

METALLURGY AND APPLICATION OF ASTM A707 FORGINGS

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Keywords

High Strength Forgings, Sour Service, SSC, Weldability, HAZ hardness, Copper Ageing, Precipitation hardening, Niobium Microalloying.

Abstract

The 50 year history of copper ageing steels is reviewed. Early developments were focused on linepipe and fittings whereas more recent interest has been in heavy section ultra high strength forgings. The metallurgical basis for the original steels is presented and compared with the approaches used for extending the concept to forgings. Modifications include higher nickel contents and niobium-molybdenum age hardening to complement the effects of copper. Mechanical property and weldability data are presented along with test results for sour service variants of the forgings.

Introduction

ASTM A707¹⁾ Forgings have been used extensively in the offshore industry since the late 1980's. The steel is based on the Ni-Cu-Nb alloy system which dates back to the early 1960's. The early steels in this family were used in plate form and later in rails, forgings and other products. Forgings were limited in strength to about 65 ksi until the late 1980's when the alloy was redeveloped by the author⁽²⁾ for use in very heavy forgings (up to 15" thick) having yield strengths between 75 – 100 ksi. In later applications additional modifications were made to adapt the steel for sour service applications. The metallurgy and evaluation of the ASTM 707 family of alloys is discussed in the present paper.

History & Metallurgical Basis

ASTM A707, Grade L5¹⁾, is a low-carbon steel that develops its mechanical properties via a combination of ferrite grain refinement and copper precipitation hardening. The steel was developed by the International Nickel Company (INCO) in the early 1960's. During its existence, the steel has been identified by a series of related generic and proprietary names that include:

Ni-Cu-Nb(Cb) Steel
IN787 (INCO)
Ni-COP (Armco)
Ni-Cu-Age
HSLA 80 (U.S. Navy)

ASTM A710 – Plate
 ASTM A707 – Forgings
 ASTM A736 – Pressure Vessels
 INCRASTEEL

The chronology of development of the different alloys is shown in Figure 1.

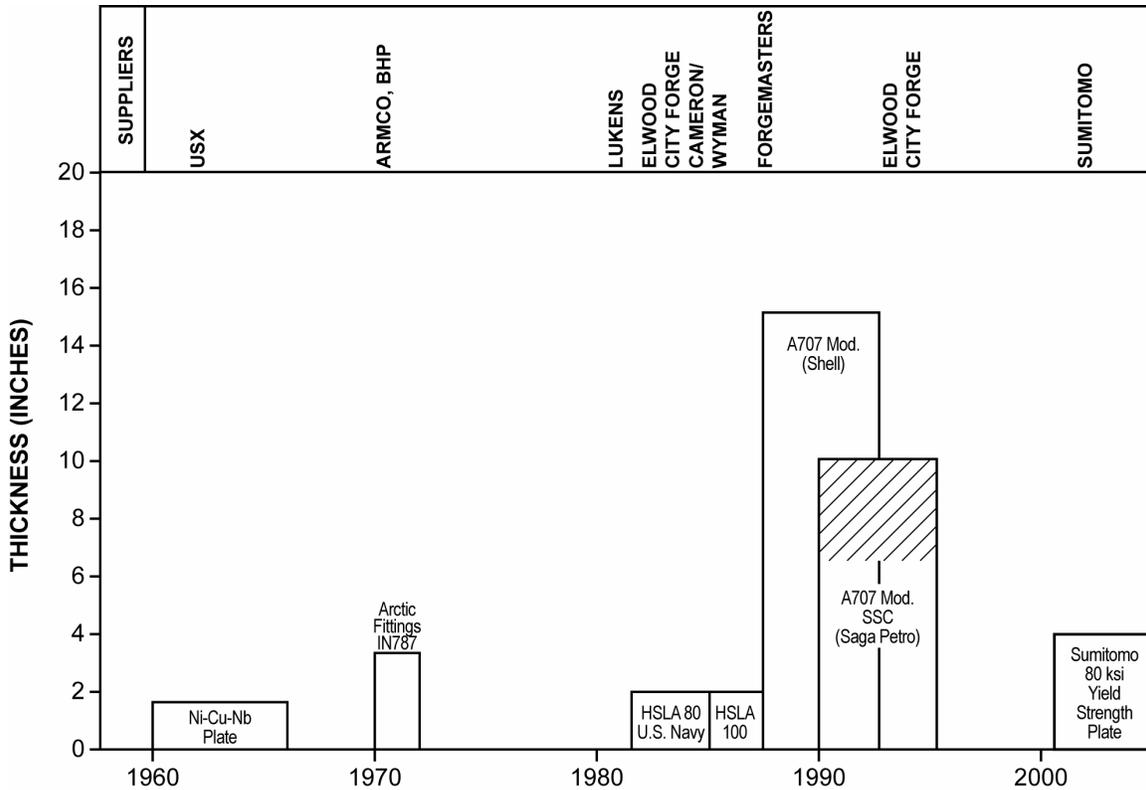


Figure 1. Chronology of Development, Copper Ageing Steels

A typical chemical composition of the original Ni-Cu alloy steel is as follows:

<u>C</u>	<u>Mn</u>	<u>Cu</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>
0.04	0.50	1.00	0.90	0.60	0.25

The steel had a lower manganese content than traditional high-strength, low-alloy steels and this has led to higher manganese variants as a means of increasing strength. The early steels were hot-rolled and aged (tempered) at 1050-1100°F. Another strength enhancing option included quenching and tempering whereas normalizing and tempering was used to improve notch toughness, particularly in thick plate but at the expense of achieving high strength.

Early uses were in structural plate, Arctic fittings in thicknesses up to 3 in., offshore platform components up to 2.5 in., plates for naval ships with strengths up to 100 ksi and in rails and low strength forgings up to 15 in.

In these and other applications, modifications were made to the chemical composition to satisfy requirements relating to properties or economics and in the case of elimination of chromium as a result of strategic material initiatives. Some of the chemical compositional and process changes are referenced below:

Improved Deoxidation – U.S. Steel, Monroeville, (1966-1970)
 Increase Manganese – Lukens, Armco, BHP, NKK
 Higher Niobium – INCO, INCRA
 Lower Niobium – NKK, BHP
 Higher Cooper – INCRA
 Higher Silicon – INCRA
 Titanium Treatment – NKK, BHP
 Controlled Rolling – NKK, BHP, Lukens
 Accelerated Cooling – NKK, Kobe, BHP
 Higher Ni & Mo – AMAX (U.S. Navy Contract)
 Elimination of Cr – U.S. Navy, BHP, NKK

Development of Higher Strength ASTM 707 Forgings

Prior to the development of ASTM 707 MOD in 1988/1989 thick wall forgings for the offshore industry were generally manufactured from low alloy steels, typically Ni-Cr-Mo-V or Cr-Mo types⁽³⁾. These steels had been developed in the power generation and pressure vessel industries and generally were not welded.

Such steels were used to produce threaded connectors for the Conoco Hutton and Joliet field developments. Typical chemical compositions and mechanical properties are shown in Table I⁽³⁾. The desire for a forging steel to match the weldability of tendon and riser pipe led to a gradual reduction of carbon content in these conventional low alloy (Cr-Mo) and HY80 (Ni-Cr-Mo-V) steels in Table I. As a result the steels were used for the first welded tethers in the Snorre TLP.

Table I. Typical Chemical Compositions and Mechanical Properties of Steels for Offshore Forgings⁽³⁾

Steel Type	CHEMICAL COMPOSITION (Wt%)														MECHANICAL PROPERTIES		
	C	Si	Mn	P	S	Cr	Mo	Ni	V	Cu	Nb	Al	CE	Pcm	Yield Strength MPa	UTS, MPa	Charpy V Notch FAToC
31/2% Ni-Cr-Mo-V	.27	.25	.40	.010	.010	1.6	.45	3.5	.12	-	-	-	1.0	0.48	850	950	-100
3% Ni-Cr-Mo (HY80)	.18	.25	.30	.010	.010	1.6	.45	3.0	-	-	-	.030	.85	0.36	600	730	-50
3% Ni-Cr-Mo Modified HY80	.10	.08	1.0	.005	.005	1.0	.45	2.8	-	-	-	.030	.75	0.28	500	620	-50
3% Ni-Mo	.07	.08	1.0	.005	.005	-	.45	2.8	-	-	-	.030	.52	0.20	450	600	-40
21/4% Cr-Mo	.12	.05	.40	.005	.005	2.25	1.0	-	-	-	-	-	.85	0.32	400	550	-70
MnNiCrMoCuNb A707 Modified	.04	.20	1.30	.010	.005	.70	.45	1.6	-	1.1	.045	.02	.70	0.21	600	700	-70
CMnNb	.12	.20	1.30	.010	.005	-	-	-	-	-	.045	.010	.40	0.20	320	450	-30

The strength potential (hardenability) of these low-carbon low alloy steels was not adequate to meet the new industry requirements (yield strength 75-85). Thus the initiative turned to precipitation hardening systems based on epsilon copper. The early users of ASTM 707 forgings applied the traditional low manganese variant shown in the Table II below.

Table II. Steel Composition, weight percent

<u>Heat No.</u>	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Cu</u>	<u>Nb</u>
A	.040	.51	.010	.008	.29	.89	.74	.20	1.19	.036
B	.040	.49	.010	.016	.18	.91	.74	.18	1.20	.020
C	.069	.54	.010	.016	.23	.87	.76	.19	1.06	.030
D	.046	.61	.012	.015	.25	.91	.77	.20	1.21	.100

Mechanical properties after quenching and tempering are presented in Table III below.

