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Iron-Base Alloys Strengthened by Laves Phases as Substitutes for Stainless Steels

By J. S. Dunning, M. L. Glenn, and W. L. O'Brien

UNITED STATES DEPARTMENT OF THE INTERIOR

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IRON-BASE ALLOYS STRENGTHENED BY LAVES PHASES AS SUBSTITUTES FOR STAINLESS STEELS

by

J. S. Dunning,[1] M. L. Glenn,[1] and W. L. O'Brien[1]

ABSTRACT

One Federal Bureau of Mines research goal, to minimize requirements for domestically scarce mineral commodities through conservation and substitution, can be accomplished by utilizing more abundant elements such as iron, molybdenum, and titanium. An example of this research is the study of precipitation-hardening, iron-base alloys containing molybdenum and titanium, as substitutes for the high-tonnage stainless steels that are high in imported nickel and chromium.

The precipitation-hardened iron-base alloys are strengthened by a dispersion of the ternary Laves phase, $Fe_2(Mo, Ti)$. Aluminum and chromium additions changed the solid solubility limits of molybdenum and titanium in α-iron and affected the composition of precipitating phases. A baseline composition of Fe-7Mo-2Ti was selected to study the effects of aluminum and chromium additions on the precipitation-hardening mechanism and microstructure and was also used in studies of mechanical properties and oxidation resistance.

The study yielded workable, precipitation-hardening alloys, with elevated temperature strengths equivalent to or superior to types 304 and 316 stainless steels. Chromium and aluminum additions in combination were more effective in providing oxidation resistance than either addition was alone.

INTRODUCTION

The Bureau's overall goal is to maintain an adequate supply of minerals to meet the economic and strategic needs of the United States. Important segments of the economy are vitally dependent on chromium, but there are currently no substitutes for chromium in high-temperature metals, corrosion-resistant alloys, and various other critical products. Although the known reserves of chromium are ample, they are concentrated in South African and Southern Rhodesian deposits; there are no significant U.S. chromium deposits. The research goal described in this report is to devise substitutes for stainless steel used in high-temperature application. These substitutes are are significantly lower in chromium than the high-tonnage stainless steels,

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such as types 304 and 316. Under current conditions of ready availability and modest cost of chromium, the alloys described should not be considered economically competitive with stainless steel, and rapid commercialization of the alloys is not foreseen. However, the on-the-shelf alloys could be rapidly commercialized and could reduce the various short- and long-term effects of a drastic curtailment of chromium supplies.

The concept of strengthening iron-base alloys with dispersions of binary Laves[2] phases is not new. However, by combining two additions that form Laves phases with iron, Bureau researchers have successfully furthered the state-of-the-art by using strengthening techniques based on ternary Laves phases, such as $Fe_2(Mo, Ti)$ (2-3).[3] In using dispersions of the ternary Laves phase, $Fe_2(Mo, Ti)$, to strengthen an iron matrix, the magnitude of hardening of the binary iron-titanium system can be combined with the stability of hardening of the binary iron-molybdenum system to yield a readily workable precipitation-hardening alloy. Aluminum and chromium were also added to provide oxidation resistance, and the effect of these additions on the hardening mechanism is described in some detail. Chromium additions were held to a minimum to meet the goal of limiting dependence on strategic imported materials.

MATERIALS AND EXPERIMENTAL PROCEDURES

Alloys were prepared from electrolytic iron, chromium, and titanium and high-purity molybdenum and aluminum. These materials were double-vacuum arc melted in the form of 3-inch-diameter, 10-pound ingots. The ingots were scalped and cleaned, forged to 1- by 3-inch slabs at 1,100° C, and then rolled to 0.4- and 0.25-inch sheet at 1,000° C. The alloys were cut into specimen blanks, solution treated at 1,250° C, water quenched, and aged to maximum hardness at 700° C. Tensile and stress-rupture specimens were prepared from the 0.25- and 0.4-inch specimen blanks following American Society for Testing and Materials standards E8-78 and E139-70, respectively.

RESULTS AND DISCUSSION

Precipitation Hardening in the Fe-Mo-Ti System

The precipitation hardening of iron alloys with ternary Laves phases, as opposed to binary intermetallics, has been described in earlier publications (1, 7). Bureau interest in developing iron-base alloys, strengthened with domestically available alloying additions, led to studies of the Fe-Mo-Ti system. The research goal was to determine if the stable hardening of binary iron-molybdenum alloys could be combined with the high magnitude of hardening at low alloy additions of binary iron-titanium alloys.

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[2] Laves phases are binary AB_2 or ternary $(A, A_1)B_2$ intermetallic compounds, with components with atomic diameters d_A and d_B in the ratio 1.2:1.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

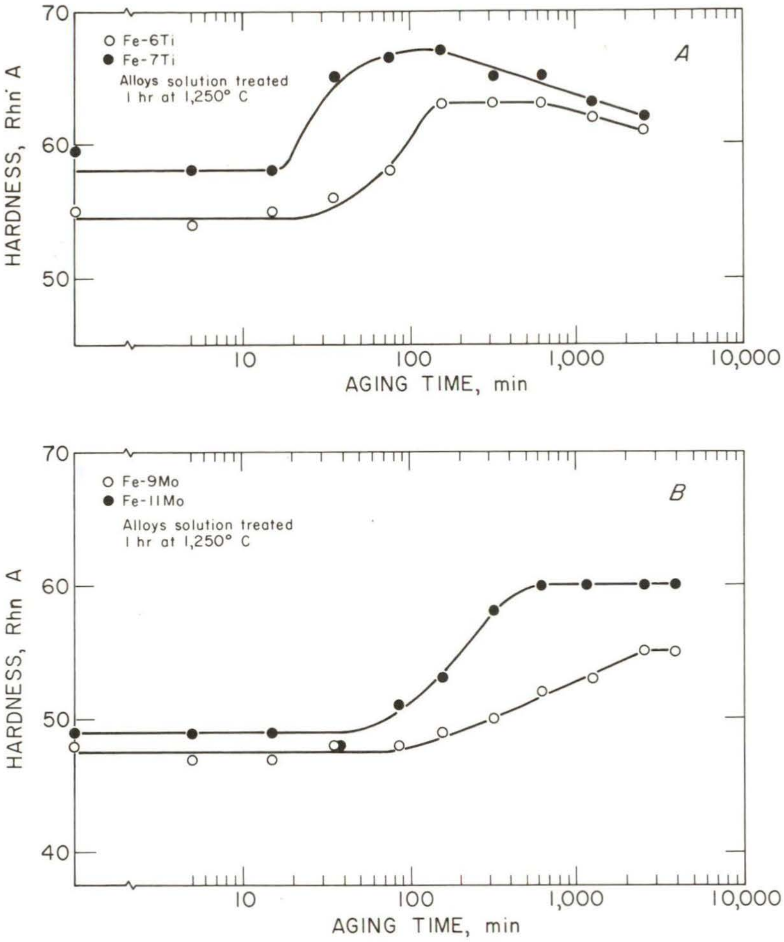

FIGURE 1. - Hardening curves for some binary iron alloys. The alloys were solution treated and aged at 700° C, *A*, Fe-Ti alloys, *B*, Fe-Mo alloys.

The aging characteristics of binary iron-titanium and iron-molybdenum alloys are typified by the hardening curves shown in figure 1. Curves are shown for iron-titanium alloys, with 6 and 7 wt-pct titanium and for iron-molybdenum alloys, with 9 and 11 wt-pct molybdenum. The alloys were all solution treated in the α-phase field for 1 hour at 1,250° C, water quenched, and aged at 700° C. The alloys quenched from the α-phase field have a homogeneous, coarse-grained, ferritic microstructure. Differences in the aging curves are readily apparent. Iron-titanium alloys age rapidly, reach a peak hardness, and rapidly overage as indicated by a decline in hardness. The precipitating phase is the Laves phase, Fe_2Ti.

