mar-M-509 (Alloy C) After Aging for Indicated Times at 950°C. Magnification x 500.

H-72209



a) 10 Hours

b) 100 Hours



c) 500 Hours

d) 1000 Hours

H-72210

Figure 7. Microstructures of Mar-M-509 (Alloy C) After Aging for Indicated Times at 1100°C. Magnification x 500.

H-72210

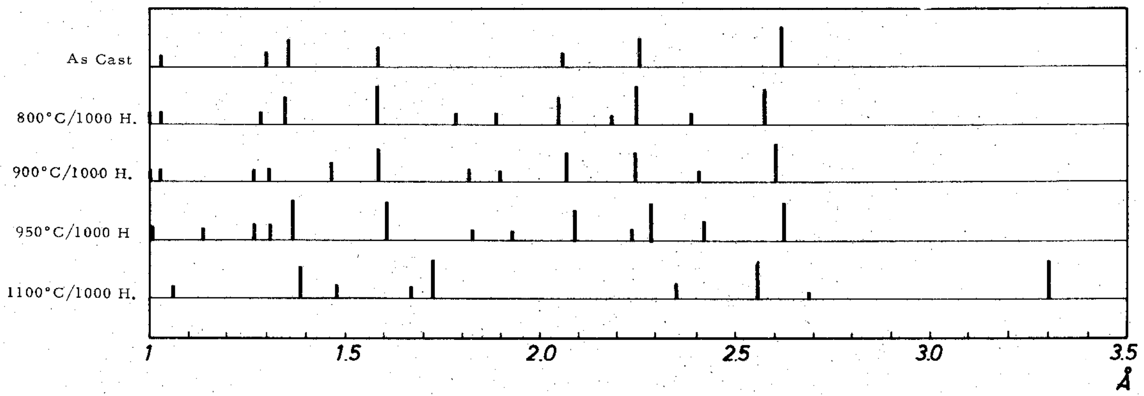
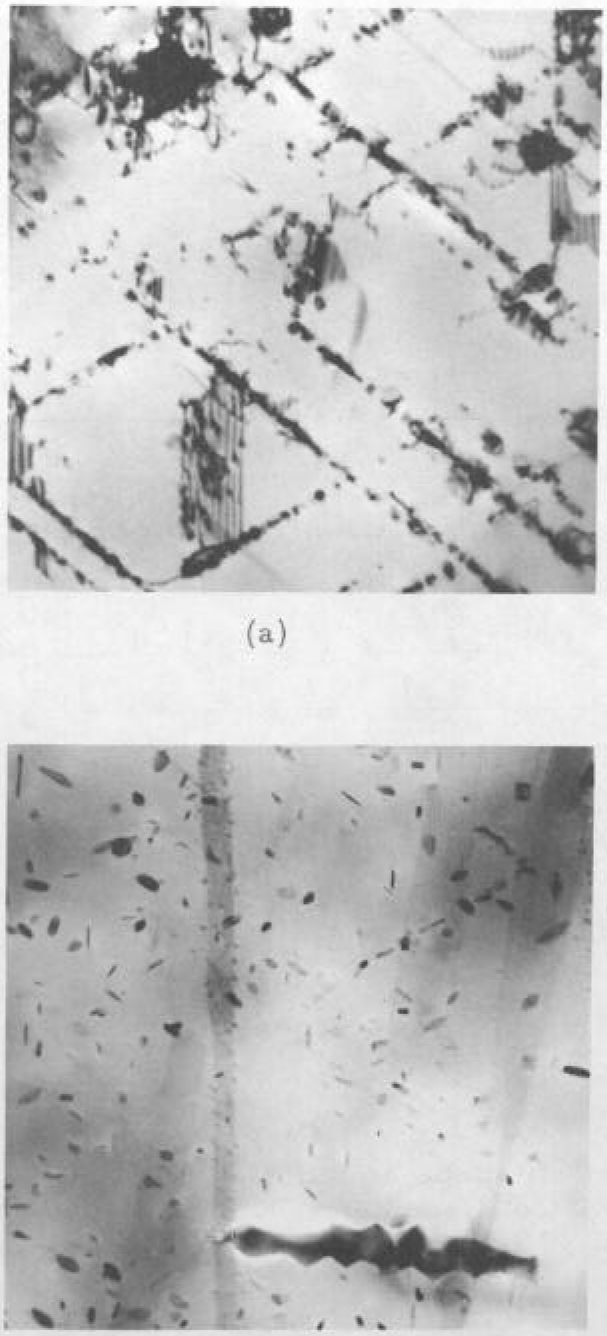


Figure 8. Schematic Representation of X-Ray Diffraction Diagrams Obtained on Isolated Precipitates in Mar-M-509 (Alloy C) as Cast and Aged as Shown.


