The Influence of Sulfur Concentration Below 0.006% Along With Sulfide Shape Control on the Charpy V-Notch Properties of Normalized and Stress Relieved TC128 Grade B Steel Plate

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Abstract

A consortium consisting of Dow Chemical, Union Pacific and Union Tank Car is collaborating with the Department of Transportation Federal Railroad Administration to develop a more puncture resistant railroad tank car for use in the transportation of hazardous chemicals. New designs and new steels are under consideration for this puncture resistant tank car. Ways to improve the toughness of the currently used TC128 Grade B tank car steel are also being explored. It has been proposed to increase puncture resistance by increasing the Charpy V-notch upper shelf energy. One way to achieve this increased shelf energy is to decrease the sulfur content of the steel and employ sulfide shape control. Currently TC128 Grade B pressure tank car steel limits sulfur to 0.015% max. This work was conducted to look at the Charpy V-notch shelf energy achievable in TC128 Grade B steel with reduced sulfur content (0.006% max) and sulfide shape control. Transverse Charpy V-notch data have been collected from TC128 Grade B plates with sulfur levels ranging from 0.001% to 0.006% that have been calcium treated for shape control. The results are presented and discussed.

Introduction

Existing railroad tank cars are made with AR TC128 Grade B normalized steel. This steel has performed satisfactorily for many years, but it is always possible to improve the engineering performance of tank cars and the steels from which they are made. A consortium consisting of Dow Chemical, Union Pacific Railroad and Union Tank Car is collaborating with the Department of Transportation Federal Railroad Administration to develop a more puncture resistant railroad tank car to be used for the transportation of hazardous gases. New low carbon steels and new tank car designs are under consideration for this puncture resistant tank car. While these developments are underway, alternatives to improve the toughness of the currently used normalized TC128 Grade B steel are also being explored.

One measure of improved steel toughness is increasing the Charpy V-notch upper shelf energy. One way to increase the upper shelf energy is to lower the sulfur content of the steel and to achieve sulfide shape control.

At present the sulfur content specified for the TC128 Grade B steel used for pressure tank car construction is 0.015% max. No sulfide shape control is specified although steel producers must meet transverse Charpy test requirements at -34° C.

The steelmaking technology developed for high strength high toughness linepipe steels can be utilized for the improvement of the TC128 Grade B steel. This steelmaking technology is used in the production of linepipe grades up to API X-120. It is not uncommon to see sulfur levels in these steels at 0.001% or even below.

This work was conducted to quantify the Charpy V-notch upper shelf energy achievable in the TC128 Grade B plates with reduced sulfur content, 0.006% max, and calcium treatment for sulfide shape control. The upper shelf energy data obtained from these steels should be of use to the FEA modeling work on the tank car puncturing process. Hopefully, the modelers will be in a position to determine if the Charpy V-notch upper shelf energy attainable in the 0.006% max sulfur, sulfide shape controlled steels is high enough to attain the desired puncture resistance. The sulfur content necessary for fitness of the required puncture resistance would still have to be determined. It might turn out that cost and availability of very low sulfur shape controlled TC128 Grade B steel will direct efforts towards the use of a lower carbon higher toughness steel for increased tank car puncture resistance.

In this work transverse Charpy V-notch data have been collected from commercial TC128 Grade B plates with sulfur content ranging from 0.001% to 0.006% and with sulfide inclusion shape control. These plates were tested in both the normalized and normalized plus stress relieved conditions.

Experimental Procedure

The TC128 Grade B steel plate samples involved in this investigation originated from commercial 201 Mg BOF heats. The steels were made to a 0.006% S max specification. The compositions of these steels are given in Tables 1 and 2.

