June 4, 1968 T. L. JOHNSTON ET AL 3,386,862

HIGH STRENGTH STRUCTURAL STEEL

Filed June 22, 1966 2 Sheets-Sheet 1



FIG. 1

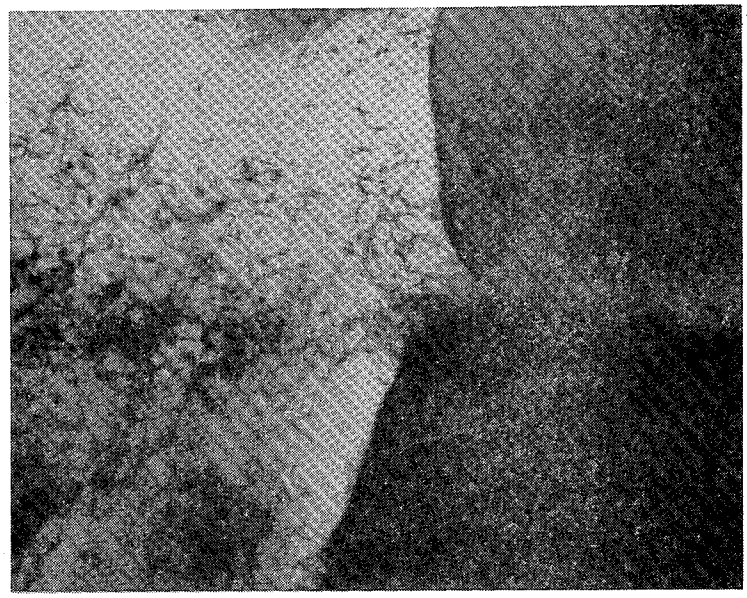


FIG. 2

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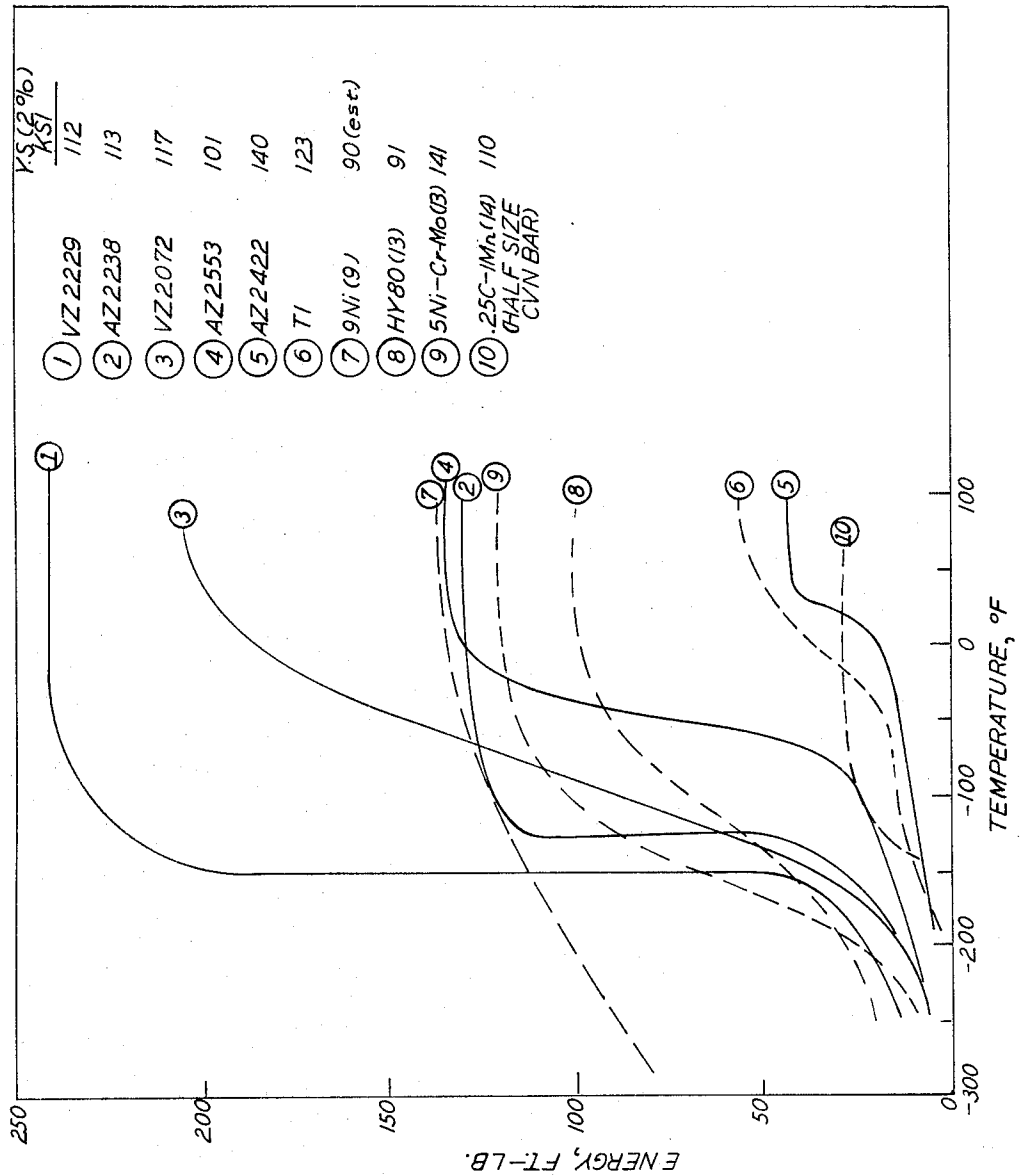


FIG. 3

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3,386,862

HIGH STRENGTH STRUCTURAL STEEL

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Continuation-in-part of application Ser. No. 459,320, May 27, 1965. This application June 22, 1966, Ser. No. 560,049

6 Claims. (Cl. 148—12)

This application is a continuation-in-part of application Ser. No. 459,320 filed May 27, 1965, and assigned to the assignees of this application and now abandoned.

