Sulfide Shape Control in High Strength Low Alloy Steels

LEON LUYCKX, JOHN R. BELL, ALEX McLEAN, AND MICHAEL KORCHYNSKY

Directionality of mechanical properties—such as toughness and bend formability—is typical of hot rolled steels processed on modern, hot strip mills. In aluminum killed steels, directionality results mainly from elongated (type II) manganese sulfide inclusions. Directionality can be reduced by retaining the original globular shape of the precipitated sulfides. This can be accomplished by promoting the formation of sulfides which are more stable and have a higher melting point than that of manganese sulfide. Thermodynamic considerations indicate that additions of Ti, Zr, Ca, Mg, and rare earths are suitable for this purpose. Experimental work on laboratory heats containing 0.020 to 0.25 pct S involved mainly additions of rare earths (mischmetal or silicides) to a V-Al-N high strength, low alloy steel. Other strong sulfide formers were not utilized either because of too high vapor pressure at steelmaking temperatures or because of their strong interaction with nitrogen. For cerium contents of 0.03 to 0.04 pct, the shape of inclusions, identified as rare earth sulfides, was globular. Control of sulfide shape contributed to a marked improvement in toughness and formability of steel in the direction transverse to the rolling direction. The results have been verified in full scale plant trials.

AMONG structural steels, the family of hot rolled high strength low alloy (HSLA) steels, with guaranteed minimum yield strengths from 45,000 to 80,000 psi, shows a most remarkable growth.[1] In developing these steels, strength is only one of the properties considered. To satisfy diversified customer requirements and be competitive, a "balanced package of properties" must be offered, Table I.

Table I. Balanced Package of Properties for High Strength Low Alloy Steels

1) Strength
2) Formability
3) Weldability
4) Fatigue Resistance
5) Toughness
6) Corrosion Resistance

Two of these properties—toughness and bend formability—are adversely affected by inclusions elongated during hot rolling. Fig. 1 illustrates this effect on toughness; impact curves are plotted for both longitudinal and transverse Charpy V-notch, 1/2 size specimens. In longitudinal specimens, the impact energy at 100 pct shear, commonly called the shelf energy, is in excess of 40 ft-lb; in transverse specimens, it is 15 ft-lb. This difference is caused primarily by the presence of elongated inclusions which are oriented parallel to the plane of fracture in the transverse specimens. Fig. 2 shows the effect of elongated inclusions on bend formability. In transverse specimens (bend axis parallel to the rolling direction), severe cracks appear in a sample bent over a radius equal to two times the plate thickness, but in a longitudinal specimen bent over the same radius, no cracking occurs.

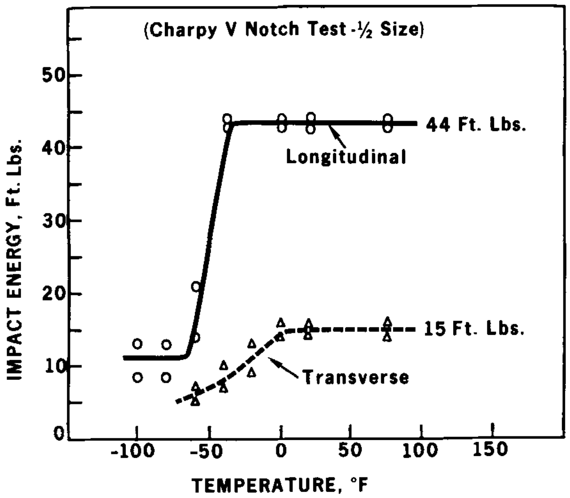

Fig. 1—Typical impact curves for high strength low alloy steel. These curves were determined on Charpy V-notch (1/2 size) specimens machined parallel (longitudinal) and perpendicular (transverse) to the rolling direction. The directionality is illustrated by comparing the longitudinal shelf energy (44 ft-lb) with the transverse shelf energy (15 ft-lb).

This effect of directionality caused by flat, elongated inclusions was highlighted during the development of an 80,000 psi yield strength low alloy steel. The steel was an aluminum killed, Mn-V-N type, in which the predominant inclusions were identified as manganese sulfides. To assure an adequate bend forming performance, the sulfur content was lowered to approximately 0.010 pct by carefully controlled steelmaking practices. For some advanced part designs however, it was desirable to develop bend forming performance comparable to that of mild steel.

To achieve this objective, several methods of minimizing the harmful effect of the plastic manganese sulfides were considered. In the as cast condition, these inclusions belong to the type II manganese sulfides described previously by Sims.[2] During hot rolling, the major factor affecting the plasticity of manganese based sulfides is the oxygen content of the steel. As schematized in the left part of Fig. 3, the higher the oxygen, the lower the plasticity.[3] However, it is not

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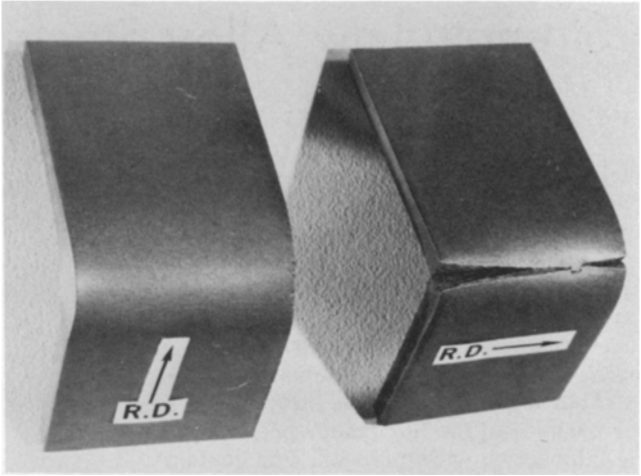


Fig. 2—Directionality of bend formability in high strength low alloy steels. The sample on the right was bent over a radius equal to two times plate thickness (*T*) with the bend axis parallel to the rolling direction and exhibits severe cracking. The sample on the left was bent over the same radius (2*T*) with the bend axis perpendicular to the rolling direction and exhibits no cracking.

