

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

DESIGN OP STRONG TOUGH Fe/Mo/C MARTENSITIC STEELS AND THE EFFECTS OF COBALT

### Permalink

<https://escholarship.org/uc/item/7sz6s31t>

### Authors

Clark, R.A.

Thomas, G.

### Publication Date

1974-03-01

DESIGN OF STRONG TOUGH Fe/Mo/C MARTENSITIC  
STEELS AND THE EFFECTS OF COBALT

R. A. Clark and G. Thomas

RECEIVED

LIBRARY

AUG 21 1975

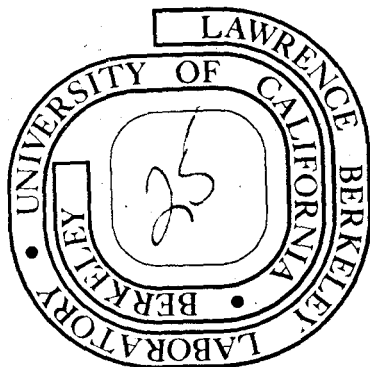
March 1974

LIBRARY AND  
DOCUMENTS SECTION

Prepared for the U. S. Energy Research and  
Development Administration under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division.*



## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LB 2-2504  
1975-138

# Design of Strong Tough Fe/Mo/C Martensitic Steels and the Effects of Cobalt

R. A. CLARK AND G. THOMAS

The microstructures and mechanical properties of a series of vacuum melted Fe/(2 to 4) Mo/(0.2 to 0.4) C steels with and without cobalt have been investigated in the as-quenched fully martensitic condition and after quenching and tempering for 1 h at 673 K (400°C) and 873 K (600°C); austenitizing was done at 1473 K (1200°C) in argon. Very good strength and toughness properties were obtained with the Fe/2 Mo/0.4 C alloy in the as-quenched martensitic condition and this is attributed mainly to the absence of internal twinning. The slightly inferior toughness properties compared to Fe/Cr/C steels is attributed to the absence of interlath retained austenite. The two 0.4 pct carbon steels having low Mo contents had approximately one-half the amount of transformation twinning associated with the two 0.4 pct carbon steels having high Mo contents. The plane strain fracture toughness of the steels with less twinning was markedly superior to the toughness of those steels with similar alloy chemistry which had more heavily twinned microstructures. Experiments showed that additions of Co to a given Fe/Mo/C steel raised  $M_s$  but did not decrease twinning nor improve toughness. Molybdenum carbide particles were found in all specimens tempered at 673 K (400°C). The Fe/Mo/C system exhibits secondary hardening after tempering at 873 K (600°C). The precipitate is probably  $Mo_2C$ . This secondary hardening is associated with a reduction in toughness. Additions of Co to Fe/Mo/C steels inhibited or eliminated the secondary hardening effect normally observed. Toughness, however, did not improve and in fact decreased with Co additions.

THIS paper is another in a series of systematic investigations on the effects of substitutional solutes on the microstructures and mechanical properties of Fe/C alloys.<sup>1-4</sup> In previous papers it has been shown that experimental ternary alloys of Fe/C/X vacuum melted and austenitized at a high enough temperature (at 1373 K to 1473 K) so as to dissolve all carbides, can have high strength and toughness in the as-quenched martensitic condition, provided the martensite is mainly dislocated, not twinned. This means that the total solute content (C+X), has a limiting value beyond which the as-quenched toughness deteriorates. The results also indicated that interlath retained austenite is beneficial to toughness. A recent paper summarizes the main factors which are involved.<sup>5</sup> The best alloy discovered so far in this sequence of investigations<sup>1-4</sup> has been Fe/4 Cr/0.35 C. In view of the interest in molybdenum<sup>6,7</sup> due to its abundance in the USA, alloys of Fe/Mo/C with and without cobalt were chosen for this investigation. Previous work on Fe/Ni/C/Co<sup>1</sup> and Fe/Cr/C/Co<sup>2</sup> showed that Co has no beneficial effect on toughness; but since Co is generally assumed to raise  $M_s$  and might possibly reduce internal twinning, it was decided to investigate whether or not cobalt could be beneficial in Fe/Mo/C steels. Since Mo is a gamma-loop forming element, the choice of alloy compositions was made so that the attainment of 100 pct martensite could be ensured in all alloys. The alloy compositions are given in Table I.

An interesting aspect in the study of Mo-containing steels is that Mo is a strong secondary hardener.<sup>8,9</sup> Secondary hardening is associated with the precipita-

tion of a coherent<sup>10-16</sup> alloy carbide, but is accompanied by a reduction in toughness.<sup>9,17</sup> The precipitate responsible for secondary hardening in molybdenum-containing steels has been identified to be  $Mo_2C$ .<sup>8-10,13-16,18,19</sup> Detailed investigations of the nature and identification of this precipitate have been conducted by Raynor, *et al.*<sup>20</sup> According to Irvine,<sup>9</sup> Mo is preferred as a secondary hardening element over other secondary hardeners, notably W and V, because Mo is cheaper than W and is more easily taken into solution than V.

This investigation entails measurements of yield and ultimate tensile strength, plane strain fracture toughness, Charpy values, hardness, and detailed analyses of the microstructures using optical and electron metallography. The steels were examined in their as-quenched fully martensitic condition and after tempering for one hour at 673 K (400°C) and 873 K (600°C).

## I. EXPERIMENTAL PROCEDURE

Table I lists the compositions and measured  $M_s$  temperatures of the alloys examined in this investigation. The alloys and their chemical analysis were kindly supplied by the Republic Steel Corporation.

Table I. Alloy Compositions and  $M_s$  Temperatures

Alloy	C	Mn	Si	Mo	Co	$M_s$ Measured °C
C198	0.18	0.30	0.15	3.85	—	435
C214	0.41	0.35	0.15	4.2	—	341
C215	0.43	0.34	0.15	3.85	9.0	465
C216	0.43	0.33	0.15	2.2	—	332
C217	0.42	0.33	0.15	2.1	5.2	397

R. A. CLARK and G. THOMAS are Graduate Student and Professor, respectively, University of California, Department of Materials Science and Engineering, Hearst Mining Building, Berkeley, Calif. 94720.

Manuscript submitted March 11, 1974.

Each material was vacuum melted and initially cast in 22.7 kg (50 lb) ingots. The ingots were subsequently hot rolled to nominally 1.3 cm (0.5 in.) plate and after sandblasting any scale off all surfaces, the plates were vacuum homogenized at 1473 K (1200°C) for 48 h then furnace cooled. At this point, mechanical test specimens for Charpy V-notch, tensile, and plane-strain fracture toughness ( $K_{IC}$ ) were rough machined. Rough machining for tensile specimens consisted of squaring blocks of material, with similar dimensions to the  $K_{IC}$  specimens, and placing four center holes in each block to delineate future machining. This procedure ensured that during subsequent heat treatment, heating and cooling rates in both tensile and fracture toughness specimens would be closely comparable, so allowing microstructures and mechanical properties to be correlated in the two types of test specimens.