This invention is concerned with a high strength structural steel and the method by which this steel is produced. This high strength structural steel is weldable and in the as-rolled condition possesses a minimum yield strength of 80 K.s.i. and an impact energy absorption at —40° F. of 40 foot pounds. This alloy is economical of expensive alloying ingredients and may be prepared either by air melting or vacuum melting techniques. No particular rolling procedures are required.

The unique properties of these high strength structural steels as compared to ordinary low alloy structural steel are readily apparent from a study of the three figures of drawing in which

FIGURE 1 is an electron beam transmission micrograph of the high strength structural steel of this invention. The structure is a massive martensite which is essentially ferrite containing a high density of dislocations. The magnification employed is × 20,000. The chemistry of this sample is:

	Percent
Carbon	0.02
Nickel	3.00
Molybdenum	3.00
Manganese	0.70
Silicon	0.30
Niobium	0.05

Remainder essentially all iron.

In this alloy both nickel and manganese serve to depress the austenite to massive martensite transformation temperature, while molybdenum serves to inhibit the transformation of austenite to equiaxed ferrite and pearlite prior to the transformation of austenite to massive martensite. The molybdenum may also serve as a carbide former. Chromium may be substituted in part for the more expensive molybdenum. To be commercially acceptable, each alloy should contain sufficient nickel or manganese or a combination of both metals to provide an acceptable austenite to massive martensite transformation temperature. The alloy should also contain a carbide forming metal which should be either chromium or molybdenum or a combination of these two metals which serves to inhibit the transformation of austenite to equiaxed ferrite and pearlite prior to the transformation temperature.

FIGURE 2 is a comparable electron beam transmission micrograph of a low alloy structural steel having a like thermal history. The structure is equiaxed ferrite containing a low density of dislocations. The magnification employed is × 20,000. The nominal chemistry of this alloy is:

	Percent
Carbon	0.02
Nickel	3.00
Silicon	0.30
Manganese	0.70

Remainder essentially all iron.

In contrast to heat treated alloy steels containing in excess of 0.1% carbon which derive their strength from quenched and tempered martensite or lower bainite, we have found that comparable yield strengths together with excellent impact toughness and weldability in the as-rolled condition can be obtained in very low carbon massive martensite steels. The carbon content of these steels should not exceed 0.07%. These steels are alloyed so as to transform on air cooling to massive martensite. The carbon content is minimized, and the alloying elements are selected to avoid the transformation to equiaxed ferrite during rolling or cooling. The austenite should be stable during processing. On subsequent cooling, the alloy should transform from austenite to massive martensite. The temperature at which this transformation takes place should not exceed 1200° F., and the preferred range is 960 to 1150° F. In general the yield strength varies inversely as the austenite to massive martensite transformation temperature.

The strength properties of air cooled plates are relatively insensitive to rolling temperatures below the austenite grain coarsening range at about 1700 to 1800° F. Impact properties are sensitive to the prior austenite grain size because the latter controls the density of grain boundary impurities. This dictates that excessive soaking times are to be avoided after completion of rolling at temperatures above 1700° F.

All heats were of one size, 20 lbs., with the exception of one 40 lb. heat, and were made in induction furnaces either in air or in vacuo. In air melts, chromium, manganese, silicon, molybdenum and carbon were added as ferro alloys. In vacuum melts, all alloying additions were in elemental form.

In air melts, after the melt down of the base charge of (Armco) iron, electrolytic nickel, and ferro-molybdenum, an addition of 0.05% aluminum was made. This addition was followed by ferro additions of chromium, manganese, silicon and vanadium, carbon and pure niobium as required. Prior to pouring at 2800–2850° F., an additional 0.05% aluminum was added.

In vacuum melts, the starting charge was electrolytic iron and electrolytic nickel. After melt down in a vacuum of the order of 0.1 mm. Hg, an argon atmosphere at a pressure of 500 mm. Hg was introduced prior to the addition of manganese and silicon. Manganese has a high vapor pressure, and the presence of the argon atmosphere reduces its loss from the melt due to vaporization. The argon atmosphere was maintained while further additions of other desired elements were made and the melt poured.

For both air and vacuum melts, the ingots were cast in tapered chill molds with a mean diameter of 2⅝ inch and were allowed to cool in the molds at room temperature. After removal from the molds the ingots were sectioned transversely to provide two—ten pound cylinders for rolling. Both visual and X-ray examination of selected ingots indicated them to be essentially free of casting defects.

ROLLING PROCEDURE

The usual rolling practice consisted of annealing the ingot halves at 1775° F. for 40 minutes after which they were box-rolled to 2 inch square bars using flat rolls with ⅛ inch reductions in roll opening and 5 minute reheats at 1775° F. after alternate passes. The bar temperature was not allowed to drop below 1400° in this stage. After box-rolling, the square bar was rolled to ⅝ inch plate either in the temperature range of 1700–1775° F. with intermediate reheats, or was air cooled to 1400° F. and rolled without reheats. The finishing temperature in the latter case was approximately 1350° F. In both rolling sequences the resultant 2 x 14 inch plate was air cooled to room temperature.

The mechanical properties such as yield strength, tensile strength, percent elongation and the reduction in area were determined on the basis of tensile tests of ⅛ inch diameter specimens. The elongation values were determined over a .8 inch gage length (7D), rather than over a usual 4D gage length. Hence the values obtained are about two-thirds that expected for a value measured over the smaller gage length.

The impact tests were made on standard 45°-V-notch Charp bars. However, because of the large number of alloys investigated, complete transition curves were not always obtained. For purposes of screening, a single test at −40° F. was often used.

Certain of the alloys which were produced in the investigation of this class of alloys are defined below in Table 1. In this table V indicates a vacuum melt and A an air melt.