Aging characteristics in the iron-molybdenum system typically show a slower onset of hardening, and overaging is slow relative to other iron-base binary alloys. Peak hardness is maintained even after several hours of exposure at the 700° C aging temperature. There has been some conjecture over the precipitating phase in this system, but a recent study (6) has indicated that the Laves phase, Fe_2Mo, is the stable phase in equilibrium with α-iron, up to temperatures of 950° C. Molybdenum additions of approximately 10 wt-pct or greater are necessary to provide hardening of useful magnitude. Molybdenum additions less than 9 wt-pct result in negligible hardening, because the solid solubility limit for molybdenum in α-iron at 700° C is approximately 8 wt-pct.

The high molybdenum additions necessary for useful hardening have limited application of the binary iron-molybdenum system because of limited workability; further additions, such as aluminum or chromium for oxidation resistance, are not feasible. It has also been observed that in iron alloys containing aluminum, additions of molybdenum in excess of 8 wt-pct tend to degrade oxidation resistance (1).

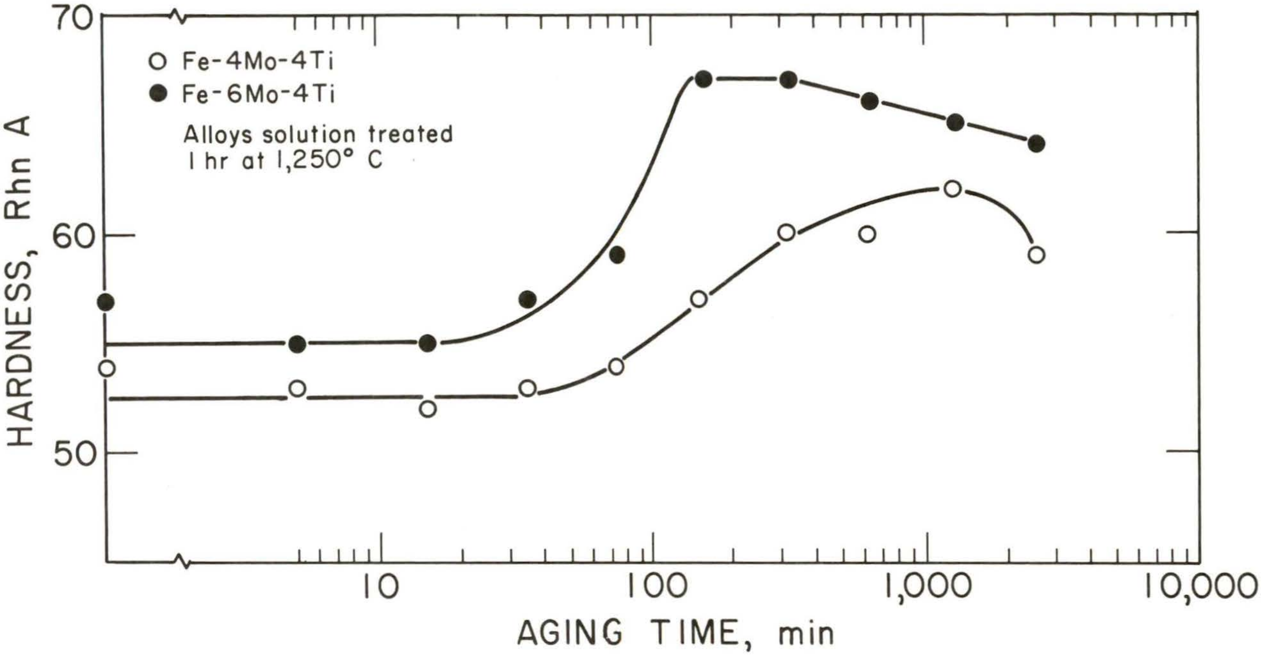

FIGURE 2. - Hardening curves for two Fe-Mo-Ti alloys. The alloys were solution treated and aged at 700° C.

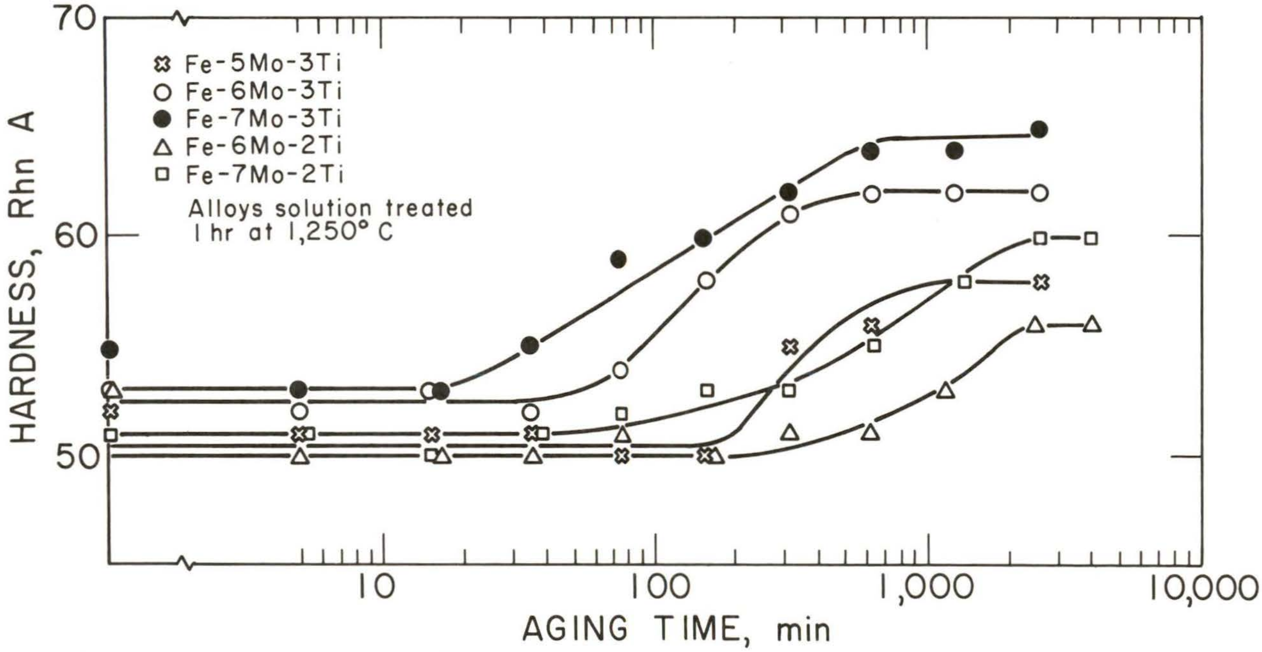

FIGURE 3. - Hardening curves for a series of ternary Fe-Mo-Ti alloys. Alloys were solution treated and aged at 700° C.

Studies of the ternary Fe-Mo-Ti system indicate small additions of titanium can be combined with molybdenum additions of less than 8-wt-pct to produce hardening characteristics of good magnitude and resistance to overaging typical of the binary iron-molybdenum system. Aging curves for ternary Fe-Mo-Ti alloys are shown in figures 2 and 3. Optimum hardening characteristics are defined in terms of (a) magnitude of hardening, from the solution heattreated, to the fully aged condition and (b) stability, or an absence of early overaging. Stability of the hardening response is the most important factor; a finely dispersed precipitate, uniformly distributed, can effectively strengthen the matrix even with a comparitively low magnitude of hardening, 5 to 6 points Rockwell A (R_A).

