Northwestern University Department of Materials Science and Engineering

SUPER-TOUGH STEEL FOR BRIDGES AND OTHER APPLICATIONS

Final Report

by

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Introduction

Higher toughness in steels permits the presence of longer fatigue cracks prior to rupture making it less likely that they would escape detection. Since steels become brittle at cryogenic temperatures, a steel with higher fracture toughness at low temperatures than existing steels is of interest for infrastructure applications such as bridges and tank cars that transport cryogenic liquids such as liquid chlorine or compressed natural gas. A steel (ASTM A710 Grade B) was previously developed at Northwestern University with FHWA and ITI financial support and with IDOT participation for bridge and other infrastructure applications and was successfully used in construction of a bridge at Lake Villa, Illinois. This A710 Grade B steel is produced by hot-rolling and air-cooling (i.e. without costly quench and temper or thermo-mechanically-controlled processing), is easily weldable without pre- and post-heating, is very corrosion-resistant and possesses very good fracture toughness at low temperatures (appr. 100 ft-lbs @ -40°F; the A709 Bridge Steel Standard requires 30 ft-lbs @-30°F). During the development of A710 steel in 1990's, we investigated the effects of different elements on the mechanical properties of the steel. In one steel composition, we added 0.1% titanium to further improve the welding properties. That steel had phenomenal fracture toughness; none of the Charpy specimens (used to estimate the fracture toughness of the steel) fractured down to -100°F.

During performance of this project, the effect of addition of various levels of titanium on mechanical and fracture properties and microstructure of A710 Grade B steel was investigated. The "super-tough" steel also was extensively tested for tank-car application. The steel was marketed to Northern DOTs and steel companies. This work is described below.

Further Development of "Super-Tough" Steel

The effect of varying Ti concentration on mechanical and fracture properties of A710 Grade B steel was investigated. This study resulted in an invited paper for American Society for Metals Materials and Technology Conference, M&TC 2009 (full paper is attached to this report). The highlights of this work are summarized here.

The research involved significant contribution from Riad Asfahani, staff scientist from Research & Technology Center of the United States Steel (US Steel) Corporation. US Steel produced three 100-lb steel heats based on our original A710 Grade B steel with variable Ti concentration: 0.03, 0.07 and 0.10 wt.% (Table 1). The strength and fracture toughness of these steels were measured and microstructure characterized. It was found that while the strength is not affected by addition of Ti, the fracture toughness is significantly improved by such addition; the more Ti is added the better the lowtemperature fracture toughness of the steel is. It is seen from Figure 1 that none of Charpy specimens fractured at 24°C (room temperature). At -23°C, steel that contained 0.07 and 0.10% Ti did not fracture, and at -40°C, the steel specimen containing 0.10 Ti did not fracture. It is important to note that the Charpy absorbed fracture energies for these three steels significantly exceed the requirements for bridge steels --- 40-50 J at -23 to -40°C (depending on the climate zone). Figure 2 shows a Charpy A710 Grade B steel specimen with 0.10 % Ti after being tested at -40°C. The specimen stopped the Charpy hammer without fully fracturing; the fracture surface was completely ductile. Metallographic analysis of these steels demonstrated that addition of Ti to steels results in a reduction of the amount of pearlite (dark areas in Figure 3) in the microstructure. It is well known that pearlite in the ferritic steels results in decreased fracture toughness. There are observations that reduction of the amount of pearlite in steels leads to increased corrosion resistance¹. We did not perform corrosion studies under this contract.

Table 1. Compositions of A 710 B steel (wt.%) with varying Ti content made at United
States Steel Corporation's Research & Technology Center

Steel	С	Si	Mn	Cu	Ni	Nb	Ti	Р	S
A710 B w/0.03% Ti	0.05	0.39	0.50	1.30	0.90	0.06	0.03	0.01	0.005
A710 B w/0.07% Ti	0.06	0.39	0.50	1.29	0.90	0.06	0.07	0.01	0.005
A710 B w/0.10% Ti	0.06	0.39	0.50	1.30	0.90	0.06	0.10	0.01	0.005



Figure 1. Charpy absorbed impact energy versus testing temperature for steels containing different amount of Ti