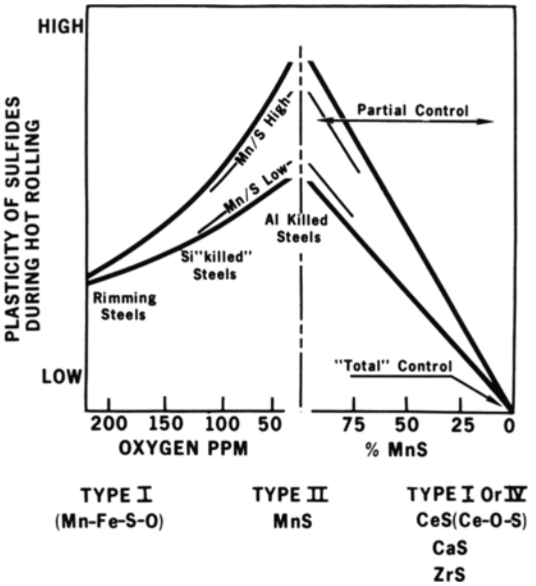


Fig. 3—Effect of oxygen content, manganese-to-sulfur ratio, and sulfide modifier on the plasticity of sulfides during hot rolling.

possible to take advantage of this effect without losing the benefit of the controlled oxide morphology associated with aluminum killed steels. In these steels, the oxide morphology is well controlled in contrast to silicon deoxidized steels where large, low melting point, manganese silicates present a problem. As shown in Fig. 3, at low oxygen levels, the plasticity of the sulfide is also affected to some extent by the manganese to sulfur ratio of the steel.[4] The smaller this ratio, the lower the plasticity. Thus, inclusions which are less susceptible to deformation can be obtained by decreasing the manganese and/or increasing the sulfur. However, manganese provides significant solution strengthening and low sulfur levels are required to ensure that the size and number of inclusions are not excessive. In view of these limitations, further consideration was restricted to the following approaches:

1) Reduction in Quantity and Size of Inclusions

This can be accomplished by a further reduction in the sulfur content. To reduce directionality of properties to an acceptable level would require sulfur levels of less than 0.005 pct. For low cost high strength low alloy steels, this is currently uneconomical.

2) Modification of Inclusion Morphology

a) The shape of manganese sulfide inclusions can be partially altered by cross rolling. This method is being used on plate mills for producing high quality steel. Even when this technique is used, the sulfide shape control is incomplete since inclusions still retain a biaxial ellipsoidal shape. Furthermore, cross rolling on modern continuous hot strip mills is currently impractical.

b) The shape of sulfide inclusions can be altered from elongated to globular by chemical means. This is accomplished by adding an element which forms a high melting point sulfide, more stable than manganese sulfide and not as readily deformable at hot rolling temperatures. As the concentration of the sulfide modifier increases, the amount of elongated MnS formed gradually decreases, until the elongated sulfides are completely replaced by more stable, globular or blocky inclusions. The relationship between sulfide morphology and inclusion plasticity is shown schematically in the right hand portion of Fig. 3. This approach based on chemical control has been adopted in the present investigation.

THEORETICAL ASPECTS

Although the thermodynamic data are limited, practical experience would indicate that zirconium and titanium can be used to alter sulfide morphology. From the data of Elliott and Gleiser,[5] Fig. 4, it appears that the elements magnesium, calcium, and ce-

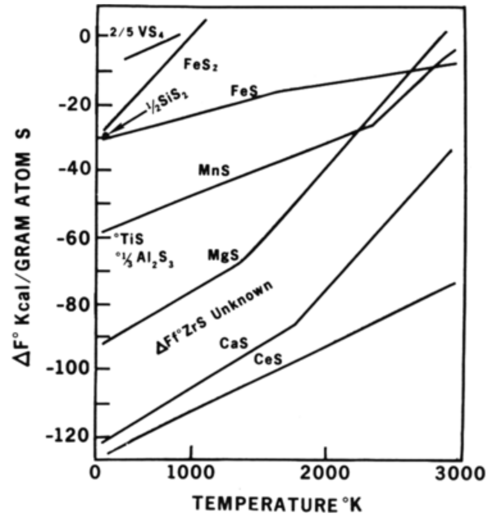


Fig. 4—Standard free energy of formation of various metal sulfides.

rium, among others, form stable high melting point sulfides. It is possible that each of these elements could be used to form sulfide inclusions which would not elongate during hot rolling. Before introducing these additives to a specific alloy system, however, other factors must be considered. For example, since the steel in question derived its strength properties in part from precipitation of vanadium nitrides, it was postulated, in screening the potential strong sulfide formers, that the additive should have a weak affinity for nitrogen. In general, the following criteria are important: interactions of the additions with oxygen, nitrogen, and carbon,[5,6] Figs. 5 to 7, also their solubility in molten steel, vapor pressure, availability, and cost. The relevance of these factors to the various strong sulfide formers will be discussed individually.

1) Zirconium

Historically, zirconium has been used in Germany as far back as World War I in order to increase the toughness of armor plate.[7] At that time, the mechanism by which this minor addition improved steel properties was not understood.[8] Since the late 1950's zirconium was used in several commercial steels to enhance physical properties especially for applications in which directionality of properties was critical. A discussion of the mechanism involved in the successful control of directionality by zirconium was published by Lichy *et al.*,[9] Bucher *et al.*[10]

Zirconium has a high affinity for oxygen, Fig. 5, and thus predeoxidation of the steel with aluminum and manganese is essential for good recovery of this additive. When zirconium is added to Al/Mn deoxidized steel, it will react with nitrogen before combining with sulfur. Metallographic evidence for this has been shown by Lichy *et al.*[9] The high affinity of zirconium for nitrogen, and its tendency to form coarse particles precludes the use of this element in hot rolled steels strengthened by finely dispersed nitride precipitates. Despite the high stability of ZrC, there is no evidence that Zr-C interactions adversely affect mechanical properties for carbon levels below 0.2 pct. However, at higher carbon levels, and for zirconium concentrations in excess of 0.1 pct, lath shaped crystals of ZrC and $Zr_4C_2S_2$ can cause embrittlement.[11] Zirconium is readily available, and is generally added to deoxidized steel in the form of scrap or as zirconium-silicide.