$M_s$  temperatures were measured to  $\pm 3^\circ\text{C}$  on a Dilatronic IIR gas quenching dilatometer. All tests were conducted in vacuum to avoid specimen decarburization. Results are listed in Table I.

Heat treatment of all specimens consisted of austenitizing for 1 h at 1473 K (1200°C) in an argon atmosphere then quenching into an agitated ice-10 pct brine solution. Immediately afterward specimens were refrigerated in liquid nitrogen to ensure complete transformation to martensite. Tempering, for those specimens requiring it, was done soon after the initial heat treatment. All alloys were fully hardened in the largest sections used, as confirmed by hardness tests. No retained austenite was discernible using either X-ray or electron microscopy techniques. Tempering for 1 h at 673 K (400°C) or 873 K (600°C) was conducted in closely controlled neutral salt baths. After tempering specimens were air cooled.

Upon completion of heat treatment, specimens were finish machined. The faces of the plane strain fracture toughness specimens were wet ground to eliminate any possible decarburized layer, and required notches were ground in. Tensile specimens were wet ground to their final dimensions. All machining and grinding operations employed flood cooling to minimize heating. The surface of tensile specimen gage sections were buffed just prior to testing using kerosene soaked 600 grit emery paper to eliminate any scratches present.

Carbon analysis was conducted on each alloy at three junctures. The plate as received from Republic Steel was tested. Analysis was conducted a second time on the plate after homogenizing. The final analysis was on samples cut out of the gage section of tested tensile specimens. A maximum 0.01 pct loss of carbon occurred.

All mechanical test specimens, Charpy V-notch, tensile, and plane-strain fracture toughness ( $K_{IC}$ ), were designed to ASTM standards. The 0.635 cm (1/4 in.) gage diam tensile specimens were pulled on a 1.33 MN (300 Kip) MTS at a head speed of 0.3 cm/min. The fracture toughness specimens ( $K_{IC}$ ) were fatigue pre-cracked and pulled according to ASTM designation E399-72.<sup>21</sup> Charpy impact testing was conducted on a 304J (224 ft-lb) capacity impact device. All mechanical testing was conducted at room temperature 296 K (23°C). All results reported are averages for two or more tests of similar specimens.

Microstructural determination was conducted using optical and transmission electron microscopy. Specimens for optical metallography were polished using standard techniques and etched in 2 pct nital. Foils for transmission electron microscopy were mechanically sectioned from previously tested  $K_{IC}$  specimens. Sectioning was conducted under flood cooling conditions to prevent tempering. Cut slices were wet ground parallel and then chemically thinned in an  $\text{H}_2\text{O}_2$ -HF solution to 0.13 mm (0.005 in.) thick. Final polishing was accomplished in cooled chromic-acetic acid solution employing the window technique. Foils from several regions of each alloy were examined using a Siemens Elmiskop IA operated at 100 kV and an Hitachi high voltage microscope operated at 650 kV. Fracture surfaces of all  $K_{IC}$  and Charpy impact specimens were examined using a JSM-U3 Scanning Electron Microscope (SEM) operated at 25 kV in the back scattered electron mode.

Attempts were also made to study the modes of deformation using compression specimens which had been carefully polished. All surfaces were examined in the SEM and replicated using acetate replicating tape prior to deformation of the specimens. The specimens were plastically deformed 5 pct, after which the surfaces of the specimens were again viewed in the SEM and replicated. Next, the specimens were electropolished for 30 min, again viewed in the SEM and replicated. The series of surface replicas was then examined in a Siemens Elmiskop IA electron microscope operated at 40 kV.

## II. RESULTS

### A. Mechanical Properties

Table II summarizes the tensile data for the various alloys. The characteristic secondary hardening peak is observed after 873 K (600°C) tempering of alloys 214, 216, and 198. However, alloys 215 and 217, which contained Co, did not exhibit secondary hardening. Since secondary hardening in Fe/Mo/C steels is associated with precipitation of  $\text{Mo}_2\text{C}$ , it appears that Co either inhibits or modifies this precipitate. Upon examining the elongation data in Table II, it is seen that at the 873 K (600°C) tempering level alloys 216 and 217 (2 pct Mo) show fair amounts of ductility. This suggests that these two alloys may be starting to overage. Irvine<sup>9</sup> and Pickering<sup>22</sup> have found that increasing the Mo level shifts the tempering temperature for peak secondary hardening to higher values. Thus, tempering at temperatures leading to peak secondary hardness in high Mo steels would lead to overaging in low Mo steels tempered similarly.

Results of the plane-strain fracture toughness tests are summarized in Table III. The average values of these results are shown plotted in Fig. 1. In all alloys, except 217, the toughness dropped after 873 K (600°C) tempering. This observation is in agreement with previous researchers<sup>17,23-25</sup> who also found that fracture toughness decreased around the secondary hardening peak. Alloy 217 showed no drop in toughness with 873 K (600°C) tempering; but alloy 215, which contains more Co and also considerably more Mo, does not exhibit a similar effect. It is also noteworthy that the alloys without Co are always tougher than the comparable

Table II. Mechanical Properties Data\*

Alloy	Heat Treatment†	Tensile Yield Strength		Ultimate Tensile Strength		Tensile Elongation, Pct	Charpy Impact Resistance	
		ksi	MN/m <sup>2</sup>	ksi	MN/m <sup>2</sup>		Ft./Lbs.	Joules
214	AQ	257	1772	322	2220	2.0	4.1	5.56
214	473 K	—	—	—	—	—	7.6	10.3
214	673 K	205	1413	251	1731	7.1	8.2	11.1
214	873 K	271	1868	279	1924	0.6	3.5	4.75
215	AQ	246	1696	283	1951	1.6	4.1	5.56
215	473 K	—	—	—	—	—	4.7	6.37
215	673 K	257	1772	278	1917	1.0	4.7	6.37
215	873 K	198	1365	198	1365	0.2	4.6	6.24
216	AQ	258	1779	309	2130	2.5	4.7	6.37
216	473 K	—	—	—	—	—	7.6	10.3
216	673 K	197	1358	229	1579	5.8	11.0	14.9
216	873 K	206	1420	223	1538	10.7	8.7	11.8
217	AQ	253	1744	306	2110	1.6	5.3	7.19
217	473 K	—	—	—	—	—	8.1	11.0
217	673 K	248	1710	277	1910	3.1	6.4	8.68
217	873 K	240	1655	253	1744	2.5	5.8	7.86
198	AQ	160	1103	198	1365	12.6	11.1	15.0
198	473 K	—	—	—	—	—	8.2	11.1
198	673 K	153	1055	183	1262	13.9	9.9	13.4
198	873 K	193	1331	205	1413	8.5	5.2	7.05

\*Averages of two or more tests.