Figure 2 shows two curves for Fe-Mo-Ti alloys at the 4 wt-pct titanium level. At this titanium level, there is a definite tendency for the binary iron-titanium hardening characteristics to dominate and for early overaging to occur. Lowering the titanium level to 3 wt-pct (fig. 3) results in a stable hardening response over a range of molybdenum contents. If the titanium content is further reduced to 2 wt-pct, the characteristics of the binary iron-molybdenum system dominate, and a slower, stable hardening response is observed. An Fe-7Mo-2Ti alloy offered stable hardening of good magnitude (10 points R_A) during aging at 700° C. This composition was selected as a baseline composition to determine the effects of aluminum and chromium additions on the hardening mechanism.

Effect of Chromium and Aluminum Additions on Fe-Mo-Ti Alloys

Chromium and/or aluminum additions to Fe-Mo-Ti alloys should improve their oxidation resistance. The minimum amount that gives plain carbon steel good resistance to scaling at 600° to 700° C is 7 pct Cr (5, 8). The chromium and aluminum additions chosen were expected to give approximately the same oxidation protection as 7 pct Cr to steel. Oxidation tests, covering a range of aluminum plus chromium additions, were conducted and are reported in a subsequent section. This part of the report will evaluate the effects of chromium and alumium additions on the hardening characteristics, microstructure, and mechanical properties of these alloys. The alloys evaluated were the base alloy Fe-7Mo-2Ti, Fe-7Mo-2Ti-7Cr, Fe-7Mo-2Ti-4Cr-2Al, Fe-7Mo-2Ti-3Cr-3Al, and Fe-7Mo-2Ti-5Al. All the alloys studied were solution treated at 1,250° C for 1 hour, water quenched, and aged at 700° C.

The precipitation-hardening characteristics of the alloy series are shown in figure 4. A solution-treated (1,250° C, 1 hour water quenched) Fe-7Mo-2Ti alloy had a R_A 50 hardness, which after aging (700° C for 42 hours) increased to R_A 60. Addition of 7 pct Cr increased the hardness of the solution-treated alloy to R_A 55 and of the aged alloy to R_A 65. Additions of 5 pct Al resulted in a solution-treated hardness of R_A 60 and an aged hardness of approximately R_A 63. Thus, a 7-pct Cr addition added a component of solid solution hardening to the as-quenched hardness, but the magnitude of precipitation hardening remain unchanged. On the other hand, 5 pct Al added a significant, 10 points Rockwell hardness number A component of solid solution hardening, but the magnitude of precipitation, 3 points Rhn A was significantly reduced. Mixed aluminum and chromium additions resulted in intermediate changes between these two extremes (fig. 4).

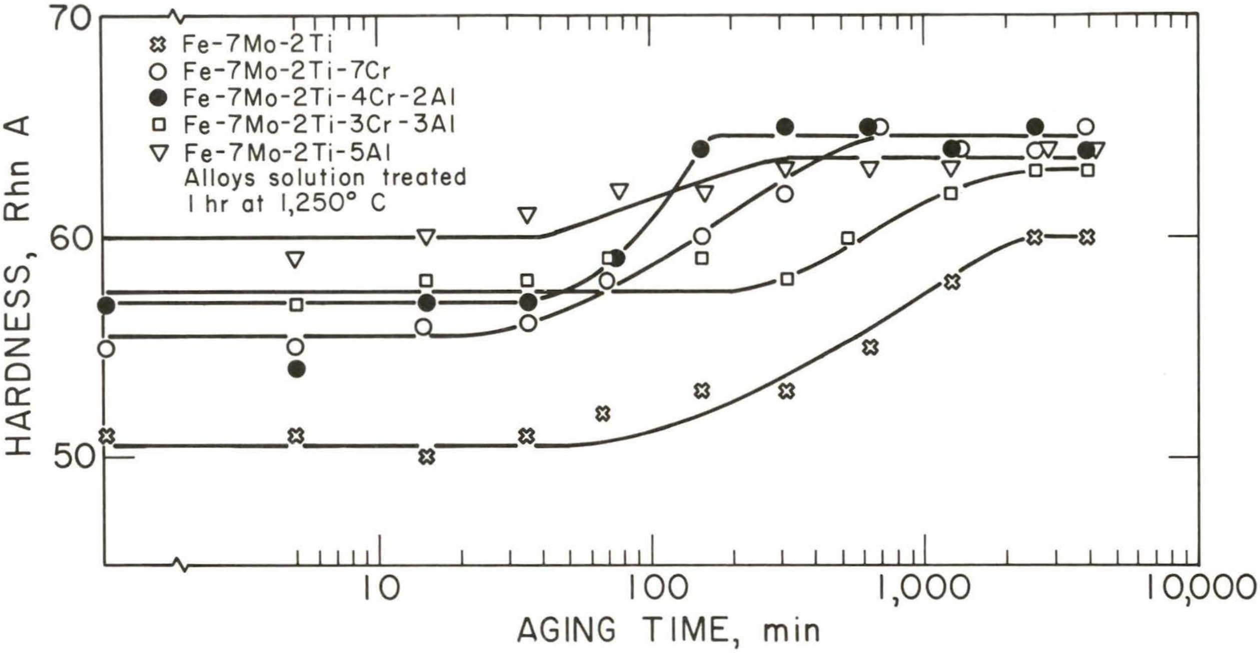

FIGURE 4. - Hardening curves for a series of Fe-Mo-Ti alloys with varying chromium and aluminum additions. Alloys were solution treated, quenched, and aged at 700° C.

A metallographic examination of the alloy series in the fully aged condition of 700° C for 42 hours indicated that aluminum and chromium had a significant effect on both the size of the precipitates and the vol-pct of precipitation. This effect is seen in figure 5 at 400 magnification and in figure 6 at 1,400 magnification. In the lower left-hand corner of both figures, the solution-treated microstructure is essentially a single-phase ferritic solid solution, which is typical of all the alloys. Grain boundaries etched rapidly in all the alloys. They contained a semi continuous network of Laves phase precipitate, which manifests itself in the extremely brittle behavior during room-temperature testing. During aging, general precipitation occurs through the body of the ferrite grains, but the grain boundaries remain unaffected. Whereas the grain boundary films are not readily apparent in optical microstructures, they are clearly visible in electron micrographs included in the final section of this report. In this final section, a spheroidizing heat treatment that induces room-temperature ductility is also described.

Photomicrographs (fig. 5-6) of the aged alloys are shown with the aluminum content increasing and the chromium content decreasing from left to right. An addition of 7 pct Cr resulted in a finer sized precipitate with an increased vol-pct of precipitation, typical of a good age-hardening alloy. Aluminum had the opposite effect: the size of the precipitates increased, and the vol-pct of precipitation decreased. This alloy age hardened to a lesser extent, and the coarse precipitate size and reduced amount of precipitate could both be anticipated to reduce the strengthening of the ferritic matrix. A mixture