2) Titanium

As with zirconium, predeoxidation of steel is required for good recovery. To achieve this objective, protection with aluminum alone without the additional

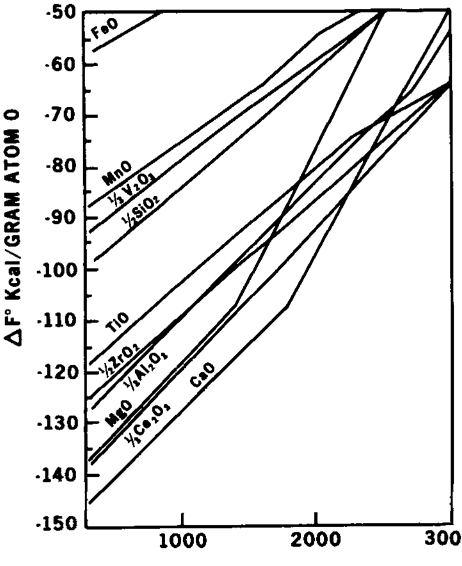


Fig. 5—Standard free energy of formation of various metal oxides.

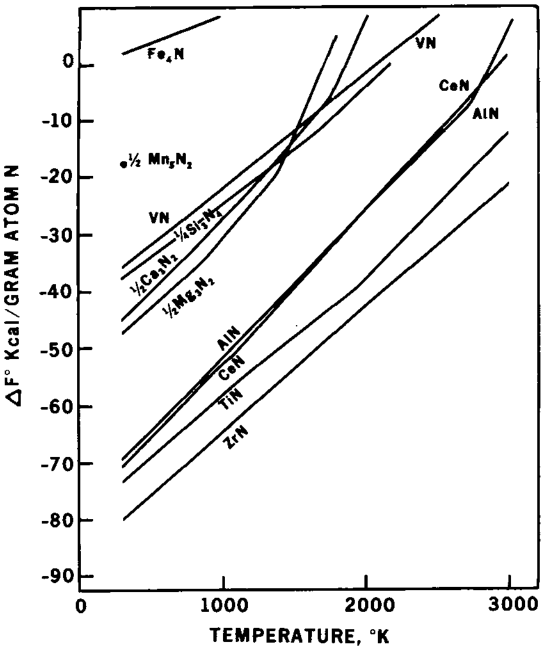


Fig. 6—Standard free energy of formation of various metal nitrides.

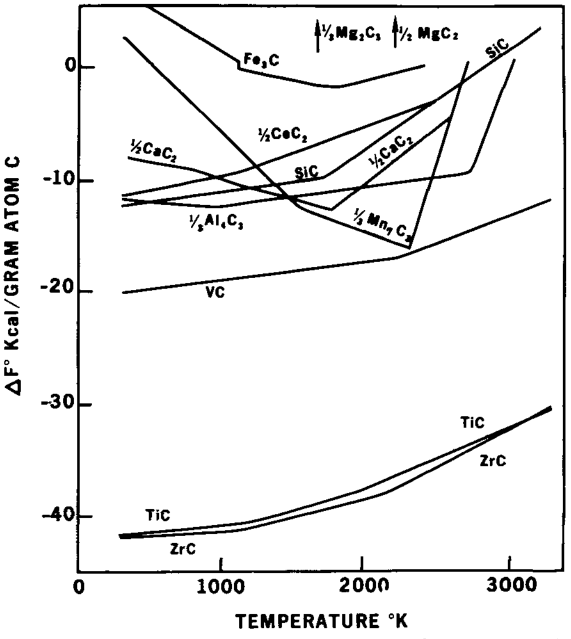


Fig. 7—Standard free energy of formation of various metal carbides.

effect of manganese is probably sufficient.[12] Titanium nitride is less stable than zirconium nitride and the high temperature precipitate in steel is generally a carbonitride rather than pure nitride. Almost total precipitation of the nitrogen must occur before sulfide morphology can be changed. Furthermore, the exact mechanism by which the change in sulfide morphology takes place is still uncertain[13] and direct substitution of manganese by titanium in the sulfide has not been clearly established. Nevertheless, titanium is being used commercially for sulfide shape control in steel. However, two side effects may preclude its use in certain grades. First, since titanium combines with nitrogen in the molten steel, it cannot be used in steels which rely on solid state nitride precipitation for strengthening. Second, titanium will combine with carbon in the solid state to form a carbide precipitate which may strengthen the steel. Finally, there are indications that (Ti, Mn, Fe) $4C_2S_2$ precipitates can be formed[11,14,15] and these, like the similar zirconium compounds could cause embrittlement. Large supplies of titanium are available at moderate cost but the reactivity of titanium with O, S, C, and N makes an accurate control of final properties of HSLA steels with this element somewhat difficult.

3) Magnesium

Thermodynamic data indicate that magnesium forms a high melting point, stable sulfide and has little tendency for nitride or carbide formation. Because of its low boiling point (2043°F), however, addition of magnesium to molten steel is hazardous and extremely difficult. Therefore, no further consideration was given to the use of this element in the present study.

4) Calcium

The sulfide of calcium is more stable than that of magnesium and the tendency for nitride or carbide formation is quite weak. The boiling point at 2718°F is higher than that of magnesium, although the solubility in molten steel at atmospheric pressure is low. Calcium is readily available at moderate cost, and exploratory work with this element was regarded as justified.

5) Rare Earths (Lanthanides)

The heavy elements of group IIIA, in particular the lanthanides, commonly referred to as rare earths, form extremely stable sulfides and oxysulfides.[14] The melting points of these compounds for the major rare earth elements are shown as a function of atomic number in Fig. 8. The best known element of this series is cerium and the melting point of its sulfide, CeS, is about 4440°F.

