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EFFECT OF COMPOSITION ON THE CORROSION RESISTANCE OF SOME ULTRA-HIGH STRENGTH METASTABLE AUSTENITIC STEELS

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### Authors

Padilla, Fred  
Challande, J.F.  
Ravitz, S.F.

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EFFECT OF COMPOSITION ON THE CORROSION RESISTANCE  
OF SOME ULTRA-HIGH STRENGTH METASTABLE AUSTENITIC STEELS

Fred Padilla,\* J.-F. Challande,† and S. F. Ravitz

Inorganic Materials Research Division, Lawrence Radiation Laboratory  
Department of Materials Science and Engineering, College of Engineering,  
University of California, Berkeley, California

ABSTRACT

The corrosion resistance of some ultra-high strength metastable austenitic Cr-Ni-C and Cr-Ni-Mo-C steels having unusually high ductility was investigated by an anodic-polarization test procedure. The ductility was the result of transformation of austenite to martensite during deformation (transformation-induced plasticity--the "TRIP" phenomenon). Increasing the chromium or molybdenum content, within the concentration ranges studied, very markedly increased both the ease with which the steels became passive and their corrosion resistance in the passive state. Increasing the nickel content or adding manganese, however, had relatively little effect. A steel containing 11 pct Cr, 8 pct Ni, 4 pct Mo, and 0.26 pct C, with a yield strength of 223,000 psi and an elongation of 31 pct, had corrosion-resistance properties, as measured by the anodic polarization tests, closely approaching those of type 316 stainless steel.

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\* Present address: Chairman, Metallurgy Technology Department, Don Bosco Technical Institute, Rosemead, California.

† Present address: French military service

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Fred Padilla and J.-F. Challande, formerly Research Assistants, Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, are now Chairman, Metallurgy Technology Department, Don Bosco Technical Institute, Rosemead, California, and member of the French military service, respectively. S. F. Ravitz is Professor of Metallurgy, Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley.

Certain metastable austenitic steels, after suitable thermo-mechanical processing, develop high yield strengths (of the order of 200,000 psi and higher) and tend to transform to martensite during straining. If the transformation begins before necking starts, a high rate of strain hardening results and the steel continues to deform plastically at high stress levels. This results in high values of elongation.<sup>(1-3)</sup> The term "TRIP" steels (from transformation induced plasticity) has been suggested for steels that exhibit such behavior.<sup>(1)</sup>

Most of the work on TRIP steels thus far has been devoted to determining their mechanical characteristics as functions of thermo-mechanical treatments and microstructures.<sup>(1,4)</sup> The present investigation was undertaken to provide information concerning the effect of

composition on corrosion resistance and on tensile properties. Because of the large number of possible variables (including, for example, wide ranges in composition, the temperature and amount of deformation, and the quenching conditions in the thermomechanical treatment), a very limited number of alloy compositions was selected and uniform treatment and testing procedures were adopted. A study such as this one can be considered as only a start toward delineating some of the effects of composition. Much more extensive studies are needed, including investigations of the effect of strain-induced martensite on corrosion resistance.

## EXPERIMENTAL PROCEDURES

### Alloy Preparation

Alloys were prepared from electrolytic iron and alloying constituents of comparable purity by induction-melting under argon in a magnesia crucible and casting under argon in a copper mold. The ingots, about 2½ in. in diameter and weighing 10 to 16 lb, were forged at 1100°C into plates 2½ to 3 in. wide and ½ to ¾ in. thick. The plates were cross-rolled at 1100°C to 0.4 in. thickness. They were then heated in stainless steel bags 1 to 2 hr at 1200°C, after which they were quenched in ice brine to prevent precipitation of carbides.

The thermomechanical treatment consisted of rolling the 0.4-in. steel at 450°C in successive reductions of 10 to 15 mils (with reheating to 450°C after each pass) to a final thickness of 0.080 in. (80% reduction), and then quenching in water. The material was essentially all in the austenitic state after this treatment.

### Corrosion Testing

The corrosion resistance of the steels was evaluated by a polarization-potential method developed by Edeleanu, (5,6) in which the anodic polarization current of the metal in a suitable electrolyte is measured as a function of applied potential. (7-9) This method provides in a few hours significant data on the corrosion properties of metals that exhibit passivity and has therefore become a valuable tool for the study of corrosion.

