

Update on Ballot for Titanium Grade 12 NACE MR0175 / ISO 15156-3

Chris Wilson, Technical Director, Uniti Titanium

Background



The International Titanium Association (ITA) sponsored a project to remove restrictions on Grade 12 titanium within the NACE MR0175 / ISO 15156-3 Standard.

- The current standard has the following restrictions on hardness and annealing:

UNS R53400 shall be in the annealed condition. Heat treatment shall be annealing at $(774\pm14)^{\circ}\text{C}$ [$(1,425\pm25)^{\circ}\text{F}$] for 2 h followed by air-cooling. Maximum hardness shall be 92 HRB.

- Continuous annealed product is currently not permitted.
- Hardness values greater than 92 HRB are not permitted.

Ballot Results

FIRST BALLOT VOTE:

MR0175 / ISO 15156-3 Maintenance Panel meeting in Krakow Poland on September 3, 2018.

FAILED – (2 Positive votes / 10 Negative votes)

SECOND BALLOT VOTE:

Maintenance Panel vote in January 2019.

PASSED – (11 Positive votes / 3 Negative votes)

THIRD BALLOT VOTE:

TG299 Task Group vote in May 2019.

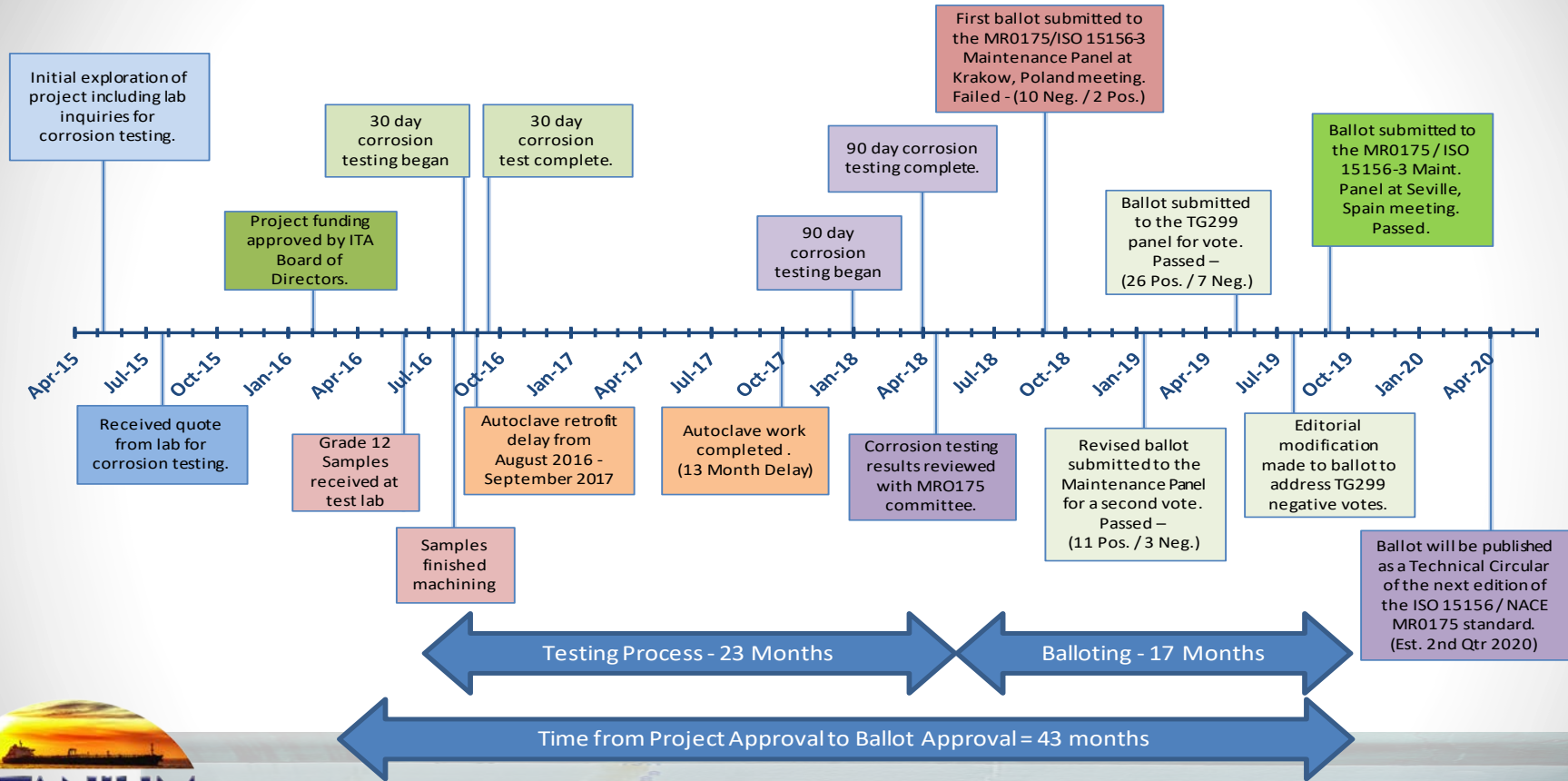
PASSED – (26 Positive / 7 negatives)

