THE UNIVERSITY OF MICHIGAN

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ADDITIVE EFFECTS OF ALLOYING ELEMENTS UPON THE MECHANICAL PROPERTIES OF CAST AUSTENITIC ALLOYS AT 1500°F

D. L. Sponseller
R. W. Kraft
R. A. Flinn

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SUMMARY

An iron-base, cast heat-resistant alloy has been developed which exhibits three times the stress rupture strength at 1500°F of conventional cast alloys of similar nickel plus chromium levels. The approach consisted of first determining the properties of a simple single-phase austenitic base material (18% Ni, 18% Cr, balance Fe) and then determining the changes in structure and properties when B, C, Mo, Al, Cb, Ti and N were added singly. From these data, alloys were calculated containing combinations of the most promising elements. Surprisingly, in many cases the individual effects were completely additive. In this way, an analysis containing 18% Ni, 18% Cr, 0.3% C, 1.25% B, and 5% Mo was developed which exhibits approximately 30,000 psi 100-hour rupture strength at 1500°F. Adequate ductility was obtained by investigating the effects of spheroidizing heat treatments and variations in this analysis upon structure and properties.

INTRODUCTION

In the development of alloys for use at elevated temperatures, the approaches that have been used vary from the factorial experiment type in which the effects of multiple changes in chemical analysis are correlated with mechanical properties to the more basic type in which the effects of single elements upon the structure and properties of pure iron are considered.

In the present investigation, in which the objective was to develop maximum 100-hour rupture strength at 1500°F in a moderately alloyed iron-base material, a somewhat different approach was employed. First, instead of pure iron a relatively simple, single-phase austenitic composition was sought which would contain minimal amounts of alloying elements, yet be stable when modest (1-5%) amounts of other alloys were added later. It was also desired that the alloy be sufficiently oxidation resistant so that this effects would not obscure the mechanical properties at 1500°F. Accordingly, an 18% nickel, 18% chromium iron-base composition was developed.

After selection of this base composition the approach was to add alloying elements singly and to observe the effects upon properties and microstructure. Then heats with combinations of the more promising elements were tested to determine the relation between the simple and the combined effects. Cast specimens were used so that forgeability was not a problem and therefore wide variations in brittle precipitates such as borides and carbides could be tested.

The literature regarding cast and wrought compositions similar to the 18% nickel 18% chromium base analysis has been reviewed recently in reference (1). It will suffice here to list the typical properties of some commercial alloys of related composition and structure for comparison (2).

COMPARATIVE PROPERTIES OF COMMERCIAL ALLOYS
AND SIMPLE BASE ALLOY

	Cr	Ni	C	1500° F 100-Hr Rupture Strength, psi
HI alloy	28	15	0.35	10,000
HK alloy	26	20	0.40	10,000
HT alloy	15	35	0.55	12,500
Base alloy	18	18	0.[illegible]	4,600

It is apparent that the base analysis is much lower in strength than the commercial alloys. This only serves to emphasize the need for evaluation of the effects of relatively small amounts of "residual" elements. It will be demonstrated that although the properties for the simple base alloy are half those of the commercial material, the properties eventually developed by systematic exploration of single and combined effects are nearly three times those of the commercial alloys.

EXPERIMENTAL PROCEDURE

The procedure employed has been described in detail in reference (1). Briefly, small high-frequency induction furnace heats using the highest purity commercially available elements were melted under an argon blanket. Ethyl silicate-bonded investment molds containing eight separately risered test bars were poured under rigidly controlled conditions. All bars were inspected by a critical x-ray technique before approval for testing.

It was found that by using virgin materials and rigidly standardized melting practice, the aim analyses could be achieved within close limits. Selected heats were analyzed, and the results for those heats referred to in this report which were analyzed are given in Table I.

TABLE I

CHEMICAL ANALYSIS OF EXPERIMENTAL HEATS

Heat No.	Aim Analysis(Wt. Percent)	Cr	Ni	C	B	Mo
R45	18 Cr, 18Ni	17.4	17.2	-	-	-
R48	18 Cr, 18Ni, 0.1C	N.A.(1)	N.A.	0.09		-
R81	18 Cr, 18Ni, 0.5C	16.9	18.5	0.43		-
R101	18 Cr, 18Ni, 15 Mo	N.A.	N.A.	-		13.3
R105	18 Cr, 18Ni, 0.5B	N.A.	N.A.	-	0.31(2)	-
R122	18 Cr, 18Ni, 1.0C	N.A.	N.A.	0.81	-	-
R180	18 Cr, 18Ni, 1.0B	17.0	17.5	-	0.66	-
R275	18 Cr, 18Ni, 0.5C, 2B, 5 Mo	16.4	18.2	0.52	1.48	4.67
R305	18 Cr, 18Ni, 0.5C, 0.5 B, 5Mo	N.A.	N.A.	0.37	0.22	N.A.
R313	18 Cr, 18Ni, 0.4C, 2B, 5 Mo	16.4	15.3	0.44	1.48	4.82
R317	18 Cr, 18Ni, 0.3C, 2B, 5 Mo	N.A.	N.A.	0.33	1.52	4.73
R351	18 Cr, 18Ni, 0.3C,1.25B, 5Mo	17.2	18.1	0.35	1.19	5.30
R364	18 Cr, 18Ni, 0.3C,1.25B,5Mo	N.A.	N.A.	0.29	0.99	4.97

(1) Not analyzed.

(2) The low values for boron may be due to the difficulty encountered in analyzing for this element.

DISCUSSION OF RESULTS

The data may be discussed conveniently in three sections:

1. Effect of elements added singly upon mechanical properties at 1500° F.
2. Effect of elements added in combination upon mechanical properties.
3. Experiments to improve ductility.

1. Effect of Elements Added Singly Upon Mechanical Properties at 1500° F.

The elements of principal interest are boron, carbon, molybdenum, aluminum, titanium, columbium and nitrogen, and the effects may be discussed in this order:

a. Boron. As boron is added, the strength at 1500° F improves continuously as indicated by Table II and Figure 1. At 2% boron the 100-hour rupture strength is over three times that of the base alloy. The details of this effect have been discussed.(1) Briefly, a complex boride containing Fe_2B, Cr_2B and CrB is present at the 0.5% boron level and increases in thickness as boron increases, Figure 2. It would not be expected in general that further boron additions beyond the level necessary to establish a continuous network would continuously improve the strength as the data indicate. It has been found(1) that the amount of boride dispersed within the austenite grains, particularly at subgrain boundaries, also increases with the added boron. While this effect would not be possible in a two-component condensed system under equilibrium conditions, it is readily explainable either on the basis of more than two components, or from non-equilibrium freezing. This observation is