These steels all conform to the AAR TC128 Grade B composition specification for pressure tank cars. The low sulfur TC128 Grade B steels shown in Table 1 were used for the full transition curve CVN determinations. These determinations were made using transverse CVN specimens.

| Steel ID | С | Mn | Р | S | Si | V | Al | Cr | Мо | Ν |
|-------------|------|------|-------|-------|------|-------|-------|------|-------|-------|
| 5 | 0.22 | 1.38 | 0.010 | 0.002 | 0.34 | 0.06 | 0.035 | 0.17 | 0.06 | 0.008 |
| 6 | 0.21 | 1.38 | 0.009 | 0.002 | 0.34 | 0.06 | 0.029 | 0.17 | 0.06 | 0.005 |
| 7 | 0.22 | 1.37 | 0.006 | 0.003 | 0.33 | 0.06 | 0.033 | 0.17 | 0.06 | 0.003 |
| 10 | 0.21 | 1.36 | 0.012 | 0.002 | 0.35 | 0.06 | 0.035 | 0.17 | 0.05 | 0.004 |
| 20 | 0.22 | 1.38 | 0.009 | 0.003 | 0.35 | 0.06 | 0.034 | 0.17 | 0.06 | 0.006 |
| ABA | 0.21 | 1.38 | 0.008 | 0.001 | 0.35 | 0.059 | 0.033 | 0.17 | 0.06 | 0.004 |
| AAW | 0.23 | 1.37 | 0.009 | 0.002 | 0.33 | 0.066 | 0.031 | 0.17 | 0.06 | 0.003 |
| AAY | 0.21 | 1.38 | 0.005 | 0.004 | 0.38 | 0.062 | 0.045 | 0.17 | 0.064 | 0.003 |

 Table 1 Chemical Composition of the Commercial Low Sulfur, 0.006% max, TC128 Grade B Steels used in this Investigation for Transition Full Curve CVN Determinations

The low sulfur TC128 Grade B steels in Table 2 were used for the Plate Mill transverse CVN determinations at -34° C and for the full curve longitudinal and transverse CVN transition curve comparisons. In Table 2 there are three groupings consisting of three heats each. The first three steels have sulfur levels of 0.001%. The second group has a sulfur concentration range of 0.002 to 0.003% S. The third group, with the highest sulfur content range, had sulfur levels of 0.003 to 0.004% S.

| | | - | | | | | | | | |
|-------------|------|------|-------|-------|--------|-------|------|------|------|-------|
| Steel ID | С | Mn | Р | S | Si | Al | V | Мо | С | Ν |
| 670 | 0.22 | 1.38 | 0.010 | 0.001 | 0.34 | 0.026 | 0.06 | 0.06 | 0.17 | 0.004 |
| 680 | 0.21 | 1.37 | 0.013 | 0.001 | 0.34 | 0.031 | 0.06 | 0.06 | 0.17 | 0.003 |
| 040 | 0.21 | 1.38 | 0.008 | 0.001 | 0.35 | 0.033 | 0.06 | 0.06 | 0.17 | 0.004 |
| | | | | | | | | | | |
| 570 | 0.23 | 1.37 | 0.009 | 0.002 | 0.35 | 0.031 | 0.06 | 0.06 | 0.17 | 0.005 |
| 770 | 0.23 | 1.39 | 0.009 | 0.002 | 0.36 | 0.039 | 0.06 | 0.06 | 0.17 | 0.004 |
| 030 | 0.21 | 1.36 | 0.010 | 0.003 | 0.34 | 0.037 | 0.06 | 0.06 | 0.17 | 0.005 |
| | | | | | | | | | | |
| 010 | 0.22 | 1.39 | 0.006 | 0.004 | 0.36 | 0.034 | 0.06 | 0.06 | 0.18 | 0.005 |
| 020 | 0.21 | 1.38 | 0.005 | 0.004 | 0.45 | 0.045 | 0.06 | 0.06 | 0.17 | 0.005 |
| 790 | 0.21 | 1.40 | 0.010 | 0.003 | 0.0522 | 0.052 | 0.07 | 0.06 | 0.17 | 0.004 |

Table 2 Chemical composition of steels to obtain Plate Mill CVN Data at -34°C and the Longitudinal and Transverse CVN Transition Curve Data

The low sulfur levels were obtained by reacting the molten steel in the ladle with a desulfurizing slag. The molten steel at the Ladle Metallurgy Facility was subjected to electromagnetic stirring as well as by top lance injection of argon while in contact with the desulfurizing slag. The time of this treatment determines the amount of desulfurization. While at the Ladle Metallurgy Station, calcium wire was then fed into the steel in order to provide sulfide shape control.