TABLE 1

Heat Number	Alloy Compositions, w/o														°F.[1]
	C	Ni	Mo	Mn	Cr	Si	Nb	Al	Ti	V	P	S	N	O	
VZ1736	.0133	2.98		.68		.32					.001	.007	.003	.001	1,304
VZ1981	[2].01	3.05		2.54		.39	.062				.001	.006	<.001	.008	1,077
VZ1996	.0053	3.05	2.85	.73		.46	.060				.002	.005	<.001	.001	1,033
VZ2009	.0031	3.08	1.85	.73		.43	.055				.001	.005	<.001	.001	
VZ2010	.0027	3.05	.95	.75		.41	.050				.003	.008	<.001	.002	1,212
VZ2011	.004	3.00	2.95	.72		.52			.093		.001	.006	<.001	.003	1,156
VZ2017	.0493	3.00	2.85	.70		.46	.050				.001	.006	<.001	<.001	954
VZ2038	.0014	3.30	.63	.72		.30	.040				.001	.008	<.001	.009	1,238
AZ2039	.0015	2.90	2.70	.50		.23	.030	.035			.012	.013	.005	.010	
VZ2043	.0019	3.00	2.82	.68		.23	.047				.001	.006	<.001	.006	1,041
VZ2044	.0386	2.82	2.82	.69		.27	.055				.001	.006	<.001	.002	958
VZ2045	[2].02	3.12	1.40	1.52		.29	.045				.001	.006	<.001	.001	1,027
VZ2052	.0032	2.95	2.75	.65		.30	.030				.001	.008			1,060
VZ2071	.006			2.40	2.90	.27	.065				.003		<.001		1,197
VZ2072	.049			2.37	2.88	.29	.065				.004		<.001		
VZ2116	.071	2.93	2.79	.69		.28	.049				.001	.007	<.001	.001	
VZ2117	.0355	2.96	1.98	.72	.95	.34	.046				.002				957
VZ2179	[2].02	2.90	2.75	.65		.39	.075	.11							
VZ2180	[2].03	2.85	2.70	.67		.22	.080		.20						1,112
VZ2181	[2].03	2.95	2.82	.67		.39	.080			.49					
VZ2182	[2].03	2.85	2.80	.67		.39	.075	.10		.50					1,065
VZ2183	[2].02	2.85	2.75	.67		.41	.070	.10	.18						1,082
VZ2184	[2].01	2.90	2.75	.67		.38	.080		.18	.50					
VZ2185	[2].02	2.95	2.70	.67		.38	.075	.070	.18	.49					
AZ2186	.0108	2.80	2.70	.36		.17	.050	.015			.006	.022			
AZ2187	.0042	2.80	2.70	.53		.24	.070	.080	.11		.005	.022	<.001		1,075
AZ2188	.0125	2.85	2.65	.48		.22	.065	.075		.19	[2].015	[2].015	.0032		
AZ2189	.0148	2.80	2.75	.58		.25	.065	.075	.14	.41	.005	.020			
AZ2190	.0104	2.95	2.70	.59		.22	.070	.065			.012	.035	.003	.02	
AZ2191	[2].03	2.95	2.70	.64		.30	.070	.071	.05		.022	.040	.002	.01	936
AZ2192	.0147	2.95	2.70	.64		.24	.060	.070		.23	.022	.041	.002	.02	1,006
AZ2193	[2].03	2.95	2.65	.59		.22	.050	.080	.12	.26	.023	.040	.002	.01	
AZ2229	.0261	2.90	2.90	.73		.30	.046				.002		<.001		
AZ2238	.0133	3.05	2.95	.66		.31	.033				.006		.0023		
AZ2239	.0170	1.70	1.65	1.73	1.15	.34	.046	.070			.012		.0033		
VZ2240	.0497	1.68	1.55	1.42	1.48	.30	.052				.011				
AZ2241	.0127	2.10	2.90	.74		.30	.030	.095			.006		.0015		
AZ2242	.0142	1.18	2.95	.77		.32	.032	.11			.007		.0032		
AZ2243	.0423	2.15	3.05	.98	.49	.36	.035	.13			.006		.0034		
AZ2252	.0177			2.60	3.02	.27	.057	.035			.016		<.001		903
AZ2253	.0194			2.65	3.30	.29	.040	.065			.015		.005	.008	881
AZ2260	.0252	3.10	2.10	.81	.99	.35	.045	.15			.012		.003		916
AZ2261	.0369	3.10	1.08	.79	.90	.32	.045	.055			.008		.0022		951
AZ2262	.0301	3.05	1.05	.82	1.70	.32	.048	.060			.013		.0022		914
AZ2312	[2].09	1.95	1.10	1.88	.49	.29	.020	.020			.011	.017			
AZ2313	[2].06	4.00	1.00	.96	.46	.32	.02	.020			.011	.018			935
AZ2352	[2].05	[2]3	[2]3	[2].7		[2].3	[2].05	[2].1							
AZ2353	[2].05	[2]3	[2]3	[2].7		[2].3	[2].05	[2].1							
AZ2354	[2].05	[2]3	[2]3	[2].7		[2].3	[2].05	[2].1							
AZ2355	[2].05	[2]3	[2]3	[2].7		[2].3	[2].05	[2].1							
AZ2422	.1040			2.35	2.75	.21	.03	.03		.19	.011	.012	.005	.010	
AZ2423	.0830			2.28	2.90	.14	.03			.18	.011	.014			
AZ2424	[2].05			2.56	3.00	.27	.05	.04							
AZ2425	[2].05			2.56	3.02	.27	.05								
AZ2475	[2].05		.52	2.30	2.33	.08	.040	.040		.13					
AZ2476	[2].05		.55	2.58	3.00	.14	.055	.048							
AZ2477	.0134			2.62	3.01	.24	.055	.045		.17	.014	.014	.005	.011	
AZ2519	[2].05			2.50	2.90	.25	.060			.19					
AZ2520	[2].05			2.39	3.01	.22				.19					
AZ2553	.0128			2.62	3.05	.32	.055	.040		.19					
AZ2554	.0163			2.55	3.22	.31	.057			.16					
AZ2555	.0135			2.54	3.20	.28	.060	.035							
AZ2556	.0154			2.70	3.11	.42				.17					
AZ2557	.0138			2.60	3.03	.34		.035							
AZ2559	[2]0			[2]2.5	[2]3	[2].3		[2].1		[2].1					

[1] Temperature at which Transformation Starts on Cooling. [2] Nominal composition.

Table 2 has been prepared to demonstrate the effect of rolling temperature upon certain of these alloys.