†AQ = as quenched in iced-brine; otherwise quenched and tempered 1 h at the indicated temperature.

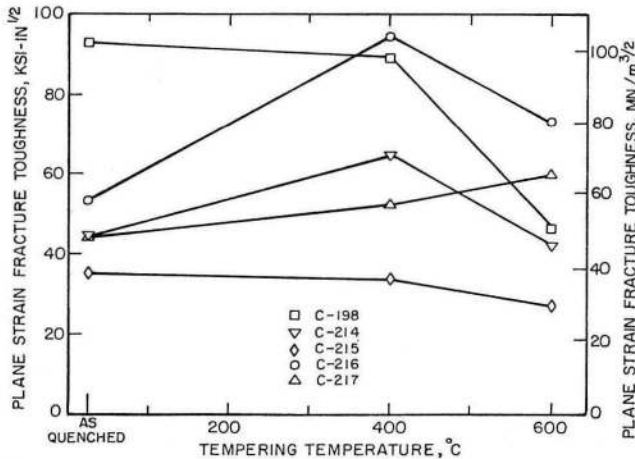


Fig. 1—Room temperature plane-strain fracture toughness as a function of tempering temperature.

alloy containing Co, e.g. 216 is always tougher than 217. Thus, Co is definitely detrimental to toughness.

Charpy impact values are given in Table II. The most interesting point here is that impact values are uniformly low, a maximum of only 15 joules (11 ft-lbs) was recorded. Thus, reasonably high plane strain fracture toughness values such as obtained for alloys 216 and 198 do not guarantee a correspondingly high impact resistance.

### B. Microstructures

1. Martensite. The microstructure of each alloy in each of the heat treatment conditions was examined using transmission electron microscopy techniques. Typically, the 0.4 carbon alloys (214, 215, 216 and

Table III. Plane Strain Fracture Toughness Data

Alloy	Heat Treatment, K*	$K_{Ic}$ or $K_Q^\dagger$		$P_m/P_Q$
		ksi-in <sup>1/2</sup>	MN/m <sup>3/2</sup>	
214	AQ	42.9	47.1	1.04
214	AQ	45.5	50.0	1.01
214	673	57.6	63.3	1.01
214	673	70.5	77.5	1.01
214	873	45.7	50.2	1.03
214	873	38.2	42.0	1.00
215	AQ	33.4	36.7	1.01
215	AQ	36.6	40.2	1.01
215	673	31.2	34.3	1.06
215	673	36.6	40.2	1.02
215	873	27.2	29.9	1.01
215	873	26.5	29.1	1.03
216	AQ	55.0	60.4	1.03
216	AQ	52.3	57.5	1.11
216	673	94.0	103.3	1.01
216	673	94.5	103.9	1.03
216	873	68.6	75.4	1.16
216	873	78.0	85.7	1.10
217	AQ	41.9	46.0	1.05
217	AQ	46.3	50.9	1.01
217	673	53.6	58.9	1.02
217	673	45.3	49.8	1.04
217	673	57.4	63.1	1.00
217	873	58.2	64.0	1.03
217	873	61.7	67.8	1.02
198	AQ	91.6	100.7	1.05
198	AQ	94.9	104.3	1.03
198	673	91.8	100.9	1.02
198	673	86.1	94.6	1.03
198	873	46.0	50.6	1.23
198	873	41.6	45.7	1.17
198	873	48.2	53.0	1.00
198	873	44.0	48.4	1.01

\*Tempered 1 h at given temperature after quenching.

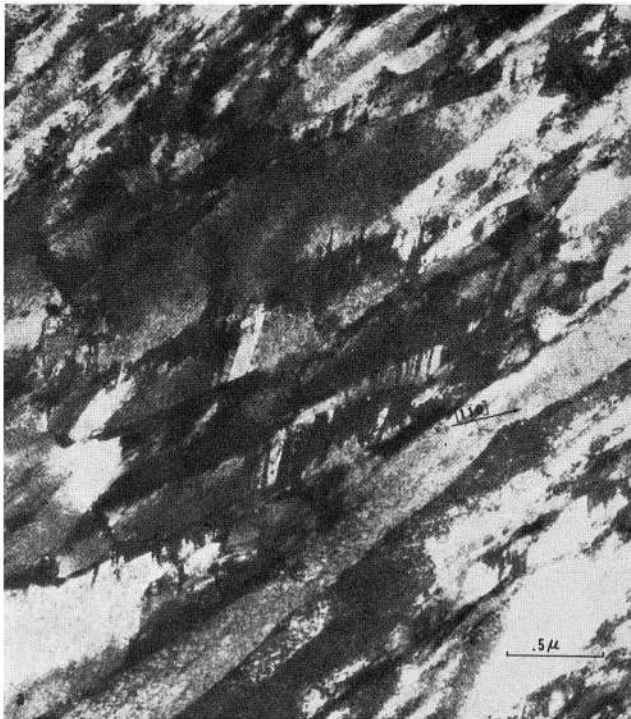
† $K_Q$  when  $P_m/P_Q > 1.10$ .

217) in the as-quenched condition exhibited a mixture of dislocated lath martensite and twinned plate martensite. Fig. 2(a) thru (d) are representative of these structures.

The lath martensite often occurs as packets of closely oriented parallel laths. Also, the two Co containing alloys (215 and 217) appear, on the average,

to have a finer microstructure, smaller plates and laths, than the similar alloys without Co as shown in Fig. 3(a) and (b).

The laths in the noncobalt bearing alloys 214 and 216 range in size from  $0.1\mu$  to  $0.5\mu$  wide while those in the Co-bearing alloys are typically  $0.1$  to  $0.2\mu$  wide. Prior austenite grain size for all alloys was



(a)



(b)



(c)



(d)

Fig. 2—As-quenched microstructures of 0.4C alloys. Bright field micrographs (a) alloy 214; (b) alloy 216; (c) alloy 215; (d) alloy 217.

similar, ASTM 1-2. Due mainly to the fact that the amount of twinning observed in any one picture is strongly dependent on foil orientation<sup>26</sup> and contrast conditions vary widely from plate to plate, it was found impossible to determine precisely the relative amount of twinned vs untwinned martensite in any one



(a)



(b)

Fig. 3—As-quenched microstructure of (a) 214 and (b) 215 showing the effect of Co additions on average lath and plate size.

alloy. However, after careful visual examination of many pictures of each alloy, it was apparent that alloys 214 and 215 have about the same amount of twinning, and alloys 216 and 217 have about the same amount of twinning. However, alloys 214 and 215 exhibit approximately twice as much twinned area as alloys 216 and 217.