FINAL BALLOT VOTE:

MR0175 / ISO 15156-3 Maintenance Panel meeting in Seville Spain on September 6, 2019.

PASSED

Timeline of NACE MR0175 Project for Grade 12 Titanium



Revised Wording

Current
Wording



UNS R53400 shall be in the annealed condition. Heat treatment shall be annealing at $(774 \pm 14)^{\circ}\text{C}$ [$(1,425 \pm 25)^{\circ}\text{F}$] for 2 h followed by air-cooling. Maximum hardness shall be 92 HRB.

New
Wording



UNS R53400 shall be in the annealed condition.

Table A.41 – Environmental and materials limits for titanium used for any equipment or component

Individual alloy UNS number	Temperature	Partial pressure H ₂ S pH ₂ S	Chloride conc.	pH	Sulfur- resistant?	Remarks
	max ° C (° F)	max kPa (psi)	max mg/l			
R50250 R50400 R56260 R53400 R56323 R56403 R56404 R58640	See "Remarks" column	See "Remarks" column	See "Remarks" column	See "Remarks" column	Yes	Any combination of temperature, pH ₂ S, chloride concentration, and <i>in situ</i> pH occurring in production environments is acceptable.
R55400	288 (550)	3 450 (500)	180 500	See "Remarks" column	Yes ^a	Any <i>in situ</i> production environment pH is acceptable for $p_{CO_2} + p_{H_2S} \leq 7\,000\text{ kPa (1\,000 psi)}$
R53400	205 (401)	3 450 (500)	180 500	See "Remarks" column	Yes ^a	Any <i>in situ</i> production environment pH is acceptable for $p_{CO_2} + p_{H_2S} \leq 7\,000\text{ kPa (1\,000 psi)}$

These materials shall also comply with the following:

- a) UNS R50250 and R50400 shall have a maximum hardness of 100 HRB;
- b) UNS R56260 shall have a maximum hardness of 45 HRC and shall be in one of the three following conditions:
 - 1) annealed;
 - 2) solution-annealed;
 - 3) solution-annealed and aged.
- c) UNS R53400 shall be in the annealed condition. Heat treatment shall be annealing at $(774 \pm 14)^\circ\text{C}$ $[(1\,425 \pm 25)^\circ\text{F}]$ for 2 h followed by air-cooling. Maximum hardness shall be 92 HRB;
- d) UNS R56323 shall be in the annealed condition and shall have a maximum hardness of 32 HRC;
- e) wrought UNS R56403 shall be in the annealed condition and shall have a maximum hardness of 36 HRC;
- f) UNS R56404 shall be in the annealed condition and shall have a maximum hardness of 35 HRC;
- g) UNS R58640 shall have a maximum hardness of 42 HRC;
- h) UNS R55400 shall be used in the Solution-Treat plus Age (STA) condition, and have a maximum hardness of 41 HRC.
- i) UNS R53400 shall be in the annealed condition.

Grandfathered Grade 12 will remain in standard with no restrictions on temperature and H2S concentration.

Footnote i): New Grade 12 listing. No restriction on processing, however NACE Level VII limitations on temperature and H2S concentration.

^a Sulfur resistant as tested in accordance with Group 1 as defined in NACE Conference paper 95047 and EFC 17, Appendix S1.