TABLE 2

Heat Number	C, w/o	Si, w/o	Nb, w/o	Al, w/o	V, w/o	Rolling Temperature, °F.	Y.S. (.2%), K s.i.	T.S., K s.i.	ε, percent	R.A., percent	Charpy (−40° F.), ft.-lb.
VZ2117						1,400	108	139	12	71	222
						1,750	111	141	12	69	238
VZ2191						1,400	116	139	11	56	91
						1,750	113	137	12	57	26
AZ2238						1,400	113	130	12	59	131
						1,750	113	131	11	69	126
AZ2239						1,400	110	134	11	59	58
						1,750	109	132	11	62	72
VZ2240						1,400	113	155	12	63	140
						1,750	115	153	12	63	178
AZ2243						1,400	115	142	11	45	100
						1,750	114	148	11	54	44
AZ2260						1,400	115	144	11	57	36
						1,750	111	142	11	67	61

TABLE 2—*Continued*

Heat Number	C, w/o	Si, w/o	Nb, w/o	Al, w/o	V, w/o	Rolling Temperature, ° F.	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, percent	R.A., percent	Charpy (−40° F.), ft.-lb.
AZ2261						1,400	96	127	12	59	59
						1,750	99	124	13	70	35
AZ2262						1,400	111	143	11	58	58
						1,750	110	138	11	58	64
AZ2312						1,400	120	155	11	50	48
						1,750	112	152	10	45	41
AZ2313						1,400	103	139	12	48	58
						1,750	100	139	13	50	72
VZ2071	.006	.27	.065			1,400	67	81	19	71	239
AZ2252	.0177	.27	.057	.035		1,400	110	135	10	58	17
AZ2253	.0194	.29	.040	.065		1,400	118	141	9	54	11
						1,700	112	136	11	60	10
AZ2553	.0128	.32	.055	.040	.19	1,400	101	116	12	70	94
						1,700	99	115	11	74	116
AZ2477	.0134	.24	.055	.045	.17	1,400	106	124	11	64	115
						1,700	105	124	11	74	95
AZ2555	.0135	.28	.060	.035		1,400	105	123	11	70	48
						1,700	100	117	11	75	100
AZ2554	.0163	.31	.057		.16	1,400	112	131	10	67	20
						1,700	110	130	10	71	95
AZ2559	[1] 0	[1] .3		[1] .1	[1] .1	1,400	113	135	10	71	19
						1,700	113	132	10	73	5
AZ2556	.0154	.42			.17	1,400	118	142	10	64	16
						1,700	113	135	10	72	11
AZ2557	.0138	.34		.035		1,400	107	128	11	73	41
						1,700	102	121	11	75	15
VZ2072	.049	.29	.065			1,400	117	149	12	67	135
						1,700	114	143	11	72	150
AZ2425	[1] .05	.27	.05			1,400	143	176	10	54	13
						1,700	136	171	11	59	14
AZ2424	[1] .05	.27	.05	.04	.01	1,400	140	176	10	53	21
						1,700	132	170	11	49	8
AZ2422	.1040	.21	.03	.03	.19	1,400	140	178	10	36	14
						1,700	135	171	11	50	18
AZ2423	.0830	.14	.03	.01	.18	1,400	141	167	11	55	17, 30, 14
						1,700	131	165	11	61	39, 21, 10
AZ2519	[1] .05	.25	.060		.19	1,400	143	180	10	60	17
						1,700	134	173	10	61	25
AZ2520	[1] .05	.22			.19	1,400	133	175	11	62	22
						1,700	132	172	11	65	13
AZ2475 [2]	[1] .05	.08	.040	.040	.13	1,400	130	169	10	64	36
						1,700	128	167	11	64	30
AZ2476 [2]	[1] .05	.14	.055	.048		1,400	141	179			27
						1,700	139	179	11	64	30

[1] Nominal composition. [2] .5 Mn addition.

Table 3 has been prepared to illustrate the effect of cooling at different rates from 1400° F.

TABLE 3

[Alloy (VZ2052)—.0032C-2.95Ni-2.75Mo]

Cooling Rate, ° F. min.$^{-1}$	Cooling Procedure	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
1,400	Estimated for water quench following rolling.	100	109	12	77	238
100	Average for air cooling following rolling.	99	109	14	79	151
6	½ hr. at 1775° F. followed by furnace cool at constant rate.	94	99	12	79	24
2½	Furnace cool following rolling	69	89	24	78	239

The results of tests of determine the effect of the rolling temperature on the mechanical properties are contained in Table 2. Below 1750° F. down to 1350° F., a range in which the alloys are austenitic, there appears to be little effect of the rolling temperature on the properties. For both the Mo-Ni alloy and the Cr-Mn alloy, yield strengths in excess of 100,000 p.s.i. are obtained. The impact values are higher in vacuum melts than in air melts, but in both cases the toughness is high as shown in FIGURE 3 where some of the present results are plotted and compared with the impact properties of T–1, 9Ni,[5] HY–80, [9] 5Ni-Cr-Mo-V,[9] and 1Mn[10] steels. The reduction in area of the low carbon alloys is high, a direct indication that particle effects in ductile fracture are small. In addition, a high reduction in area has often been correlated with a high value of the shelf energy.

The transformation product observed in both the 3Mo-3Ni and the 3Cr-2.5Mn alloys was predominantly massive martensite. The leaner alloys start to transform at higher temperatures and they contain a much greater proportion of equiaxed ferrite. Whenever equiaxed ferrite formed in large amounts, the transformation range was not only higher, but also much broader than that observed for a transformation to massive martensite. In FIGURE 1 the structure as examined by electron transmission microscopy is seen to consist of ferrite plates containing a high density of dislocations. Such a configuration of unpinned dislocations existing in a matrix relatively free of particles imparts both strength and toughness to the alloy. The macroscopic yield strength is strongly dependent upon the high strain hardening rate associated with such dislocation arrays. High toughness results from the ability of the dislocations to accommodate the imposed high strain rates of the Charpy test by rapid relaxation of stress concentrations. The relaxation rate depends in turn on the allowable plastic strain rate, ϵ, which is a fraction of the density of dislocation, n, and their velocity v, as given by:

$$\dot{\epsilon}=nbv \qquad (9)$$

where b is the Burgers vector. A high initial value for n leads to a spreading out rather than a concentration of shear deformation, and reduces the average velocity of motion required. This latter effect is a particularly important consideration in iron based alloys at low temperatures where the velocity of motion of a dislocation as a function of stress decreases sharply. The influence of cooling rate on the mechanical properties is shown in Table 3 for 3Ni-3Mo steel. A rapid quench did not affect the tensile properties, but some improvement in toughness compared to air cooling was noted. If the alloy is very slowly cooled after rolling, the amount of equiaxed

ferrite will of course increase. The grain size is much larger than the needles of massive martensite. The appearance of the equiaxed structure is shown in FIGURE 2 for a 3Ni alloy. Examination of thin foils reveals a marked decrease in dislocation content as compared to massive martensite. As a consequence both the impact and tensile properties are lessened. Similarly, if the alloys are either reheated after rolling and held at a temperature high in the ferrite range (1200–1400° F.) or furnace cooled from the rolling temperature, there is a loss in strength. The properties as a function of tempering temperature are listed in Table 4.

TABLE 4.—EFFECT OF TEMPERING TEMPERATURE ON IMPACT TOUGHNESS

[Alloy (VZ1996)—.0053C-3.05Ni-2.85Mo Plate A rolled at 1250° F. and Plate B rolled with cooling from 1850° to 1700° F.]

Condition	Temperature, ° F.	Time, hr.	Hardness R.A.	Charpy (−184° F.), ft.-16 lb.
A			61	240
A	600	1	61	209
A	1,000	1	62	240
A	1,200	4	60	65
A	1,400	1	50	240
A	1,700	2	61	161
A	1,900	1	60	9
B			62	60
B	1,600	1	60	240
B	1,700	1	61	86
B	1,800	1	61	35

When the material is reaustenitized there is no loss in properties provided that the temperatures and times are such as to avoid grain coarsening. For example, the properties after heat treatment at 1700° F. are much superior to those obtained at 1900° F.

The effect of varying the carbon content on the mechanical properties of the base alloys, 3Ni-3Mo-.7Mn-3Si-.05Nb, and 2.5Mn-3Cr-.3Si-.0.5Nb is shown in Table 5.

TABLE 5.—EFFECT OF CARBON CONTENT ON PROPERTIES

(A) Base Alloy 3Ni-3Mo Rolled at 1,400° F.

Heat Number	C, w/o	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
VZ2043	.0019	84	96	15	71	170
VZ2052	.0032	99	109	14	79	151
VZ2229	.0261	112	133	13	65	239
VZ2044	.0386	108	135	12	71	175
VZ2017	.0493	111	144	13	65	148
VZ2116	.071	110	158	13	56	59

(B) Base Alloy 3Cr-2.5Mn Rolled at 1,400° F.

VZ2071	.006	67	81	19	71	239
VZ2072	.049	117	149	12	67	135
AZ2253	.0194	118	141	9	54	11
AZ2555	.0135	105	123	11	70	48
AZ2477*	.0134	106	124	11	64	115

*.1V addition.

These results shown an increase in yield and tensile strengths with an increase in carbon content with air melted alloys generally stronger than those vacuum melted. The results of the impact tests are less straightforward. In vacuum melted 3Ni-3Mo alloys the impact strength remained high up to the 0.07 carbon level, but in the vacuum melted 2.5Mn-3Cr series there was a drop in impact resistance when the carbon level was increased even from .01 to .05. It is noteworthy that the addition of 0.1Al and 0.1V to air melt AZ2477 has increased the impact resistance at −40° F. to the 100 ft.-lb. range.

NICKEL AND MANGANESE

The results of a series of tests on 3Mo-.7Mn-.3Si-.05Nb low carbon alloy heats in which the nickel content was varied are shown in Table 6.

TABLE 6.—EFFECT OF NICKEL CONTENT ON PROPERTIES

[Base alloy—.02C-3Mo rolled at 1400° F.]

Heat Number	Ni, w/o	Y.S. (.2%) K s.i.	T.S. K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
AZ2242	1.18	76	88	16	60	14
AZ2241	2.10	87	108	16	64	138
AZ2039	2.90	113	130	12	59	131

It is seen that an increase of nickel content for the same carbon level leads to an increase in the strength properties. Except for heat AZ2242, all of these alloys possess an impact strength at −40° F. in excess of 100 ft.-lbs.

Results of a similar series of the 3Cr-Mn alloys in which the manganese content has been systematically varied have not been obtained. However, it is expected that the influence of manganese should be similar to that of nickel.

An important influence of molybdenum is to increase hardenability, and since this can also be accomplished by an increase in the manganese content, several heats were made of a 3Ni alloy in which both the molybdenum and manganese contents were varied. The results are given in Table 7.

TABLE 7.—EFFECT OF MOLYBDENUM AND MANGANESE CONTENT ON PROPERTIES

[Base alloy—.02C-3Ni rolled at 1400° F.]

Heat Number	Mo, w/o	Mn, w/o	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
VZ1981	2.54	75	87	17	83	238	
VZ2045	1.40	1.52	91	103	13	77	235
VZ2052	2.75	.65	99	109	14	79	151

These results indicate that manganese alone (VZ1981) can lead to high toughness, but that in order for the yield strengths to reach to 100K s.i. level, the presence of a carbide forming element (e.g., molybdenum) in this base alloy is needed.

MOLYBDENUM AND CHROMIUM

These two elements have a similar effect on properties. Both increase hardenability, but chromium is also effective in lowering the M_s temperature and both form alloy carbides in the same temperature range. These carbides are believed to form within the ferrite during the air cool after rolling.

The effect of molybdenum content on the properties is shown in Table 8.

TABLE 8.—EFFECT OF MOLYBDENUM CONTENT ON PROPERTIES

[Base alloy—.02C-3Ni rolled at 1400° F.]

Heat Number	Mo, w/o	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
VZ1736*		47	62	32		240
VZ2038	.63	56	70	23	75	113
VZ2010	.95	68	81	18	75	240
VZ2009	1.85	83	93	16	72	240
VZ2052	2.75	99	109	14	79	151

*⅝ inch rod heated at 1,650° F. for .5 hour and air cooled.