An important point with regard to mechanical properties is that the more heavily twinned martensites, those of alloys 214 and 215, have lower toughness than the less twinned martensites of alloys 216 and 217. A good idea of the effect of twinning can be obtained by comparing the toughness in the as-quenched condition, of alloy 214 with 216 and alloy 215 with 217, thus limiting the effect of Co in the comparison.

Fig. 4 shows the typical as-quenched microstructure of alloy 198, the low carbon alloy. The microstructure consists of virtually 100 pct dislocated martensite. Alloy 198 was investigated to help isolate the effects of C content on microstructure. Since the object of the research program was development of a high strength tough steel a 0.4 pct C level was used in the other alloys to attain the desired regime of yield and ultimate tensile strength. No retained austenite was detected even after very careful selected area diffraction and dark field studies.

All of the as-quenched microstructures exhibited some autotempering and the carbide was determined to be  $\text{Fe}_3\text{C}$ , along  $\{110\}$   $\alpha$  planes. A further discontinuous  $\text{Fe}_3\text{C}$  precipitate occurred in the boundaries between packets of martensite laths, but never between the laths within a packet. Fig. 5(a) and (b) illustrate the structure of an autotempered martensite plate.

2. Tempered Martensites. Tempering at 673 K (400°C) resulted in additional Widmanstätten matrix

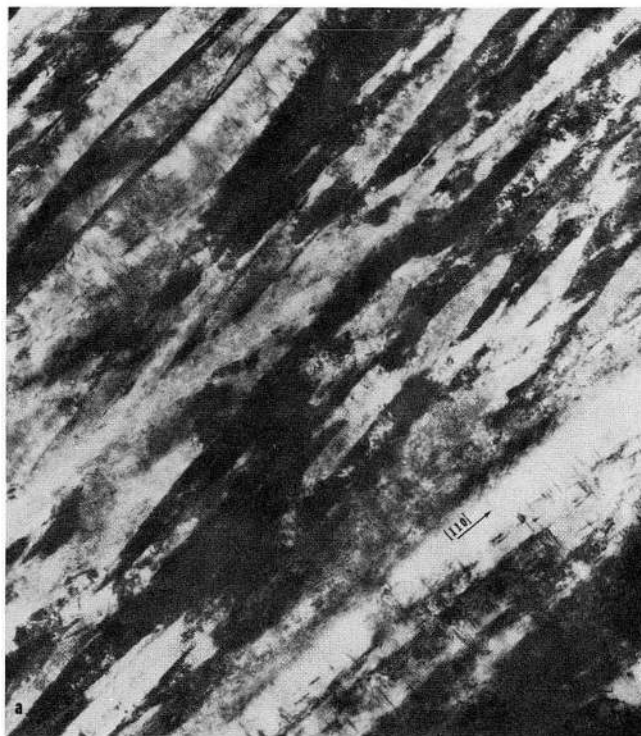
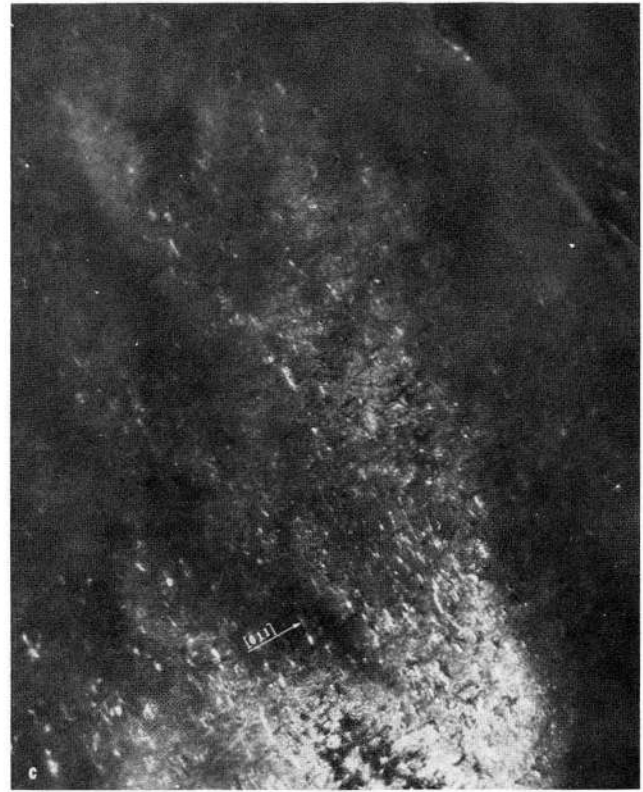


Fig. 4—Bright field micrograph of typical as-quenched structure in alloy 198.





(a)

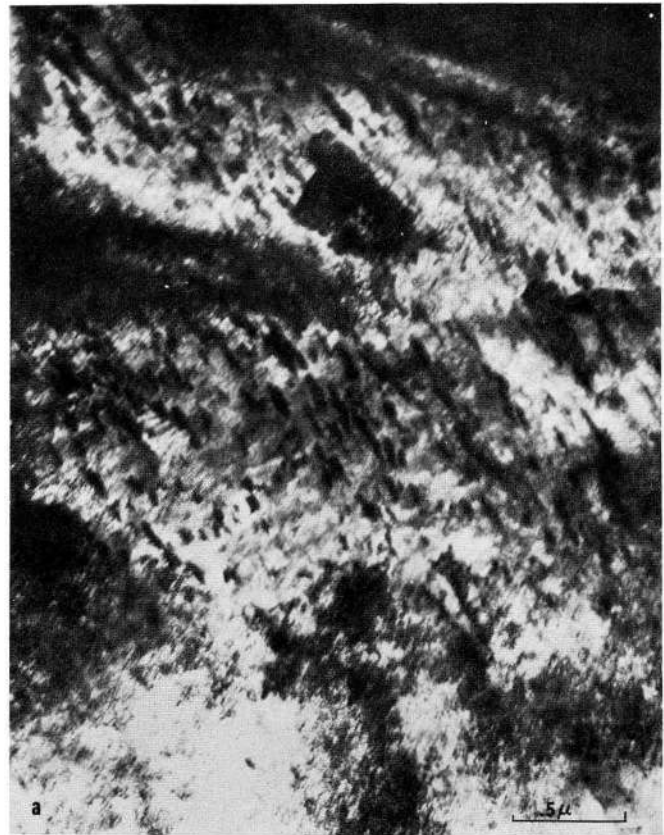


(b)

Fig. 5—Bright field (a) and dark field (b) illustrating autotempering present in as-quenched alloys. Alloy 198.