Table III. Mechanical Properties

<u>Heat No.</u>	<u>Section Thickness Inches</u>	<u>Water Quench, °F</u>	<u>Aging Temp, °F</u>	<u>Tensile Strength, ksi</u>	<u>Yield Strength, ksi</u>	<u>Charpy Energy, ft-lb</u>	<u>Temp., °F</u>
A	2.5	1600	1150	92.0	76.0	165	-20
B	8	1650	1150	75.0	62.0	210	-50
B	15	1650	1100	77.8	65.2	140	-20
C	10	1600	1150	81.5	69	85	-20
D	9	1700	1100	83.1	73.2	45	-20

The standard low-manganese formulation produces a yield strength of less than 65 ksi in thicknesses between 8 to 15 inches even though the toughness was very good at low temperatures.

Analysis of available data for forgings and plate revealed loss of toughness and inadequate yield strength as section thickness increased.

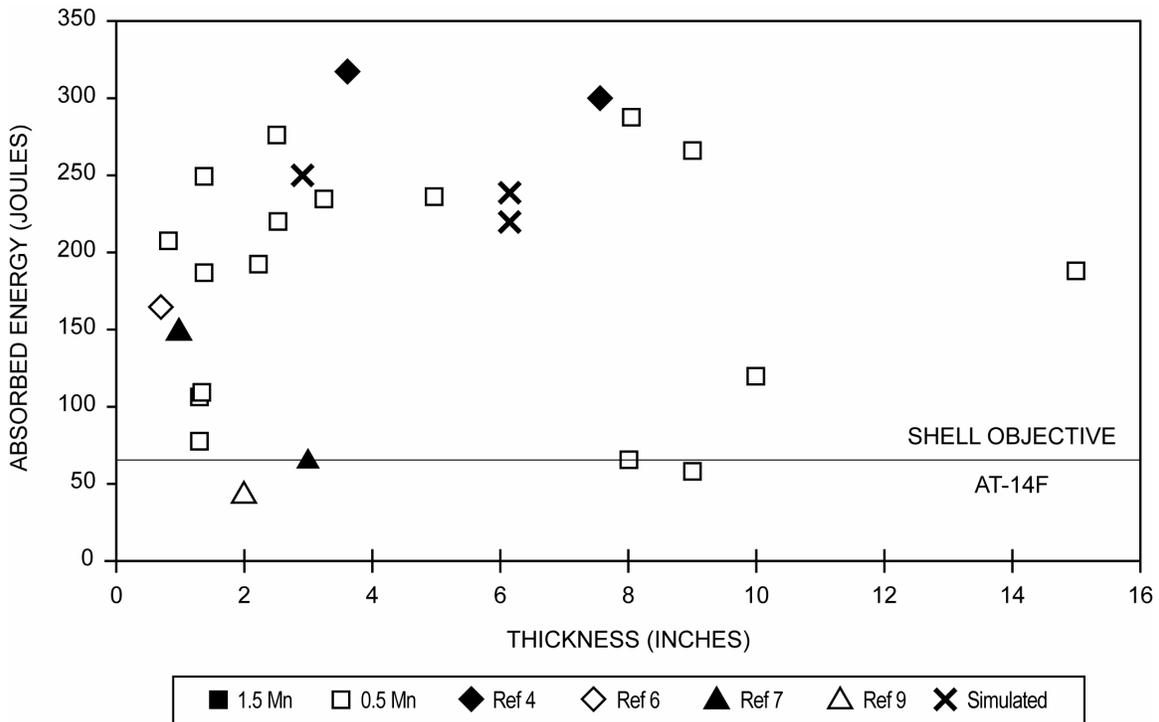


Figure 2. Effect of material thickness on the Charpy V-notch absorbed energy of Ni-Cu-Nb steels.⁽²⁾

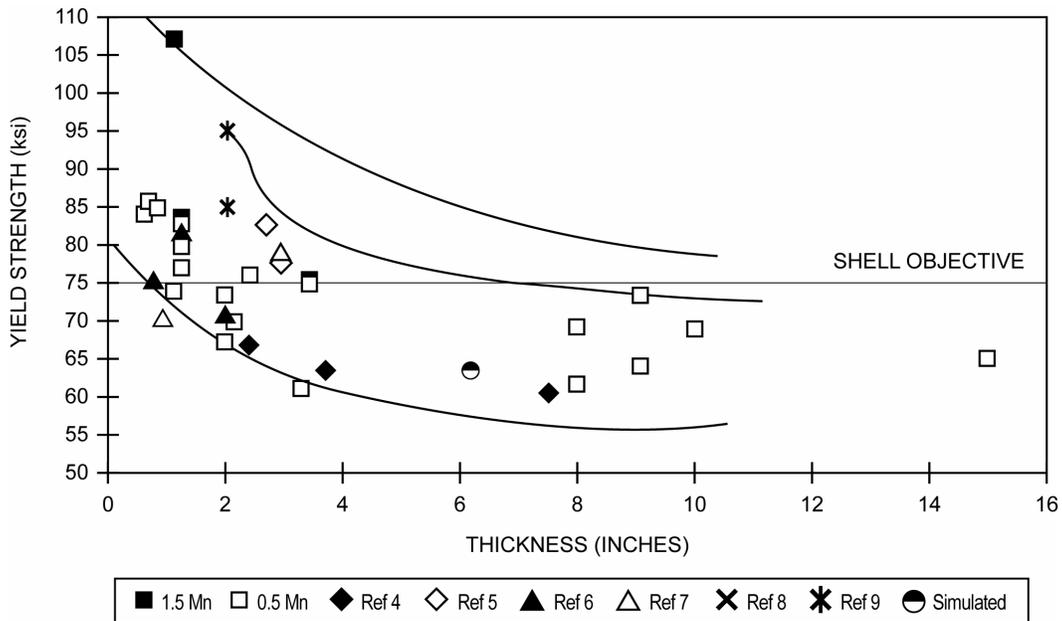


Figure 3. Effect of material thickness on the yield strength of Ni-Cu-Nb steels.⁽²⁾

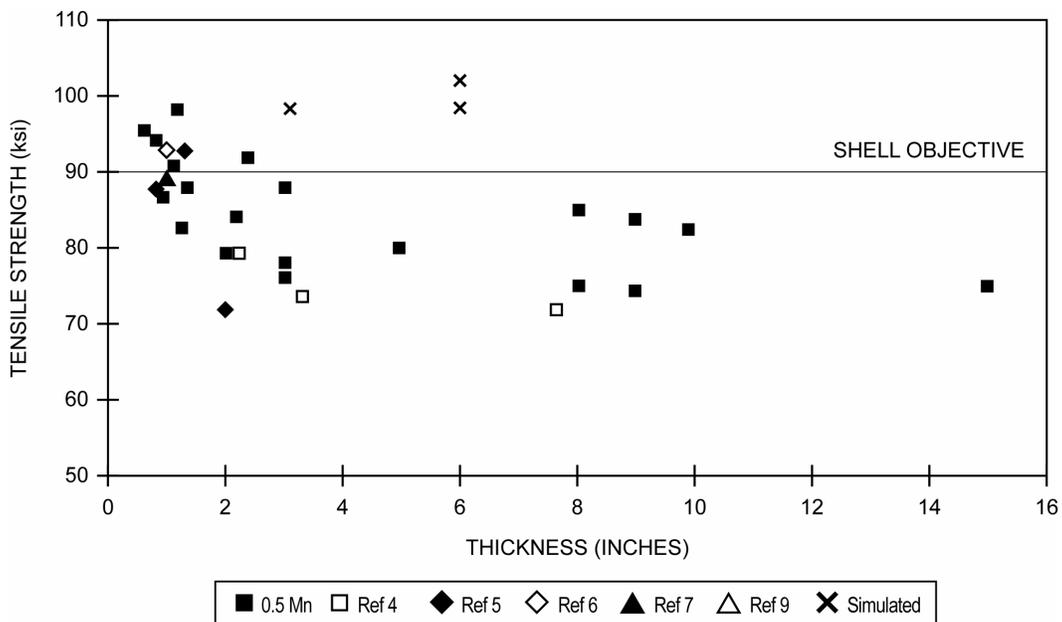


Figure 4. Effect of material thickness on the tensile strength of Ni-Cu-Nb steels.⁽²⁾

In order to increase yield strength a variety of metallurgical approaches was adopted which are summarized below.

- (a) The original Ni-Cu-Nb steel was developed around a reliance on nickel, both to increase hardenability and to offset the effect of copper on hot shortness. An increase in manganese to more normal levels was adopted, following the lead of Armco^{4,6)}, Lukens⁹⁾, NKK⁷⁾, and BHP⁸⁾. The beneficial effect is illustrated in Figure 5.