TABLE II

EFFECTS OF INDIVIDUAL ELEMENTS UPON MECHANICAL PROPERTIES OF BASIC 18% Cr - 18% Ni ANALYSIS

			1500°F. Properties					
Heat No.	Addition to Basic 18% Cr 18% Ni Analysis (Wt. Pct.)	Rm. Temp. T.S. (psi)	T.S. (psi)	Increase over Base Analysis	10-Hr. R.S. (psi)	Increase over Base Analysis	100-Hr. R.S. (psi)	Increase over Base Analysis
Base Analysis								
R26, R37, R40, R45	-	51,700(1)	16,000	-	6,500	-	4,600	-
Boron								
R105	0.5 B	68,000	23,200	45%	12,500	92%	8,800	91%
R180	1.0 B	72,800	27,500	72%	15,000	131%	10,900	137%
R192,R328	2.0 B	-	37,200	133%	18,900	189%	12,300	167%
Carbon								
R48	0.1 C	-	19,400	21%	9,100	40%	5,900	28%
R81,82	0.5 C	63,300	30,400	90%	21,000	223%	11,600	152%
R122	1.0 C	73,500	34,300	114%	25,100	286%	20,000	335%
Molybdenum								
R63,R304	5.0 Mo	-	23,300	46%	17,800	174%	11,300	146%
R94,R101	15.0 Mo	77,000	58,000	262%	24,000	269%	16,600	261%
Other Elements								
R41	5.0 Al	-	20,400	28%	10,100	55%	7,500	63%
R93,R127	5.0 Ti	-	34,200	114%	20,000	208%	11,200	143%
R253	4.0 Cb	-	34,000	113%	12,800	97%	8,600	87%
R138	0.5 N	73,100	28,000	75%	13,600	109%	8,500	85%

(1) Rm. Temp. T. S. obtained by extrapolation of carbon series to zero carbon.

TABLE III

EFFECTS OF SELECTED COMBINATIONS OF ELEMENTS UPON MECHANICAL PROPERTIES OF BASIC 18% Cr - 18% Ni ANALYSIS

			1500°F. Properties					
Heat No.	Addition to Basic 18% Cr 18% Ni Analysis (Wt. Pct.)	Rm. Temp. T.S. (psi)	T.S. (psi)	Increase over Base Analysis	10-Hr. R. S. (psi)	Increase over Base Analysis	100-Hr. R. S. (psi)	Increase over Base Analysis
R26, R37, R40, R45 (Avg)	0(Base Analysis)	(51,700)	16,000	-	6,500	-	4,600	-
R164	0.5 C, 0.5 B	-	38,600	141%	21,000	223%	13,800	200%
R273	0.5 B, 5 Mo	71,700	34,600	116%	21,300	228%	13,300	189%
R305	0.5 C, 0.5 B, 5 Mo	-	51,000	219%	29,400	352%	25,000	444%
R233, R275 (Avg. of both)	0.5 C, 2.0 B, 5 Mo	72,500	65,000	306%	42,700	557%	32,100	598%

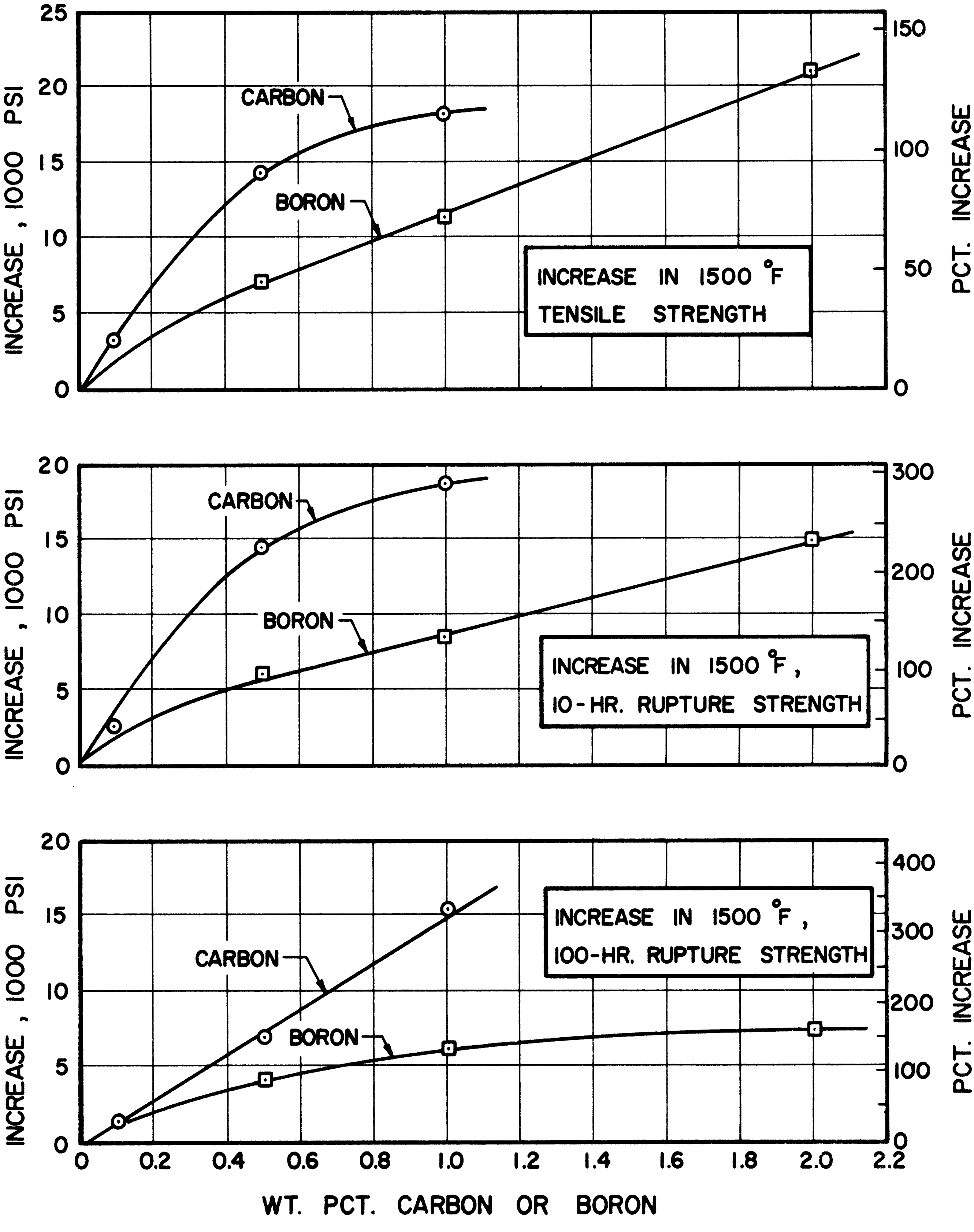
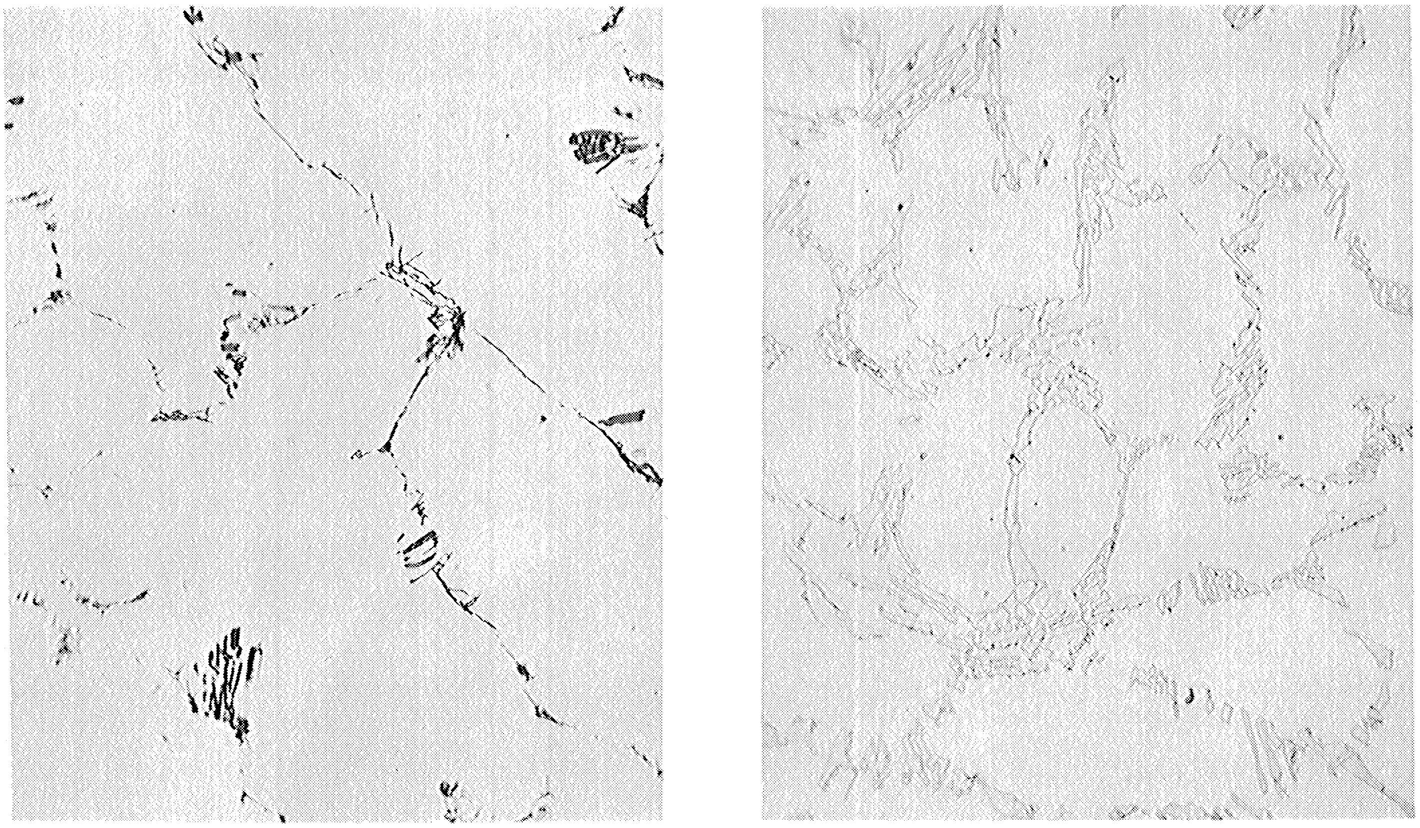