For the corrosion tests, specimens about 1.4 cm square were cut from the 0.080-in. sheet, and a 21-gauge copper wire was soldered to the back of each specimen. The specimen, after being mounted in a self-curing resin ("Koldmount") was polished on silicon-carbide papers (through 600-grit) and then with a one-micron diamond paste on a canvas wheel, washed ultrasonically in water and in ethyl alcohol, and rinsed thoroughly in ethyl alcohol.

The polarization cell consisted of three enclosed glass cylinders, one containing the briquetted specimen (mounted vertically in a hole in the cylinder wall), another a similarly arranged platinum counter-electrode approximately 1.4 cm square, and the third a saturated calomel reference electrode. To minimize contamination, the first and second compartments were connected near the bottom by a 10-mm glass tube about 8 cm long, in the middle of which was sealed a 2-mm-thick medium-coarse fritted glass disk, while the first and third were connected by a 2-mm glass capillary tube 10 cm long. The electrolyte was 10-pct (2-normal) sulfuric acid solution prepared from reagent-grade concentrated sulfuric

acid and triple-distilled water. To eliminate air, purified hydrogen was bubbled rather vigorously through the electrolyte for about an hour before each test and at the rate of one or two bubbles per second during the test. The specimen was immersed in the electrolyte for 15 min before the start of the measurements to establish the steady-state corrosion potential (i.e., the potential that exists between the specimen and the saturated calomel electrode (SCE) in the absence of an applied potential\*).

The potential between the specimen and the calomel electrode was controlled with a potentiostat and was continuously recorded, together with the corresponding polarization current between the specimen and the platinum counter-electrode, on an x-y recorder. The potential was varied automatically at the rate of 1.3 v per hr, starting near the corrosion potential (about -0.3 to -0.4 v) and ending at a potential of about 1.8 v. With the aid of a logarithmic converter, a set of suitable resistances, a selector switch, and a low-pass filter, polarization currents ranging from one-half microampere to one ampere could be recorded smoothly and uninterruptedly.<sup>(10)</sup> All measurements were made at  $22^{\circ} \pm 1^{\circ}\text{C}$ .

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\* Potentials are expressed here relative to the saturated calomel electrode, with the convention that the more positive the potential the stronger the oxidizing power of the electrolyte with respect to the specimen.



### Interpretation of Corrosion Test Data

An idealized anodic polarization curve and a typical actual curve are shown in Fig. 1. As the potential is increased above the corrosion potential,  $E_{\text{corr}}$ , at which no external current flows, the current density rises to a maximum (the critical anodic current density,  $I_{\text{cr}}$ ) at the primary passive potential,  $E_{\text{pp}}$ . The current density then drops rapidly to the passive range AB, where it remains more or less constant at the passive current density,  $I_{\text{p}}$ , before rising again in the transpassive region. The lower the passive current density, the lower the corrosion rate of the passivated metal in the test solution; in a prolonged test on a TRIP steel in this investigation, the measured weight loss corresponded to a corrosion rate of approximately 0.5 mil per yr (0.013 mm per yr) for each microampere per sq cm, in very good agreement with the rate calculated for steels by Faraday's law. The lower the critical current density,  $I_{\text{cr}}$ , and the primary passive potential,  $E_{\text{pp}}$ , the less strong are the oxidizing conditions required to make the metal passive and the less likely is the metal to become depassivated by changes in its environment. Steels can become passive spontaneously in a solution saturated with air if the critical current density is less than approximately  $100 \mu\text{a}/\text{cm}^2$ .<sup>(11)</sup>

Data obtained by the corrosion test procedure described above on samples of commercial stainless steels are given in Table I, together with data for similar stainless steels estimated from curves presented by Fontana and Greene.<sup>(12)</sup> The passive current density and especially the critical current density are very sensitive to the chromium content,

Table I. Corrosion-Test Data for Commercial Stainless Steels

Stainless Steel type no.*	Data source	Passive curr. dens., $\mu\text{a per sq cm}$	Critical curr.dens., $\mu\text{a per sq cm}$	Prim. pass. potential, v vs SCE
304	Present investigation	5	80	-0.22
304L	Fontana and Greene <sup>(12)</sup>	3	200	-0.27
316	Present investigation	5	15	-0.18
316	Fontana and Greene <sup>(12)</sup>	2	15	-0.18

\* Nominal composition (in addition to maxima of 2 pct Mn, 1 pct Si, 0.045 pct P, and 0.03 pct S):

Type no. 304: 18-20 pct Cr, 8-12 pct Ni, 0.09 pct C max.