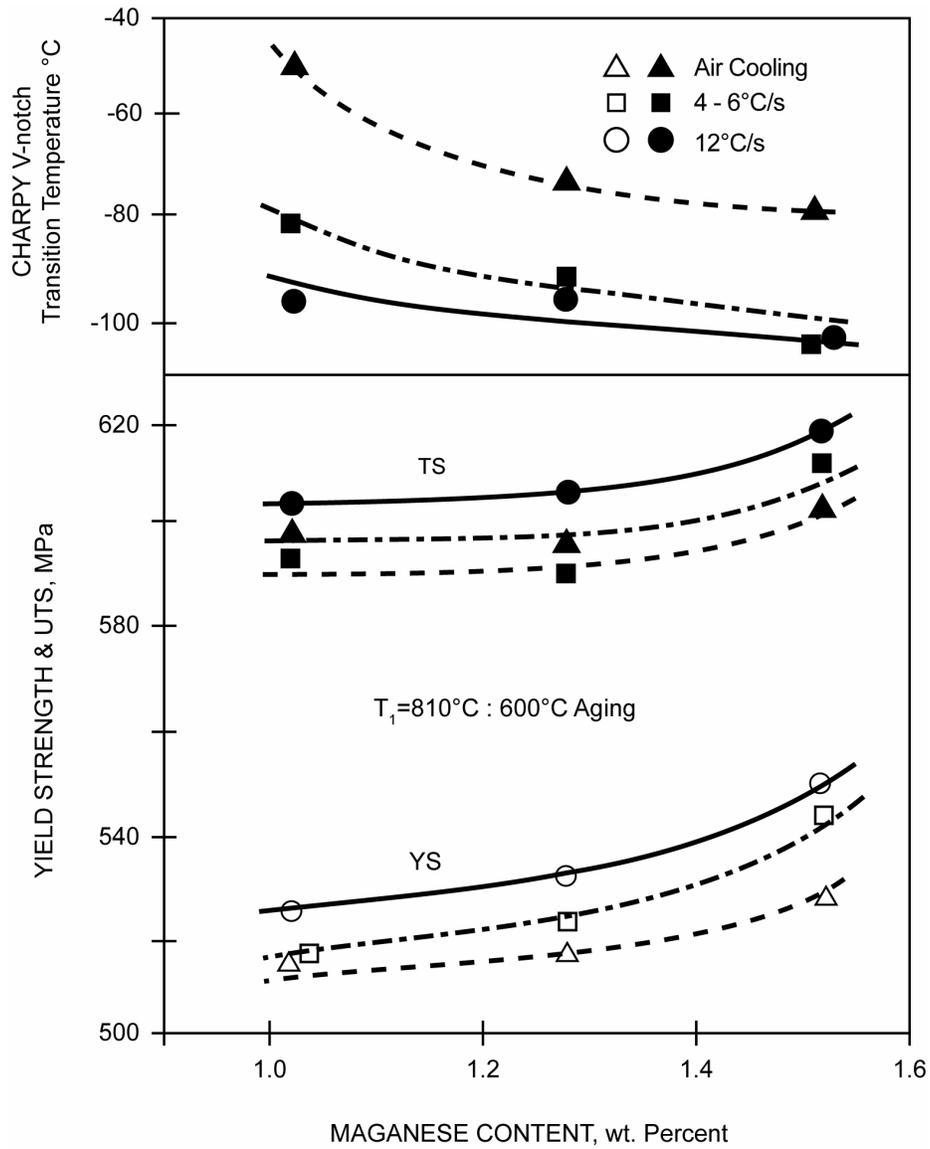


Figure 5. Effect of Manganese on the properties of Ni-Cu-Nb hot-rolled steels.⁽⁷⁾

- (b) A slightly higher carbon content was introduced based on the plate data of Hamburg et al⁹⁾ Figure 6.

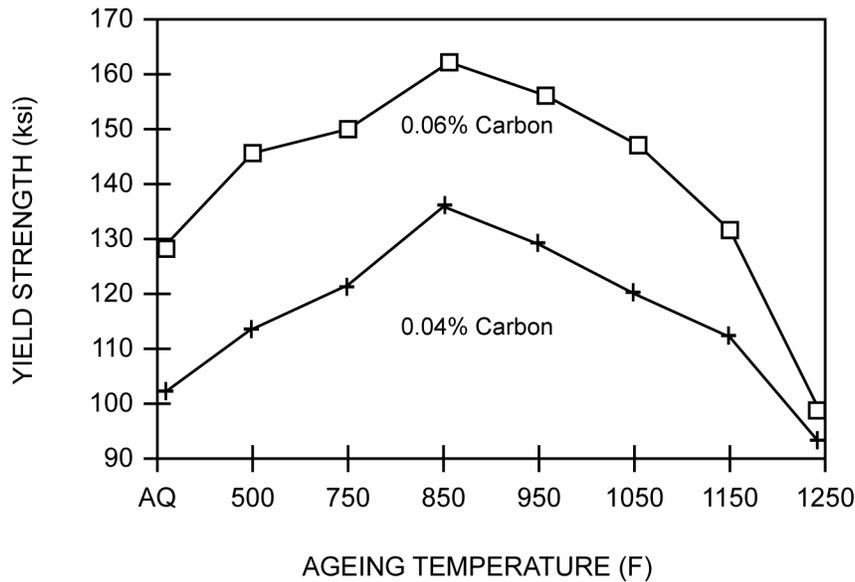


Figure 6. Yield strength of 0.04%C compared to 0.06% HSLA-100 as a function of the aging temperature.⁽¹⁰⁾

(c) Niobium

This element was studied extensively by the International Nickel Co. and by Armco Steel who evaluated contents up to 0.10 percent, mainly in hot rolled steels. A higher niobium content was adopted for the modified ASTM 707 L5 alloy for several reasons.

- (i) To lower austenite to ferrite transformation temperature when taken into solution at high quenching temperatures this mechanism was facilitated by the use of low carbon and low free nitrogen contents).
- (ii) To combine with molybdenum and to produce intense secondary hardening in the presence of molybdenum due to the formation of $(\text{Nb Mo})_4\text{C}^{(3, 12, 13)}$. This strengthening mechanism has been used extensively by Nippon Steel in its HT 80 (80 kg/mm² UTS) Q & T steel but elsewhere it remains obscure and virtually unknown to this date. The Mo-Nb-C phase diagram is presented below. Figure 7. Kanazawa et al^(12, 13) showed that when steels were quenched from low austenitizing temperatures (900-925°) well below the dissolution temperature for niobium carbonitrides, there was a remarkable secondary hardening effect when molybdenum was also present. The precipitating phase appeared to be $\delta(\text{Nb Mo})\text{CN}$ having a NaCl type crystal structure believed to results from partial replacement of niobium and carbon by molybdenum and nitrogen respectively in $\delta\text{-NbC}$. This phase was later found by the author in hot rolled steels⁽¹⁵⁾.

(d) Increased Nickel

This was adopted to improve hardenability and to access the traditional benefit to toughness.

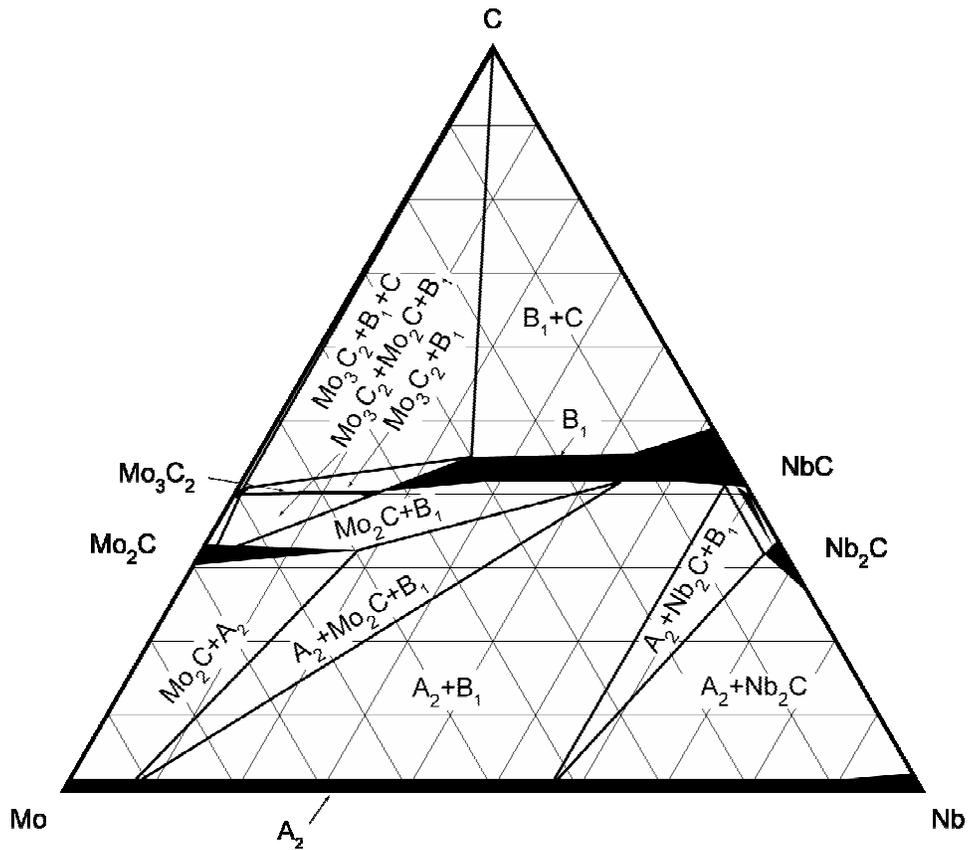


Figure 7. Phase diagram of Nb-Mo-C alloy at 1900°C (by Rudy.⁽¹⁴⁾)

- (e) Consideration was given to further increasing copper content to increase the volume fraction of E copper precipitation. However apart from the hardening by precipitation, copper additions also seriously increase hardenability, Figure 8, and can result in unacceptable HAZ hardnesses unless proper welding and PWHT procedures are used. For this reason it was decided to maintain the copper content at the traditional level around 1.10 percent