Specific guidelines shall be followed for successful applications of each titanium alloy specified in this part of ISO 15156. For example, hydrogen embrittlement of titanium alloys can occur if these alloys are galvanically coupled to certain active metals (e.g. carbon steel) in H₂S-containing aqueous media at temperatures greater than 80 ° C (176 ° F). Some titanium alloys can be susceptible to crevice corrosion and/or SSC in chloride environments. Hardness has not been shown to correlate with susceptibility to SSC/SCC. However, hardness has been included for alloys with high strength to indicate the maximum testing levels at which failure has not occurred.

What does this mean?

- Removed Barriers for Grade 12 Titanium Producers
 - No restrictions on annealing cycle
 - No maximum hardness requirement
 - Increased supply availability for NACE MR0175 sour service market.
- Improved Mechanical Properties over Grade 2 / 2H.
- Improved Corrosion Resistance over Grade 2 / 2H.
- Potential Project Cost Savings over Grade 2 / 2H.

Grade 12 Titanium

CORROSION ADVANTAGES

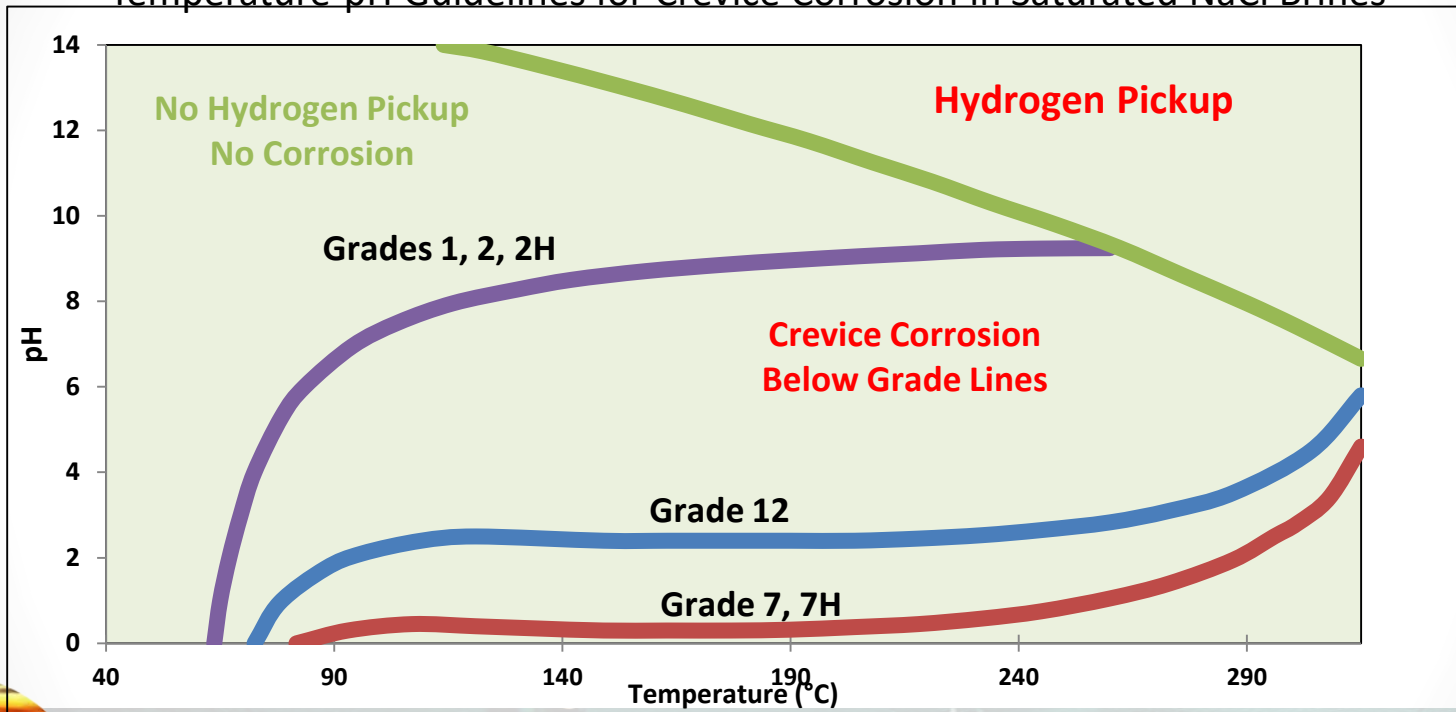