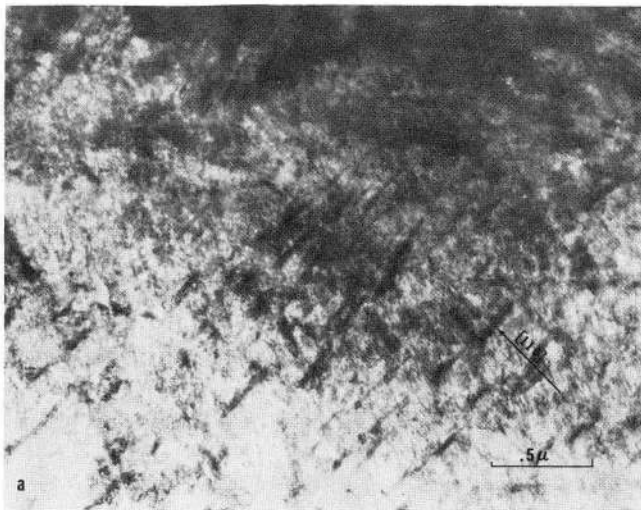


(a)

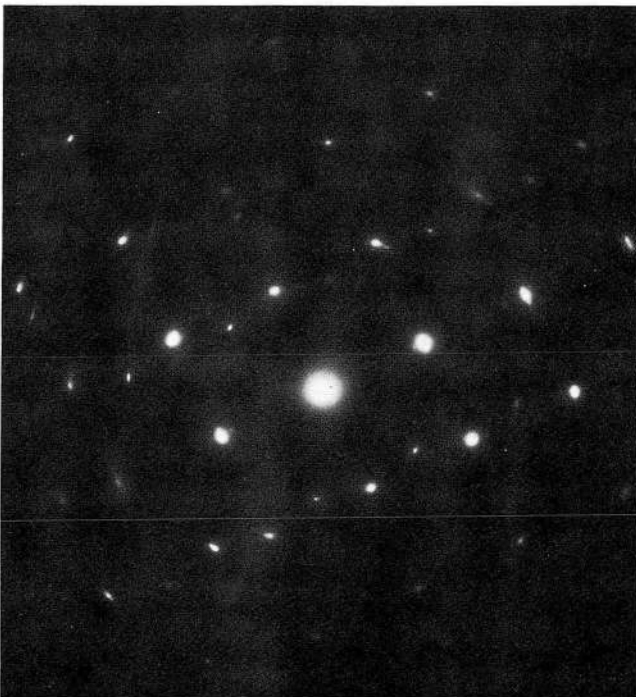


(b)

Fig. 6—Bright field micrographs showing typical microstructures in alloys tempered at 400°C for 1 h. (a) alloy 214; (b) alloy 215; (c) alloy 216, (d) alloy 198. 6(e) is a selected area diffraction pattern showing the streaks which were used to identify the presence of the MoC precipitate.



(c)



(e)

Fig. 6-Continued.

precipitation and further lath boundary precipitation of  $\text{Fe}_3\text{C}$ . There was also cementite precipitation at the matrix-twin interfaces as previously reported by other researchers.<sup>1-4,27</sup> Fig. 6(a) thru (d) show microstructures typical of the 673°K tempering condition. Analysis of streaks in electron diffraction patterns (Fig. 6(e)) led to the conclusion that very small amounts of a molybdenum carbide were also present in all the alloys with this tempering treatment. The formation of a  $\text{MoC}$  precipitate under similar conditions has been previously noted.<sup>18,23</sup>

Tempering at 873 K (600°C) resulted in very fine precipitation of an alloy carbide associated with secondary hardening. This precipitate produced streaking in the diffraction patterns and is identical to the results obtained by Dyson, *et al.*<sup>20</sup> It is tentatively



(d)

concluded therefore that the precipitates are  $\text{Mo}_2\text{C}$ . Precipitation of the  $\text{Mo}_2\text{C}$  phase was accompanied by resolution of the cementite precipitate. Microstructures characteristic of this tempering condition are shown in Fig. 7(a) and (b). Some cementite was still present in the 0.4 pct alloys though none was observed in the 0.18 C alloy. Also, the low Mo alloys, 216 and 217, appeared to have more retained  $\text{Fe}_3\text{C}$  than the higher Mo alloys, 214 and 215. This is seen in Fig. 8(a) and (b). The remaining cementite spheroidized considerably so that it no longer existed as a continuous interlath precipitate.

The fracture surfaces of tested  $K_{IC}$  specimens were all remarkably similar. A typical fracture surface is illustrated by Fig. 9. The fracture surfaces invariably consisted of low level and small dimples mixed with somewhat varying amounts of flat cleavage-like areas. This type of fracture morphology has been attributed by Low<sup>28</sup> to a void coalescence mechanism. This mechanism appears to adequately explain how a dimpled rupture surface, generally associated with ductile failure, can be obtained in the brittle failure of a high strength alloy.

An attempt was made by plastic deformation of compression specimens to establish if deformation occurred via slip or by twinning. This information would help determine if the twinning in the observed microstructures was all due to transformation effects or included contributions from deformation twinning. Observations of surface replicas taken from the compression specimens showed only slip lines. However, the detection of fine deformation twins in the martensite laths or plates may be beyond the resolution limitations of these experiments.

### III. DISCUSSION

The results of this work support the general conclusions of previous investigations concerning the correlation of microstructure with mechanical prop-

erties. A common feature is that in martensite the presence of internal twinning is detrimental to toughness and that the tendency to increased twinning and decreased toughness increases with total solute content. Based on this work and that of Goolsby<sup>17</sup> and