Since the early twenties, rare earths have been used to improve hot and cold formability of carbon, alloy, and stainless steels.[16-18] Problems encountered with rare earth additions, inconsistent recovery and poor cleanliness, hampered a broader use of these elements.[19-21] Cerium forms an extremely stable oxide, Fig. 5, and this is one of the reasons for its poor recovery under steelmaking conditions. For optimum recovery, it is essential that the steel be thoroughly deoxidized prior to rare earth addition. Even with the combined effect of aluminum and manganese, some further deoxidation of the steel by cerium is to be expected. Free energies of formation of the nitrides suggest that aluminum and cerium have similar behavior. Since no problems related to nitride formation have been encountered in the past with aluminum at levels typical of killed steels, no difficulty was anticipated with rare earths. This assumption has been substantiated by several investigators.[22-23] In view of the low free energy of formation of rare earth carbides, it is unlikely that carbide formation would be a problem.[6] Paradoxically, "rare earths" are plentiful, and these elements are marketed mainly as a mixture known as mischmetal, or as a ferrosilicide of these elements. In these forms, rare earths are the only metals of group IIIA available for commercial use in steelmaking, and these additives were included in the experimental program.

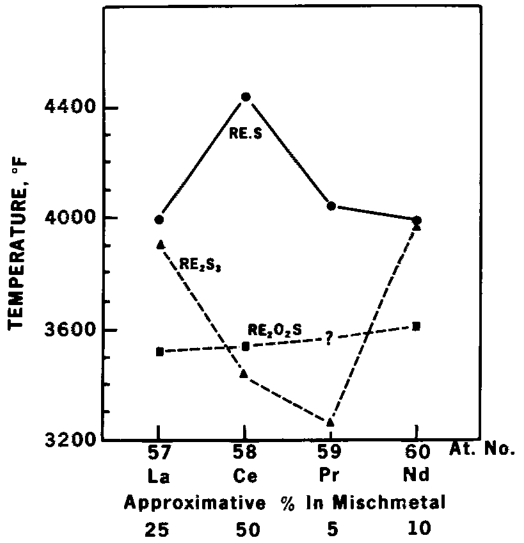
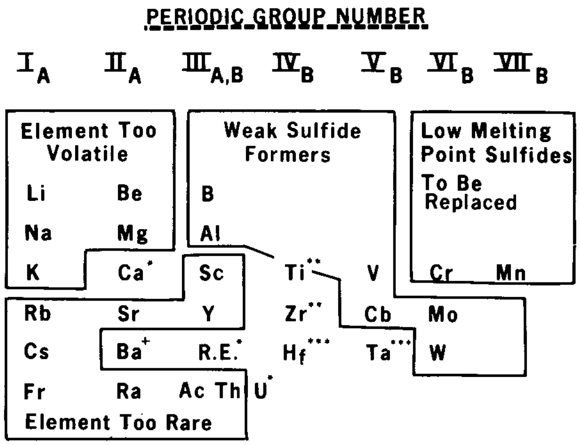


Fig. 8—Melting points of rare earth sulfides and oxy-sulfides.

6) Other Elements

From the standpoint of sulfide stability, there are several other elements which could be used for sulfide shape control. Practical considerations, however, preclude their use. The common elements from group IA, such as lithium, sodium, and potassium, have a high vapor pressure; the other elements of the group, rubidium, cesium, and francium, are scarce and expensive. In group IIA, beryllium, strontium, and barium are unacceptable from the standpoints of cost and health hazards. In group IIIA, elements other than the rare earths such as scandium, yttrium, and the actinides, particularly uranium, although attractive from the standpoint of their properties, are unacceptable because of restricted availability and handling hazards.

In view of these overall considerations, which are summarized in Fig. 9, the experimental program was limited to studies on the influence of calcium and rare earth metals on the sulfide morphology in a high strength, low alloy steel strengthened by vanadium-nitride precipitation.



*Ca, R.E.,U: Potential Sulfide Formers
**Zr,Ti: Undesirable Interaction With N and C
***Hf,Ta: Rare and Undesirable Interaction With C ar
+Ba: Low Solubility In Carbon Steel

Fig. 9—Potential sulfide formers for HSLA steels.

EXPERIMENTAL ASPECTS

1) Melting Procedure

The laboratory program included 27 heats of basic composition typical for a V-Al-N* high strength-low alloy steel[24] except for sulfur which was increased to 0.020 to 0.025 pct:

Composition, pct							
C	Mn	Si	P	S	V	Al	N
0.16	1.30	0.40	0.008	0.020/0.025	0.11	0.060	0.017

In addition three heats were made in which the sulfur content was about 0.015 pct. The melts were produced in a 100-lb medium frequence induction furnace, using magnesia crucibles. To simulate more closely the conditions likely to be encountered in practice, no precautions were taken to protect the metal by argon shrouding or vacuum processing. The sequence of addition, after melt down of low carbon scrap together with some pig iron necessary to attain the carbon specification is shown in Fig. 10. To determine changes in the oxygen content of the steel at different stages, four suction samples were taken in the majority of heats. The time interval between samples is also included in Fig. 10. The furnace was tapped within 1½ min after the last addition. The total time lag between the addition of aluminum and tap was about 5 min.

Results of oxygen determinations by means of inert gas fusion analysis are summarized in Fig. 11. The oxygen contents before and after the rare earth addition were: 73 and 48 ppm, respectively (geometric average). Because of the very short time allowed for oxide separation, these values representing total oxygen are higher than the equilibrium values. The dissolved oxygen level in both cases should be very much less and for this reason, the interaction between the sulfide control agent and oxygen should be minimal.

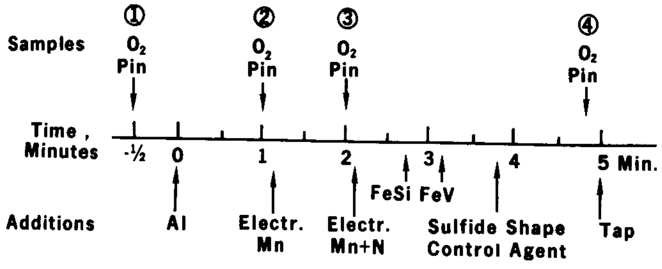


Fig. 10—Sequence of additions and sampling for heat made at 2880° to 2900°F.