Type no. 304L: 18-20 pct Cr, 8-12 pct Ni, 0.03 pct C max.

Type no. 316: 16-18 pct Cr, 10-14 pct Ni, 0.08 pct C max, 2-3 pct Mo.

as will be shown later. Thus, in view of the possible differences in composition indicated by the nominal composition ranges shown at the bottom of Table I, the agreement between the present results and those of Fontana and Greene may be considered reasonable.

#### Mechanical Testing

Specimens of one-in. gauge length were machined from the 0.080-in. sheet and tested at room temperature on an Instron testing machine at a cross-head speed of 0.04 in. per min. Each specimen was tested for ferromagnetism within the gauge length with a small hand magnet before and after the tensile testing.

#### RESULTS

A series of alloys containing 13 pct. Cr, 6 to 11 pct. Ni, and varying amounts of Mo and Mn were prepared and tested as described above; their compositions and the results of the tests are summarized in Table II. All the alloys exhibited the TRIP effect except alloys B and C, which necked down rapidly during the tensile test and exhibited low elongations. After the tests, alloys B and C were strongly magnetic only in the necked-down region, whereas all the others were strongly magnetic throughout the gauge length.

All the alloys showed very good passive corrosion resistance, the passive current densities being  $10 \pm 2 \mu\text{a}$  per sq cm, corresponding to a corrosion rate of only 0.005 in. per yr. Comparison with the data in Table I indicates that these alloys approach types 304 and 316 stainless steels in passive corrosion resistance. There are wide differences,

Table II. Effect of Composition on Properties of Metastable Austenitic Steels\*

Containing 13 pct Cr and 0.25±0.01 pct C

Alloy	Percent			Passive	Critical	Primary	Strength,		Elong.,	Reduction
	Ni	Mo	Mn	current density	current density	passive potential <sup>†</sup>	Yield	Tensile	pct in 1 in.	in area, pct
				µa per sq cm	µa per sq cm	v vs SCE	kpsi			
A	8	-	-	12	1,000	-0.34	164	253	28	32
B <sup>‡§</sup>	11	-	-	11	750	-0.32	187	187	8	51
C <sup>‡§</sup>	10	1	-	12	100	-0.31	194	194	11	51
D	9	2	-	12	35	-0.27	200	209	46	44
E <sup>§</sup>	8	1	-	12	75	-0.32	190	264	27	35
F	8	3	-	8	15	-0.25	187	231	38	38
G	7	4	-	10	15	-0.24	185	249	34	42
H	6	3	2	9	30	-0.28	185	231	40	33
I <sup>§</sup>	6	3	4	10	35	-0.38	186	188	46	42

\* Before being tested, all alloys were homogenized at 1200°C, quenched in ice brine, reduced 80 pct in thickness at 450°C, and quenched in water.

† The corrosion potential was consistently 0.04 to 0.05v more negative.

‡ Not a TRIP steel

§ Slightly magnetic, before being tested (all others were nonmagnetic).

however, in the critical current densities and in the tensile properties. These properties are discussed below.

#### Effect of Increasing the Nickel Content.

Increasing the nickel content from 8 pct (alloy A) to 11 pct (alloy B) had relatively little effect on the critical current density but had a profound effect on the tensile properties, changing the alloy from a TRIP steel with a yield strength of 164,000 psi and an elongation of 28 pct to a non-TRIP steel with a yield strength of 187,000 psi and an elongation of only 8 pct.

#### Effect of Addition of Molybdenum.

The addition of molybdenum to the alloy A composition had a profound effect on the critical current density but only a moderate effect on the tensile properties. With 1 pct Mo (alloy E), the critical current density dropped from 1000  $\mu\text{a}$  per sq cm to 75  $\mu\text{a}$  per sq cm, a value comparable to that of 18-8 stainless steel (Table I) and with 3 pct Mo (alloy F), the critical current density was only 15  $\mu\text{a}$  per sq cm, a value comparable to that of type 316 stainless steel. The yield strength was raised somewhat by 1 pct and 3 pct Mo, and the elongation was increased by 3 pct Mo.