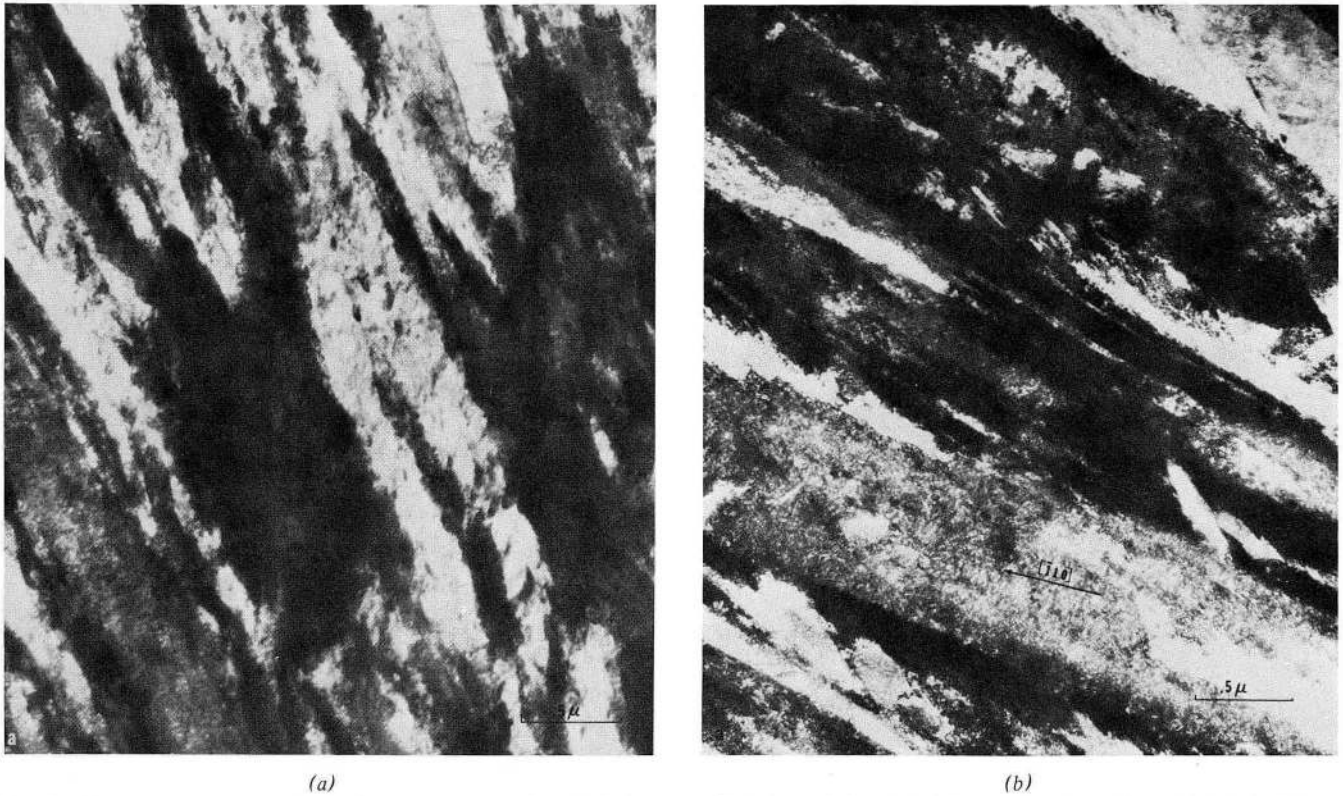


Fig. 7—Microstructures typical of alloys tempered at 600°C. Bright field (a) of alloy 217 shows structure characteristic of low Mo alloys. Bright field (b) shows structure characteristic of high Mo alloys.

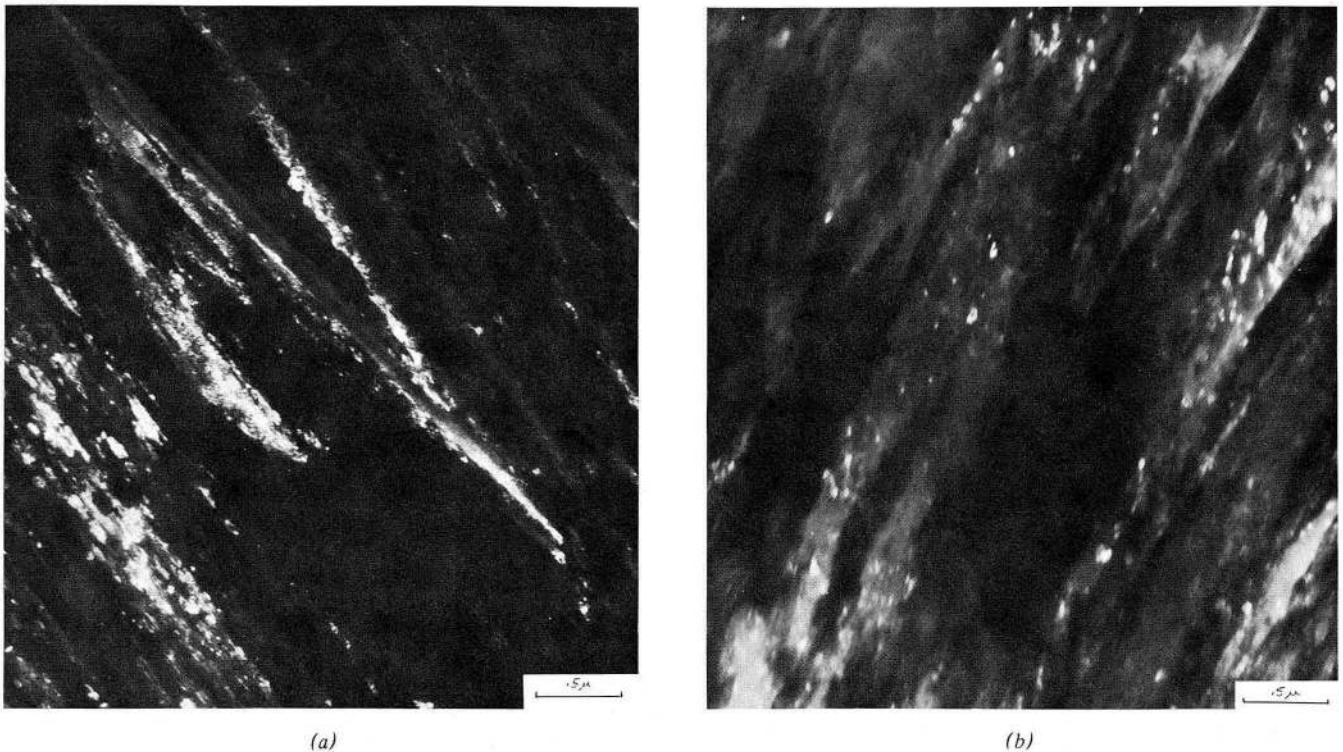


Fig. 8—Dark field micrographs of carbide spots in alloys tempered at 600°C for 1 h. (a) low Mo alloy and (b) high Mo alloy.

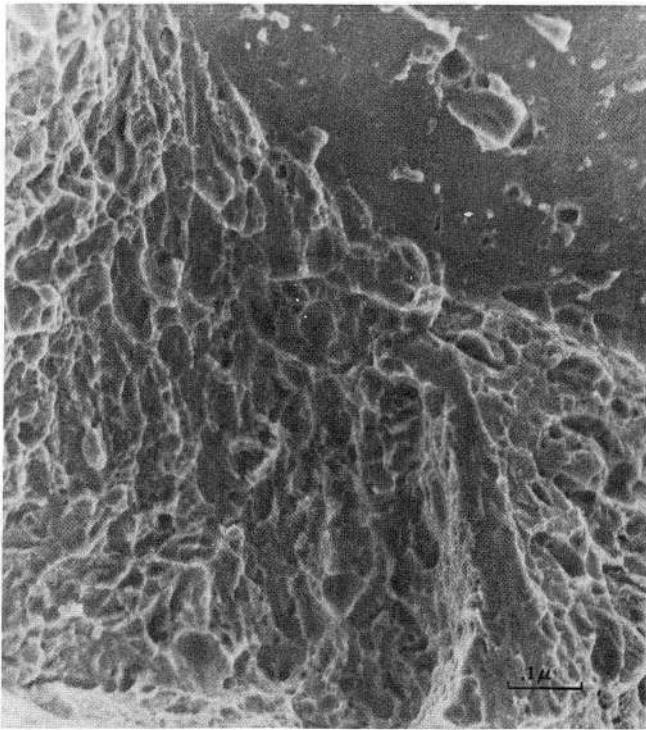


Fig. 9—Scanning electron micrograph showing typical fracture surface exhibited by all fracture toughness specimens. The fracture surface is a mixture of low level dimples mixed with varying amounts of flat cleavage areas.