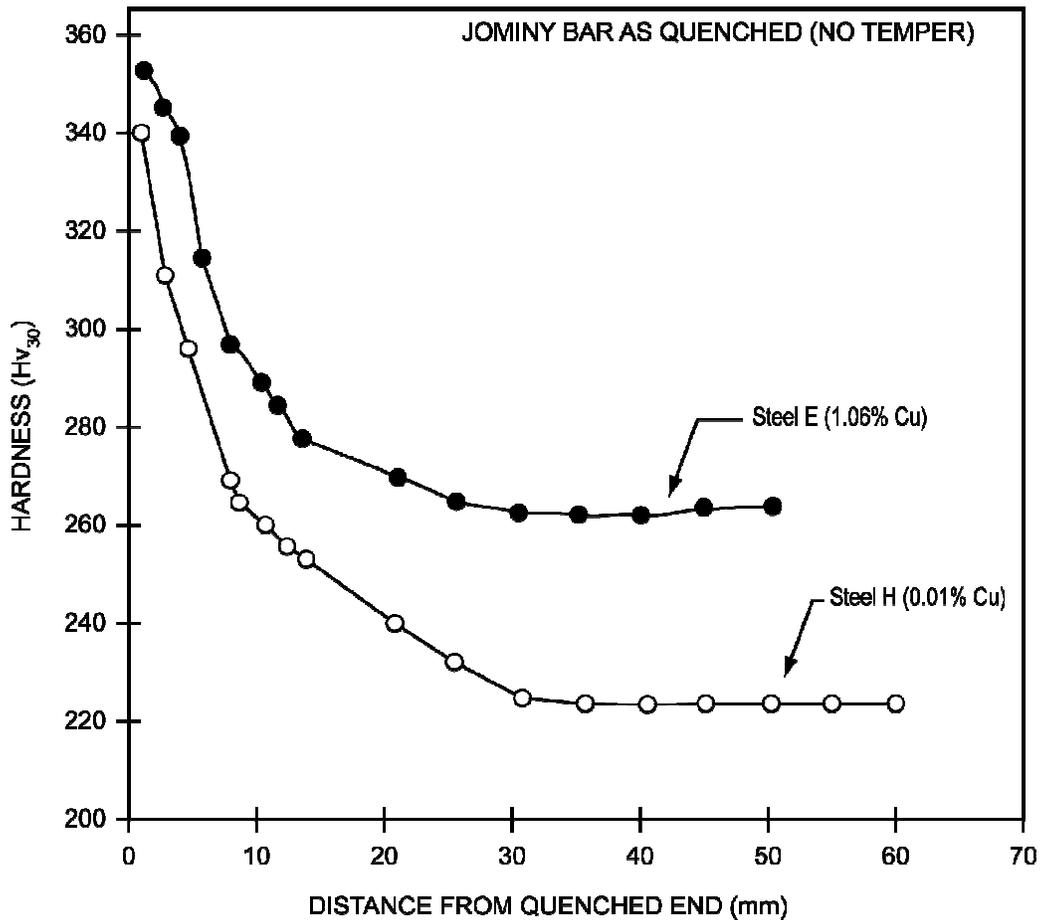


Figure 8. Effect of Copper on As Quenched Hardness

The first experimental steels using these strengthening concepts had chemical compositions shown in Table IV below.

Table IV

	C	Mn	Si	Ni	Cu	S(1)	P(1)	Nb	Mo	N	Cr	Al	Ti
A	0,05	1.55	0.40	0.95	1.10	0.005	0.008	0.07	0.30	LAP	0.80	0.03	0.01-0.015
B	0.075	1,55	0.40	0.95	1.10	0.005	0.008	0.07	0.30	LAP	0.80	0.03	0.01-0.015
C	0.05	0.50	0.40	1.70	1.10	0.005	0.008	0.07	0.30	LAP	0.80	0.03	0.01-0.015

(1) maximum

LAP = Least Amount Possible

The results of the early trials have been published by Smith et al¹⁶⁾ and led to the adoption of a very low carbon, 1.7 percent nickel 1.5 manganese Nb-Mo alloy design by the offshore industry.

Typical mechanical properties of early production forgings utilized by Shell Oil³⁾ are presented below.

Table V. Mechanical Properties

	0.2 YS MPa	UTS MPa	A %	Z %	CVN @ -10°C (J)	FATT °C
Specification	520	620	20	40	INF	INF
Component	Min	Min	Min	Min		
Riser Tensioner Joint	656	704	26	74	184,194,203	-77
Tendon Extension	552	642	27	79	215,216,198	-35
Riser Connector	600	642	27	67	221,221,221	-50

Since the early beginnings the ASTM A707 alloy has been modified several times to meet key objectives such as achievement of even higher strength or greater section thickness, lower Charpy FATT transition temperatures or enhanced resistance to H₂S. A summary of actual chemical compositions used to date is presented in Table VI.

Table VI

Summary of Chemical Compositions for Ni - Cu - Nb (ASTM 707-Type) Steels

Designation (Ref.)	In Figures	C	Mn	P	S	Si	Cr	Ni	Mo	V	Cu	Nb	Ti	Al	N	B	CE	Pcm	Comments
ASTM 707 L5 ⁽¹⁾	A	0.07	0.70	0.025	0.025	0.35	0.90	1.00	0.25	0.05	1.30	0.03 ⁺	-	-	-	-	-	0.27	Heat Analysis, max.
ASTM 707 L6 ⁽¹⁾	B	0.07	2.20	0.025	0.025	0.15	0.30	0.40	0.35	0.05	0.40	0.10	-	-	-	-	-	0.26	Heat Analysis, max.
707 MOD-Gray ⁽²⁾	C	0.05	1.55	0.008	0.005	0.40	0.80	0.95	0.30	-	1.10	0.07	0.011	0.03	0.005	0.0002		0.27	Aim Composition
707 MOD-Gray Shell ⁽³⁾	D	0.05	1.55	0.008	0.005	0.40	0.80	1.70	0.30	-	1.10	0.07	0.011	0.03	0.005	0.0002		0.29	Aim Composition
707 MOD (*Forgemasters)	E	0.05	1.56	0.010	0.005	0.29	0.71	0.96	0.45	-	1.06	0.043	-	0.03	?	-	0.68	0.26	Actual Composition
707 MOD-Gray (**SSC)	F	0.05	1.30	0.010	0.006	0.38	0.10	1.00	0.40	0.01	1.20	0.05	0.02	0.05	0.009	-		0.24	Aim Composition
Saga Petroleum	G	0.04	1.17	0.005	0.002	0.23	0.02	0.96	0.35	0.005	1.15	0.04	0.014	0.026	0.006	-		0.21	Actual Composition
Forgemasters (No Cu)	H	0.045	1.55	0.010	0.005	0.29	0.70	0.96	0.45	-	0.01	0.047	-	0.03	?	-	0.49	0.22	Actual Composition
Ni Cu Age	J	0.05	0.47	-	-	-	-	0.87	0.20	-	1.02	0.01	-	?	?	?		0.16	Actual Composition

+ Minimum

* Forgemasters (Sheffield)

** Saga Petroleum

Steels C and D (ASTM A707 MOD) in Table VI above have the maximum strengthening potential and are suitable for very heavy section forgings.

Steels F and G have lower manganese and niobium contents and have been shown to resist sulfide stress cracking in severe H₂S environments. The strength-hardness balance for Steel D is shown in Figure 9.

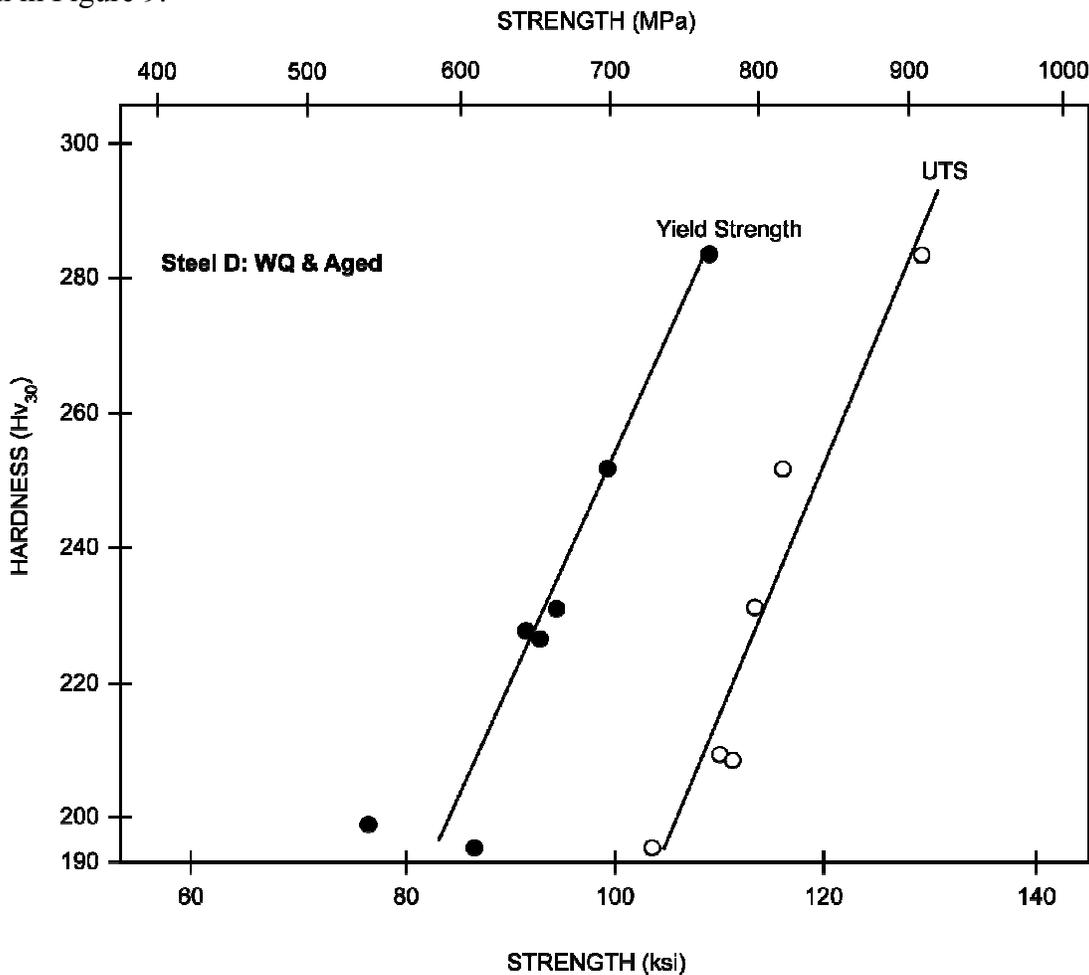


Figure 9. Strength – Hardness Correlation for ASTM A707 MOD Steel.