¹ Y.T. Zhao et al., The Mechanical Properties and Corrosion Behaviors Of Ultra-Lo w Carbon Microalloying Steel, Materials Science And Engineering A-Structural Materials Properties Microstructure and Processing, <u>454</u>, p. 695, 2007



Figure 2. Charpy specimen made of A710 Grade B steel with 0.10 % Ti after being tested at -40°C. The specimen stopped the Charpy hammer without fully fracturing. The fracture surface is completely ductile



Figure 3. Effect of Ti addition on microstructure of ASTM A710 Grade B ferritic steel: A - 0.03% Ti, B - 0.07% Ti, C -0.10% Ti

Testing of "Super-Tough" Steel for Tank-Car Applications

Based on the test results for three steels produced at US Steel Company, a 300-lb heat of the steel containing 0.11% Ti was melted, hot-rolled to ½-inch thick plates and then air-cooled at Sophisticated Alloys, Inc., Butler, PA for further testing at Union Tank Car Company (UTLX) for tank cars carrying cryogenic liquid applications. The chemical composition of the steel is shown in Table 2.

Table 1. Chemical composition (wt.%) of steel produced for 01LX tests								
С	Mn	Si	Cu	Ni	Nb	Ti	S	Р
0.05	0.57	0.51	1.33	0.55	0.08	0.11	< 0.005	< 0.005

Table 1. Chemical composition (wt.%) of steel produced for UTLX tests

The tensile and fracture properties of this steel were tested at Northwestern University and other property such as a puncture resistance in a drop weight test was tested at Miner Enterprises (and paid by UTLX). Figure 4 shows the results of tensile testing: the 0.2% offset yield strength was 74 ksi, ultimate tensile strength was 81ksi and elongation to failure more than 33%. These properties significantly exceed requirements for steels for bridges and tank cars.



Figure 4. Stress-strain curves for two specimens made of 'super-tough" steel produced at Sophisticated Alloys for UTLX

A710 Grade B steel modified with Ti has very high fracture toughness. The Charpy testing machine at Northwestern University has limit of 264 ft-lbs, therefore Charpy tests were performed at MSI Inc on a machine with 700 ft-lbs limit. At testing temperatures down to -60°F, none of the specimens fractured (Figure 5). During testing specimens bent and were pushed with the Charpy hammer through the machine. Thus the machine measured not the energy to fracture the specimen but the energy to bend it and push through the machine. Therefore, the absorbed fracture energy for the steel exceeds 700 ft-lbs at all temperature down to $-60^{\circ}F$.



Figure 5. Charpy absorbed fracture energy versus testing temperature (arrow indicates that specimen did not fracture) for steel produced at Sophisticated Alloys, Inc

The optical micrographs of the steel (Figure 6) show a typical ferritic microstructure. Practically, no pearlite is present in the steel (note that this steel contains 0.11% Ti vs 0.10% Ti in steel produced by US Steel Company). As before, the remarkable

high fracture toughness of the steel could be attributed to the suppression of pearlite formation by an addition of titanium to the steel.



Figure 6. Microstructure of the steel produced at Sophisticated Alloys, Inc: A - low magnification, B - higher magnification

UTLX included this steel in their program to test a number of steels for application in tank cars that transport cryogenic liquids such as chlorine and liquefied natural gas. This program also includes our original A710 Grade B steel, highperformance bridge A709 steels (A709 HPS70 and A709 HPS100), and a few steels that are currently used for tank-car construction. Previously (in 2006-2007), the mechanical and fracture properties of the steels (except for 'super-tough" A710 Grade B steel which was not available at that time) were tested at Bodycote, Houston (UTLX funded that), at Southwest Research Institute and at American Railroad Association. The original A710 Grade B (with 0.03% Ti) fracture properties at low temperatures significantly exceeded these of all steels in the program. As this report shows, the A710 Grade B steel modified with 0.10-0.11% Ti has even better fracture properties than original A710 Grade B steel.

While some of the tests performed by UTLX or its contractors are still in progress or being analyzed, some results of drop tests are available and are described below. This non-standardized test was designed by UTLX to test the steel penetration resistance to a 2-inch-diameter punch that free-falls onto a plate of steel. This test simulates a penetration of a tank car by a steel object during a crash. While this test does not mimic the real crash, it allows qualitative ranking of the steels as to their puncture resistance. This test is very severe therefore it was expected that the steel rod would punch a hole in all steel plates, but the appearance of the punched hole and the energy absorbed during the tests would let the ranking of the steels in the test.