Over this range of molybdenum contents there is a monotonic increase in yield strength with increase in molybdenum content. The impact properties are a maximum in the 1–2% Mo range in this table; however, on occasion in alloys of higher molybdenum content with the same nominal compositions as VZ2052, e.g., VZ1996, impact values of 240 ft.-lbs. at −40° F. have been obtained.

The effects of chromium on the properties can be seen in the following Table 9.

TABLE 9.—EFFECT OF CHROMIUM CONTENT ON PROPERTIES

[Base alloy—.05C-1.5Ni-1.5Mo-1.5Mn rolled at 1,400° F.]

Heat Number	Cr, w/o	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
VZ2240	1.48	113	155	12	63	140
AZ2239	1.15	110	134	11	59	58
AZ2312	.5	120	155	10	50	48

TITANIUM—ALUMINUM—VANADIUM—NIOBIUM

The effects of small additions of elements such as Ti, Al, V and Nb are difficult to specifically isolate because of the many complex interactions possible. These elements have been generally added in quantities consistent with usual alloy steel practice. Throughout this investigation Nb has been a standard alloying element in the amount of 0.05 w/o. This usage of Nb is based upon preliminary work with rod material which revealed both an increase in the yield strength as well as the impact strength of alloys containing .02 w/o C. This effect of Nb can also be seen in the data for alloys VZ2011 and VZ2180, Table 10.

TABLE 10.—EFFECT OF TITANIUM, ALUMINUM, VANADIUM AND NIOBIUM CONTENT ON PROPERTIES

[Base alloy—3Ni-3Mo rolled at 1,400° F.]

Heat Number	C, w/o	Ti, w/o	Al, w/o	V, w/o	Nb, w/o	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, percent	R.A., percent	Charpy (−40° F.), ft.-lb.
VZ2011	.004	.093				83	96	17	72	238
VZ2180	*.03	.20			.080	98	108	15	73	238
VZ2181	*.03			.49	.080	95	107	16	74	239
VZ2182	*.03		.10	.50	.075	88	100	19	71	239
VZ2183	*.02	.18	.10		.070	88	101	17	74	238
VZ2184	*.01	.18		.50	.080	81	94	19	67	239
VZ2185	*.02	.18	.070	.49	.075	83	95	18	68	207
VZ2229	.0261				.046	112	133	13	65	239
AZ2187	.0042	.11	.080		.070	102	115	13	67	117
AZ2188	.0125		.075	.19	.065	116	128	12	65	122
AZ2191	*.03	.05	.071		.070	116	139	11	56	91
AZ2192	.0147		.070	.23	.060	122	135	11	61	34
AZ2193	*.03	.12	.080	.26	.050	111	125	13	57	186
AZ2039	.0015		.035		.030	110	127	11	58	126

*Nominal.

The addition of Nb raises the yield strength and does not impair impact properties at −40° F. This effect of Nb is thought to be due to its role in refining the grain size of austenite. In these low carbon alloys not enough of the NbC phase is formed to adversely affect impact strength as has been found in the case of higher carbon alloys. Refinement of the grain size of the austenite will result in a smaller needle length of the massive martensite, and will also tend to distribute impurity particles over a larger total grain boundary surface area. Both of these effects will be beneficial insofar as toughness is concerned. Any loss in hardenability due to the refinement of austenitic grain size does not appear to be significant in these alloys.

In the vacuum melts there is no beneficial effect imparted by the addition of elements Ti, V and Al. In fact these additions can reduce the yield strength (e.g., VZ2185). This reduction may be due to the complete removal from solution of carbon by vanadium. In air melts, the addition of vanadium to alloys low in phosphorus and sulfur, has a beneficial effect on yield strength and the impact properties at −40° F. remain high (AZ2188). In fact the properties of all of the air melts are good, with the exception of AZ2192 which showed a reduction in impact strength for a high phosphorus and vanadium content. The addition of Ti and Al to air melts appears to be beneficial. Results of a similar study with Cr-Mn alloys are shown in Table 11.

TABLE 11.—EFFECT OF VANADIUM, ALUMINUM AND NIOBIUM CONTENT ON PROPERTIES

[Base alloy—OC-3Cr, 2.5Mn rolled at 1,400° and 1,750° F.]

Heat Number	V, w/o	Al, w/o	Nb, w/o	Rolling Temperature, ° F.	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40°F.), ft.-lb.
AZ2477	.17	.045	.05	1,400	106	124	11	64	115
				1,750	105	124	11	74	95
AZ2553	.19	.040	.055	1,400	101	117	12	70	94
				1,750	99	115	11	74	116
AZ2554	.16		.057	1,400	112	131	10	67	20
				1,750	110	130	10	71	95
AZ2555		.035	.060	1,400	105	123	11	70	48
				1,750	100	117	11	75	100
AZ2556	.17			1,400	118	142	10	64	16
				1,750	113	135	10	72	11
AZ2557		.035		1,400	107	128	11	73	41
				1,750	102	121	11	75	15

The properties of the first two heats indicate that the attainment of high impact strengths in Cr-Mn alloys is reproducible. These properties compare favorably with those of 3Mo-3Ni air melts. The omission of either vanadium or aluminum does not adversely affect the properties provided that the rolling temperature is at least 1700° F. (Heats AZ2555 and AZ2554.) The higher rolling temperature may facilitate the removal from solution of nitrogen by these elements. The absence of Nb leads to a decrease in impact resistance, particularly at the higher rolling temperature (Heats AZ2556 and AZ2557).

THE EFFECT OF PHOSPHORUS AND SULFUR

The amount of phosphorus and sulfur in these alloys was generally kept to less than 0.015 percent each. In order to determine the effects of these elements in larger quantities, a series of air melted alloys was prepared with phosphorus contents of up to .0.022 percent and sulfur up to 0.040 percent. The properties of these alloys are listed in Table 12.

TABLE 12.—EFFECT OF PHOSPHORUS AND SULFUR CONTENT ON PROPERTIES

[Base alloy—.02C-3Ni-3Mo rolled at 1,400° F.]