Tom,<sup>29</sup> in Fe/Mo/C steels the optimum Mo content at 0.4 pct C is about 2 pct. In such an alloy, good combinations of tensile and fracture properties are attained in as-quenched, untempered (*i.e.* not process tempered) martensites (Fig. 10). This result shows that as-quenched martensites are not inherently brittle, as is often assumed.

The as-quenched yield strengths of all alloys containing  $\approx 0.4$  pct C (alloys 214 to 217) were virtually identical as expected. However, the fracture toughness of alloy 214 was only 80 pct that of alloy 216. It will be recalled that although neither alloy exhibited extensive twinning, there was approximately twice as much twinned volume in alloy 214 as there was in alloy 216. A similar correlation is apparent between the alloys 215 and 217 though the unique determination of the cause of the toughness reduction is hampered here by the large and varying Co concentration.

Thin films of retained austenite around martensite laths can be detected by careful electron diffraction and dark field even when unresolved by X-rays.<sup>4,5</sup> However no retained austenite was detected in any of the alloys studied in this work. Since this is the only significant microstructural difference between the as-quenched martensites in these Fe/Mo/C steels and those of Fe/Cr/C reported earlier<sup>4</sup> and since Fe/Mo/C dislocated martensites have slightly lower toughness than the Fe/Cr/C dislocated martensites at similar yield strengths it is concluded that superior toughness is associated with such interlath films of retained austenite. Future alloy design programs will investigate this possibility in more detail.

The consequence of varying alloy constituents is best resolved in terms of the individual effects of dif-

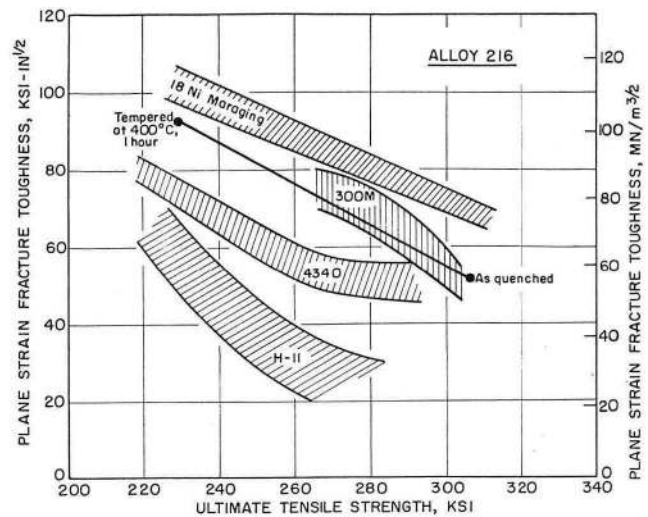


Fig. 10—Comparison of ultimate tensile strength and plane strain fracture toughness of alloy 216 with the strength and toughness properties of several ultrahigh-strength commercial steels.

fering Mo or differing Co contents. The effect of increasing Mo in the absence of Co and at a constant C content ( $\approx 0.4$  pct) is illustrated by comparing alloys 214 and 216. Alloy 214 with the higher Mo content of the two alloys has increased amounts of twinned martensite. Higher Mo content does contribute to an increased secondary hardening effect with 600°C tempering, as noted in Table II. No discernible difference was apparent in the amount of autotempering as a function of Mo content. Also no effect on hardenability attributable to varying Mo content was noted, as all specimens were fully hardened in the dimensions employed.

Co additions to the Fe-Mo-C ternary system produced some interesting results. First, no effect on the amount of twinned martensite was apparent when comparing alloys 216 and 217. Alloy 217 is identical to alloy 216 except that 217 has a 5.2 wt pct addition of Co. Measurements showed that Co additions did raise the  $M_s$  temperatures (Table I). However, Co additions did not appear to influence tensile yield or ultimate strength properties, in either direction. Those alloys containing Co exhibited less tensile elongation compared to similarly treated alloys without Co. In the as-quenched condition Co additions caused moderate drops in the plane-strain fracture toughness ( $K_{Ic}$ ) of an alloy. In the quench and tempered condition, the addition of Co caused large decreases in plane strain fracture toughness for 673 K (400°C) tempering and moderate toughness reductions with 873 K (600°C) tempering. In addition, comparing alloy 214 with 215 and alloy 216 with 217 in Fig. 11, it is observed that the alloy without Co in each pair (214 and 216) always had better combinations of tensile yield and fracture toughness properties than the alloy containing Co (215 and 217). For example, it appears possible to temper alloy 216 such that it has a higher yield strength at a given fracture toughness level than would be attainable with alloy 217.

Another interesting facet of Co additions is the apparent effect of hindering the Mo secondary hardening reaction. As observed in Table II, neither alloy 215 nor 217 exhibited secondary hardening when tempered

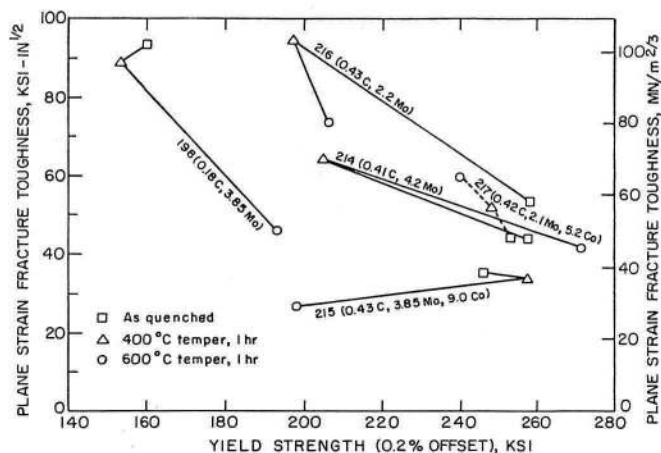


Fig. 11—Room temperature plane-strain fracture toughness vs tensile yield strength for each of the tempering conditions.

for 1 h at 873 K (600°C). Similar alloys, however without any Co, 214 and 216, exhibit the expected secondary hardening reaction. Thus, cobalt must somehow effect the coherent precipitation of  $\text{Mo}_2\text{C}$  responsible for secondary hardening in Fe/Mo/C systems. Examination of electron micrographs of the several alloys studied suggested that Co enhanced interlath carbide precipitation, *i.e.* Co containing alloys exhibited the greatest amounts of interlath  $\text{Fe}_3\text{C}$  precipitation. Thus, Co may act to stabilize  $\text{Fe}_3\text{C}$ . Also greater amounts of interlath carbides could act as fracture paths lowering toughness. In addition, a stabilized  $\text{Fe}_3\text{C}$  would hinder the uniform precipitation of the secondary hardening  $\text{Mo}_2\text{C}$  phase by preventing a homogeneous solution of C in the iron matrix.