Figure 1. Effect of Boron and Carbon Additions Upon the 1500°F Properties of the Basic 18% Chromium - 18% Nickel Analysis.



(a) Heat R105, containing 0.5% boron, shows a limited amount of gram boundary constituent.

(b) At the 1.0% boron level of heat R180, the grain boundary network is quite extensive. A multiphase nature is evident in this constituent.

Figure 2. Effect Upon As-Cast Microstructure of Boron Additions to the Basic 18% Chromium - 18% Nickel Analysis. X500.

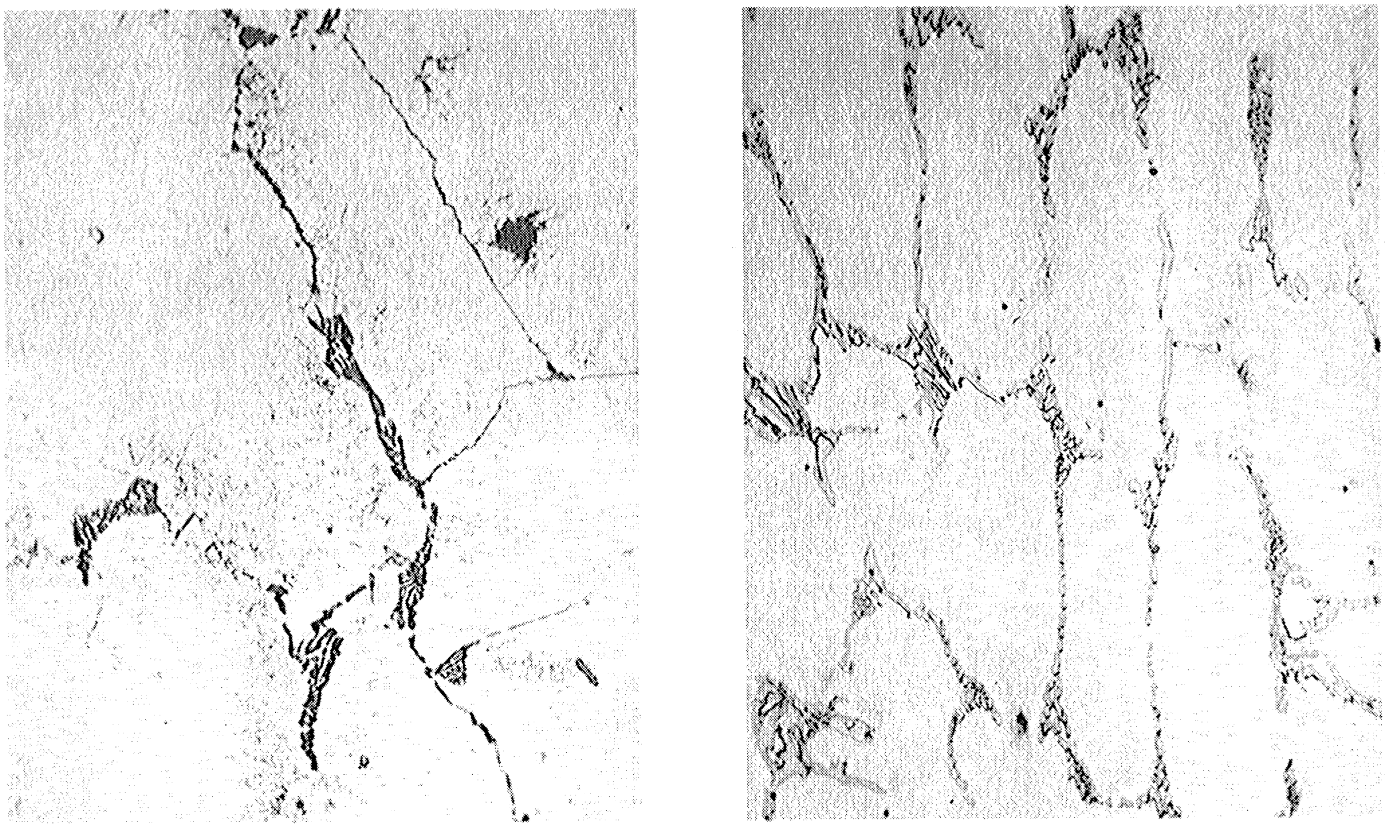
of more than passing importance because it is encountered in the other systems to be discussed.

b. Carbon. The effect of relatively large amounts of carbon is even stronger than that of boron. Increases in strength at 1500° F of up to 335% above the base level were observed at 1% carbon, as seen from Table II and Figure 1. In the microstructure of the 0.5% carbon analysis pictured in Figure 3(a), a limited amount of carbide is evident at grain boundaries, and a fine precipitate is distributed throughout the matrix. At 1% carbon, an extensive grain boundary network is encountered, Figure 3(b).