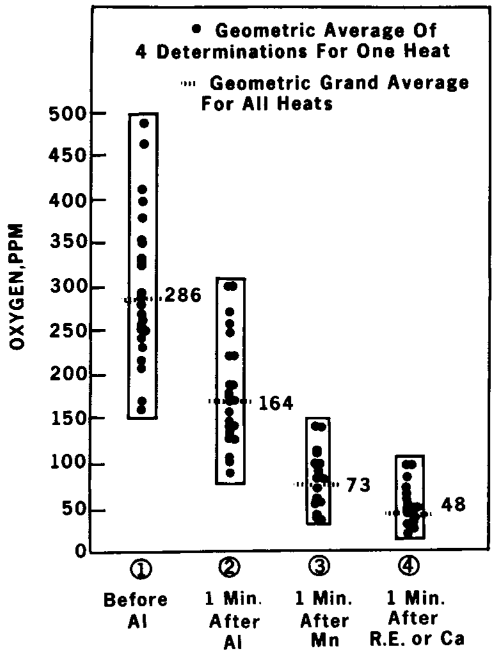


Fig. 11—Oxygen content of steels at various stages during the heat.

The steel was poured into two 50-lb hot topped steel casting molds. The small ingot size promoted very fast solidification and precluded most of the flotation and segregation effects which normally occur in commercial ingots. Compared to large ingot practice, the laboratory experiments offered less opportunity for incomplete mixing and stream reoxidation. On the other hand, the laboratory experiments were more severe from the standpoint of cleanliness and degree of desulfurization.

Samples for chemical analysis were taken from the tap stream in ceramic and cast steel molds. Several check analyses made on the rolled product were in good agreement with the liquid steel samples.

2) Exploratory Program

In nine preliminary heats, the effects of various amounts of CaSi, CaBaSi, $Ca(CN)_2$, mischmetal, and rare earth silicide on sulfide shape were compared to a reference heat made without a sulfide shape control agent. Table II lists the sulfide control agent, the amount of addition, and final analysis of the steel. Efforts were made to maximize interaction between the fully deoxidized steel and the volatile calcium alloys by dividing the additions into two to four equal parts, wrapping each lot in steel foil and plunging to the bot-

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*Steel of this composition is known under the trade name: VAN-80 steel.

tom of the crucible with a steel rod. Even with very large additions of calcium alloys (*e.g.*, 20 lb per ton CaSi), metallographic examination revealed that only 60 pct of the sulfides were converted to a globular shape. The ineffectiveness of calcium is attributed to its high vapor pressure and low solubility in this steel. Since the same degree of sulfide shape control was achieved with much smaller additions of rare earth, efforts were centered on the effect of rare earth additions for the remainder of the program.

3) Rare Earth Experiments

A systematic program of twenty-one heats was set up in which rare earth was added in two forms: 1) *mischmetal* (containing 50 pct Ce, 25 pct La, 10 pct Nd, 5 pct Pr, and other rare earths) and 2) *rare earth silicide* (containing approximately 35 pct Fe, 30 pct Si, and 34 pct rare earths of about the same composition as mischmetal). In sulfide formation the other rare earth elements presumably react similarly to cerium.

Table II. Exploratory Program

Heat No.	Sulfide Shape Control Addition			Composition,* Wt Pct.										Ce Recovery, Pct	Pct Ce/ Pct S	Pct Sulfide Shape Control‡
	Agent	Amount Added, lb./ton	Calcium or Rare Earth, lb./ton	C	Mn	Si	S	P	V	Al	N	O	Ce			
1	None	–	–	0.16	1.27	0.41	0.021	0.010	0.11	0.077	0.013	–	0.002 (residual)	–	–	0
2	CaSi	18.0	6.5	0.15	1.27	0.39	0.019	0.007	0.11	0.060	0.011	0.005	–	–	–	30
3	CaSi	18.0	6.5	0.15	1.32	0.45	0.019	0.007	0.12	0.058	0.017	0.006	0.004 (residual)	–	–	60
4	CaSi	18.0	6.5	0.063†	1.35	0.44	0.021	0.007	0.11	0.083	0.017	–	–	–	–	50
5	$Ca(CN)_2$	3.5	1.5	0.13	1.34	0.42	0.022	0.007	0.11	0.069	0.006	0.003	–	–	–	20
6	CaBaSi	20.5	3.5	0.16	1.35	0.43	0.021	0.007	0.11	0.063	0.015	0.003	–	–	–	40
7	Mischmetal	0.5	0.5	0.012†	1.19	0.41	0.021	0.008	0.11	0.061	–	0.006	0.017	100	0.81	60
8	R.E.Si	0.5	0.2	0.15	1.27	0.45	0.021	0.008	0.12	0.079	0.015	0.010	0.007	100	0.33	20
9	R.E.Si	3.0	1.0	0.15	1.28	0.39	0.022	0.008	0.11	0.062	0.014	0.004	0.020	75	0.91	70

*Calcium less than 0.005 pct for heats 1 to 6.
†Carbon rimmed out during melting.
‡Metallographic estimate.