(a)

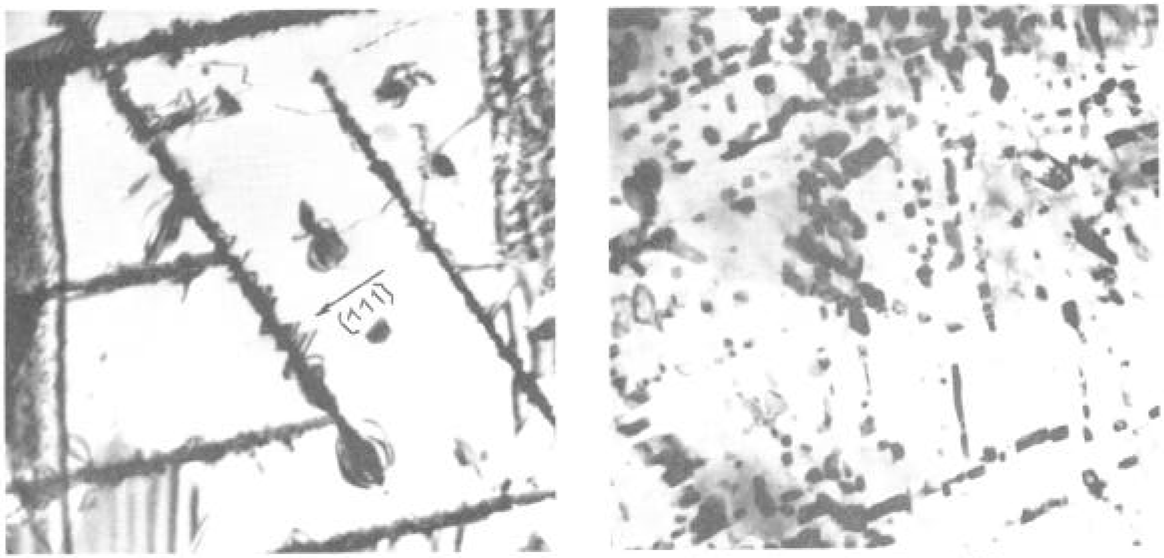
(b)

Figure 9. Thin Foil Transmission Electron Micrographs of the Mar-M-509 Alloy After 800°C/100 h/Water. Magnification x 40,000.