After strand casting, this steel was hot rolled into 16 mm thick plates with finishing temperatures around 982°C.

The tensile properties obtained from some of the 16 mm low sulfur, 0.006% max, TC128 Grade B plates can be seen in Table 3. Examination of these results shows that the minimum requirements of 345 MPa for the yield strength and 558 MPa for the ultimate tensile strength specified for TC128 Grade B steel, were met in all cases.

| Steel ID | 0.2% Offset Y.S. (MPa) | Ultimate Tensile Strength (MPa) | % Elongation G. L. 203 mm |
|----------|---------------------------|------------------------------------|------------------------------|
| 5 | 434 | 576 | 17 |
| 6 | 400 | 572 | 23 |
| 7 | 407 | 564 | 19 |
| 10 | 407 | 563 | 24 |
| 20 | 400 | 570 | 23 |

| Table 3 Tensile Properties of Commercial Low Sulfur | , 0.006% max, TC128 Grade B Steels Used for Full | | | | | |
|---|--|--|--|--|--|--|
| CVN Curve Determination | | | | | | |

Charpy V-notch impact tests were performed on plate samples produced from the low sulfur BOF heats. The plates used for the full curve transverse CVN determinations and the mill transverse CVN determinations were normalized from 900°C and stress relieved for one hour at 620°C. The steel plates used for the full curve longitudinal and transverse CVN comparisons were normalized from 900°C.

Plate samples from five different heats were used for full curve transverse Charpy Vnotch determinations. The test temperatures ranged from -51° C to room temperature. The room temperature CVN test results were used for the upper shelf energy values because all these Charpy specimens exhibited 100% fibrous fracture characteristic of Charpy tests conducted on the upper shelf. Transverse CVN impact testing at -34° C is specified for TC128 Grade B pressure tank car steel plates. As a result, Plate Mill CVN data were compiled at this temperature. High, medium and low sulfur values within the 0.006% S max range were selected and plotted.

Plate samples from three different heats of the 0.006% max sulfur TC128 Grade B were used for both the longitudinal and transverse full curve CVN determinations. This testing was done in order to show how closely the transverse CVN values approach the longitudinal values when the TC128 Grade B steel sulfur levels are low and sulfide shape control is also obtained.

Results & Discussion

The transverse CVN data obtained from the 16 mm thick plates produced from five commercial heats of low sulfur TC128 Grade B steel are given in Table 4 and plotted in Figure 1.



Figure 1 Depiction of the Transverse CVN data obtained from the five heats of Low Sulfur, 0.006% max, TC128 Grade B Plates in the Normalized (900°C) and Stress Relieved Condition (620°C at 1 hour).