The continuous strengthening by carbon, even after the first appearance of grain boundary carbide, is considered to be similar in principle to that of boron.

c. Molybdenum. Molybdenum concentrations of 5 and 15% improve strength considerably, Table II. At the 5% level, the strengthening is due presumably to solid solution effects exclusively, because virtually no grain boundary constituent is present. The greater strengths resulting from the 15% molybdenum addition to the base analysis are accompanied by a very large amount of grain boundary constituent. This higher molybdenum level was not explored further because of poor oxidation resistance at elevated temperatures.

d. Other Elements. Aluminum, columbium, titanium and nitrogen were also added individually to the basic iron-chromium-nickel analysis. The data of Table II show that each of these elements improves properties of the base analysis. Of these elements, only titanium had a pronounced strengthening effect. It was not given further consideration, however,



a) Heat R80, containing 0.5% carbon, exhibits very little grain boundary carbide, and some fine matrix precipitate.

(b) Considerably more grain boundary carbide is evident at the 1.0% carbon level of heat R122.

Figure 3. Effect Upon As-Cast Microstructure of Carbon Additions to the Basic 18% Chromium - 18% Nickel Analysis. X500.

because of its detrimental effect upon casting quality, producing a very poor surface.

2. Effect of Elements Added in Combination Upon Mechanical Properties

After reviewing the effects of elements added singly, combinations of the more promising elements carbon, boron and molybdenum were chosen for further investigation.

Data for a few selected alloys in this category are listed in Table III. Here it is seen that very large increases in strength at 1500° F can be realized by appropriate multiple additions to the base analysis. Most notable of these is the seven-fold increase (to 32,000 psi) in 100-hour rupture strength which is brought about by the addition of 0.5% carbon, 2% boron and 5% molybdenum to the base analysis.

The data for various carbon and boron levels with 5% molybdenum are presented in Figure 4. As an attempt at correlation the individual strengthening effects at various alloy levels were simply added and plotted as dashed lines for comparison with the experimental values. Here three of the six experimental curves lie above the calculated curves, and two experimental curves lie very close to the calculated curves. In just one case, that of the 10-hour rupture strength at the 0.5% boron level, does the experimental curve lie significantly below the calculated curve.

Unfortunately the microstructure of the final alloy is rather complex, so that a complete correlation between structure and properties is not possible. Although a better fit could probably be obtained, this would be as empirical as the simple addition procedure. The important feature is that by the approach of testing individual alloys singly,

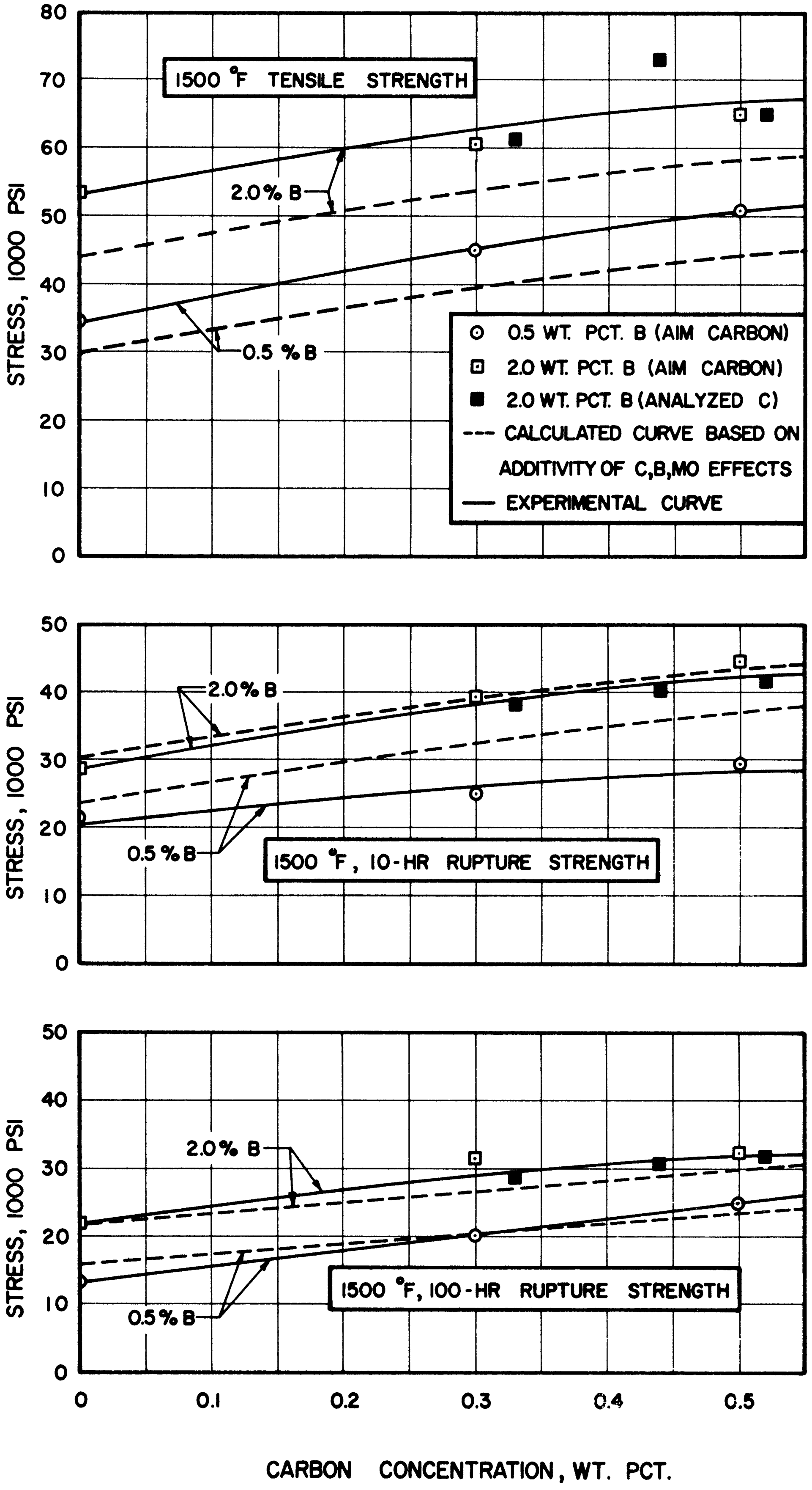


Figure 4. Comparison of Calculated and Observed Effects of Alloying Elements. The calculated curves are based on simple additivity of the effects of 5% molybdenum and varying amounts of boron and carbon on properties of the basic 18% chromium - 18% nickel analysis.

improvement factors can be developed which are approximately additive in the ranges tested.

3. Experiments to Improve Ductility

The analysis which provided the highest strength at 1500° F (0.5% C, 2% B, 5% Mo) lacked ductility, particularly at 70°F. To improve upon this condition, certain compositional changes and heat treatments were investigated.

a. Initial Reduction of Carbon and Boron Concentrations. As a first attempt at improving ductility, carbon and boron concentrations were reduced from the levels just described for the R233 analysis to the levels of the R351 analysis, 0.3% carbon and 1.25% boron. This change was accompanied by a considerable reduction in the amount of grain boundary constituent. For the sake of comparison, key properties are given in Table IV. The limited amount of room temperature testing failed to show an improvement in ductility due to the compositional change. Ductility in rupture tests run at 30,000 psi did show considerable improvement, although it is recognized that ductility in this type of test need not be uniquely related to room temperature ductility.