Figure 7 shows how a steel-plate (gray) in a form of a disk is clamped horizontally in a holder. This holder is placed in a press under a raised frame that holds a 2-inch-diameter punch aimed onto the middle of the plate (Figure 8). The punch is raised to a predetermined height and then the upper frame with the punch is released for a free fall. The plate is removed from the holder after the test with a punch still in the plate. Then the plate is photographed. The punch is pushed out with a smaller press, and the plate is subjected to further visual and microscopic analyses at UTLX and at Arcelor-Mittal Global R&D Division. This detailed analysis is not completed yet.

Figure 9 compares "super-tough" A710 Grade B with competingA709 HPS100 steel after room-temperature puncture testing. The surface of "super-tough" steel around the punched-out hole is clean and does not contain any cracks, while A709 HPS100 steel contains numerous cracks around the punched-out hole. This indicates that in a tank-car crash the long cracks could form and propagate at low temperatures in A709 HPS100 steel leading to a release of chemical transported in the tank car, while "super-tough" steel would provide much better protection of the cargo. Further puncture tests are planned by UTLX with a redesigned set-up to closer reflect the conditions of tank car crash in the field.

The stress and displacement values were recorded during the puncture tests and energy absorbed by steel plates was calculated. Preliminary results demonstrate that "super-tough" steel absorbed approximately 20% more energy of impact than other steels of the same thickness, thus indicating that this steel could fare better in tank-car crashes than other steels.

UTLX plans to continue the testing of the steels with a redesigned setup to better simulate conditions of tank-car crashes in the field and also to perform welding studies. If "super-tough" A710 steel outperforms other steels in these tests, UTLX plans to build one or two experimental tank cars for testing in field using this steel.



Figure 7. Assembly of the plate into holder for a penetration test



Figure 8. Placement of the plate into press prior to penetration test



Figure 9. Punctured "super-tough" A710 Grade B (A) and A709 HPS100 (B) steel plates

Marketing of the Steel to Northern DOTs and Communication with Steel Companies

During the performance of this project, we contacted numerous Northern DOTs to market the "super-tough" steel for bridge construction. These states included Minnesota, North Dakota, Alaska, Wisconsin, and Montana. None of these state DOTs expressed interest in immediate use of the steel. The major impediment to using this steel is that steel is not commercially available. We communicated with aggressive mini-mill companies, Nucor Steel Company and Steel Dynamics, and we visited Steel Dynamics to discuss the production of a commercial heat of steel. These companies agreed to produce a 150-ton commercial heat, but they want this heat to be substantially sold. If tests of the "super-tough" steel are successful at UTLX and UTLX orders 30-60 tons of steel to build one or two experimental tank cars, then steel companies might be more willing to produce commercial heats and market the steel to the DOTs.

Summary

Addition of small amounts of titanium (0.10-0.11%) to A710 Grade B steel significantly increases absorbed fracture energy at cryogenic temperatures.

The "super-tough" steel significantly outperformed other steels tested in UTLX program in search for advanced steels for tank cars that transport cryogenic liquids such as liquid chlorine or compressed natural gas. Further tests are underway. UTLX plans to build one ore two experimental tank cars if further testing is successful.

Attachment

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Effect of Ti on Charpy Fracture Energy and Other Mechanical Properties of ASTM A 710 Grade B Cu-Precipitation-Strengthened Steel

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Abstract

Addition of titanium (Ti) to ASTM A710 Grade B Cu-precipitation-strengthened steel significantly increases the impact absorbed fracture energy and reduces the ductile-to-brittle transition temperature. The effect of Ti correlates with the reduction of the amount of pearlite in the ferritic microstructure. A thorough study of the mechanical properties of Ti-modified A 710-B steel is presented.

Introduction

The ductile to brittle transformation in steels depends on interplay of the fracture stress and the flow stress. In steels the flow stress depends on temperature and strain rate because the motion of screw dislocations is function of temperature and strain rate. In this work the fracture stress has been assumed essentially independent of temperature and strain rate. At high temperatures and low strain rates thermal energy is sufficient to give plastic flow at stresses below the fracture stress, but this is not so at low temperatures and strain rates; thus there is ductile to brittle transformation temperature as shown in Figure 1.