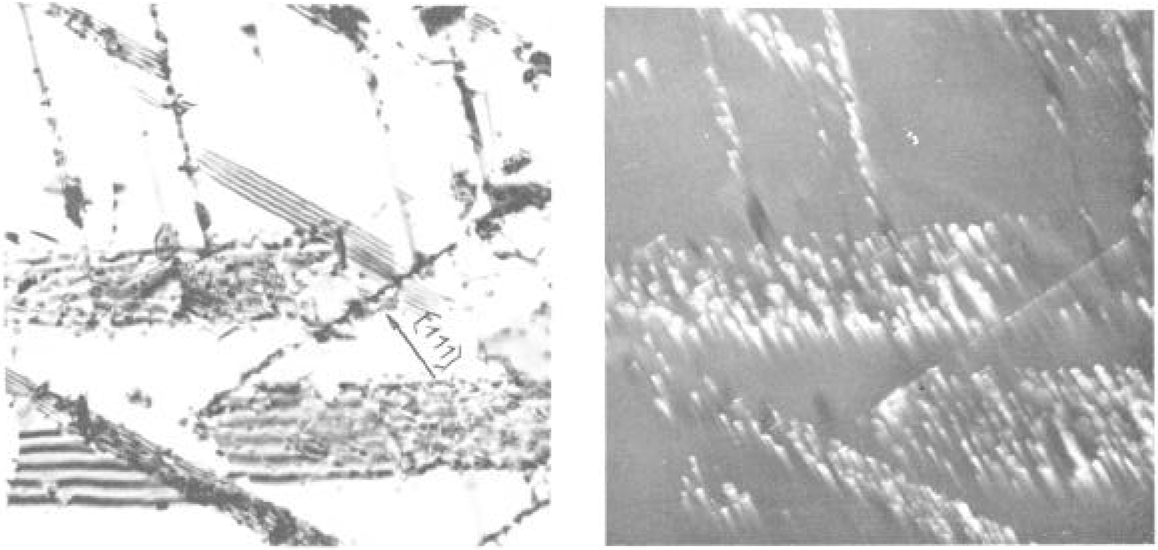
H-72211

H-72211

H-72212



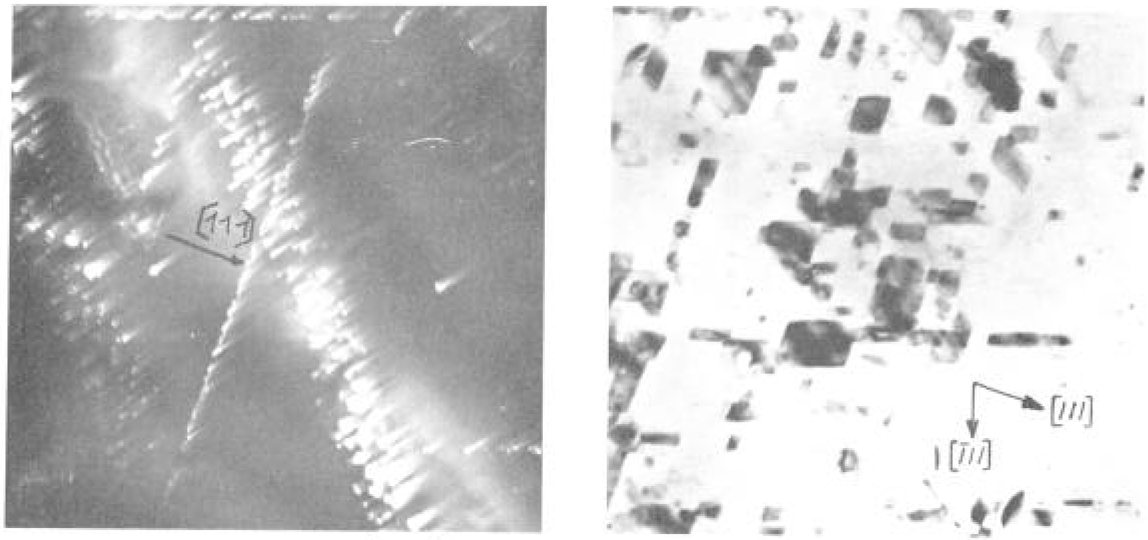
(a) MC Carbides (b) $M_{23}C_6$ Carbides



(c) Bright Field (d) Dark Field (MC Carbides).

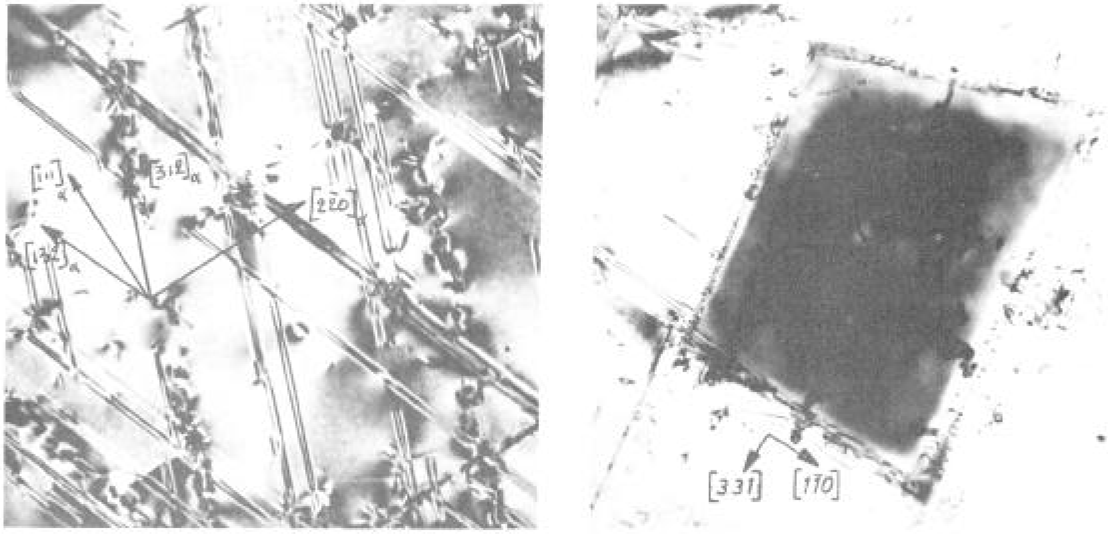
Figure 10. Thin Foil Transmission Electron Micrographs of the Mar-M-509 Alloy After 800°C/250 h/Water. Magnification x 40,000.