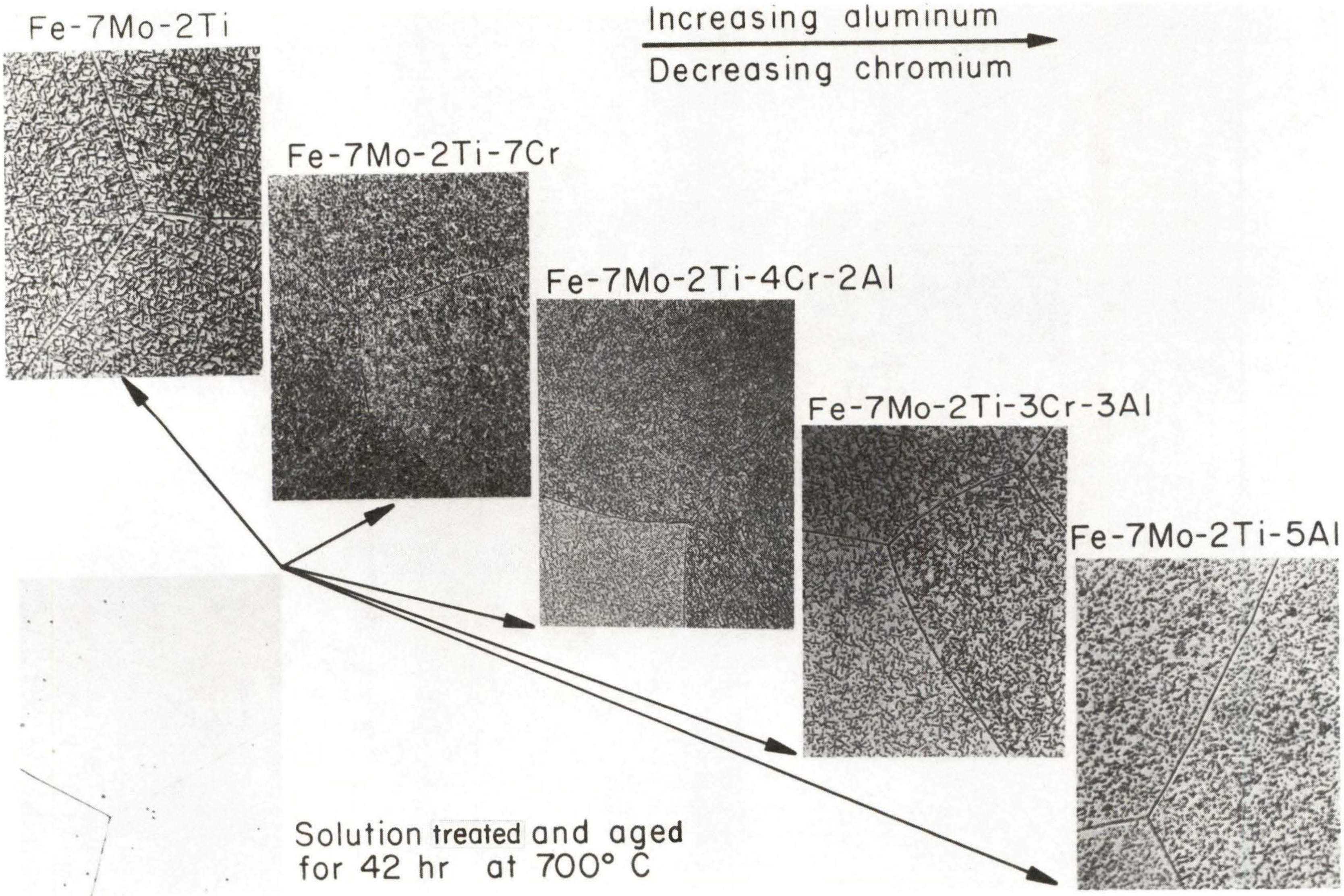

FIGURE 5. - Fe-Mo-Ti alloy series with aluminum and chromium additions, solution treated (lower left) and aged at 700° C (X 400).

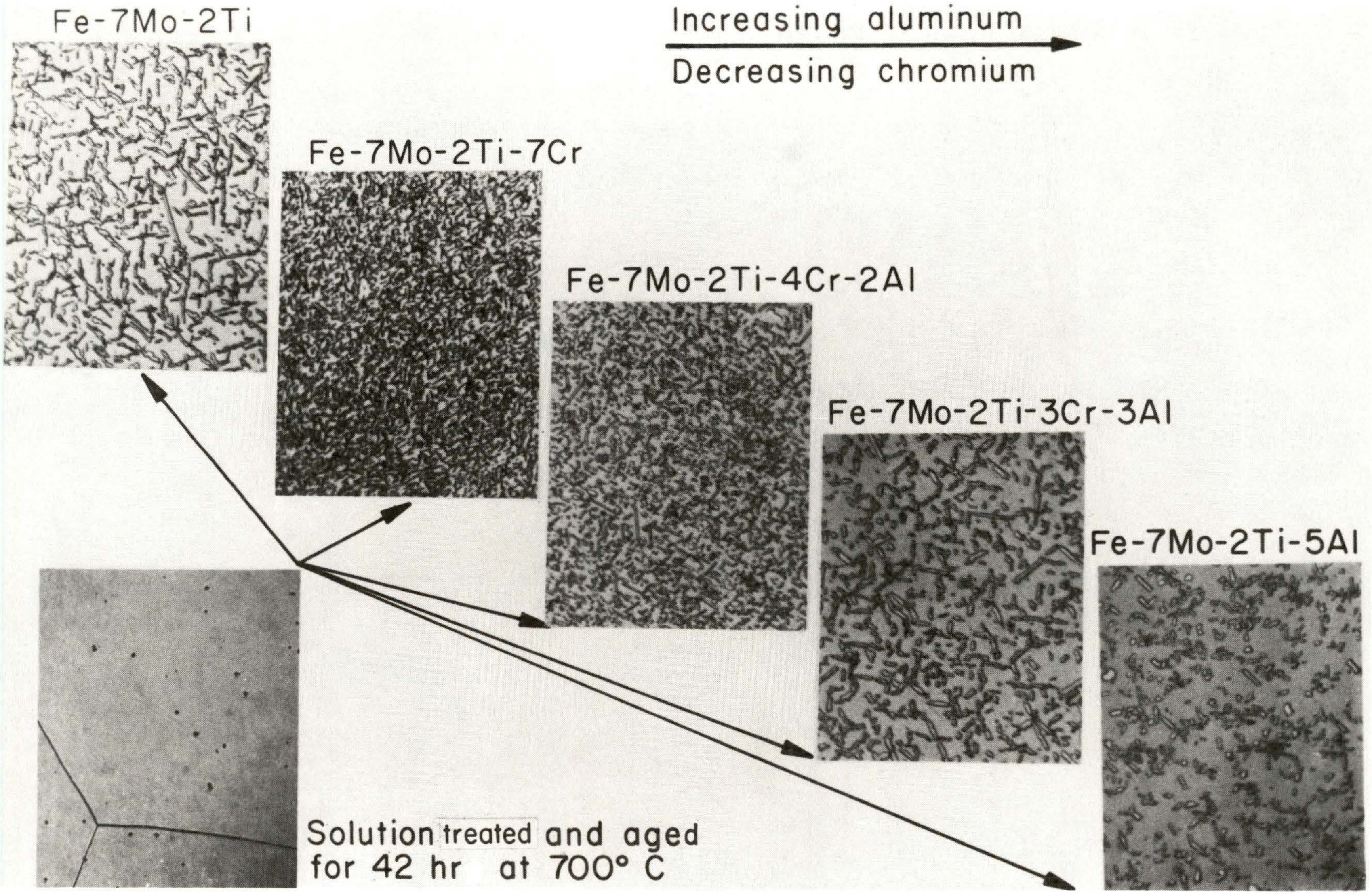

FIGURE 6. - Fe-Mo-Ti alloy series in solution-treated (lower left) and aged condition at high magnification (X 1,400).

of chromium and aluminum had counteracting effects. Both the size and vol-pct of precipitates in the Fe-7Mo-2Ti-3Cr-3Al alloy closely approximated those of the base alloy. The size of the precipitates of the alloys aged at 700° C were too fine for electron microprobe analysis, so the precipitates were coarsened by solution treating the alloys at 1,250° C for 1 hour and furnace cooling to room temperature. Photomicrographs of four furnace-cooled compositions, Fe-7Mo-2Ti; Fe-7Mo-2Ti-7Cr; Fe-7Mo-2Ti-5Al; and Fe-7Mo-2Ti-3Al-3Cr, are shown in figure 7.