A moderate reduction in 100-hour rupture strength at 1500° F is noted, which would be expected on the basis of the additivity considerations discussed earlier. The microstructure of the R351 type, lower carbon, lower boron analysis is shown in Figure 5.

b. Effect of Spheriodizing Heat Treatment upon Ductility. As another approach toward improving ductility, spheroidizing treatments at 2150° F were conducted for different intervals upon the 0.3% carbon, 1.25% boron, 5% molybdonem analysis. The series of specimens of Figure 6

TABLE IV

COMPARISON OF MECHANICAL PROPERTIES AT TWO LEVELS OF CARBON AND BORON

	Rm. Temp. Properties(1)			Average 1500°F Properties		
				100-Hr. Rupture Strength (psi)	30,000 psi Test to Rupture	
Analysis	T.S.	Elong. (Pct.)	R.A. (Pct.)		Elongation (Pct.)	R.A. (Pct.)
R 233 Type (18% Cr, 18% Ni, 0.5% C, 2.00% B, 5% Mo, Bal. Fe)	72,500	1.5	-(2)	31,900	8.5	9.0
R 351 Type (18% Cr, 18% Ni, 0.3% C, 1.25% B, 5% Mo, Bal. Fe)	83,200	1.25	2.7	29,700	12.3	15.2

(1) Rm. temp. properties for the R233 analysis are the results of a single test; those for the R351 analysis are the average values of two tests.

(2) Broke at gage mark.

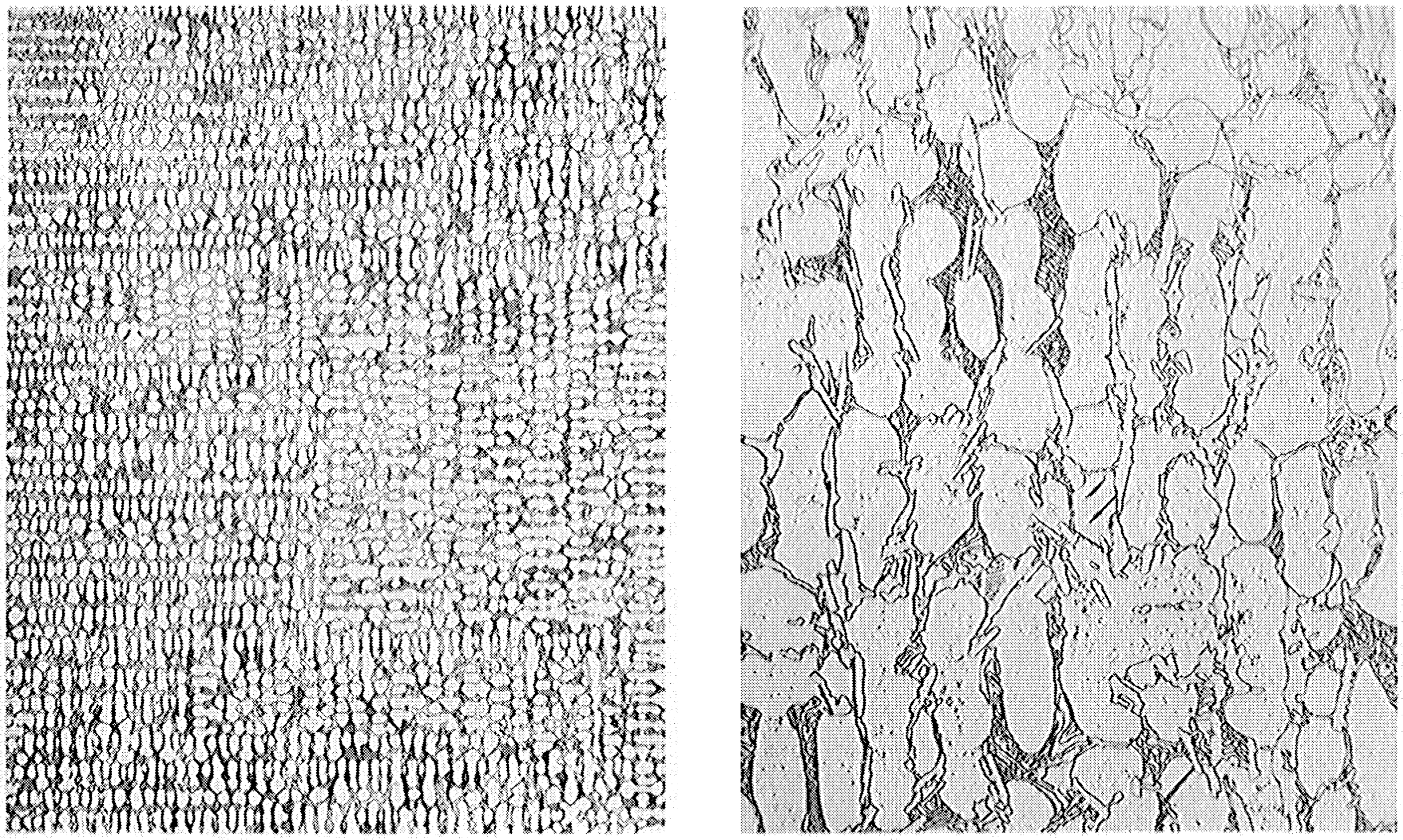
TABLE V

EFFECT OF 2150°F/1 HR. HEAT TREATMENT UPON PROPERTIES OF R351-TYPE ANALYSIS

(18% Cr, 18% Ni, 0.3% C, 1.25% B, 5% Mo, Bal. Fe)

Heat No.	Condition	Rm. Temp. Elong. (Pct. in 1 inch)	Rm. Temp. R.A. (Pct.)	1500°F Life under 30,000 psi Stress, Hr.
R404	2150-1-AC(1)	2.5	1.5	157
R405	2150-1-AC	3.0	4.5	115
R421	2150-1-AC	2.0	2.5	144
		Avg. 2.5	Avg. 2.83	Avg. 139 (100 Hr. R.S. ≃ 31,100)
R351	As-Cast	1.5	3.0	96
R364	As-Cast	-	-	92
R421	As-Cast	1.0	1.5	81
		Avg. 1.25	Avg. 2.25	Avg. 90 (100 Hr. R.S. ≃ 29,600)