The base metal hardnesses, (<240H_{v30}) even when considering yield strengths in excess of 80 ksi are compatible with moderate H₂S environments. However, after welding with heat inputs in the range 1.37 to 1.7 kJ/mm the HAZ hardness increases to >280H_{v10} Figures 10 and 11 which is not reflective of satisfactory H₂S resistance.

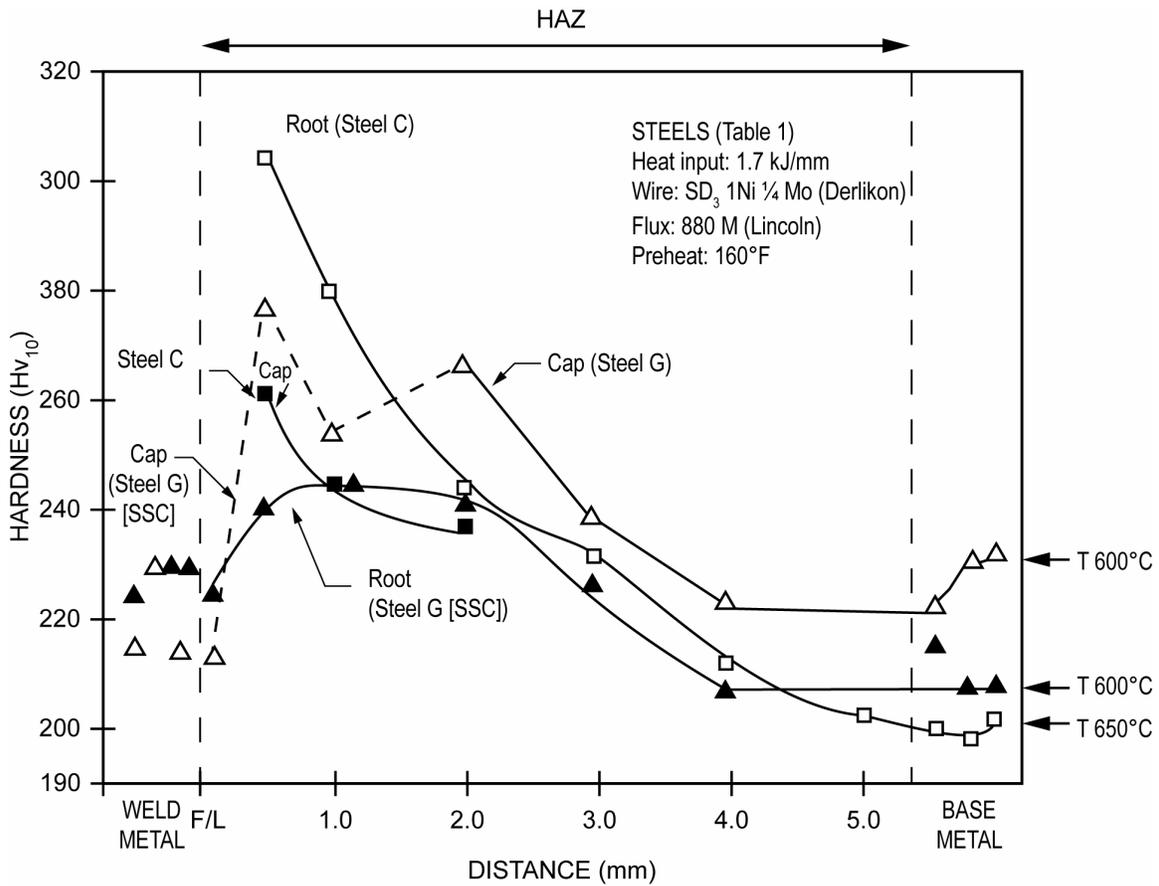


Figure 10. Hardness Results for ASTM A707 MOD and ASTM 707 SSC Steels.

In contrast the ASTM A707 SSC variant of the alloy (Steel G), redeveloped by EWI/Microalloying International, and applied for the riser flex joint of the Saga Petroleum Snorre TLP, has hardnesses generally <260H_{v10}, Figures 10 and 11, combined with excellent Charpy V-notch toughness, Figure 12.

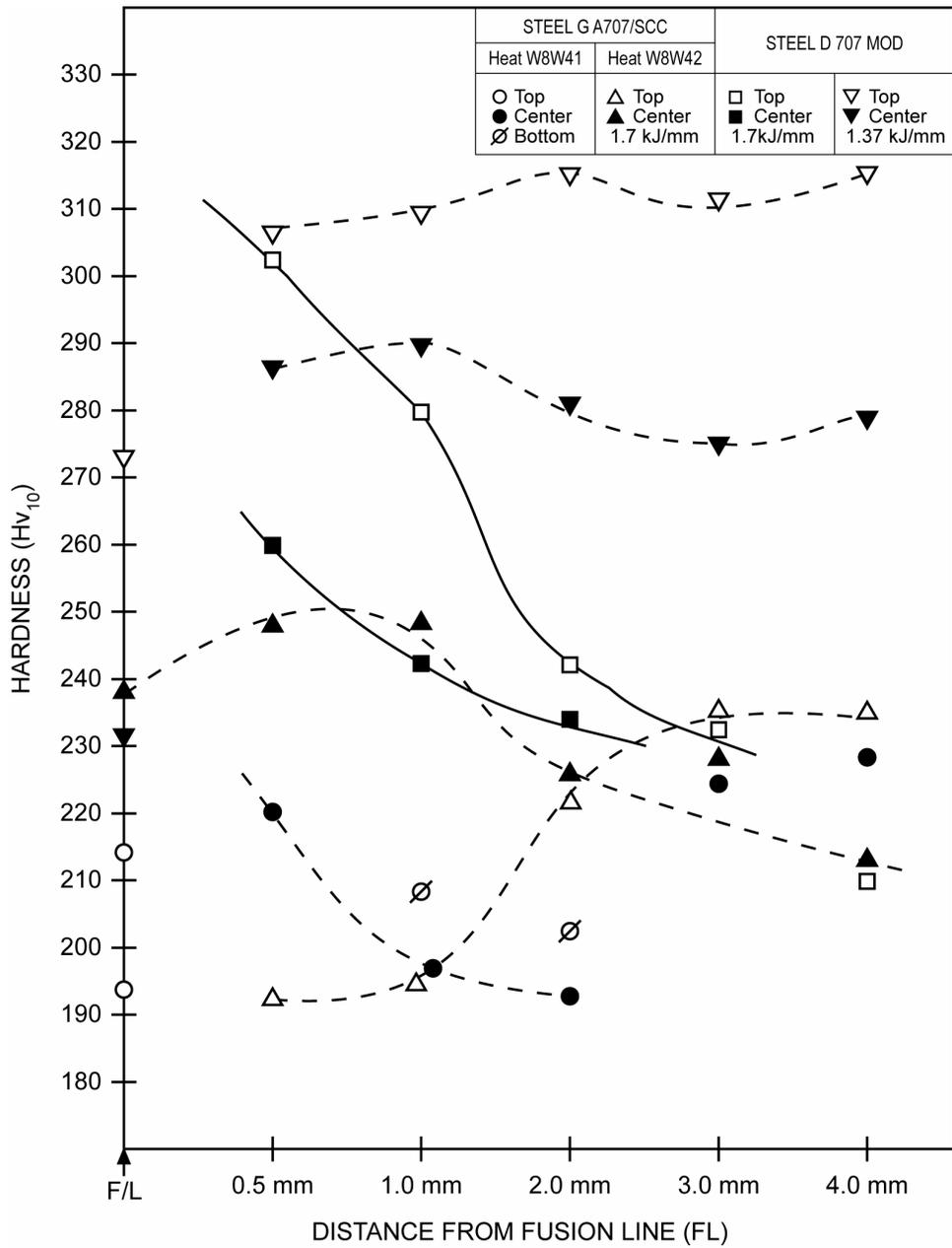


Figure 11. HAZ Hardness Results for ASTM A707 MOD and ASTM A707 SSC Steels.