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Crevice Corrosion

Temperature-pH Guidelines for Crevice Corrosion in Saturated NaCl Brines



Source: R.W. Schutz, Mater. Perform., Vol 24 (No. 1) Jan 1985, p 39-47

Grade 12 Titanium

MECHANICAL PROPERTY ADVANTAGES

NACE MR 0175 - Approved Ti Grades

UNS Number	Titanium Grade	C	O	N	H	Fe	Al	V	Pd	Ru	Ni	Mo	Cr	Zr	Sn	Ti
R50250	Grade 1	0.10	0.18	0.03	0.015	0.2	—	—	—	—	—	—	—	—	—	Bal.
R50400	Grade 2	0.10	0.25	0.03	0.015	0.3	—	—	—	—	—	—	—	—	—	Bal.
R53400	Grade 12	0.08	0.25	0.03	0.015	0.3	—	—	—	—	0.6 to 0.9	0.2 to 0.4	—	—	—	Bal.
R56403	Grade 25 (Ti-6Al-4V + Pd & Ni)	0.10	0.2	0.05	0.015	0.4	5.5 to 6.75	3.5 to 4.5	0.04 to 0.08	—	0.3 to 0.8	—	—	—	—	Bal.
R56323	Grade 28 (Ti-3Al-2.5V + Ru)	0.08	0.15	0.03	0.125	0.25	2.5 to 3.5	2.0 to 3.0	—	0.08 to 0.14	—	—	—	—	—	Bal.
R56404	Grade 29 (Ti-6Al-4V ELI + Ru)	0.08	0.13	0.03	—	0.25	5.5 to 6.5	3.5 to 4.5	—	0.08 to 0.14	—	—	—	—	—	Bal.
R58640	Grade 19 Beta C (Ti-3Al-8V-6Cr-4Mo-4Zr)	—	—	—	—	—	3	8	—	—	—	4	6	4	—	Bal.
R56260	Ti-6246	—	—	—	—	—	6	—	—	—	—	6	—	4	2	Bal.

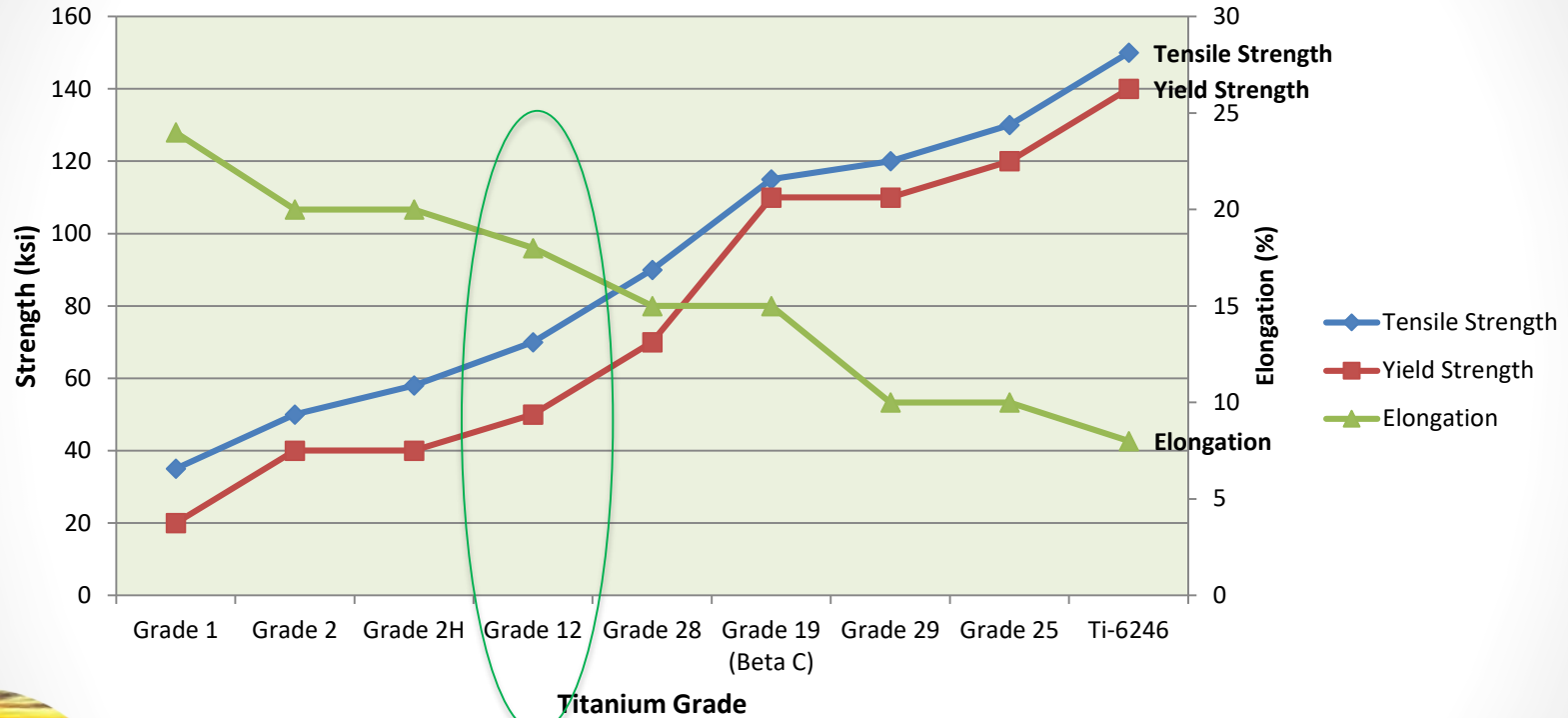
Mechanical Properties Requirement (ASME SB265)