#### Effect of Partial Replacement of Nickel by Molybdenum.

Alloys B, C, D, F, and G represent a series in which, starting with 11 pct Ni, part of the nickel was replaced successively with molybdenum in steps of 1 pct by weight. Major changes occurred in both the corrosion and tensile properties. The critical current density dropped

rapidly from 750  $\mu\text{a}$  per sq cm in alloy B to 15  $\mu\text{a}$  per sq cm in alloys F and G. There was also a slight (but perhaps not significant) drop in the passive current density, and there was a steady change in the primary passive potential from -0.32 v in alloy B to -0.24 v in alloy G.

As mentioned previously, alloy B, containing 11 pct Ni and no Mo, was not a TRIP steel. Substitution of 1 pct of molybdenum for a corresponding amount of nickel (alloy C) had relatively little effect on the tensile properties, as may be seen in Fig. 2. Substitution of another percent (alloy D, with 9 pct Ni and 2 pct Mo), however, caused an abrupt change, restoring the TRIP effect and giving the highest yield strength and one of the highest elongations of all the alloys listed in Table II. Further replacement of nickel by molybdenum (alloys F and G) caused moderate decreases in yield strength and elongation but produced a substantial increase in tensile strength.

#### Effect of Manganese.

Alloy H is similar to alloy F, but with 2 pct of manganese substituted for an equal quantity of nickel. This substitution doubled the value of the critical current density but had virtually no effect on the tensile properties. Addition of 2 pct more manganese without further changing the nickel content (alloy I) had little or no effect on the critical current density or on the yield strength, but decreased the tensile strength to about the same value as the yield strength while at the same time it increased the elongation substantially.

Effect of Chromium.

The chromium content was not varied in the alloys listed in Table II. However, during the development of the corrosion-testing procedure that was finally adopted, tests were made on TRIP steels available from other investigations. Among these was a series containing 8 to 16 pct Cr, 8 pct Ni, and  $0.26 \pm 0.02$  pct C, which had been prepared and thermomechanically treated in essentially the same manner as described previously. The anodic polarization test procedure used, however, was somewhat different.\* The results for this series are summarized in Table III. Alloy A in this table is the same as in Table II. The passive current density found for this alloy in both series was  $12 \mu\text{a}$  per sq cm. The critical current density for this alloy, however, was  $3000 \mu\text{a}$  per sq cm in the Table III series compared with  $1000 \mu\text{a}$  per sq cm in the Table II series. The difference is very likely due to the differences in test procedure, which could affect the nature of the film on the surface of the metal and thus the current density required to form a passive film.

The data in Table III show that the critical current density was extremely sensitive to the chromium content, dropping from the very high value of  $200,000 \mu\text{a}$  per sq cm at 8 pct Cr to the low value of

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\* The applied potential was started at about 0.6 v and was changed at the rate of 3 v per hr to -0.8 v, then to +1.8 v, and finally back to the starting voltage, whereas for the data in Table II the potential was started at -0.3 to -0.4 v and was increased at the rate of 1.3 v per hr to 1.8 v.

Table III. Effect of Composition on Properties of Metastable Austenitic Steels Containing 8 Pct Ni and 0.26±0.02 Pct C

Alloy	Percent		Passive	Critical	Primary	Strength,		Elong.,
	Cr	Mo	current density µa per sq cm	current density µa per sq cm	passive potential v vs SCE	Yield	Tensile	pct in 1 in.
J*	8	-	100	200,000	+0.17	196	271	17
K†	11	-	40	30,000	0.00	198	242	35
A*‡	13	-	12	3,000	-0.30	164	253	28
L*	16	-	9	10	-0.24	-	-	-
M*§	9	4	10	50	-0.25	-	-	-
N*	11	4	10	20	-0.07	223	241	31
O*§	13	4	6	6	+0.12	-	-	-

\* Pretreatment essentially as in first footnote of Table I.

† Pretreatment same, except quenched to -196°C after homogenization.

‡ Same alloy as A of Table II.

§ Also contained 2 pct Si and 1 pct Mn.



10  $\mu\text{a}$  per sq cm at 16 pct. The chromium content had a strong effect also on the passive current density, which dropped from 100  $\mu\text{a}$  per sq cm at 8 pct Cr to 9  $\mu\text{a}$  per sq cm at 16 pct. The tensile test data are incomplete but indicate that a decrease in yield strength may be associated with an increase in chromium content.