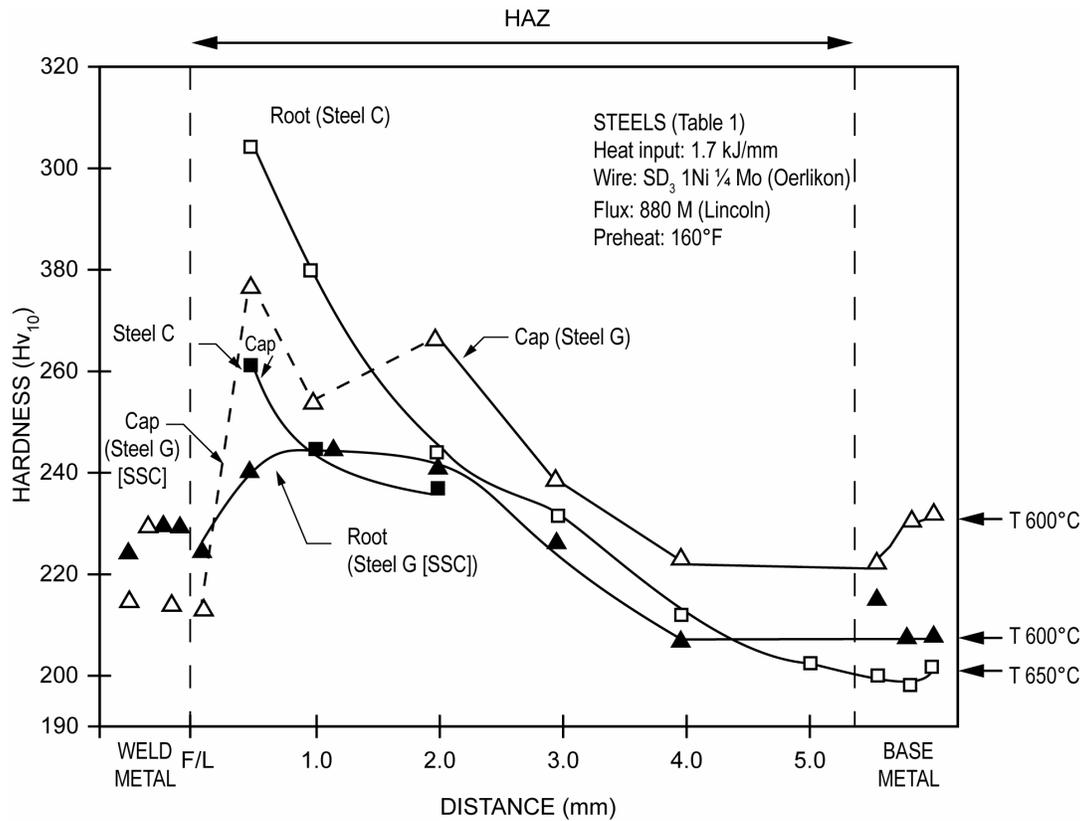


Figure 12. Charpy Properties for Weld Cross Section ASTM A707 SSC

In contrast to the original Ni-Cu-Nb steel which shows a peak hardness (strength) and a toughness trough at tempering (ageing) temperatures of 450-475°C Figures 13 and 14, the Nb-Mo modified ASTM A707 alloy shows a strong secondary hardening response at 600-640°C Figure 15

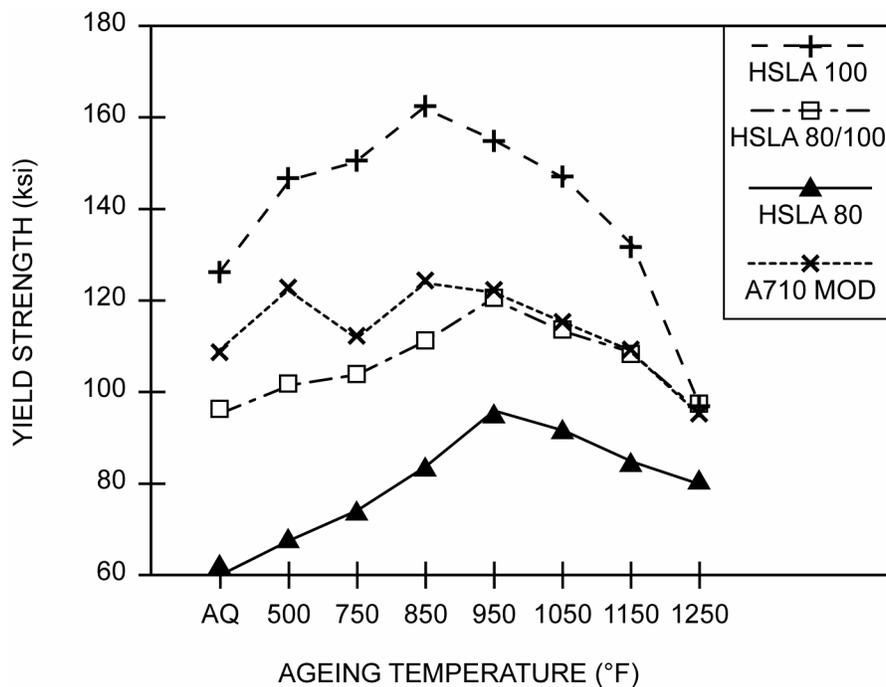


Figure 13. Yield strength of HSLA steels as a function of the ageing temperature.⁽²⁾

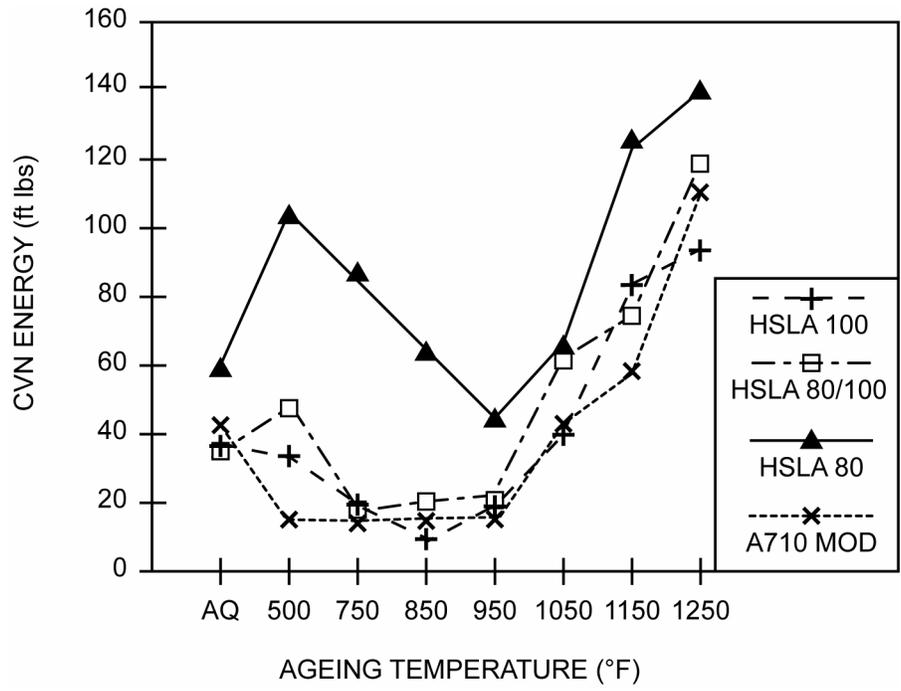


Figure 14. Charpy V-notch energy at -120°F of HSLA steels as a function of aging temperature.⁽⁹⁾

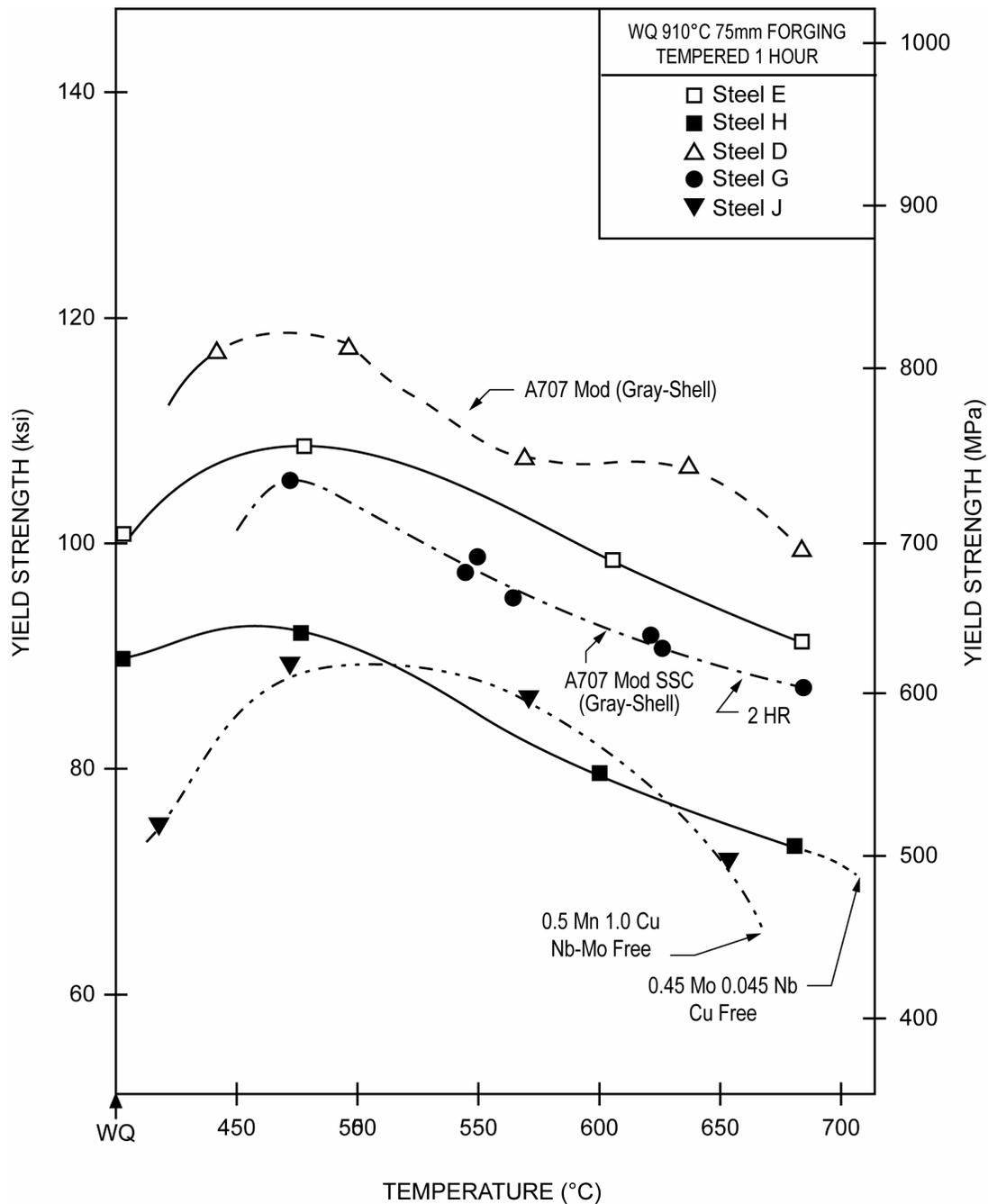


Figure 15. Ageing Behavior of ASTM A707 Forgings.