The effect of chromium and aluminum additions on the precipitation in the furnace-cooled alloys correlated well with the same alloys in the aged condition. Chromium additions decreased the size of the precipitates, but increased their vol-pct; aluminum additions increased the precipitate size, and decreased their vol-pct. The amount of precipitation and the size of the precipitates for the base alloy and for the base alloy plus 3 pct Cr plus 3 pct Al was about the same. The composition of precipitates and the matrix of the solution-treated and furnace-cooled alloys, as determined by microprobe analysis, is shown in table 1. These results must be considered semiquantitative (especially in regard to the analysis of the fine precipitates), but they do explain the effects of the chromium and aluminum additions to the Fe-Mo-Ti system.

TABLE 1. - Electron microprobe analysis of Fe-Mo-Ti alloys with aluminum and chromium additions. Alloys were solution treated and furnace cooled to approximate equilibrium precipitation.

	Fe	Mo	Ti	Al	Cr
	Matrix (wt-pct)				
Fe-7Mo-2Ti	92.3	6.1	1.6	0	0
Fe-7Mo-2Ti-7Cr	87.2	4.9	1.0	0	6.9
Fe-7Mo-2Ti-5Al	85.5	7.5	2.3	4.7	0
Fe-7Mo-2Ti-3Al-3Cr	87.7	4.9	1.4	3.0	3.0
	Matrix precipitates (wt-pct)				
Fe-7Mo-2Ti	61.4	27.7	10.9	0	0
Fe-7Mo-2Ti-7Cr	57.6	28.5	8.8	0	5.1
	50.7	22.2	22.7	0	4.4
Fe-7Mo-2Ti-5Al	61.5	25.9	10.8	1.8	0
Fe-7Mo-2Ti-3Al-3Cr	58.8	25.8	12.4	1.0	2.0
	Matrix precipitates (at-pct)				
Fe-7Mo-2Ti	61.8	17.8	14.1	0	0
Fe-7Mo-2Ti-7Cr	64.2	18.4	11.4	0	6.0
	53.3	13.7	28.0	0	5.0
Fe-7Mo-2Ti-5Al	66.3	16.2	13.5	4.0	0
Fe-7Mo-2Ti-3Al-3Cr	63.6	16.3	15.6	2.2	2.3

Examining the analyses of the matrices first, it is seen that a 7 wt-pct Cr addition to the Fe-Mo-Ti system reduces the solubility of molybdenum from 6.1 to 4.9 pct and of titanium from 1.6 to 1.0 pct. Thus, more molybdenum and titanium will precipitate from solid solution as Laves phase precipitates. An aluminum addition of 5 pct has the opposite effect. The solubility of

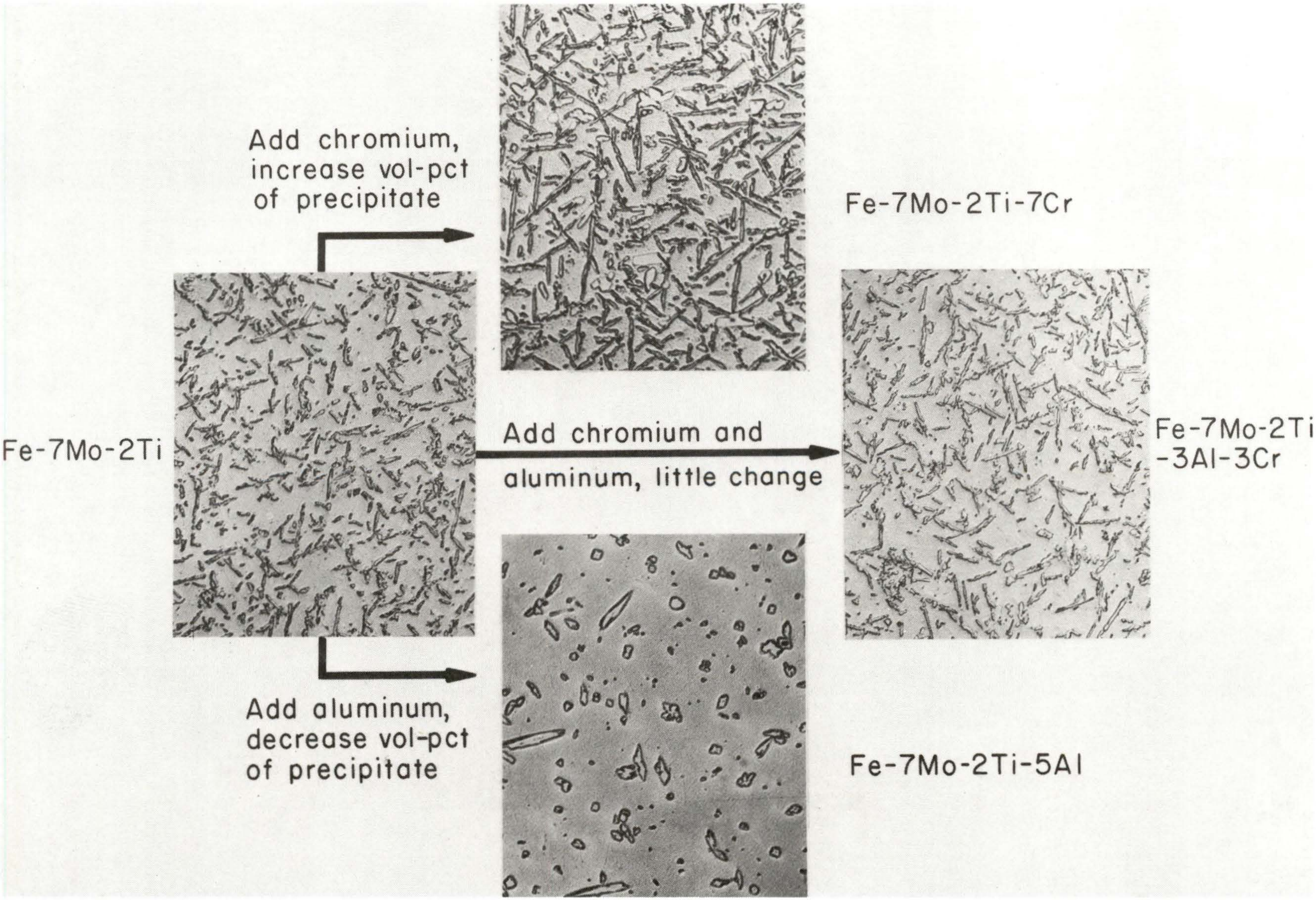

FIGURE 7. - Effect of aluminum and chromium additions on precipitation in an Fe-Mo-Ti alloy. Alloys were solution treated for 1 hr at 1,250° C, and furnace cooled to ambient temperature (X 400).

molybdenum is raised from 6.1 to 7.5 pct, and the solubility of the titanium is raised from 1.6 to 2.3 pct. This leaves less titanium and molybdenum available for precipitation. The addition of both chromium and aluminum offset each other, and the effect on solid solubility in the ferrite matrix is reduced. Analysis of the precipitate in each system showed that each alloy had precipitates in the composition range expected for the Laves phases, Fe_2 (Mo, Ti) or $(Fe, Cr)_2$ (Mo, Ti). A second precipitate, lean in iron, was detected in the 7-pct Cr alloy. There was no evidence that aluminum entered into the Laves phase precipitation. The 1.8-pct content indicated for the 5-pct Al alloy was attributed to background from the matrix and is indicative of the semiquantitative nature of the electron probe analysis of small precipitates embedded in a matrix of different composition.

The main significance of the microprobe data was in explaining the effect of aluminum and chromium on precipitation hardening in the Fe-Mo-Ti system. Aluminum decreases precipitation by expanding the range of solid solubility of molybdenum and titanium in ferritic iron. Chromium increases precipitation by decreasing solid solubility of molybdenum and titanium in the ferritic matrix, and also by substituing for some iron in quaternary intermetallic precipitates. Thus, it is evident in an Fe-Mo-Ti system containing both aluminum and chromium for oxidation resistance, all alloying additions must be balanced to produce an optimum combination of precipitation hardening, solid solution strengthening, fabricability, and oxidation resistance.