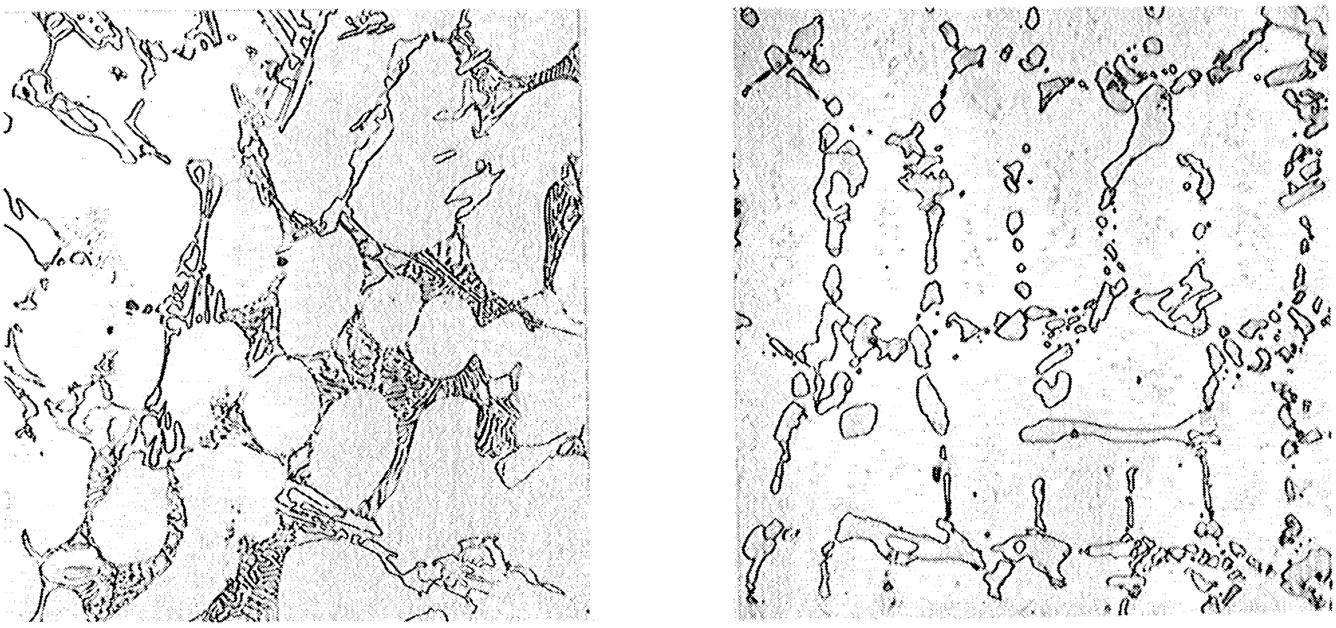
(1) 2150-1-AC means that specimens were annealed at 2150°F. for 1 hour and air-cooled.



(a) X100

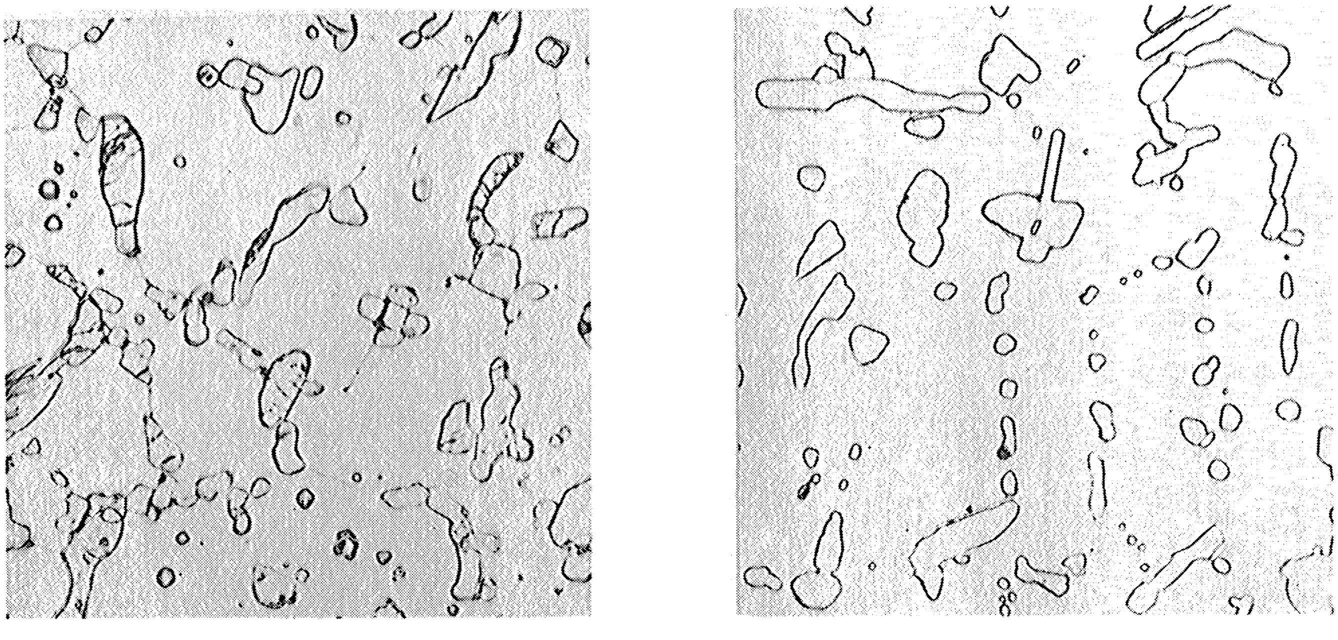
(b) X500

Figure 5. As-Cast Microstructures of R351 (18% Cr, 18% Ni, 0.3% C, 1.25% B, 5% Mo).



(a) As-cast (b) 1

(b) 2150°F, 1 hr., air cooled



(c) 2150°F, 5 hr., air cooled

(d) 2150°F, 24 hr., air cooled

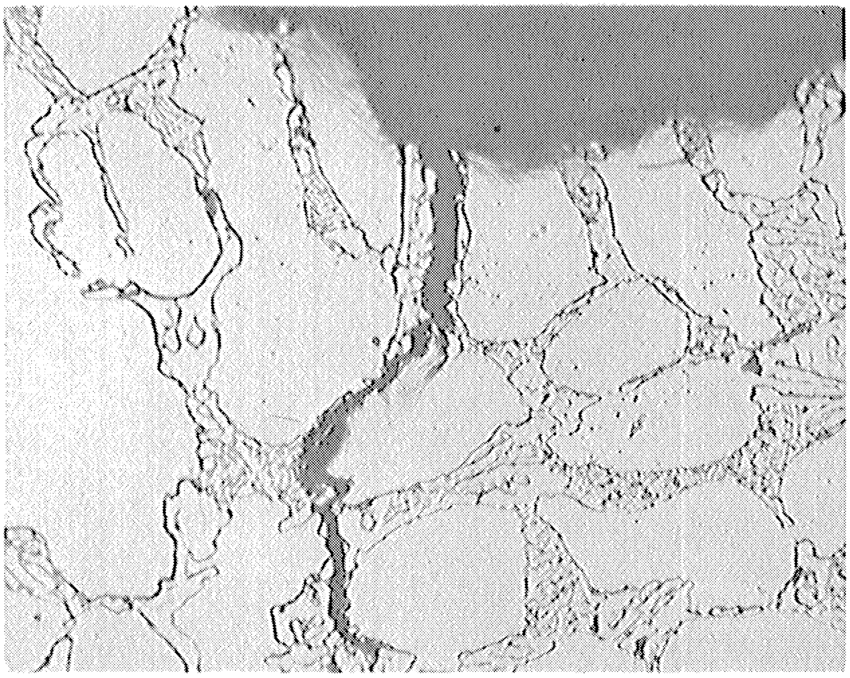
Figure 6. Spheroidization of R351 - Type Analysis (18% Cr, 18% Ni, 0.3% C, 1.25% B, 5% Mo). Heat R405 is pictured here. X500. Spheroidization of the grain boundary constituent has begun in the 1-hour specimen and is progressively more advanced after 5 and 24 hours.

shows that spheroidization is appreciable after one hour, and far advanced after 24 hours. To explore the effect of spheroidization upon ductility in more detail than possible with the tensile test, microbend specimens were prepared and observed (Figure 7) with the "strain viewer", the use of which is described in reference (3).