Table III. Rare Earth Program

Heat No.	Sulfide Shape Control Addition		Composition, Wt Pct.										Cerium Recovery, Pct	Pct Ce/Pct S
	Amount Added, lb./ton	Rare Earth, lb./ton	C	Mn	Si	S	P	V	Al	N	O	Ce		
A) Mischmetal														
10	0.5	0.5	0.14	1.23	0.43	0.022	0.007	0.11	0.040	0.015	0.008	0.015	100	0.68
11	0.5	0.5	0.16	1.23	0.43	0.021	0.007	0.11	0.058	0.017	0.006	0.009	69	0.43
12	1.0	1.0	0.16	1.22	0.42	0.021	0.009	0.11	0.058	0.014	0.004	0.022	83	1.05
13	1.0	1.0	0.16	1.25	0.43	0.021	0.008	0.10	0.064	0.015	0.004	0.025	94	1.19
14	1.5	1.5	0.16	1.26	0.39	0.020	0.009	0.11	0.049	0.015	0.002	0.030	75	1.50
15	1.5	1.5	0.15	1.26	0.44	0.025	0.008	0.12	0.048	0.015	0.003	0.031	77	1.24
16	2.0	2.0	0.15	1.24	0.43	0.021	0.005	0.11	0.057	0.018	0.004	0.040	75	1.90
17	2.0	2.0	0.16	1.28	0.44	0.020	0.007	0.11	0.070	0.018	0.007	0.042	79	2.10
18	3.0	3.0	0.16	1.28	0.43	0.021	0.005	0.11	0.052	0.018	0.004	0.061	76	2.90
19	3.0	3.0	0.16	1.22	0.42	0.020	0.006	0.11	0.059	0.017	0.002	0.064	80	3.20
B) Rare Earth Silicide														
20	3.0	1.0	0.17	1.22	0.42	0.022	0.011	0.11	0.053	0.015	0.009	0.025	94	1.14
21	3.0	1.0	0.15	1.33	0.41	0.024	0.010	0.12	0.068	0.015	0.004	0.020	75	0.83
22	4.5	1.5	0.16	1.31	0.44	0.022	0.011	0.11	0.078	0.016	0.004	0.035	87	1.59
23	4.5	1.5	0.15	1.35	0.44	0.021	0.011	0.12	0.083	0.017	0.007	0.034	85	1.62
24	6.0	2.0	0.15	1.14	0.43	0.019	0.005	0.11	0.059	0.017	0.004	0.041	77	2.13
25	6.0	2.0	0.16	1.24	0.44	0.019	0.007	0.11	0.074	0.020	0.004	0.036	68	1.90
26	9.0	3.0	0.16	1.22	0.43	0.020	0.007	0.11	0.049	0.019	0.005	0.057	72	2.85
27	9.0	3.0	0.16	1.22	0.42	0.019	0.007	0.11	0.042	0.018	0.006	0.061	77	3.21
28*	2.25	0.75	0.16	1.31	0.38	0.016	0.005	0.11	0.110	0.015	0.005	0.016	80	1.00
29*	3.00	1.0	0.15	1.31	0.42	0.015	0.005	0.11	0.110	0.022	0.003	0.026	98	1.74
30*	3.75	1.25	0.15	1.26	0.40	0.015	0.006	0.11	0.120	0.022	0.005	0.024	72	1.60

*Low sulfur heats.

The additions used in this part of the program are presented in Table III. Each practice was duplicated to check reproducibility. All elements reported, except for C, N, Ca, and Ce were determined by spectrographic analysis. Carbon and nitrogen were determined by combustion and wet chemistry techniques, respectively. Calcium was determined by atomic absorption and found to be less than 50 ppm in all cases. Presuming that recoveries would be similar for all the rare earths, only total cerium was analyzed by X-ray fluorescence. The results of the cerium analysis, plotted as a function of the amount added, Fig. 12, show recoveries ranging from 70 to 100 pct. The zero reading for reference heats were 20 to 40 ppm, and this causes recoveries to appear slightly higher than 100 pct in heats with small additions.

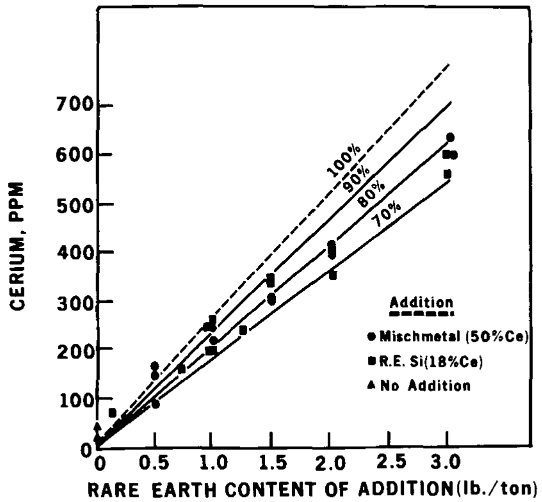


Fig. 12—Cerium content of steel for various levels of addition. Lines correspond to calculated recovery levels.

4) Metallography and Mechanical Properties

Samples from the top and bottom of each experimental ingot were hot rolled to 0.080 in., and sections taken for microscopic evaluation. In addition, samples from each heat were rolled to 0.25 in. on a laboratory mill designed to simulate processing on a hot strip mill by controlled cooling practice.[1,25] The latter samples were finish-rolled at 1650°F, cooled rapidly (30°F per sec) to 1100°F, and then cooled slowly at 50° per hr to simulate cooling conditions in a large coil. Material for tensile tests, longitudinal and transverse impact tests, and transverse bend tests was obtained from each sample. The property of major interest, the shelf energy, or energy at 100 pct shear fracture, was obtained by the Charpy V-notch impact test using 1/2 size specimens. Bend formability was also tested for each sample with the bending axis parallel to the rolling direction. To increase the severity of the bend test, the samples were sheared (rather than machined), and the shear burr was left intact on the tension side of the bend to act as a crack starter. The bend radii varied from three to one-half of the plate thickness ($3T$, $2T$, $1\frac{1}{2}T$, $1T$, and $1/2T$, T being the plate thickness).

Table IV. Results of Mechanical Testing and Quantitative Metallography

Heat No.	Sulfide Shape Control Addition, lb./ton	Yield Strength, 1000 psi	Ultimate Tensile Strength, 1000 psi	Pct Total Elongation, 2 in.	Pct Uniform Elongation	Shelf Energy*, ft-lb. Longitudinal	Shelf Energy*, ft-lb. Transverse	Pearlite, Pct	Ferrite Grain Size ASTM No.
A) Ref.									
1	None	86	105	21	10	34	15	15	11.6
B) Mischmetal									
10	0.5	81	100	25	15	–	20	4	11.4
11	0.5	85	102	25	15	40	16	5	11.0
12	1.0	85	105	24	14	–	26	7	11.2
13	1.0	85	103	23	14	39	27	8	11.3
14	1.5	86	104	24	14	37	32	8	10.7
15	1.5	87	104	22	15	–	31	10	11.3
16	2.0	76	96	28	17	–	28	8	11.0
17	2.0	76	96	27	17	38	34	12	10.8
18	3.0	79	97	22	14	–	28	8	11.1
19	3.0	82	99	24	14	37	25	5	11.0
C) Rare Earth Silicide									
20	3.0	88	105	21	13	–	24	8	11.0
21	3.0	88	106	24	14	35	22	7	10.9
22	4.5	81	100	21	14	–	32	16	11.4
23	4.5	86	103	24	14	37	31	10	11.5
24	6.0	77	96	26	16	40	30	9	10.8
25	6.0	78	96	25	14	38	30	7	11.2
26	9.0	80	97	22	12	38	27	7	11.0
27	9.0	81	100	25	14	35	25	10	11.0
28†	2.25	76	96	26	16	47	32	9	11.2
29†	3.0	76	95	28	17	44	32	8	11.0
30†	3.75	77	96	25	15	46	35	9	11.0