A correlation between the microstructure of the aged alloys and their elevated temperature strength was easily obtained. Stress-rupture specimens were prepared for the baseline alloy and for all alloys containing mixed chromium plus aluminum additions. (Because conservation of chromium was the goal, these were the alloys of primary interest.) Stress-rupture data (shown in table 2) reflected the size and distribution of precipitates. The Fe-7Mo-2Ti alloy with relatively coarse precipitates and little solid solution strengthening (as-quenched 51 Rhn A, maximum 60 Rhn A) had poor stress-rupture properties in spite of the high magnitude of hardening. The Fe-7Mo-2Ti-5Al exhibited strong solid solution strengthening (as-quenched 60 Rhn A), but the minimum hardening during aging (maximum hardness 63 Rhn A) and the coarse nature of precipitation resulted in little effective strengthening at elevated temperature, as reflected in poor stress-rupture properties. The Fe-7Mo-2Ti-3Cr-3Al alloy had an intermediate as-quenched hardness (57 Rhn A), indicating intermediate solid solution strengthening with a six-point increase in hardness to a maximum as-aged hardness of 63 Rhn A. This alloy yielded favorable stress-rupture properties even though precipitates are rather coarse, being comparable to those in the baseline composition, but finer than the Fe-7Mo-2Ti-5Al alloy. Thus, it appeared that a component of solid solution strengthening combined with approximately six points Rhn A were desirable for stress-rupture strength. The Fe-7Mo-2Ti-4Cr-2Al alloy combined these characteristics (as-quenched 57 Rhn A, maximum 65 Rhn A) with a fine precipitate size and, indeed, yielded the best stress-rupture properties. The stress-rupture data in table 2 compare favorably with a 100-hour stress-rupture life at a stress of 32.9 kips per square inch, or 227 megapascals, for type 316 stainless steel (_7_).

TABLE 2. - Stress-rupture properties of some Fe-Mo-Ti-Al-Cr alloys, solution treated and aged at 700° C. Stress-rupture tests at 650° C in an argon atmosphere

Composition and properties	Solution treated and aged to maximum hardness at 700° C
Fe-7Mo-2Ti:	
Stress...............kips per square inch..	
Test 1:	35
Test 2:	30
Life..................................hours..	
Test 1:	0
Test 2:	11
Elongation.............................pct..	
Test 1:	42
Test 2:	45
R in A...................................pct..	
Test 1:	70
Test 2:	71
Fe-7Mo-2Ti-4Cr-2Al:	
Stress...............kips per square inch..	
Test 1:	37.5
Life..................................hours..	
Test 1:	106
Elongation.............................pct..	
Test 1:	24
R in A......................................	
Test 1:	33
Fe-7Mo-2Ti-3Cr-3Al:	
Stress...............kips per square inch..	
Test 1:	40
Test 2:	35
Life..................................hours..	
Test 1:	1
Test 2:	80
Elongation.............................pct..	
Test 1:	32
Test 2:	31
R in A...................................pct..	
Test 1:	68
Test 2:	70
Fe-7Mo-2Ti-5Al:	
Stress...............kips per square inch..	
Test 1:	37.5
Test 2:	32.5
Test 3:	27.5
Test 4:	25

TABLE 2. - Stress-rupture properties of some Fe-Mo-Ti-Al-Cr alloys, solution treated and aged at 700° C. Stress-rupture tests at 650° C in an argon atmosphere--Continued

Composition and properties	Solution treated and aged to maximum hardness at 700° C
Life..............................hours..	
Test 1:	0.3
Test 2:	1
Test 3:	4
Test 4:	8
Elongation..........................pct..	
Test 1:	40
Test 2:	35
Test 3:	46
Test 4:	57
R in A..............................pct..	
Test 1:	65
Test 2:	38
Test 3:	64
Test 4:	65

R in A Reduction in area.

Chromium and/or aluminum additions to the Fe-7Mo-2Ti alloy had a significant effect on its workability hardness, microstructure, and mechanical properties. As the aluminum content was increased, workability of the alloy decreased. However, in the range studied, chromium had practically no effect on this property. Both aluminum and chromium additions increased the hardness of the Fe-Mo-Ti alloy by solid solution strengthening, and also by precipitation hardening. Aluminum increased the solid solution hardening more than chromium did, but precipitation hardening was minimal. On the other hand, the magnitude of the hardening observed during aging was much higher for the chromium additions than for the aluminum additions. Thus, the chromium alloys were harder in the aged condition. Chromium additions led to finer and more voluminous precipitation, whereas aluminum had the opposite effect: the precipitates were coarser and less voluminous. When added together, they had a counteracting effect. Chromium additions improved the stress-rupture life of the Fe-Mo-Ti alloys, whereas aluminum additions did not. The high-aluminum alloys contained coarse precipitates resulting in poor stress-rupture properties.

Oxidation tests are reported in a subsequent section of this report.

Room-Temperature Ductility

As discussed in the preceding section on solution-treated alloys, a coarse-grained, single-phase ferritic structure is observed with continuous grain boundary films in ferritic grain boundaries. During subsequent aging, precipitation occurs throughout the ferrite grains, but grain boundary films are eventually unchanged. These grain boundary films are not readily apparent in optical micrographs, but are clearly see in figure 9. The continuous grain boundary films lead to low room-temperature ductility (0 pct) in both solution-treated and solution-treated and aged alloys. Previous studies both by Bureau researchers and other laboratories indicated that a warm or cold working of the solution-treated alloys (3) or a spheroidizing heat treatment of the aged alloys (4) is necessary to restore room-temperature ductility. Room-temperature and elevated temperature tensile specimens and stress-rupture specimens were prepared from the baseline Fe-7Mo-2Ti alloy and the alloys with chromium and aluminum, and aluminum additions. Specimens were prepared from material that had been solution treated and aged to maximum hardness at 700° C and material that had been given a number of spheroidizing heat treatments. Spheroidizing the aged alloys was accomplished by holding the material for a fixed time at an intermediate temperature (below the solution heat treatment temperature), followed by air cooling. Initially, spheroidizing temperatures in the range 950° to 1,100° C were studied. The effect of the spheroidizing heat treatment on room-temperature ductility is readily apparent in room-temperature mechanical properties (table 3). In the aged condition and after spheroidizing at the lowest temperature (950° C), all alloys exhibited zero ductility. A 1-hour treatment at 1,000° C was the minimum treatment required to induce ductile behavior at room temperature. No treatment was successful in inducing ductile behavior in the Fe-7Mo-2Ti-5Al alloy. When a specimen fails prematurely with zero ductility, recorded ultimate tensile strength (UTS) showed a broad scatter band and are not representative. It was also observed that whereas a 1-hour treatment at 1,000° C induced room-temperature ductility in the Fe-7Mo-2Ti-2Al-4Cr alloy, a one-half hour treatment at 1,050° C resulted in marginal ductility. Thus, both time and temperature are important to the spheroidizing process.

TABLE 3. - Room-temperature tensile properties of aged and aged and spheroidized iron-base alloys

Composition and properties	Solution treated and aged to maximum hardness at 700° C	Aged and spheroidized			
		4 hours at 950° C	1 hour at 1,000° C	1/2 hour at 1,050° C	1 hour at 1,100° C
Fe-7Mo-2Ti:					
UTS..............kips per square inch..	50.9	ND	68.4	68.5	68.8
Elongation.......................pct..	0	ND	35	31	33
R in A...........................pct..	0	ND	48	60	48
Fe-7Mo-2Ti-2Al-4Cr:					
UTS..............kips per square inch..	ND	18.2	87.4	62.2	75.1
Elongation.......................pct..	ND	0	15	1	10
R in A...........................pct..	ND	0	11	<1	6
Fe-7Mo-2Ti-2Al-3Cr:					
UTS..............kips per square inch..	31.7	26.7	ND	ND	90.8
Elongation.......................pct..	0	0	ND	ND	20
R in A...........................pct..	0	0	ND	ND	18
Fe-7Mo-2Ti-5Al:					
UTS..............kips per square inch..	21.9	ND	39.7	31.3	25.5
Elongation.......................pct..	0	ND	0	0	0
R in A...........................pct..	0	ND	0	0	0

ND Not determined.
UTS Ultimate tensile strength.
R in A Reduction in area.