Heat Number	P, w/o	S, w/o	Ti, w/o	Al, w/o	V, w/o	Nb, w/o	Y.S. (.2%), K s.i.	T.S., K s.i.	ϵ, Percent	R.A., Percent	Charpy (−40° F.), ft.-lb.
AZ2039	.012	.013	----------	.035	----------	.030	110	127	11	58	126
AZ2190	.012	.035	----------	.065	----------	.070	117	127	11	56	126
AZ2187	.005	.022	.11	.080	----------	.070	102	115	13	67	117
AZ2191	.022	.040	.05	.076	----------	.070	116	139	11	56	91
AZ2188	*.015	*.015	----------	.075	.19	.065	116	128	12	65	122
AZ2192	.022	.041	----------	.070	.23	.060	122	135	11	61	34
AZ2189	.005	.020	.14	.075	.41	.065	89	101	16	67	118
AZ2193	.023	.040	.12	.080	.26	.050	111	125	13	57	186

*Estimated.

The effect of these additions is not systematic, but it is seen that these elements can reduce the CVN values. Titanium appears to have an effect which offsets the detrimental influence of phosphorus and sulfur on toughness.

HARDENABILITY

In order to obtain an indication of the hardenability of these alloys a 2½ inch diameter ingot (AZ2531B) was sectioned in the transverse direction after casting. A hardness traverse across the diameter of the exposed face was made and the hardness values were found to vary in a random manner from 18½ to 19½ Rc. A similar traverse was made on a section through the ingot which had been reaustenitized and air cooled from 1750° F. and similar readings were obtained. The alloy is therefore fully hardened in section sizes at least up to 2½ inch diameter in both the as-cast and the air cooled conditions.

WELDABILITY

The purposes of some initial tests on weldability were to determine is sound welds, free of cracks and blow holes could be obtained by standard welding techniques, and to assess the behavior of the heat affected zone. The welding was performed by members of the Manufacturing Development Staff. Test weldments were made using .02C-3Ni-3Mo steel plates.

The weld material was either of the same compositions as the plate with which a 75% argon-25%Co_2 atmosphere was used, or Airco No. 352, low hydrogen, covered electrodes. The results of tests listed in Table 13 indicated that crack free welds can be obtained and that the heat affected zone is still quite tough, absorbing 44 to 104 ft.-lbs. Studies with 5Ni steels indicate that the transformation temperature of the present steels is sufficiently high to avoid cracking of the weld metal interface on cooling. Furthermore, the low carbon level prevents the formation of carbides which are known to have an embrittling effect.

FORMABILITY

In order to determine the formability of these alloys, a ½ inch plate of the 3Ni-3Mo alloy was bent about a ½ inch diameter through an angle of 90°. No cracking was observed. A correlation between the formability of high strength alloys and the reduction of area in the tensile test has been established, and on this basis also the high reduction of area of the low carbon massive martensitic steels is indicative of good formability.

EFFECT OF COLD WORK

A plate of 3Ni-3Mo-.02C alloy was reduced 84% by rolling at room temperature. The yield strength of the alloy was 240K s.i., its tensile strength was 207K s.i. and the elongation in 2" was 3%, as determined on flat tensile strips. The material still appeared tough in the sense that failure was not brittle; and occurred as a result of plastic instability with considerable lateral contraction in the immediate vicinity of the fracture.

INGOT SIZE AND TRANSVERSE PROPERTIES

One 40 lb. heat of a 3Mo-3Ni-.02C alloy was vacuum melted and rolled to ⅝" plate thickness in order to make a comparison with the properties of the usual 20 lb. heats. The width of the plate was 4 inches which permitted transverse as well as longitudinal properties to be obtained. The results were as follows:

	Y.S., K s.i.	TS, K s.i.	Percent ϵ	Percent R.A.
Longitudinal	88	99	15	79
Long transverse	95	106	14	81

IMPACT PROPERTIES

Orientation of Notch	Test Temperature −40°	Test Temperature −120°
Transverse and parallel to rolling plane, ft.-lb	236	186
Perpendicular to rolling plane, ft.-lb	186	144
Longitudinal and parallel to rolling plane, ft.-lb	153	127

These results indicate about the usual sort of anisotropy associated with rolled plate products. The lower than usual value of 88K s.i. for the yield strength of the alloy is thought to be due more to variation in carbon content than to a loss in tensile properties as a result of increasing the size of the ingot from 20 to 40 lbs.

TABLE 13.—EFFECT OF WELDING ON IMPACT TOUGHNESS

[Base alloy—.02C-3Ni-3Mo rolled at 1,400° F.]

Charpy Notch Position Relative to Weld	Weldment Number—Filler Metal: VZ2179-9 base [1]	VZ2179-4 352	AZ2186-7 base [1]	AZ2186-8 Base [1]	AZ2186-6 352	AZ2188-2 Base [1]	AZ2188-5 352
1. Notch in weld adjacent parent metal	[2] 50	89	72	[2] 6	47	[2] 17	48
2. Same as 1	[2] 9	100	[2] 9	[2] 2	104	[2] 21	44
3. Notch in parent metal removed from weld	240	240	141	[2] 5	139	80	112
4. Notch in center of weld	[2] 12	6	16	[2] 8	14	12	8

[1] Holes and cracks present in weldment. [2] Partial fracture along weld interface.

AS CAST PROPERTIES

In many potential applications of high strength steels it may be desired to obtain the strength and toughness in the as-cast condition. In order to determine as-cast properties therefore, the following alloys, containing additions of either Zr or Hf for deoxidation, were cast and mechanical properties determined, Table 14.

TABLE 14.—EFFECT OF HAFNIUM AND ZIRCONIUM CONTENT ON AS-CAST MATERIAL

[Base alloy—.05C-3Ni-3Mo]

Heat Number	Hf,* w/o	Zr,* w/o	Y.S. (.05%), K s.i.	T.S., K s.i.	ϵ, percent	R.A., percent	Charpy (−40° F.), ft.-lb.
AZ2352	.05		109	130	5	10	16
AZ2353		.05	110	137	7	14	9
AZ2354	.01		110	132	7	14	14
AZ2355		.01	90	135	5	12	13

*Nominal composition.

The strengths of these as-cast alloys are similar to the alloys as-rolled, but there is a sharp decline in impact and ductility values. Nevertheless the properties seem to be of sufficient interest to warrant further investigation.