The tempering (ageing) responses of the standard ASTM A707 MOD and ASTM A707 SSC alloys are presented in Figure 16. The more highly alloyed “Shell” alloy is seen to be very resistant to softening either during ageing or PWHT. Thus if HAZ hardnesses <260H_v10 are specified, the welds must be post weld heat treated at temperatures in excess of 675-685°C (1247 to 1265°F). In contrast the ASTM A707 SSC alloy has reduced hardening potential and can be softened by ageing (PWHT) at 625° (1157°F) if necessary to meet classical hardness requirements (<Rc22) for sour service applications.

Weldability and Sour Service Properties of ASTM A707 Steels

The HAZ microstructure of ASTM A707 for heat inputs between 1.5 and 5 kJ/mm consists of acicular ferrite and bainite rather than martensite. The behavior is representative of a carbon steel rather than the low alloy steels shown in Table I according to the classification of Graville⁽¹⁷⁾ Figure 16

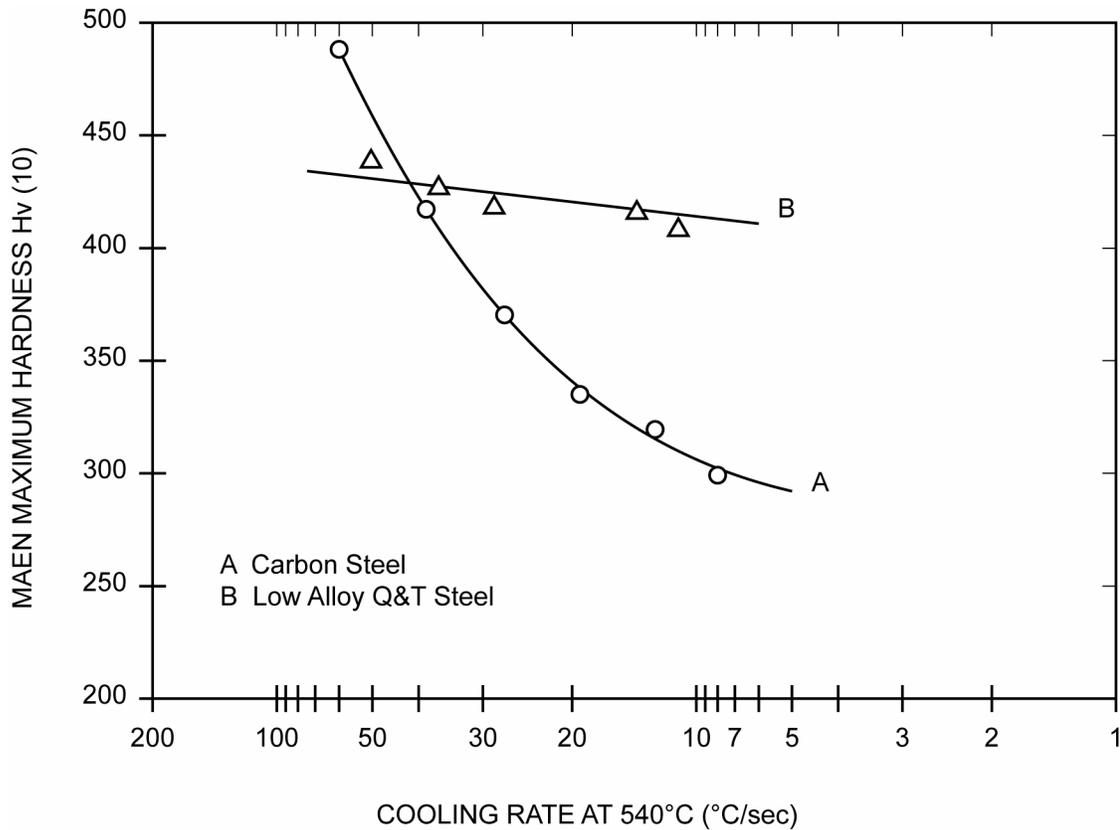


Figure 16. Typical hardening curves for two types of steel.⁽¹⁵⁾

Since martensite is not present after welding the HAZ does not soften during PWHT and in fact will usually harden due to precipitation of copper and niobium- molybdenum carbides. For standard ASTM A707 MOD, low HAZ hardnesses can only be obtained by overaging the alloy as shown in Figure 14.

The ASTM A707 family of alloys is generally tolerant of low preheat or no preheat welding procedures due to the very low carbon contents, which places the steels well into Zone I of Graville's cracking diagram, Figure 17⁽¹⁷⁾. In contrast earlier steels used for offshore forgings (Table I) are barely weldable unless modified to lower carbon contents.

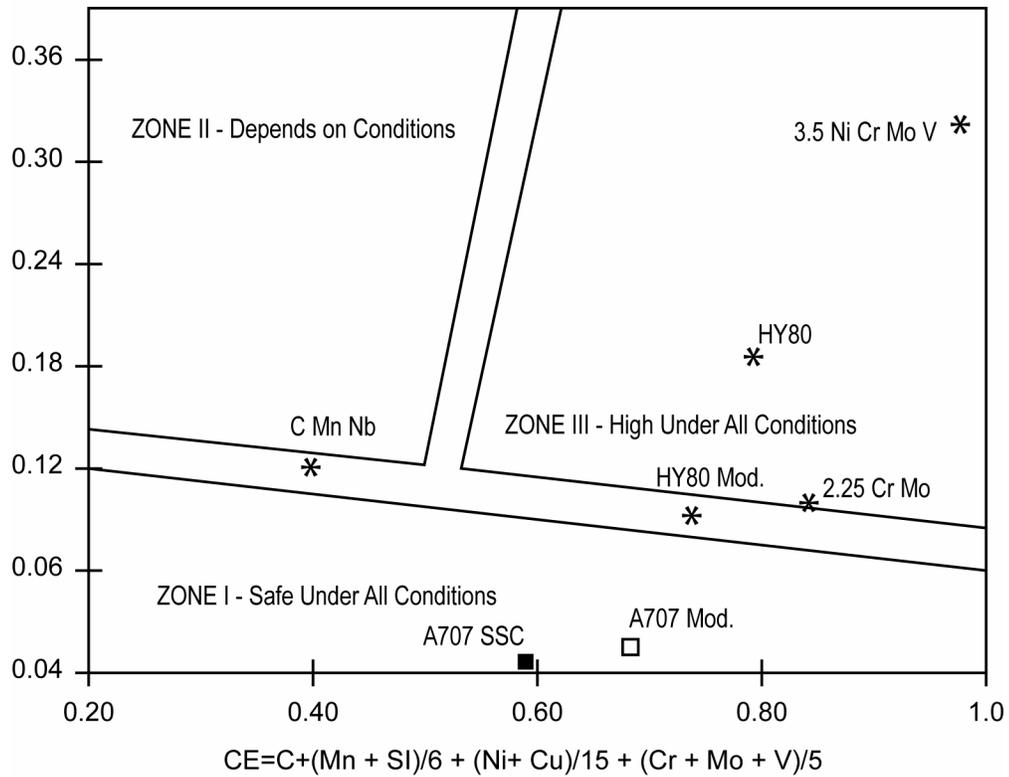


Figure 17. Weldability of steel as a function of Carbon content and Carbon Equivalent, after Graville.⁽¹⁷⁾

The performance of the ASTM A707 SSC steel (Steel G) in NACE SSC tests (Method A) is shown in Table VII. The alloy withstands the 720 hr test at stress levels approaching 80% SMYS. This behavior is distinctly superior to the standard ASTM A707 MOD variant (Steel D) and much better than traditional low alloy steels, Figure 18.

Table VII

CLI ID No.	Microalloying Identification No.	SMYS (ksi)	% SMYS	Stress Applied (ksi)	Initial pH	Final pH	Failure Time (hrs)
3033-1	6W	65.3	60	39.0	2.6	3.5	NO FAIL
3003-2	6W	65.3	60	39.0	2.6	3.5	NO FAIL
3003-3	6W	65.3	60	39.0	2.6	3.5	NO FAIL
3003-4	6W	65.3	80	52.0	2.8	3.7	165.7
3004-1	8W	65.3	80	52.0	2.6	3.8	293.0
3004-2	8W	65.3	80	52.0	2.6	3.5	NO FAIL
3004-3	8W	65.3	80	52.0	2.6	3.8	144.7
3004-4	8W	65.3	80	52.0	2.8	3.5	NO FAIL
3005-1	6 BM	72.6	60	43.5	2.6	3.4	NO FAIL
3005-2	6 BM	72.6	60	43.5	2.6	3.4	NO FAIL
3005-3	6 BM	72.6	60	43.5	2.6	3.5	NO FAIL
3005-4	6 BM	65.3	80	52.0	2.8	3.7	314.0
3006-1	8 BM	72.6	80	58.0	2.6	3.8	147.8
3006-2	8 BM	72.6	80	58.0	2.6	3.4	NO FAIL
3006-3	8 BM	72.6	80	58.0	2.6	4.0	NO FAIL
3006-4	8 BM	65.3	80	52.0	2.8	3.5	NO FAIL