The stress (Peierls stress) to move a long dislocation segment from a deep crystallographic energy valley would be very large. J. Weertman proposed many years ago that a high Peierls energy dislocation would likely move by first forming a double kink [1]. In the BCC metals the kink edges would be in the edge orientation and thus very mobile. Later he suggested that a misfit center would interact with a dislocation to help pull it from its Peierls energy valley [2]. This is depicted in Figure 2.

Such a misfit center will both give increase in yield stress at elevated temperatures where thermal energy is sufficient to nucleate double kinks along the dislocation line but decrease the yield stress at low temperatures where thermal energy is small. The misfit center helps the applied stress displace the dislocation escape from the deep energy valley. This behavior is depicted in Figure 3.



Temperature

Figure 1. The yield strength at constant strain rate is shown to increase rapidly on cooling intersecting the fracture strength giving a ductile to brittle transformation



Figure 2. A misfit center lying above or below a dislocation line segment twists it partially out of its Peierls valley reducing the flow stress

The first precipitates to form in the binary Fe-Cu alloys are BCC in structure instead of thermodynamically stable FCC Cu [3]. Further these precipitates are very small (few nanometers) and contain substantial amounts, approximately 33% of Fe [3]. Renewed interest in Cu alloy precipitation strengthened steels occurred because of the need to reduce C content in martensitic steels to achieve improved weldability in relatively high yield strength steels. This is the basis for HSLA 100 steel with 700 MPa yield strength that is used for naval applications [4]. It was found previously [5,6], that tempering of the martensite in HSLA 100 overages the Cu alloy precipitates so they under contribute to the yield strength. If the Mo and Cr are eliminated, added to HSLA 100 to attain a martensitic structure on quenching, the full strengthening effect of Cu alloy precipitates can be achieved. Investigations of this concept lead to the development of ASTM A710 Grade B steel at Northwestern University. The BCC Cu alloy precipitates are coherent and coplanar with the ferrite matrix and their activation energy for nucleation is small. They form on air cooling from hot rolling. The resulting steel A710 B, has a yield stress of 480-550 MPa in as

rolled and air-cooled condition. The strength of the steel increases on aging in 500 to 550°C temperature range [7 - 10].



Figure 3. A misfit center strengthens the steel at elevated temperatures but reduces flow stress at low temperatures thereby lowering the ductile to brittle transformation temperature

One of the 45-kg heats of steel made by the former Inland Steel Research Laboratory during development of A710 Grade B steel contained 0.10 wt % Ti. The steel had the remarkable high Charpy impact energy at dry ice and acetone temperature, -95° C. The specimens bent but did not break stopping the Charpy hammer [10]. Concept expressed in Figure 3 explains this result. Ti by reacting with C and N to form T(C, N) raised the fracture strength. The Cu alloy precipitates that are only a few nm in diameter are misfit centers that increase the yield strength at room temperature but decrease the yield stress at low temperatures, thus the lower ductile to brittle transformation temperature.

This remarkable result led us to the present study, the effect of Ti variation on the properties of low carbon nano-scale precipitation strengthened steel.

Experimental Procedure

The steel for this research was made at United States Steel Corporation's Research & Technology Center. A 135-kg vacuum induction melt was split and cast into three 45-kg ingots differing only in Ti content as shown in Table 1. The ingots dimensions were 3-inch-thick by 8-inch-width by 14-inch-length. The Ti content varied from 0.03 wt. pct., the upper limit in the A710 B specification, to 0.10 wt. pct, the amount in the Ti alloyed steel previously investigated. Each ingot was stripped from the mold upon cooling to room temperature, reheated to 1093°C, hot-rolled to 12.2-mm-thick plate with a finish rolling temperature of 871°C, and then air-cooled to room temperature.

Standard tensile and Charpy specimens were machined in rolling direction. Tensile testing was performed on MTS screw driven machine and Charpy specimens were tested in machine with a 358 J limit.

Specimens for optical microscopy were etched with 5% nitol solution.