H-72212



(a) Ta C Particles on $\{111\}$ planes (b) $M_{23}C_6$

Figure 11. Thin Foil Transmission Electron Micrographs of the Mar-M-509 Alloy After 800°C/500 h/Water. Magnification x 40,000.



(a) 250 Hours , x 40,000
MC

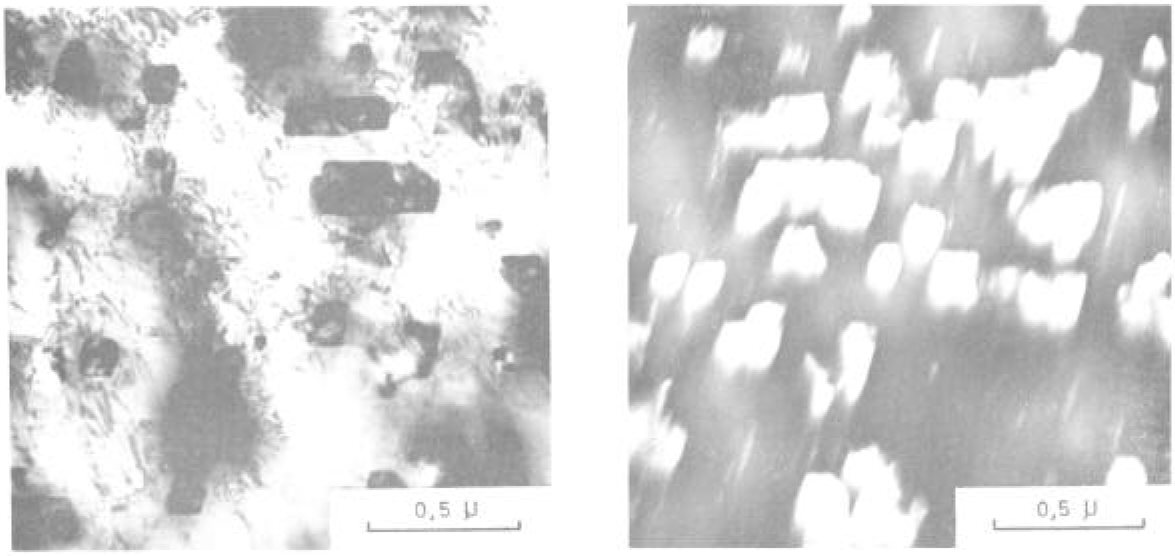
(b) 500 Hours, x 32,000
$M_{23}C_6$

Figure 12. Thin Foil Transmission Electron Micrographs of Alloy Mar-M-509 After Aging at 900°C.