| Sample # | Temperature, °C | E | Energy Ave. J | | |
|----------|--------------------|-----|---------------|-----|-------|
| 5 | 21 | 182 | 234 | 214 | 210.0 |
| 5 | -18 | 127 | 157 | | 142.0 |
| 5 | -29 | 131 | 146 | | 138.5 |
| 5 | -40 | 89 | 106 | 53 | 82.7 |
| 5 | -51 | 62 | 31 | | 46.5 |
| 6 | 21 | 211 | 192 | 184 | 195.7 |
| 6 | -18 | 120 | 76 | | 98.0 |
| 6 | -29 | 108 | 129 | | 118.5 |
| 6 | -40 | 118 | 126 | 91 | 111.7 |
| 6 | -51 | 58 | 106 | | 82.0 |
| 7 | 21 | 198 | 226 | 220 | 214.7 |
| 7 | -18 | 136 | 127 | | 131.5 |
| 7 | -29 | 112 | 130 | | 121.0 |
| 7 | -40 | 110 | 108 | 103 | 107.0 |
| 7 | -51 | 92 | 119 | | 105.5 |
| 10 | 21 | 232 | 222 | 238 | 230.7 |
| 10 | -18 | 130 | 140 | | 135.0 |
| 10 | -29 | 122 | 127 | | 124.5 |
| 10 | -40 | 108 | 68 | 82 | 86.0 |
| 10 | -51 | 96 | 81 | | 88.5 |
| 20 | 21 | 182 | 184 | 220 | 195.3 |
| 20 | -18 | 122 | 136 | | 129.0 |
| 20 | -29 | 133 | 130 | | 131.5 |
| 20 | -40 | 99 | 108 | 56 | 87.7 |
| 20 | -51 | 95 | 74 | | 84.5 |

Table 4 Transverse Charpy V-notch Data Obtained from the Low Sulfur 0.006% max TC128 GradeB Steels in the Normalized (900°C) Stress Relieved One Hour at 620°C condition

Three test temperatures are of interest; 1) room temperature, 2) -40° C and -51° C. The upper shelf energy is obtained from the room temperature data. It is anticipated that the -34° C transverse CVN test requirements for TC128 Grade B pressure tank cars may be lowered in the future to -40° C and that is why this test temperature is of interest. The Charpy V-notch testing was done at -51° C just to see how much toughness remained at a very low temperature.

The room temperature impact data show some scatter with values ranging from 182 to 230 J. The average upper shelf energy obtained from fifteen room temperature tests was 209 J. Kyed et al ⁽¹⁾ reported longitudinal CVN upper shelf energy of 196 J from a 0.009% sulfur TC128 Grade B steel that had been double normalized (900°C) and stress relieved for one hour at 620°C. The average transverse CVN upper shelf energy obtained in this work was essentially equivalent to the longitudinal upper shelf energy reported by Kyed.

Hicho and Harne⁽²⁾ obtained both longitudinal and transverse CVN data from 0.010% S TC128 Grade B plates that had been normalized and stress relieved. Their average CVN upper shelf energy absorption values were 102 J and 224 J, respectively for the transverse and longitudinal CVN tests.

The average transverse CVN upper shelf energy obtained from the five heats of low sulfur, 0.006% max, TC128 Grade B is twice that of Hicho and Harne's steel. In fact the average transverse CVN of the low sulfur steels is almost equal to the longitudinal values reported by Hicho and Harne⁽²⁾.

The transverse CVN data collected at -40° C show considerable scatter with values ranging from 53 to 110 J. The average energy absorption value at -40° C is 95 J. This value is well above the minimum transverse 20 J energy currently specified at -34° C for pressure tank car steels.

The transverse CVN data obtained at -51° C also show considerable scatter with values ranging from 31 to 119 J. The average transverse CVN value for -51° C is 81 J. This average value is close to that found at -40° C. The low value, 31 J, found at -51° C is still above the 20 J minimum value currently specified for -34° C transverse CVN tests.

Plate Mill CVN testing was done on transverse samples obtained from plates whose compositions are given in Table 2. Cumulative distribution curves of the transverse CVN energy absorption values from individual tests are plotted in Figure 2. There were forty-one transverse CVN tests run on plates from steels 670, 680 and 040. These steels had sulfur levels of 0.001%. The same number of transverse CVN tests was run on the intermediate sulfur level, 0.002% S, steels, 570, 770 and 030. Fifty-six transverse CVN tests were performed on the higher sulfur level, 0.004% S, steels, 010, 020 and 790.