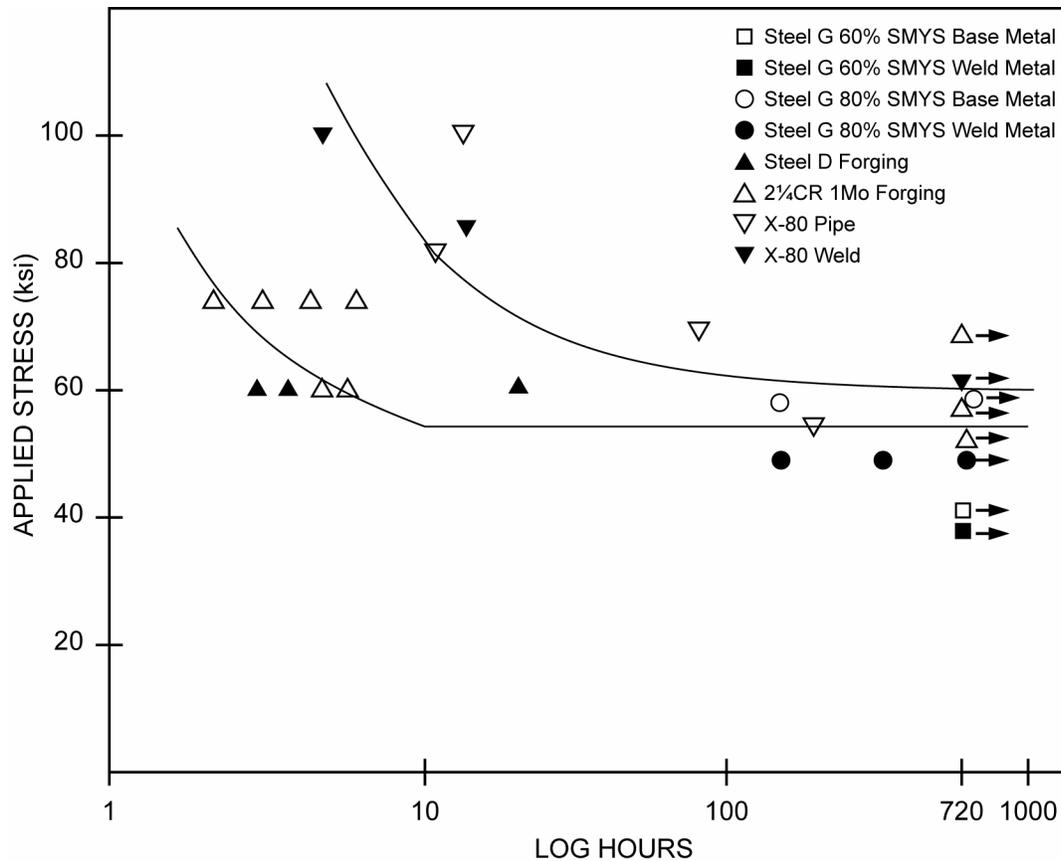


Figure 18. Sulfide Stress Cracking Results for Various Steel Types.

The behavior of the ASTM A707 SSC alloy in H₂S environments is consistent with research conducted by Microalloying International and Korrosionscentralen ATV in the early 1990's, Figure 19⁽¹⁸⁾. The research showed that HAZ hardesses as high as 275H_v5 did not lead to SSC cracking at a stress of 72 percent SMYS even when hydrogen charging rates of two times that associated with NACE Solution A were applied.

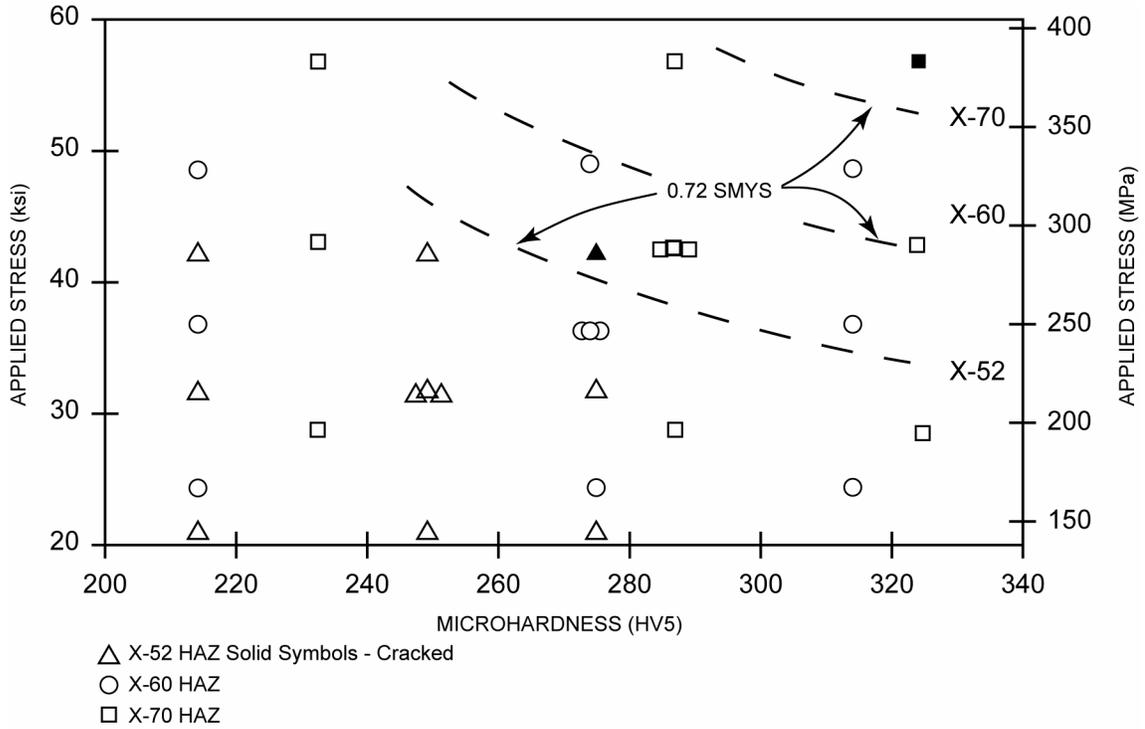


Figure 19. SSC Behavior as a Function of Applied Stress Versus Microhardness-HAZ.⁽¹⁸⁾

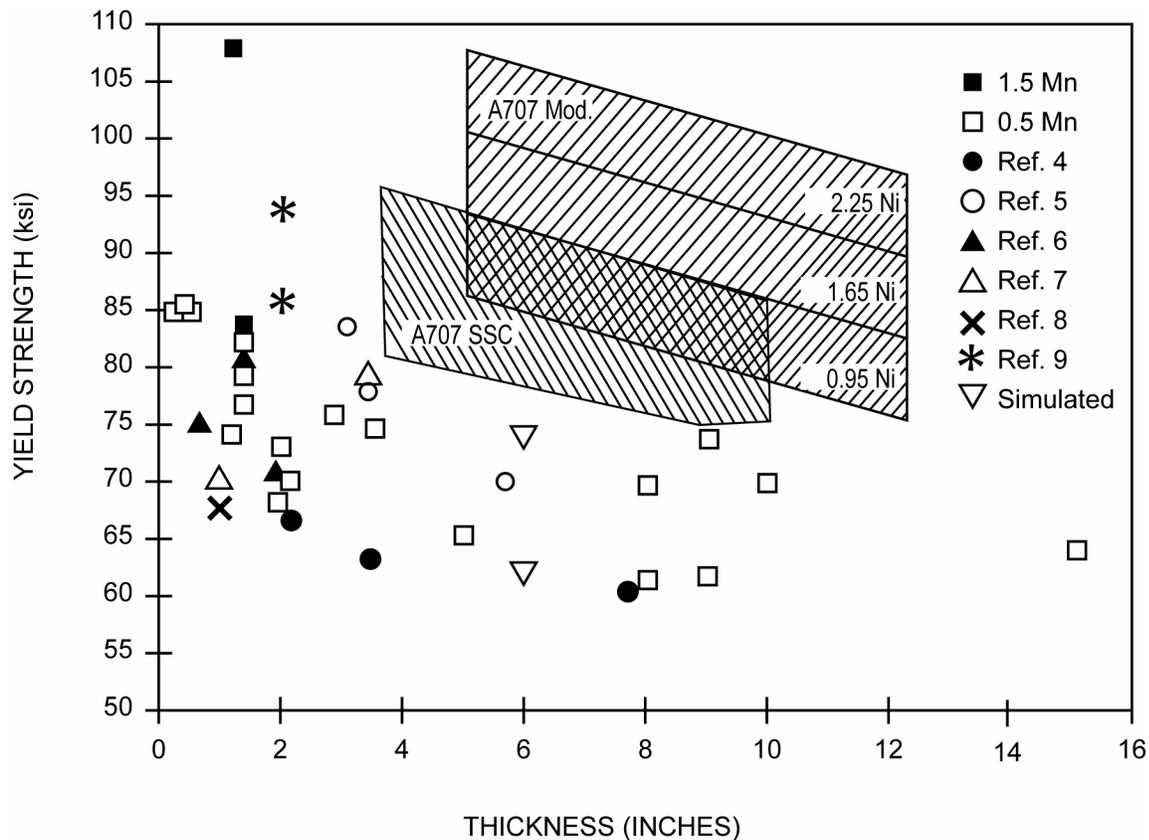


Figure 20. Effect of Material Thickness of Yield Strength of old and new ASTM A707 alloys.

Summary and Conclusions

The mechanical properties (yield strength) of the recently developed high strength forging steels, ASTM 707 MOD, for both sweet and sour service are presented in Figure 20 along with the data presented earlier in Figure 3 for literature data circa 1960-1990. The modified alloys have vastly superior section capability, higher strengths while maintaining the excellent toughness and weldability (with minimum preheat) that characterized the original steel.

The alloys have largely replaced higher carbon conventional Q & T steels and have become the workhorse for forgings for critical service in the oil and gas sector.

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