NACE MR0175 / ISO 15156 Approved Grades

UNS Number	Titanium Grade	Tensile Strength (ksi)	Yield Strength, 0.2% Offset (ksi)	Elongation in 2 in. (%)
R50250	Grade 1	35 min.	20 to 45	24 min.
R50400	Grade 2	50 min.	40 to 65	20 min.
R50400	Grade 2H	58 min.	40 to 65	20 min.
R53400	Grade 12	70 min.	50 min.	18 min.
R56323	Grade 28 (Ti-3Al-2.5V + Ru)	90 min.	70 min.	15 min.
R58640	Grade 19 Beta C (Ti-3Al-8V-6Cr-4Mo-4Zr)	115 min.	110 min.	15 min.
R56404	Grade 29 (Ti-6Al-4V ELI + Ru)	120 min.	110 min.	10 min.
R56403	Grade 25 (Ti-6Al-4V + Pd & Ni)	130 min.	120 min.	10 min.
R56260	Ti-6246	150 min.	140 min.	8 min.

Sorted by
Increasing
Tensile
Strength

Minimum Allowable Mechanical Properties NACE MR0175 / ISO 15156 Approved Titanium Grades



Data from ASME SB 265 Mechanical Property Requirements

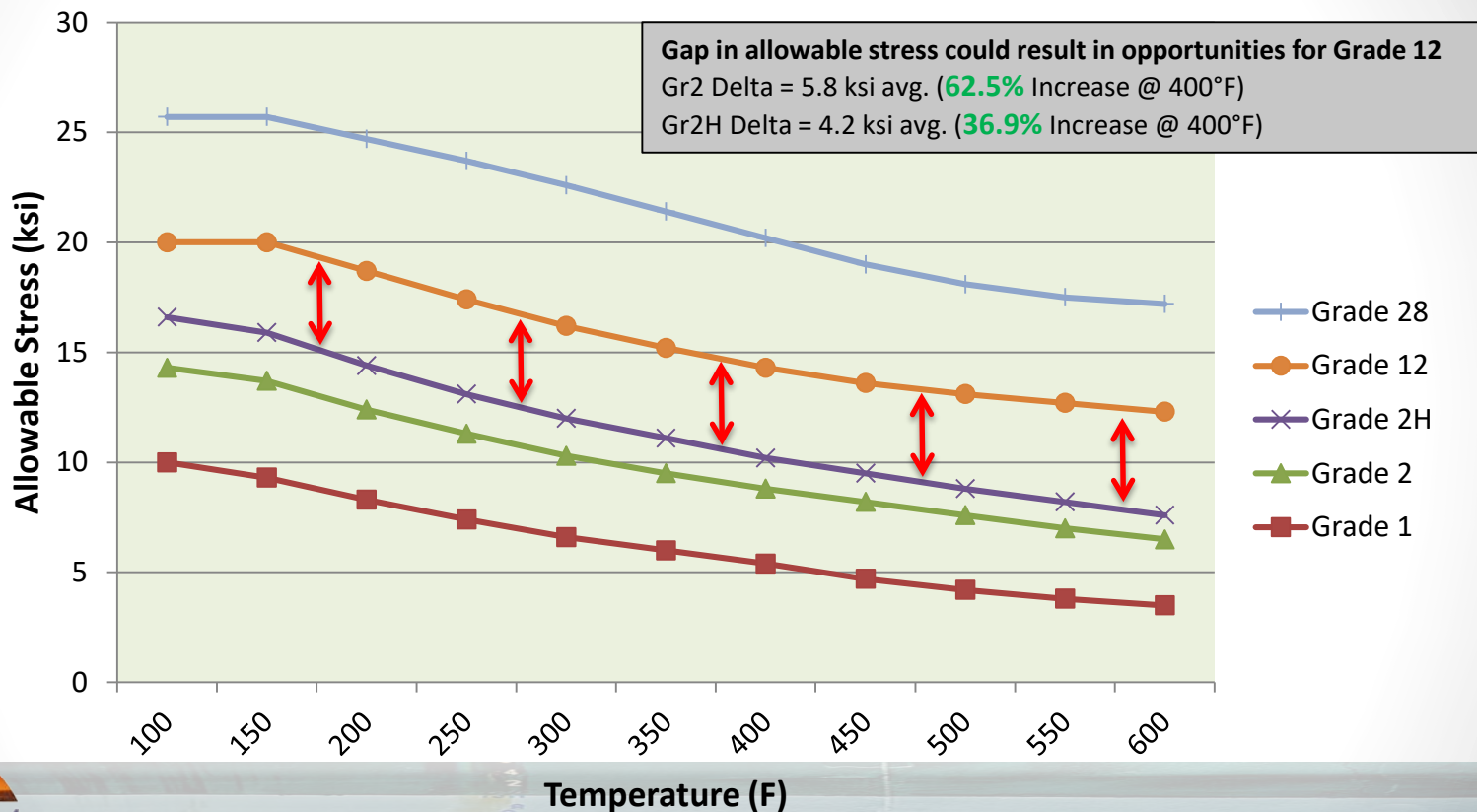
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NACE MR0175 / ISO 15156 Approved Titanium Grades Versus ASME Section VIII Division 1 Code Approved Titanium Grades

NACE MR0175 / ISO 15156 APPROVED TITANIUM GRADES		ASME Section VIII Division 1 Code Approved
R50250	Grade 1	Yes
R50400	Grade 2 / Grade 2H	Yes
R53400	Grade 12	Yes
R56403	Grade 25 (Ti-6Al-4V + Pd & Ni)	No
R56323	Grade 28 (Ti-3Al-2.5V + Ru)	Yes
R56404	Grade 29 (Ti-6Al-4V ELI + Ru)	No
R58640	Grade 19 Beta C (Ti-3Al-8V-6Cr-4Mo-4Zr)	No
R56260	Ti-6246	No

ASME Section VIII Division 1 Allowable Stress at Elevated Temperatures



Data from ASME Boiler and Pressure Vessel Code for Section VIII, Division 1 Service.