A summary of the elevated-temperature tensile properties of aged and aged and spheroidized alloys is shown in table 4. The ultimate tensile strength of the alloys was degraded slightly by the spheroidizing heat treatment, but the more significant engineering properties, yield strength and ductility, were unaffected.

TABLE 4. - Elevated temperature properties (650° C) of aged and aged and spheroidized iron-base alloys

Composition and properties	Solution treated and aged to maximum hardness at 700° C	Aged and spheroidized		
		1 hour at 1,000° C	1/2 hour at 1,050° C	1 hour at 1,100° C
Fe-7Mo-2Ti				
UTS...kips per square inch..	56.2	39.5	36.6	36.2
Yield.kips per square inch..	28.3	29.3	27.4	26.8
Elongation.............pct..	27	31	29	27
R in A.................pct..	65	77	71	74
Fe-7Mo-2Ti-2Al-4Cr:				
UTS...kips per square inch..	50.0	45.9	45.6	44.4
Yield.kips per square inch..	28.8	36.2	31.8	33.5
Elongation.............pct..	23	25	26	28
R in A.................pct..	60	63	66	70
Fe-7Mo-2Ti-3Al-3Cr:				
UTS...kips per square inch..	62.7	46.8	ND	50.7
Yield.kips per square inch..	35.8	36.9	ND	38.5
Elongation.............pct..	19	25	ND	27
R in A.................pct..	26	65	ND	64
Fe-7Mo-2Ti-5Al:				
UTS...kips per square inch..	60.3	ND	ND	57.7
Yield.kips per square inch..	34.7	ND	ND	36.8
Elongation.............pct..	19	ND	ND	26
R in A.................pct..	27	ND	ND	52

ND Not determined.
UTS Ultimate tensile strength.
R in A Reduction in area.

Stress-rupture properties of aged and aged and spheroidized alloys are summarized in table 5. The data indicate that spheroidization does degrade stress-rupture life slightly, but the aged and spheroidized Fe-7Mo-2Ti-2Al-4Cr and Fe-7Mo-2Ti-3Al-3Cr alloys did exhibit stress-rupture life equivalent or superior to type 316 stainless steels. By way of comparison, the stress-rupture life of type 316 stainless steel at 32.9 kips per square inch, or 227 megapascals, is 100 hours (7).

TABLE 5. - Stress-rupture properties of aged and aged and spheroidized alloys at 650° C

Composition and properties	Solution treated and aged to maximum hardness at 700° C	Aged and spheroidized for 1 hr at 1,100° C
Fe-7Mo-2Ti:		
Stress..kips per square inch..		
Test 1:	35	ND
Test 2:	30	22.5
Life..................hours..		
Test 1:	0	ND
Test 2:	11	381
Elongation..............pct..		
Test 1:	42	ND
Test 2:	45	30
R in A..................pct..		
Test 1:	70	ND
Test 2:	71	34
Fe-7Mo-2Ti-Cr-2Al:		
Stress..kips per square inch..		
Test 1:	37.5	37.5
Test 2:	ND	32.5
Life..................hours..		
Test 1:	106	80
Test 2:	ND	23.3
Elongation..............pct..		
Test 1:	24	28
Test 2:	ND	31
R in A..................pct..		
Test 1:	33	46
Test 2:	ND	58
Fe-7Mo-2Ti-3Cr-3Al:		
Stress..kips per square inch..		
Test 1:	40	37.5
Test 2:	35	32.5
Life..................hours..		
Test 1:	1	4
Test 2:	80	90
Elongation..............pct..		
Test 1:	32	41
Test 2:	31	30
R in A..................pct..		
Test 1:	68	87
Test 2:	70	62

TABLE 5. - Stress-rupture properties of aged and aged and spheroidized alloys at 650° C--Continued

Composition and properties	Solution treated and aged to maximum hardness at 700° C	Aged and spheroidized for 1 hr at 1,100° C
Fe-7Mo-2Ti-5Al:		
Stress..kips per square inch..		
Test 1:	37.5	ND
Test 2:	32.5	ND
Test 3:	27.5	ND
Test 4:	25	ND
Life...................hours..		
Test 1:	0.3	ND
Test 2:	1	ND
Test 3:	4	ND
Test 4:	8	ND
Elongation...............pct..		
Test 1:	40	ND
Test 2:	35	ND
Test 3:	46	ND
Test 4:	57	ND
R in A..................pct..		
Test 1:	65	ND
Test 2:	38	ND
Test 3:	64	ND
Test 4:	65	ND

ND Not determined.
R in A Reduction in area.

OXIDATION RESISTANCE

The baseline Fe-7Mo-2Ti composition was again selected to obtain an estimate of the chromium and aluminum additions necessary to provide oxidation resistance. This was considered necessary prior to beginning the optimization of the alloy composition because the precipitation-hardening mechanism provided by molybdenum and titanium additions had been shown to be dependent upon the amount of chromium and aluminum added for oxidation resistance. The alloys discussed in previous sections had chromium and aluminum additions that were estimated to be roughly equivalent to a 7-pct Cr addition the minimum that provides some scaling resistance to iron-base alloys at elevated temperature.

A series of arc-melted, 100-gram buttons of the 7Mo-2Ti base were prepared with varying chromium and aluminum additions. The buttons were remelted a minimum of three times to aid homogeneity. The homogeneity of arc-melted buttons did not compare with material from a larger ingot but because the tests were preliminary, the procedure allowed the rapid scanning of a number of compositions.

Specimens were held at 700° C for 200 hours in air. The results of the oxidation tests are plotted on the ternary diagram in figure 8. Relatively low levels of aluminum (2 pct) in combination with chromium greatly enhanced the oxidation resistance of the Fe-Mo-Ti alloy. Combinations of chromium plus aluminum were effective in providing a continuous resistant oxide film, and specimens retained a bright appearance after exposure and showed little weight gain. Neither chromium or aluminum was as effective alone as they were in combination.

It was concluded after these preliminary oxidation tests that combined additions of aluminum and chromium would be used in the final optimization process to provide oxidation resistance. To conserve chromium, the amount of aluminum should be high even though it is in contradiction with studies indicating that aluminum tends to degrade the hardening mechanism. The range of aluminum plus chromium additions selected for final optimization studies was 2 to 4 pct Al and 3 to 8 pct Cr.

The ternary Fe-7Mo-2Ti composition discussed in this report was selected on the basis of hardening characteristics to study the effect of chromium and aluminum additions. Prior to final optimization and evaluation (which will be described in a later report), it was necessary to select a range of molybdenum plus titanium additions for consideration.