H-72213

H-72213

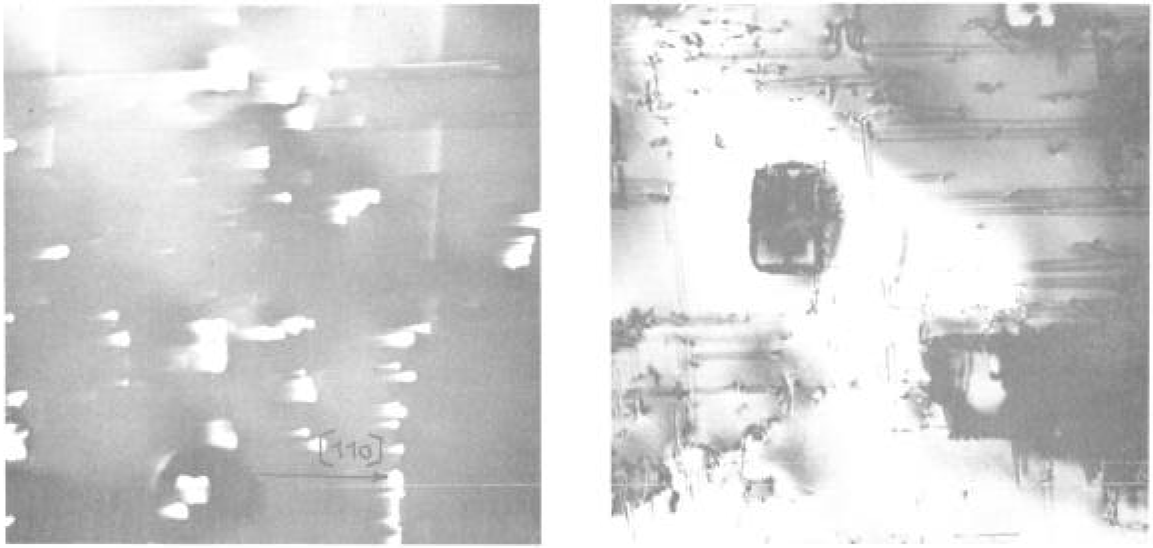
H-72214



Bright-Field Picture

Dark-Field Picture.

Figure 13. Thin Foil Transmission Electron Micrograph of Alloy M-M-509 After 1000°C/100 Hours/Water. Precipitation of $M_{23}C_6$ Carbides.

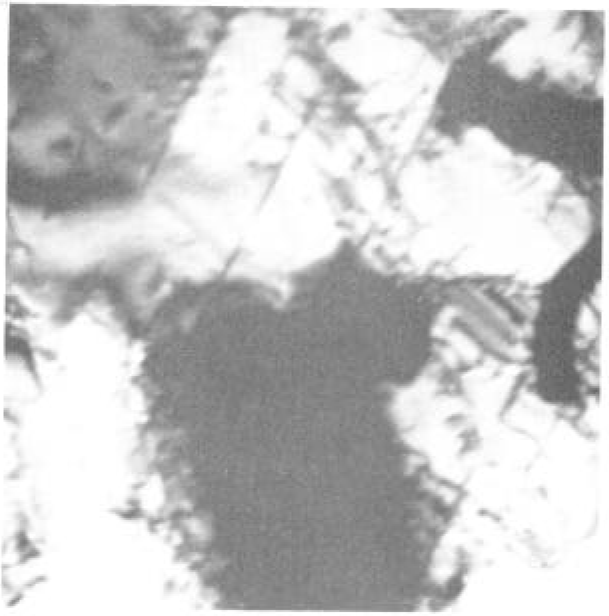


Dark-Field Picture (Ta C Particles).

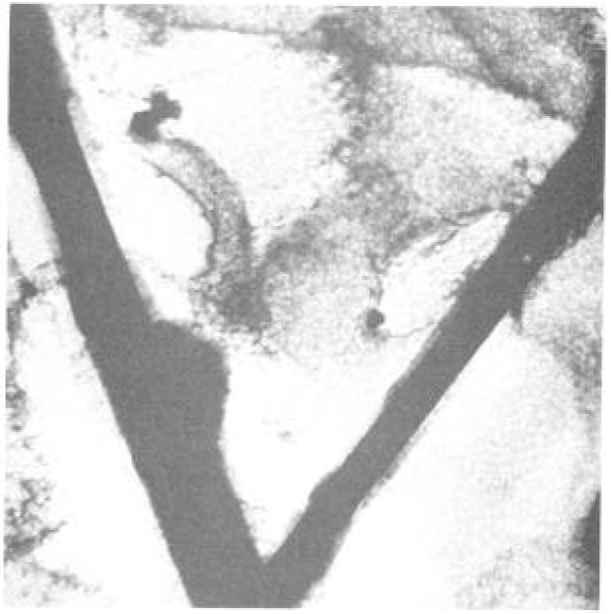
$M_{23}C_6$ Carbides.

Figure 14. Thin Foil Transmission Electron Micrographs of the Mar-M-509 Alloy After 1000°C/500 h/Water. Magnification x 32,000.