#### Effect of Chromium and Molybdenum.

Molybdenum, like chromium, was very effective in lowering both the passive and critical current densities, as shown by the data in Table III for alloys M, N, and O, which contained 4 pct Mo (alloys M and O contained also 2 pct Si and 1 pct Mn). Alloy N, with 11 pct Cr, 8 pct Ni, 4 pct Mo, and 0.26 pct C not only had a passive current density corresponding to a corrosion rate of only 5 mils per yr and a critical current density approaching that of type 316 stainless steel, but also had a yield strength of 223,000 psi and an elongation of 31 pct.

#### ACKNOWLEDGEMENT

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12. Reference 9, p. 337.

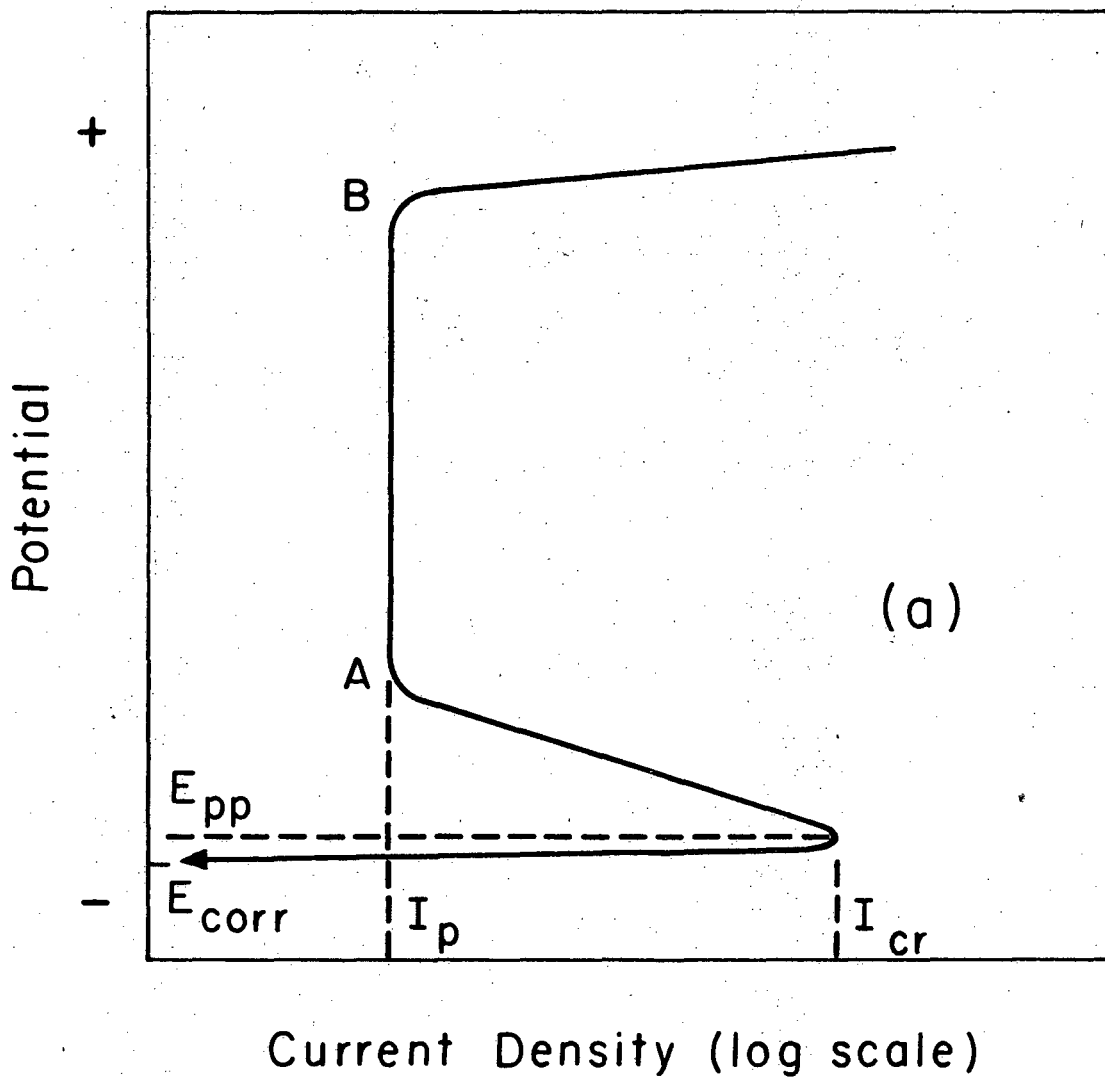
[Note to editor: Reference 4 (a) has been accepted for publication by Met. Trans..]