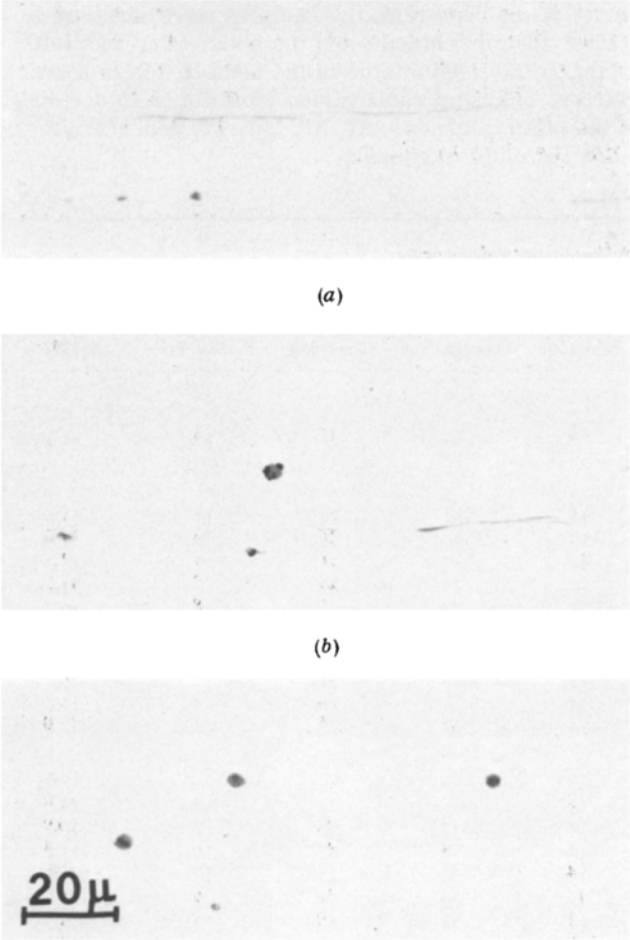
*Charpy V-notch, 1/2 size specimens.
†Low sulfur heats.

RESULTS AND DISCUSSION

Because only 1/3 of rare earth silicide is rare earth elements, additions were three times that of the mischmetal. Equivalent amounts of rare earth, whether added as silicide or mischmetal, resulted in similar recoveries and steel performance.

1) Microstructure

The rare earth additions had no influence on the microstructure of the steel matrix. The ferrite ASTM grain size number and percent pearlite for each of the heats are listed in Table IV. The oxide morphology was good and no different from that of the aluminum killed control heat. The effect of rare earth additions on the sulfide morphology is illustrated by the photomicrographs shown in Fig. 13. The reference sample, Fig. 13(*a*), typifies the elongated sulfide inclusions. A sample with Ce/S ratio of 1.0 reveals a partial change in sulfide shape, Fig. 13(*b*). Complete sulfide shape control was achieved with a Ce/S ratio of about 1.5, Fig. 13(*c*). These ratios were the same for both low and high sulfur heats. Inclusion morphology was found to be independent of the position in the ingot and reproducible in twin heats. Results of microprobe analysis of an elongated manganese sulfide and a globular rare earth sulfide are shown in Fig. 14. In the globular sulfide there is no manganese present, only rare earths as represented by cerium. At recovery levels experienced in this program for heats with sulfur levels in the range 0.020 to 0.025 pct, a $1\frac{1}{2}$ lb per ton addition of mischmetal or a $4\frac{1}{2}$ lb per ton addition of rare earth silicide will provide complete sulfide shape control.



(*a*)

(*b*)

(*c*)

Fig. 13—The effect of rare earth additions on sulfide inclusion morphology. Magnification is indicated by micron scale on the photomicrograph. (*a*) Elongated MnS inclusions in reference sample. (*b*) Partial sulfide shape control in sample with pct Ce/pct = 1.0. (*c*) Complete sulfide shape control in sample with pct Ce/pct = 1.5.

2) Mechanical Properties

a) TENSILE PROPERTIES

The rare earth additions had no effect on the tensile properties of the steel. The yield strength, ultimate tensile strength, uniform elongation, and total elongation of specimens processed from each heat are listed in Table IV. The small variations in properties are attributed to minor processing and chemistry variations and not to rare earth additions.

b) TOUGHNESS

Substantial improvements were obtained in this property as shown by impact data listed in Table IV. Effects of rare earth addition on the shelf energy are shown in Fig. 15 which represents a plot of shelf energy for longitudinal and transverse impact specimens (1/2 size Charpy, V-notch) vs Ce/S ratio. For Ce/S ratios between 1.5 and 2.0, the transverse shelf energy increased 100 pct, *i.e.*, from 15 to 30 ft-lb. These results are in accord with the microscopic observations which show complete change in sulfide morphology from elongated to globular. With Ce/S ratios greater than 2.00, the transverse shelf energy appears to decrease slightly. The longitudinal shelf energy was not affected by the level of rare earth additions.

c) BEND FORMABILITY

The effect of rare earth additions on bend formability is illustrated in Fig. 16. The samples were bent with the shear burr on the tension side of the bend. As with impact performance, bend formability is dramatically improved by sulfide shape control. The reference sample without rare earth addition completely fractured when bent over a radius equal to two times the plate thickness (2*T*). The samples with Ce/S ratios greater than or equal to 1.5 exhibited only a slight edge cracking which was restricted to the severely cold worked, sheared edge. There was no tendency for crack propagation.

3) Practical Implementation

The results of small scale laboratory experiments discussed above have been confirmed by full scale plant trials. Rare earth additions are now being used commercially to control sulfide morphology with consequent improvement in transverse toughness and bend formability in high strength low alloy steels. The practical aspects of this procedure will be discussed elsewhere.