Figure 2 Cumulative Distribution Plot of Individual Transverse CVN Test Energy Absorption Values at -34° C, showing the difference in values between the 0.004% S steel and those with Sulfur levels of 0.002% and below.

Figure 2 shows that both the intermediate and low sulfur steels had a range of CVN energy absorption values at -34° C of 46 to 138 J. The nominal 0.004% sulfur steels had CVN energy absorption values at -34° C ranging from 23 to 114 J.

As can be seen from Figure 2, the low and medium sulfur TC128 Grade B steels group together and their results are indistinguishable. The high sulfur, approximately 0.004% S, TC128 Grade B steel had significantly lower CVN energy absorption values at -34° C. The advantage of using sulfur levels of 0.003% S max for theTC128 Grade B steels is that no single CVN test fell below the 20 joule minimum value set for the TC128 Grade B pressure car specification.

The steels with the compositions presented in Table 1 were used for longitudinal and transverse full curve CVN determinations. This test series was conducted to compare the longitudinal and transverse properties obtained from the same plate sample. The longitudinal and transverse CVN impact energy absorption values as a function of test temperature are plotted in

Figures 3, 4 and 5. Figure 3 shows the comparison of longitudinal and transverse CVN properties of the 0.001% S TC128 Grade B plate samples. The transverse CVN energy absorption values of the 0.001% sulfur steel are as good as or better than the longitudinal values except for the 4°C test temperature. The longitudinal and transverse CVN energy absorption values obtained from the 0.002% sulfur steel were essentially identical as can be seen in Figure 3.



Figure 3 Comparison of longitudinal and transverse full CVN curves obtained from 0.001% S TC128 Grade B Plate.

The longitudinal and transverse CVN curves obtained from the 0.004% S TC128 Grade B steel are plotted in Figure 5. At this higher sulfur level, the longitudinal CVN energy absorption values are superior to the transverse values from room temperature to around -20° C. There is a significant difference in the upper shelf CVN values, 219 J for the longitudinal test and 131 J for the transverse test.



Figure 4 Plot of longitudinal and transverse CVN curves obtained from 0.002% S TC128 Grade B Plate.

All in all, excellent impact properties were obtained from the 0.006% S max TC128 Grade B steels. It remains to be determined if 0.006% S max TC128 Grade B steel can satisfy the still to be determined puncture resistance requirements and what sulfur level might be required. Once this has been determined, the issues of steel cost and availability will come into play.



Figure 5 Plot showing the difference in the temperature range of -18° C to 21° C CVN Energy absorption between longitudinal and transverse specimen prepared from a 0.004% S TC128 Grade B plate.

Conclusions

Consistent with expectations, lowering the sulfur content to 0.006% maximum, and applying calcium treatment for inclusion shape control on the TC128 Grade B steel, results in a significant increase in the transverse CVN properties.

With sulfur levels below 0.003% the longitudinal and transverse CVN impact properties are virtually the same.

The transverse upper shelf energy found for the 0.002 to 0.003% sulfur steels is essentially the same as the longitudinal CVN values reported by Kyed et al ⁽¹⁾ for a 0.009% S and Hicho and Harne⁽²⁾ for a 0.010% S TC128 Grade B steel, 620° C.

The Plate Mill transverse CVN data obtained at -34° C show a significant improvement in energy absorption values for the 0.002% S or lower TC128 Grade B steels compared to the 0.004% S TC128 Grade B Steel.

The average transverse CVN upper shelf energy absorption value found for steels in the 0.002 to 0.003% S range was 209 J, twice that reported by Hicho and Harne⁽²⁾ for a 0.010% S TC128 Grade B steel.

Acknowledgments

The authors would like to acknowledge the assistance given by Luis Laus, John Melton, Judy Sims, Garry Vader and Lynn Vea, all of Arcelor Mittal Steel USA. Special thanks to Fred Fletcher also of Arcelor Mittal USA for his review and helpful comments.

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