Finally, alloy 198 was chosen as a base alloy with respect to the formation of twinned martensite. Low carbon alloys such as this exhibit little or no twinning. The low carbon content also results in a relatively low yield strength. As expected, the toughness in the as-quenched condition of this low yield strength material was greater than that exhibited by the 0.4 C alloys. However, upon tempering, there was a rapid deterioration of toughness to values below those exhibited by some of the 0.4 C alloys.

#### IV. SUMMARY

The conclusions arrived at from examination of the mechanical properties and microstructures of these alloys are:

- 1) As-quenched martensites are not necessarily brittle unless they are heavily twinned.
- 2) Increasing amounts of Mo, at constant C content, resulted in increased amounts of twinning, and decreased the toughness without changing tensile strength appreciably.
- 3) Lowering C content at a constant Mo level results in a substantially reduced amount of twinning. As-quenched toughness is increased as is ductility with lower C content; however, ultimate and yield tensile strengths are drastically reduced as expected.
- 4) The fracture toughness of as-quenched Fe/Mo/C steels was not as high as was obtained in previous experimental Fe/Cr/C steels. This is attributed to the absence of resolvable amounts of interlath retained austenite in the Fe/Mo/C alloys.

5) Cobalt raises the  $M_s$  temperature in these alloys.

6) Cobalt additions do not result in any significant change in microstructure except possibly causing finer laths. The amount of twinning present when compared with a similar Fe-Mo-C alloy without Co additions is about the same.

7) Addition of Co to an Fe/Mo/C steel in the "as-quenched" condition, all other things remaining constant (*i.e.* other alloying elements, heat treatment, etc.), results in a lower plane strain fracture toughness and slightly lower yield and ultimate tensile strengths. In addition, the ductility is considerably reduced by the Co addition.

8) Cobalt additions to Fe/Mo/C steels appear to strongly inhibit the secondary hardening reaction characteristic of Mo bearing alloy steels. In addition, Co containing steels have lower fracture toughness, yield and ultimate tensile strength, and lower ductility when compared to similarly tempered noncobalt bearing steels. It may be that Co stabilizes  $\text{Fe}_3\text{C}$  with respect to  $\text{Mo}_2\text{C}$  especially along lath boundaries. The latter may account for the reduced toughness in the tempered condition.

#### ACKNOWLEDGMENTS

We wish to thank the United States Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory for financial support of this research. This work was done in partial fulfillment of the M.S. requirements at Berkeley by one of the authors (R. A. Clark).

#### REFERENCES

1. S. K. Das and G. Thomas: *Trans. ASM*, 1969, vol. 62, p. 659.
2. M. Raghavan and G. Thomas: *Met. Trans.*, 1971, vol. 2, pp. 3433-39.
3. D. H. Huang and G. Thomas: *Met. Trans.*, 1971, vol. 2, pp. 1587-98.
4. J. McMahon and G. Thomas: Third International Conf. on Strength of Metals and Alloys, *Microstructure and Design of Alloys*, vol. 1, pp. 180-84, Cambridge, England, 1973.
5. G. Thomas: *Iron and Steel International*, 1973, vol. 46, pp. 451-61.
6. R. S. Archer, J. Z. Briggs, and C. M. Loeb, Jr.: *Molybdenum: Steels-Irons-Alloys*, Climax Molybdenum Co., 1948.
7. L. Colombier: *Molybdenum in Stainless Steels and Alloys*, Climax Molybdenum Co., Ltd., 1967.
8. K. J. Irvine: *J. Iron Steel Inst.*, 1962, vol. 200, p. 820.
9. K. J. Irvine: *Heat Treatment of Metals*, ISI Special Report No. 95, p. 37, The Iron and Steel Institute, London, 1966.
10. F. B. Pickering: *Precipitation Processes in Steels*, ISI Special Report No. 64, p. 23, The Iron and Steel Institute, London, 1959.
11. R. W. K. Honeycombe: *Trans. Iron Steel Inst. of Japan*, 1966, vol. 6, p. 217.
12. P. Payson: *Trans. ASM*, 1959, vol. 51, p. 60.
13. P. Wilkes: *Metal Sci. J.*, 1968, vol. 2, p. 8.
14. R. G. Baker and J. Nutting: *Precipitation Processes in Steels*, ISI Special Report No. 64, p. 1, The Iron and Steel Institute, London, 1959.
15. R. W. K. Honeycombe: *Proceedings of the National Research Institute of Metals, Tokyo*, p. 44, 1966.
16. K. J. Irvine and F. B. Pickering: *J. Iron Steel Inst.*, 1960, vol. 194, p. 137.
17. R. Goolsby: *Relationships Between Microstructure and Fracture Toughness in a Secondary Hardening Steel*, Ph.D. Thesis, University of California, Berkeley, Lawrence Berkeley Laboratory Report-405, 1971.
18. K. Kuo: *J. Iron Steel Inst.*, 1953, vol. 173, p. 363.
19. R. W. K. Honeycombe: *Low Alloy Steels*, ISI Publication No. 114, p. 65. The Iron and Steel Institute, London, 1968.
20. D. J. Dyson, S. R. Keown, D. Raynor, and J. A. Whiteman: *Acta Met.*, 1966, vol. 14, p. 867.
21. Annual Book of ASTM Standards, Designation E399-72, p. 960, 1972.
22. K. J. Irvine, F. B. Pickering, and J. Garstone: *J. Iron Steel Inst.*, 1960, vol. 196, p. 66.

23. C. R. Simcoe and A. E. Nehrenberg: *Trans. ASM*, 1965, vol. 58, p. 378.
24. C. R. Simcoe, A. E. Nehrenberg, V. Biss, and A. P. Coldren: *Trans. ASM*, 1968, vol. 61, p. 834.
25. B. R. Banerjee: *J. Iron Steel Inst.*, 1965, vol. 203, p. 166.
26. P. M. Kelly and J. Nutting: *J. Iron Steel Inst.*, 1961, vol. 197, p. 199.
27. A. J. Baker, P. M. Kelly and J. Nutting: *Electron Microscopy and Strength of*

- Crystals*, G. Thomas and J. Washburn, eds., p. 899, John Wiley and Sons, New York, 1963.
28. J. R. Low, Jr.: *Engineering Fracture Mechanics*, 1968, vol. 1, p. 47.
29. T. Tom: *Microstructural Variables and Fracture Toughness of High Strength Mo and Mo-Ni Steels*, D. Eng. Thesis, University of California, Berkeley, Lawrence Berkeley Laboratory Report—1856, 1973.

**LEGAL NOTICE**

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720