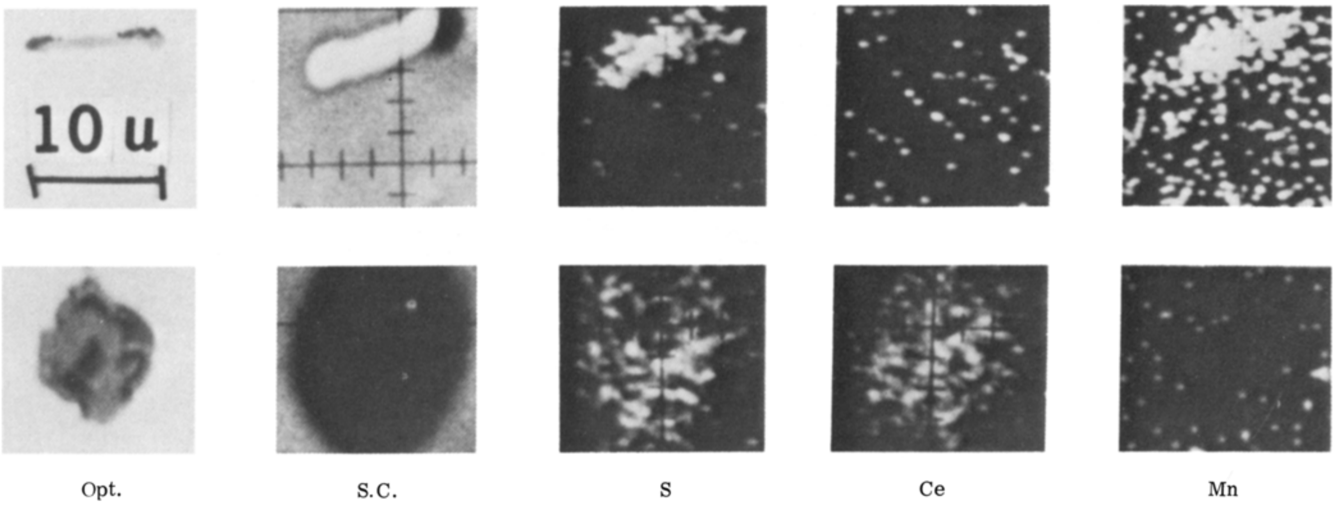


Fig. 14—Microprobe analyses of elongated (top row) and globular (bottom row) sulfide inclusions.

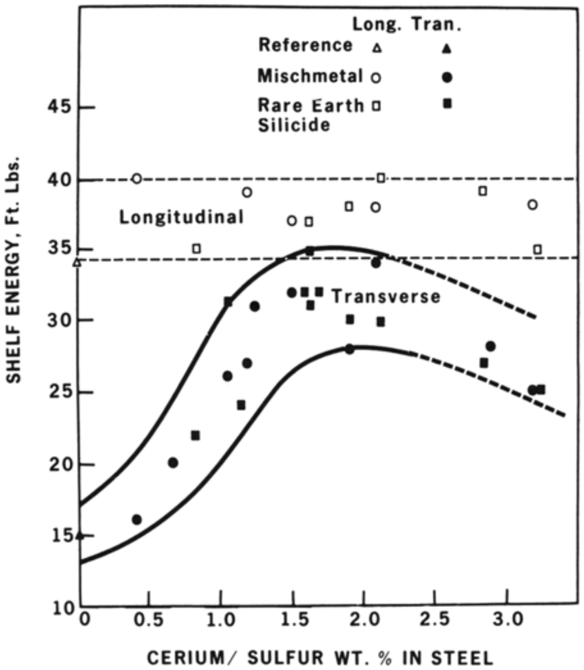


Fig. 15—Relationship between shelf energy determined on longitudinal and transverse Charpy 1/2 size V-notch specimens and cerium-to-sulfur ratio. Each data point is the average of two tests.

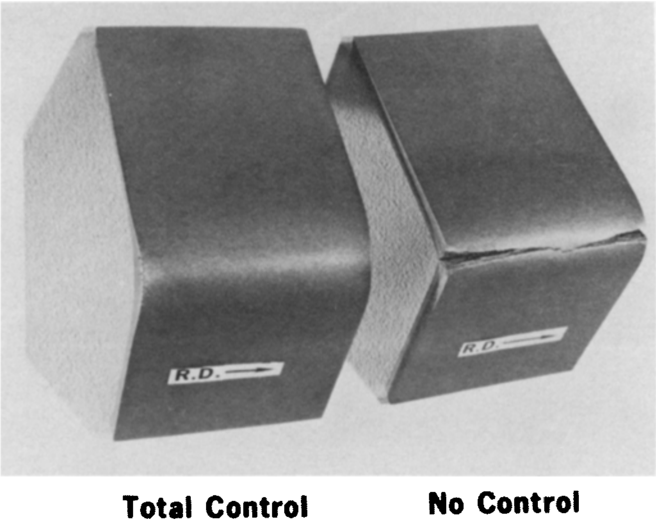


Fig. 16—The effect of sulfide shape control on transverse bend formability. The control sample (right) with elongated sulfides, when bent over a radius of two times plate thickness, is severely fractured. The sample with sulfide shape control (left) (pct Ce/pct S = 1.5) exhibits minor checking on the sheared edge only.

SUMMARY

Experimental results verified conclusions based on thermodynamic considerations that rare earth additives can be used to achieve control of sulfide morphology in aluminum killed steels. In steels with sulfur contents up to 0.025 pct, a Ce/S ratio of 1.5 in the final product will result in exclusively globular rare earth sulfides instead of elongated type II manganese sulfides. In a hot-rolled steel, strengthened to 80,000 psi yield strength in part by vanadium nitride precipitation, there was no evidence that the rare earths had any adverse effects on the strengthening mechanism. Control of sulfide shape doubled the toughness in the direction transverse to the rolling direction, as measured by the shelf energy determined on 1/2 size Charpy V-notch specimens. This improvement in toughness was coupled with a dramatic improvement in bend formability. In spite of the high strength level, sheared bend specimens were bent over a radius equal to plate thickness (bend axis parallel to the rolling direction) with only slight edge cracking. In contrast, specimens without sulfide shape control cracked when bent over a radius equal to two times plate thickness. Effectiveness of rare earth additions in improving toughness and formability of high strength, low alloy steels has been verified in full scale mill trials and incorporated into commercial practice.

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