## List of Figures

Fig. 1 - Anodic polarization curves. (a) Idealized curve. (b) Actual curve for alloy A, Table II (13 pct Cr, 8 pct Ni, 0.25 pct C).

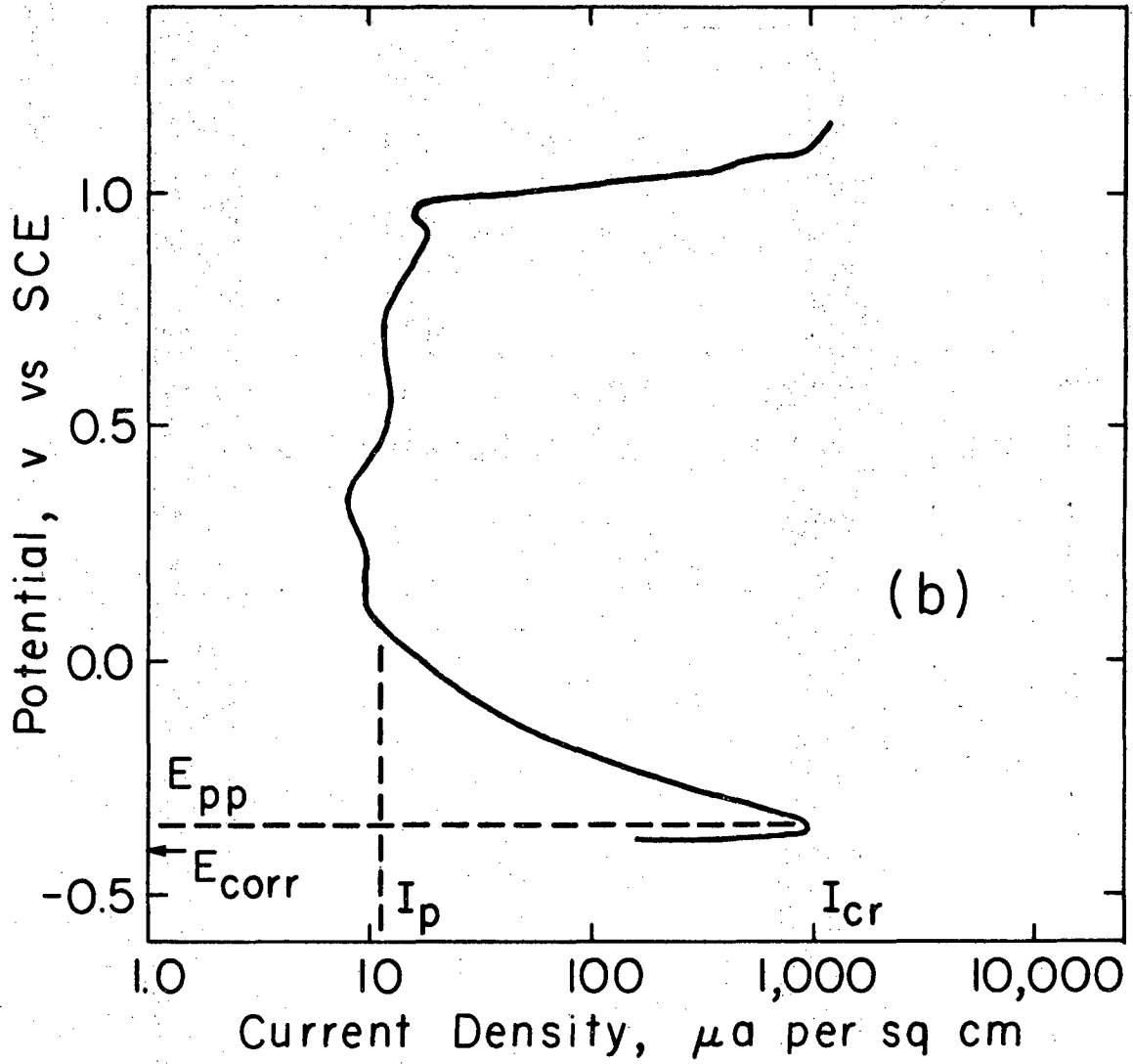
[Note to editor: Part (b) of Fig. 1 should be placed either immediately to the right of or immediately below part (a).]