Grade 12 Titanium

COST FACTORS

Material Cost Factor Equation

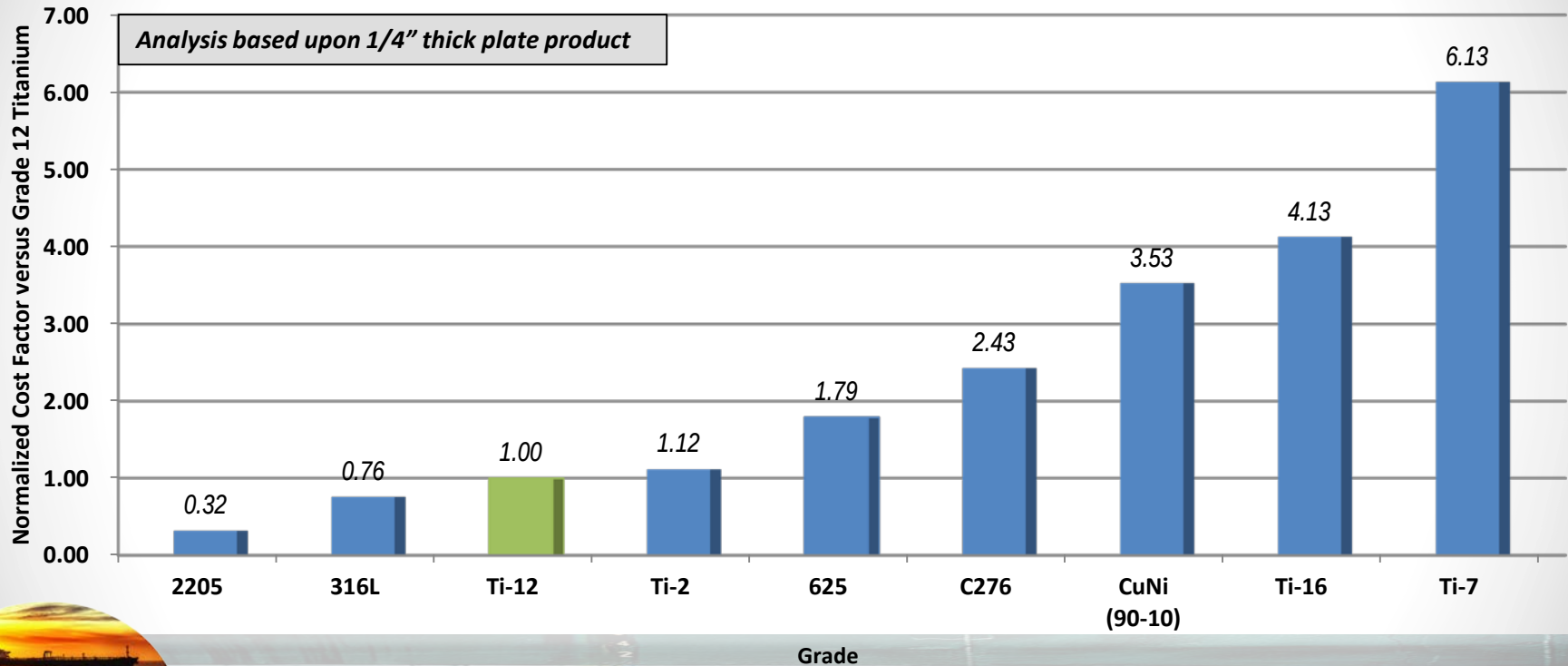
Normalized Against Grade 12 Titanium

for Density and Strength

$$\begin{array}{ccccccc}
 \text{Normalized Cost} & = & \text{Material Alloy Cost} & \times & \text{Density} & \times & \text{Thickness} & \times & \frac{144 \text{ in}^2}{\text{ft}^2} & \times & \frac{\text{Grade 12 Ti Yield Strength (lbs./in}^2\text{)}}{\text{Material Alloy Yield Strength (lbs./in}^2\text{)}} \\
 (\$/\text{ft}^2) & & (\$/\text{lb}) & & (\text{lbs./in}^3) & & (0.250 \text{ in}) & & & & \\
 \end{array}$$

Normalized Cost
of Grade 12 Titanium

Normalized Cost Factor Based upon Grade 12 Titanium Cost, Minimum Yield Strength and Density



Data Source: Tricor Metals Alloy Cost Comparison Chart , Industry Survey and ASME SB 265 minimum yield strength requirements.

Acknowledgement

- ITA Board of Directors and Staff
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- Sample Materials:
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 - ThyssenKrupp VDM
 - Uniti Titanium
- Industrial Applications Committee
 - Rob Henson, VSMPO Tirus US
 - Charles Young, Tricor Metals

Summary

- Grade 12 Modifications will be included in the next technical circular publication of the NACE MR0175 / ISO 15156 standard.
- Expect document to be published in 2nd Qtr 2019
- Key Benefits:
 - Removed Barriers for Grade 12 Titanium Producers
 - No restrictions on annealing cycle
 - No maximum hardness requirement
 - Increased supply availability for NACE MR0175 sour service market.
 - Improved Mechanical Properties over Grade 2 / 2H.
 - Improved Corrosion Resistance over Grade 2 / 2H.
 - Potential Project Cost Savings over Grade 2 / 2H.
- Grade 12 is a viable and competitive option, when all factors of the project scope are considered, such as allowable stress at elevated temperatures, density of material, cost of material, and corrosion resistance.

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