The effect of a normalizing treatment on several other cast alloys was also studied, Table 15.

TABLE 15.—EFFECT OF NORMALIZING TREATMENT ON PROPERTIES OF AS CAST MATERIAL

[Base alloy—.02C-3Ni-3Mo held ¾ hr. at temperature]

Normalizing Temperature Heat Number	As Cast		1,800° F.		1,900° F.		2,100° F.	
	Hardness, Rc	Charpy (−40° F.), ft.-lb.	Hardness, Rc	Charpy (−40° F.), ft.-lb.	Hardness, Rc	Charpy (−40° F.), ft.-lb.	Hardness, Rc	Charpy (−40° F.), ft.-lb.
VZ2180	17	5	16	4	17	5	17	6
VZ2181	17	6	14	6	17	5	18	5
AZ2190	22	8	20	9	21	8	22	8
AZ2192	25	6	22	5	23	7	21	9

These results reveal that normalizing above 1800° F. has no significant effect upon the properties. The effect of lower normalizing temperatures is being investigated.

FATIGUE PROPERTIES

Fatigue tests were performed on a 3Ni-3Mo alloy having a yield strength and tensile strength of 112K s.i. and 133K s.i., respectively. Both smooth and notched specimens were tested as rotating beams (R. R. Moore type). The unnotched fatigue strength obeys the usual rule in that the fatigue endurance at long lives is about ½ of the tensile strength. The notched specimen (theoretical notch factor of 5) exhibits about the same degree of reduction of fatigue strength as other steels of this strength level.

Because of the uniform structure of this steel it is expected that the degree of scatter of fatigue data should be less than usual at these strength levels.

Preliminary fatigue crack growth studies in sheet specimens revealed a characteristic of these steels associated with the high impact toughness. The cracks grew until the stress on the remaining section was equal to the tensile strength of unnotched material, so that the material, statically, was notch insensitive.

CARBURIZATION

In certain instances it may be desired to increase the surface hardness by carburization. The effect on the properties of a carburized .02C-3Ni-3Mo alloy (Z1755) was therefore investigated. The carburization was done by the packed method at 1700° F. for 2 hrs. The resultant surface hardness was 55 R_c and that of the interior was 20 R_c. In one case the notch was present prior to carburizing and this specimen absorbed 17 ft.-lbs. in the Charpy impact test. In a second set of specimens, the notch was machined after carburization so that the base of the notch was in a noncarburized region. These specimens absorbed 95–155 ft.-lbs., indicating that the core of the specimen retains its toughness after this heat treatment.

The following partial bibliography is presented to assist in the understanding of this invention and its technical background.

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Being not unmindful of the following patents, 2,707,680, Succop, May 3, 1955; 3,044,872, Hayes, July 17, 1962; 3,135,600, Hardwick et al., June 2, 1964; and 703,911 (British), Feb. 10, 1954, we claim as our invention:

1. The process of producing a weldable structural steel object having in the as-rolled condition, a massive martensitic structure essentially free of equiaxed ferrite, a minimum yield strength of 80K s.i. and a minimum impact energy absorption value at −40° F. of 40 foot pounds comprising fabricating an alloy having a maximum carbon content of 0.07%, a content of alloying metal selected from the group consisting of nickel, molybdenum, chromium, manganese and silicon in an amount not substantially in excess of 7%, the sum of combinations of the nickel, molybdenum, chromium and manganese not exceeding about 6%, the alloy containing significant amounts of metal selected from the group consisting of nickel, manganese and combinations of nickel and manganese such that the transformation of austenite to massive martensite is retarded at temperatures above 1300°

F., the alloy further containing significant amounts of metal selected from the group consisting of chromium, molybdenum and combinations of chromium and molybdenum such that the transformation of austenite to equiaxed ferrite is essentially absent at temperatures above the austenite to massive martensite transformation temperature, the chemistry of the object being adjusted to exhibit an austenite to massive martensite transformation temperature below 1300° F. and a rate of transformation of austenite to massive martensite such that essentially no equiaxed ferrite is produced in air cooling from the austenite to massive martensite transformation temperature to room temperature, hot working the alloy and finishing the hot working operation at a temperature sufficiently low to inhibit substantial austenite grain growth during working and cooling down to the austenite to massive martensite transformation temperature, said object exhibiting a microstructure of massive martenite containing a high density of dislocations and metallurgically indistinguishable from the structure in FIGURE 1.

2. The process recited in claim 1 in which the alloy contains about 0.05% niobium.

3. A weldable structural steel object having in the as-rolled condition a massive martensitic structure essentially free of equiaxed ferrite, a minimum yield strength of 80K s.i. and a minimum impact energy absorption value at —40° F. of 40 foot pounds, a maximum carbon content of 0.07%, a content of alloying metal selected from the group consisting of nickel, molybdenum, chromium, manganese and silicon in an amount not substantially in excess of 7%, the sum of combinations of the nickel, molybdenum, chromium and manganese not exceeding about 6%, the alloy containing significant amounts of metal selected from the group consisting of nickel, manganese and combinations of nickel and manganese such that the transformation of austenite to massive martensite is retarded at temperatures above 1300° F., the alloy further containing significant amounts of metal selected from the group consisting of chromium, molybdenum and combinations of chromium and molybdenum such that the transformation of austensite to equiaxed ferrite is essentially absent at temperatures above the austenite to massive martensite transformation temperature, the chemistry of the object being adjusted to exhibit an austenite to massive martensite transformation temperature below 1300° F. and a rate of transformation of austenite to massive martensite such that essentially no equiaxed ferrite is produced in air cooling from the austenite to massive martensite transformation temperature to room temperature, and exhibiting a microstructure of massive martensite containing a high density of dislocations and being metallurgically indistinguishable from the structure shown in FIGURE 1.

4. The weldable structural steel object recited in claim 3 and which includes a niobium content of about 0.05%.

5. The process recited in claim 1 in which the chromium, manganese, nickel and molybdenum are present in approximately equal amounts.

6. The object recited in claim 3 in which the chromium, manganese, nickel and molybdenum and present in approximately the same amounts.

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