H-72214



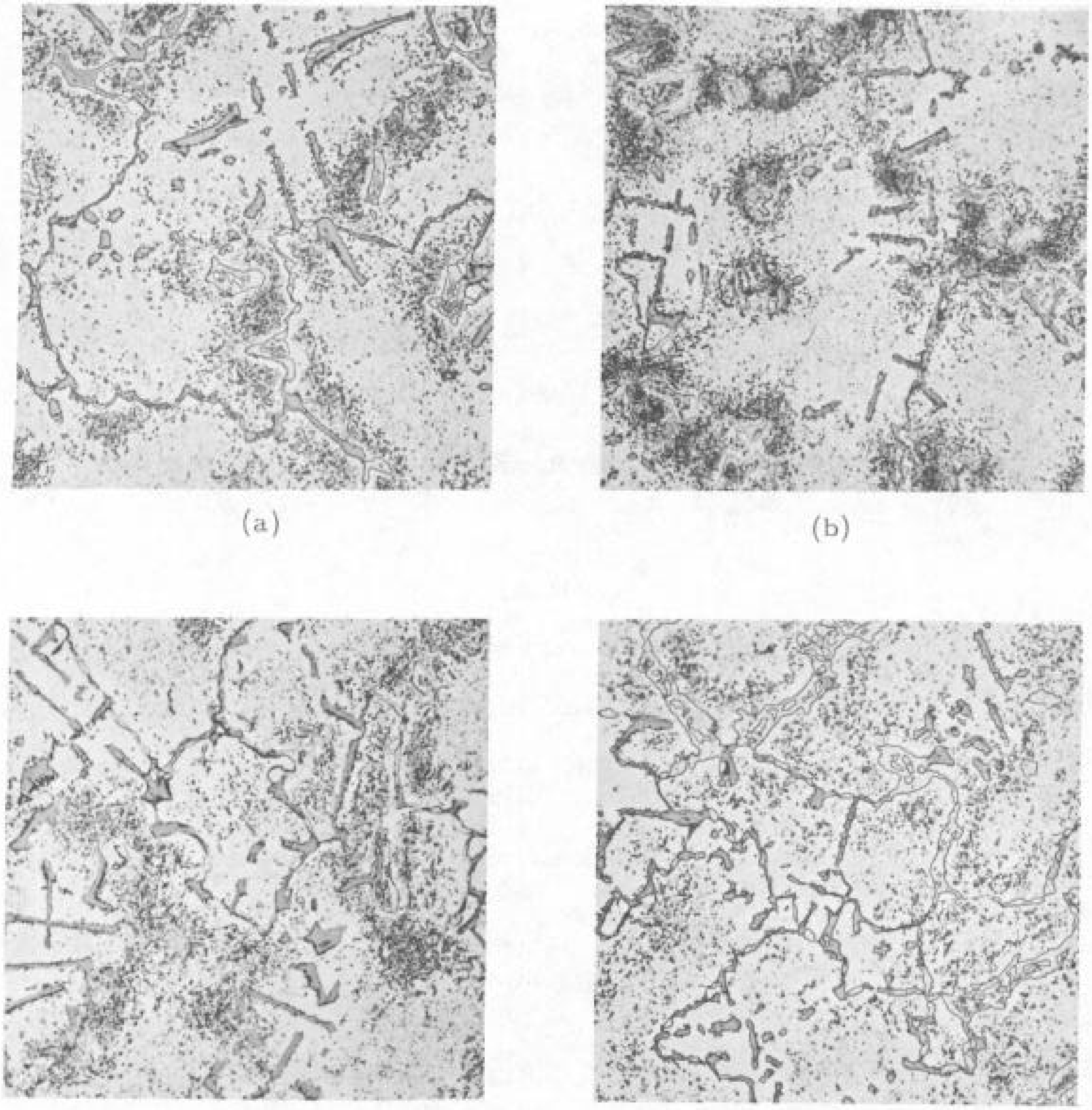
(a)-T.E.M. magnification : x 40,000



(b) T.E.M. magnification x 32,000.

Figure 15. Microstructure of Mar-M-509 Alloy After :
a) 1100°C/100 Hours/Water b) 1100°C/250 Hours/Water.

H-72215



(a) (b)

(c) (d)

Figure 16. Optical Microstructures of Mar-M-509 (Alloy C) Aged at 950°C Under 8 kg/mm2.

a) Aged During 500 Hours - Head of the Specimen
b) Aged During 500 Hours - Region under Stress
c) Aged During 1000 Hours - Head of the Specimen
d) Aged During 1000 Hours - Region under Stress.

Magnification x 500.

H-72216