Fig. 2 - Effect of replacement of Ni by Mo on tensile properties of alloys containing 13 pct Cr and 0.25 pct C.



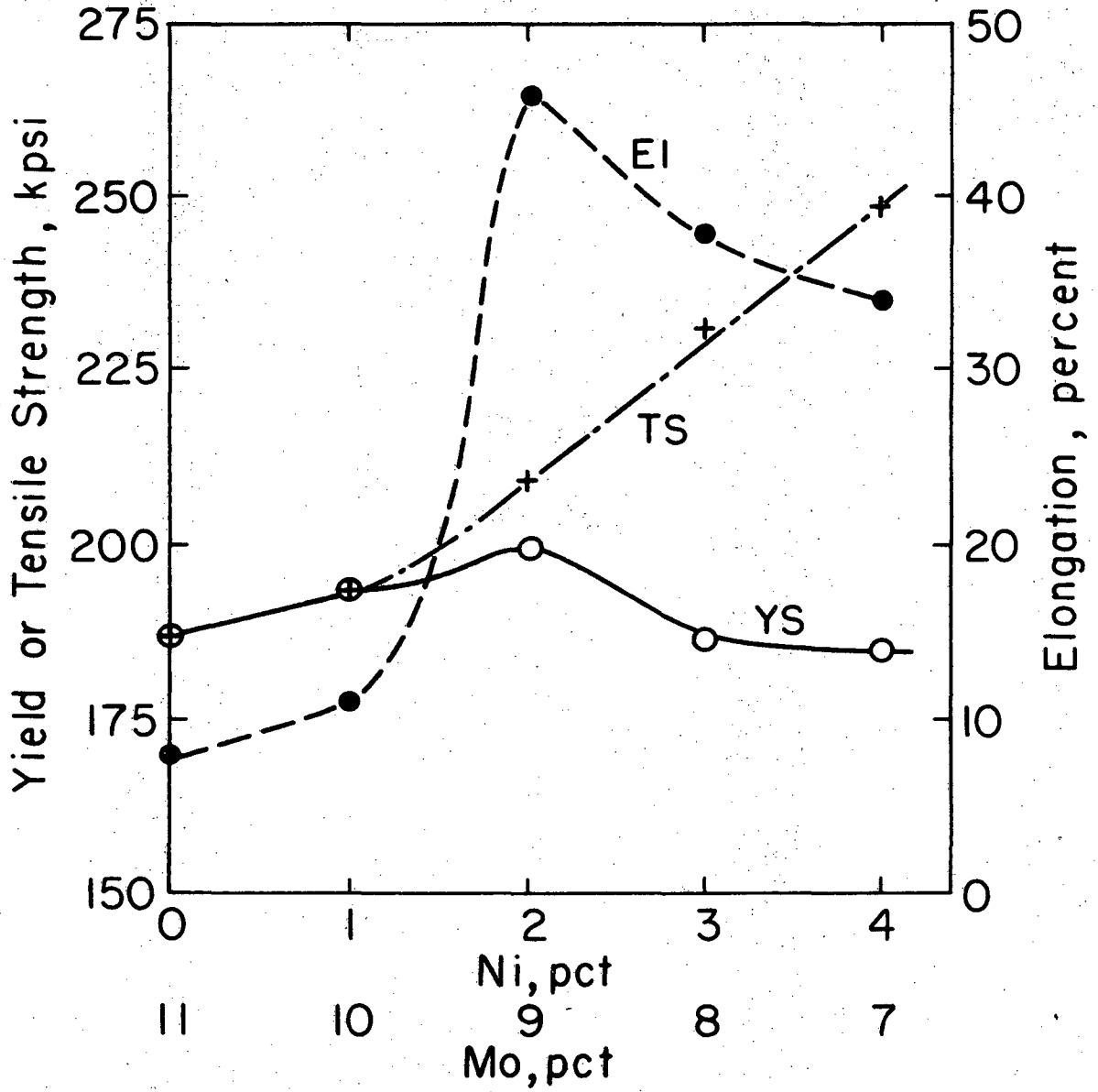
XBL 706-1275

Fig. 1(a)



XBL 706-1276

Fig. 1(b)



XBL 706-1274

Fig. 2

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