Composition ranges for alloy optimization

Several series of 100-gram ingots were prepared by arc melting. The series was based on varying molybdenum and titanium additions with aluminum

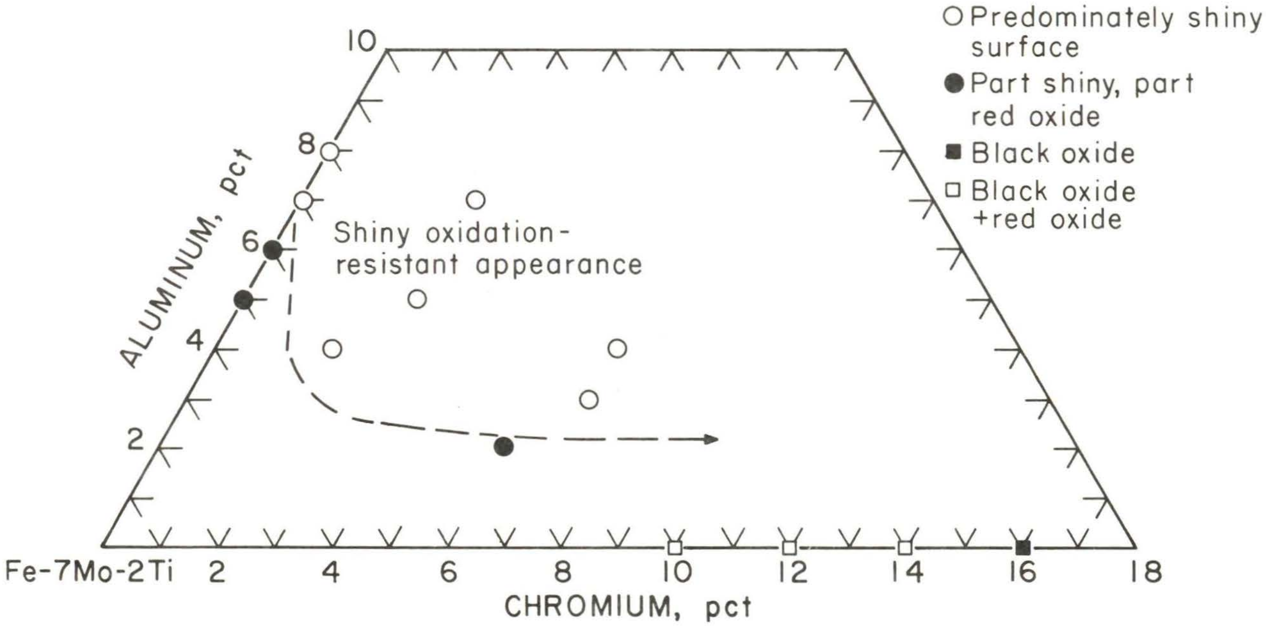

FIGURE 8. - Appearance of Fe-7Mo-7Ti alloys with various chromium and/or aluminum contents after 200 hours' oxidation at 700° C.

and chromium additions within the range selected for alloy optimization. The ingots were evaluated for hardening characteristics and workability. A typical series of compositions is outlined in table 6 for alloys containing a 3-pct Al plus 3-pct Cr addition. Similar compositions were run with 2-pct Al plus 4-pct Cr additions.

TABLE 6. - A series of Fe-Mo-Ti-Al-Cr compositions to study the effect of composition on hardening characteristics and workability

(pct, balance is iron)

Molybdenum	Titanium	Aluminum	Chromium
7	2	3	3
6.5	2.5	3	3
6	2.5	3	3
5	2.5	3	3
4	2.5	3	3
6	3	3	3
5	3	3	3
4	3	3	3
6	3.5	3	3
5	3.5	3	3
4	3.5	3	3
6	4	3	3
5	4	3	3
4	4	3	3

All the ingots were forged and rolled to 0.1-inch sheet to test workability, and specimens were cut for solution heat treatment and aging studies. Thin foils were prepared from selected compositions for transmission electron microcopy to study the size and distribution of precipitates.

All alloy compositions were workable. At titanium contents of 3.5 pct and above, some edge cracking was observed in the rolled sheet. Within the composition range 4 to 7 pct Mo and 2 to 3 pct Ti, all alloys were readily workable and a 5- to 10-point increase in hardness between the as-quenched and fully aged condition was observed. The alloys were resistant to early averaging. Precipitation hardening of this magnitude, combined with the solid solution strengthening of the chromium and aluminum additions, was anticipated to yield elevated temperature strengths equivalent to stainless steels. Transmission electron microscrope studies were conducted at the Argonne National Laboratory by Donald Potter. Solution-treated materials were dislocation-free, typical of well-annealed material. Attempts to observe a grain boundary in the solution-treated alloy were not successful, but the grain boundaries were observed in a fully aged sample, and the presence of grain boundary films was confirmed by direct observation. Several electron micrographs of the fully aged alloy Fe-4Mo-2Ti-4Cr-2Al are shown in figure 9. Uniform precipitation is observed throughout the matrix of the material, and

FIGURE 9. - Electron micrographs of fully hardened Fe-4Mo-2Ti-4Cr-2Al alloy. *A*, Precipitate particles, X 50,000; *B*, precipitate particle, X 100,000; *C*, grain boundary (white arrow), X 20,000; and *D*, black arrows show dislocation loops, X 100,000.

in two of the micrographs grain boundaries (see arrows) are clearly coated with a continuous film of precipitate. Precipitate particles are associated with clusters of dislocations, indicating a substantial difference in specific volume between the matrix and the precipitate particles. One specimen was prepared that had been aged just to the onset of precipitation. This sample showed a nonuniform precipitate dispersion (precipitation becomes uniform as aging proceeds) with precipitate particles in the size range 0.1 to 5 micro-inch size. Again, precipitate formation was accompanied by the generation of a high density of dislocations.

The uniform precipitate dispersions and the associated high-dislocation densities undoubtedly both contributed to the precipitation strengthening of the fully aged alloy.

Based on the hardening characteristics and workability of the alloy series studied and discussed above, the composition range selected for final optimization studies was narrowed to the following range:

Fe-4 to 6 pct Mo-2 to 3 pct Ti-2 to 4 pct Al-3 to 8 pct Cr.

Compositions in this range are anticipated to yield workable alloys with stable hardening of 5 to 10 points R_A. A fine, uniform precipitate typical of age hardening alloys can be anticipated with elevated-temperature strengths equivalent to the high-volume stainless steels. Room-temperature ductility will be induced by spheroidizing heat treatment. Oxidation resistance in the 600° to 700° C temperature range will be provided by the aluminum and chromium additions. Current studies are aimed at selecting a final composition in this range and fully evaluating the alloy in terms of mechanical properties, oxidation, and corrosion resistance. A report on the evaluation will be published at the conclusion of the project.

SUMMARY AND CONCLUSIONS

A ternary Fe-Mo-Ti system was studied as a potential base composition for a low-chromium, nickel-free stainless steel.

Precipitation-hardening mechanisms in the Fe-Mo-Ti stainless steel substitute system were studied in some detail. Aluminum and chromium additions to the baseline Fe-7Mo-2Ti composition were assessed in terms of hardening characteristics, workability, oxidation resistance, and mechanical properties. Conclusions of the study can be summarized as follows:

1. The stability of the hardening response in binary iron-molybdenum can be combined with the high magnitude of hardening of the binary iron-titanium system to yield a ternary alloy that has useful hardening characteristics and a broad composition range.

2. Aluminum and chromium additions have marked effects on solid solubility limits in the ternary Fe-Mo-Ti system

3. Aluminum additions increase the range of solid solubility of molybdenum and titanium in ferritic iron. The vol-pct of precipitation in solution-treated and aged material is decreased by the presence of aluminum, and the size of precipitates solution-treated and aged material is increased.

4. Chromium decreased the range of solid solubility of molybdenum and titanium in ferritic iron. The vol-pct of precipitates in solution-treated and aged alloys is increased by the presence of chromium, and at least two separate intermetallic precipitates containing chromium were observed. Chromium induces a fine precipitate in solution-treated and aged alloys.

5. For optimum stress-rupture properties, precipitate size and distribution, solid solution strengthening, and the magnitude of precipitation hardening response are all factors to be considered. Stress-rupture properties equivalent to 304 and 316 stainless steel can be achieved.

6. Based on workability, hardening characteristics, mechanical properties, and oxidation studies, a composition range of Fe-4 to 6 pct Mo-2 to 3 pct Ti-2 to 4 pct Al and 3 to 8 pct Cr was selected for optimization and characterization studies.

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