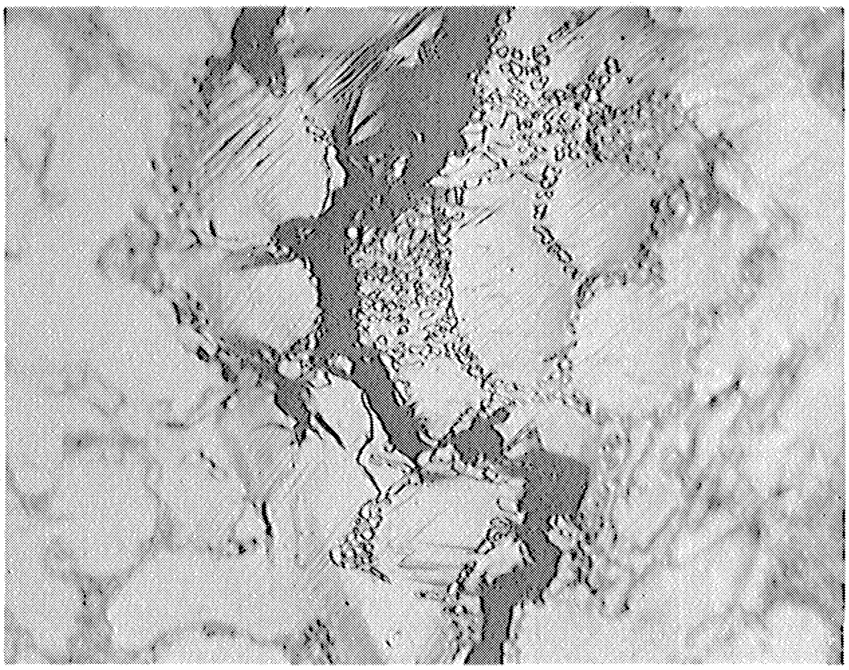
The difference between propagation of cracks in the as-cast and the spheroidized conditions is rather striking. In Figure 7(a) a crack is seen propagating through the as-cast material with virtually no deformation of the austenite matrix. Cracks in this material are quite localized as they propagate through the grain boundary constituent. Spheroidization of the grain boundary constituent results in the different mode of crack propagation seen in Figure 7(b). The crack is not as localized as in the as-cast material. Extensive plastic flow occurs in the vicinity of the crack, as evidenced by the heavy slip lines and the out-of-focus condition away from the crack caused by bending. The photograph of Figure 8 shows as-cast and spheroidized specimens, indicating the difference in ductility between the material in the two conditions.

Tensile test elongations and reductions of area are presented in Table V for the R351 analysis in the as-cast condition and as-spheroidized for one hour at 2150° F. Moderate increases in the average values of these measures of ductility are noted. Spheroidizing times of up to 24 hours did not materially improve the values of elongation and reduction of area beyond the levels for one hour.

c. Effect of Spheroidizing Heat Treatment Upon Strength Properties. Data illustrating the effect of time of spheroidization upon the 100-hour rupture strength at 1500° F are shown graphically in



(a) As-Cast



(b) 2150°F, 1 hr., air cooled; extensive deformation of the matrix is indicated by the numerous slip lines and by the out-of-focus condition away from the crack.

Figure 7. Propagation of Cracks in Side-of-Beam Microbend Specimens of R351 - Type Analysis (18% Cr, 18% Ni, 0.3% C, 1.25% B, 5% Mo). Heat R364, X350.

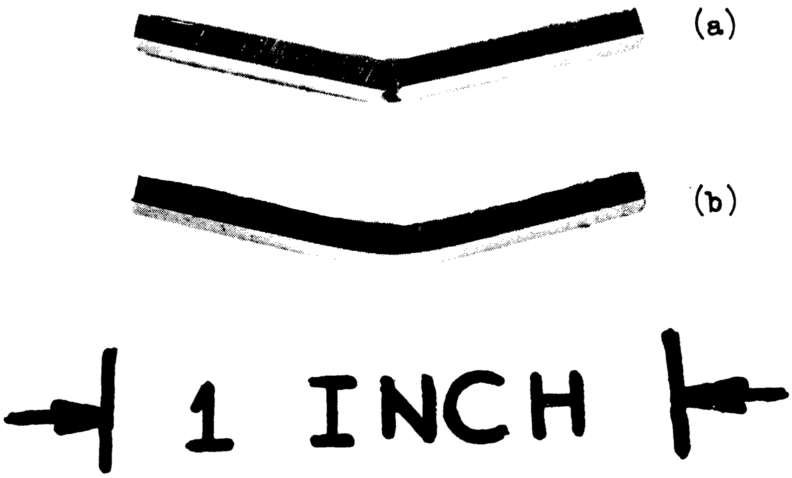


Figure 8. Microbend Specimens of Heat R364 Which Were Studied in Bottom-of-Beam Strain Viewer. Specimens are 1/16 in. square by 1 in. in length. (a) As-cast, showing lack of plastic deformation during bending. (b) 2150°F 20 hr., air cooled; this specimen exhibits a significant amount of ductility. A fine crack is present at the center of the specimen.

Figure 9. An initial increase is indicated, the curve reaching a maximum at approximately one hour. Beyond this point the curve drops steadily as the spheroidization pictured in Figure 9 becomes quite advanced.

The initial increase in rupture strength is of interest. The data of Table V for heats of the R351 type analysis in the as-cast condition and after spheroidizing one hour at 2150° F show this effect quite clearly. Bars stressed at 30,000 psi had an average life of 139 hours, as compared to 90 hours for bars in the as-cast condition. This represents an improvement of approximately 1500 psi (5.1%) in the 100-hour rupture strength at 1500° F. The reason for this strengthening effect may be similar to that proposed for iron-base nickel-chromium alloys containing large amounts (up to 1.5%) of boron (1), in which a conditioning effect was observed at 2200° F. This treatment brought about subsequent precipitation of boride precipitate at subgrain boundaries during rupture testing at 1500° F. Second-stage creep rates were greatly reduced and less microcracking was observed, causing an overall improvement in strength properties at 1500° F.

d. <u>Minor Compositional Adjustments to the R351 Analysis</u>. In an effort to further improve room temperature ductility of the R351 analysis, small compositional changes were made in a final series of heats. The changes consisted of reducing the carbon content from 0.3% to 0.25%, and in some heats reducing the boron concentration from 1.25% to 0.9%, all for the purpose of reducing the amount of grain boundary constituent. In addition, either 2% or 4% tungsten was added to four of these heats, in an effort to maintain 1500° F strength properties at the original level by solid-solution strengthening.