Corporation's Research & Technology Center									
Steel	С	Si	Mn	Cu	Ni	Nb	Ti	Р	S
A710 B w/0.03% Ti	0.05	0.39	0.50	1.30	0.90	0.06	0.03	0.01	0.005
A710 B w/0.07% Ti	0.06	0.39	0.50	1.29	0.90	0.06	0.07	0.01	0.005
A710 B w/0.10% Ti	0.06	0.39	0.50	1.30	0.90	0.06	0.10	0.01	0.005

 Table 1. Compositions of A 710 B steel (wt.%) with varying Ti content made at United States Steel

 Corporation's Research & Technology Center

Results and Discussion

The effect of increasing Ti from 0.03 to 0.10 % on the microstructure is shown in Figure 4. The Ti reacts with C to form TiC thereby significantly reducing the amount of cementite and pearlite as in interstitial free steels. The TiC particles are too small to be seen at the magnification of Figure 4. The increase in Ti had little effect on the ferrite grain size.



Figure 4. Microstructure in optical microscope of (A) A710 B with 0.03 wt pct Ti and (B) Ti-modified A710 B with 0.10 wt pct Ti

The results of room temperature tensile tests are shown in Figure 5 and summarized in Table 2. Increasing the Ti content from 0.03 wt % to 0.10 wt % gives little increase in yield stress but there is a significant increase in ultimate tensile stress. The small increase in work hardening is suggested to be due to Orowan looping around the small Ti precipitates. The elongations to failure in all three steels were almost the same, 28 to 30% in 25.4-mm- gage length specimens.

Table 2.	Yield stress, ultimate tensile strength, and elongation to failure						
Steel	0.2% Offset Yield, MPa	UTS, MPa	Elongation to Failure, %				
A710 B w/0.03% Ti	480	545	30				
A710 B w/0.07% Ti	507	590	28				
A710 B w/0.10% Ti	493	583	28				



Figure 5. Stress-strain curves for A709 Grade B with (A) 0.03% Ti, (B) 0.07%Ti and (c) 0.10%Ti

The Charpy impact energies were measured over the temperature range 25 to -73° C. The results are given in Table 3 and the average Charpy values are plotted versus temperature in Figure 6. The arrows indicate that the specimens did not break in the Charpy apparatus. The specimens bent but were only partially fractured with a ductile fracture surface. Thus the true fracture energy for these specimens is higher than 358 J, the limit of the Charpy machine. Figure 7 is a photograph of such a specimen showing its fracture surface. The unusually high shelf fracture energy at the higher test temperatures must result from the fracture stress being significantly higher than the yield stress. As shown in Table 3 and Figure 6, the >358 J level shifted to a lower temperature as the Ti content increased. The high fracture energies seen in the 0.10 Ti modified A710 B steel is not equaled by any other ferritic relatively low alloy steel as far as the authors know.

		/	
Т, ⁰С	A710 B w/0.03% Ti	A710 B w/0.07% Ti	A710 B w/0.10% Ti
24	>358	>358	>358
-23	271	>358	>358
-40	212	309	>358
-51	250, 279	290, 306	336
-62	282, 201	227, 293	252, 255
-73	135, 155	192, 252	113, 233

Charpy fracture energy (J) of A710 Grade B and the two Ti modified A710 B steels

Table 6.



Figure 6. Charpy Absorbed Impact Energy versus temperature for the three ASTM A710 steels modified by Ti



Figure 7. Charpy specimen of A710 Grade B with 0.10 % Ti tested at -40°C. The specimen stopped Charpy hammer without fully fracturing. Fracture surface is completely ductile

Final Discussion and Conclusions

The Ti modified Cu nanoscale precipitation hardened steels have remarkably high Charpy absorbed impact energies especially at cryogenic temperatures. This was attributed to Weertman's theory [2]. The interaction of slightly misfitting coherent coplanar low-nano-size Cu alloy precipitates with screw dislocations locally lowers the Peierls stress.

The addition of Ti to steel significantly reduced the cementite and pearlite in steel replacing them by small TiC particles raising the fracture stress.

Many applications for highly impact resistant steel particularly at low temperatures come to mind. Tank cars that carry refrigerated liquids and bridges in very cold climates are examples. The very high shelf fracture energy even at room temperature makes it a candidate for safety critical automobile components.

Acknowledgments

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