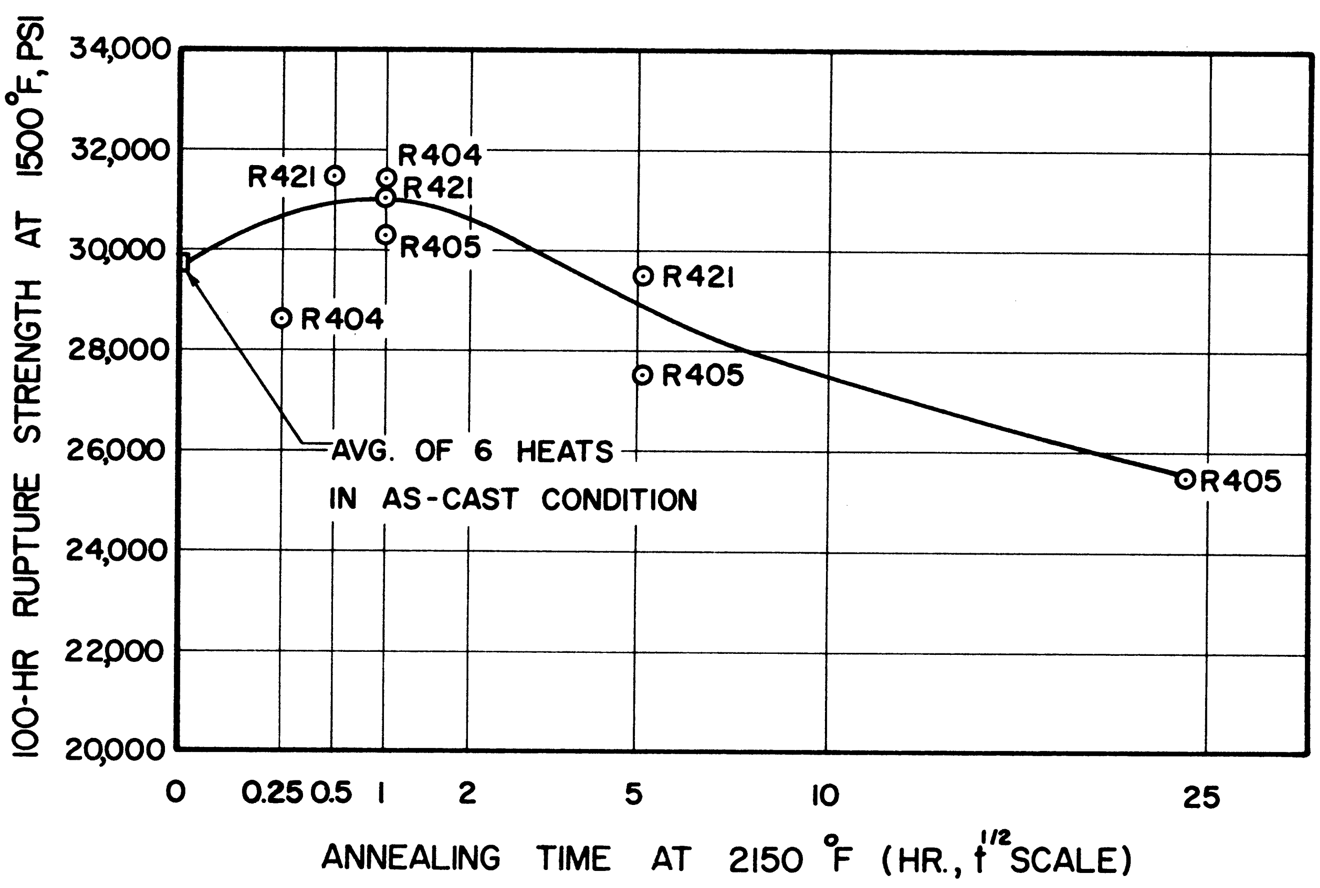


Figure 9. Effect of Spheroidizing Time at 2150°F Upon the 100-hr. Rupture Strength at 1500°F of R351 - Type Analyses.

The results obtained from this series of heats are listed in Table VI. The following observations may be made from these data, as compared to the data for the R351 analysis:

Room temperature ductility is superior to that of the R351 analysis, especially when comparing material in the heat-treated condition.

The values of as-cast 100-hour rupture strength at 1500° F are lowered by amounts ranging from 0.3% to 10%.

Tungsten has an optimum strengthening effect at the 2% concentration level.

The 1500° F 100-hour rupture strengths of all alloys are increased by heat-treating at 2150° F, but to a lower degree than for the R351 analysis.

Thus the compositional changes described here permit a definite improvement in room temperature ductility, at the price of a moderate penalty in strength at 1500° F. The 0.25% carbon, 0.9% boron, 2% tungsten analysis (R428), with 4% elongation and 4% reduction of area at room temperature, and a 100-hour rupture strength at 1500° F of approximately 28,900 psi in the heat-treated condition, seems to represent a good compromise.

TABLE VI

EFFECT OF MINOR COMPOSITIONAL CHANGES UPON PROPERTIES OF THE R351 TYPE ALLOY IN THE AS-CAST AND HEAT-TREATED CONDITIONS

Heat No.	Deviation from R351 Analysis (18% Cr, 18% Ni, 0.3% C, 1.25 % B. 5% Mo)	Condition(1)	Rm. Temp. Properties			1500°F, 100-Hr. Rupture Strength, psi(2)
			T.S. (psi)	Elong. (Pct. in 1 inch)	R.A. (Pct.)	
R351 Analysis						
R351, R364, R421	-	As-Cast	83,200 (avg.)	1.25 (avg.)	2.25 (avg.)	29,600
R404, R405, R421	-	2150-1-AC	88,100 (avg.)	2.5 (avg.)	2.83 (avg.)	31,100
Lower Carbon, Lower Boron						
R427	0.25% C, 0.9% B	As-Cast	-	-	-	~27,000
R429	0.25% C, 0.9% B	As-Cast	73,100	1.5	1.5	~27,000
		2150-1-AC	73,800	3.0	3.0	~27,500
Lower Carbon, Lower Boron, Plus Tungsten						
R428	0.25% C, 0.9% B, 2% W	As-Cast	-	-	-	~28,000
		2150-1-AC	84,300	4.0	4.0	~28,900
R430	0.25% C, 0.9% B, 4% W	As-Cast	81,900	1.5	3.0	~27,000
		2150-$\frac{1}{2}$-AC	82,300	3.0	3.0	~27,600
		2150-1-AC	78,400	3.0	3.0	~27,300
		2150-2-AC	81,600	4.0	4.0	~27,700
R431	0.25% C, 0.9% B, 4% W	As-Cast	75,300	2.0	3.0	~27,700
		2150-1-AC	83,200	4.0	5.0	~27,000
Lower Carbon, Plus Tungsten						
R433	0.25% C, 2 % W	As-Cast	-	-	-	~29,600
		2150-1-AC	87,500	3.0	3.0	~29,800

(1) 2150-1-AC, for example, means that specimens were annealed at 2150°F for 1 hour and air-cooled.

(2) Most of these values were obtained from just one test, estimating on the basis of existing curves.

CONCLUSIONS

1. The effects of carbon, boron, molybdenum, aluminum, columbium, titanium and nitrogen added singly upon the properties at 1500° F of a simple single phase cast austenitic alloy have been evaluated.
2. In many cases the effects upon strength at 1500° F are additive, leading to predictable development of high strength for this material.

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