Evaluation of HASTELLOY® alloy G-30 and ULTIMET™ alloy for Wet Process Phosphoric Acid Services

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Abstract

Advances in materials engineering have led to the development of HASTELLOY alloy G-30 and more recently to ULTIMET alloy for severe corrosion and corrosion/erosion services in wet process phosphoric acid (WPA) production. A complicating factor involved in WPA production is that equipment corrosion attack may differ significantly depending on the operations of the process and the feedstock rock used. Therefore, it is imperative that corrosion data on potential alloys for process equipment be collected in the field or in the laboratory in producer's actual process acids.

The factors affecting corrosion/erosion such as concentration, temperature, impurity levels, velocity and solid particles are discussed. Laboratory corrosion data in producer's acid are presented specifically on HASTELLOY alloy G-30, a nominally 43Ni- 30Cr- 15Fe- 5Mo- 2W alloy, which has been used successfully for several years in WPA production. Also discussed is quality cold drawn and annealed welded tubing for superior corrosion protection in the weld zone for WPA production heat exchanger tubing.

The development of ULTIMET alloy, a nominally 53Co- 26Cr- 9Ni- 3Fe- 5Mo- 2W alloy, for better resistance to both corrosion and wear is also discussed. Laboratory test results collected to date in WPA will be presented.

Introduction

Wet process phosphoric acid (WPA) manufacturing consists of a series of operations with severe corrosion and corrosion/erosion problems. An important aspect of corrosion in phosphoric acid is the difference in behavior between reagent grade acid and wet-process acid produced from the digestion of phosphate rock. Boiling tests in reagent grade acid reflect non-oxidizing conditions at all concentrations, and it has been shown that alloys containing high molybdenum and no chromium perform best.[1] The wet process acids, on the other hand, have exhibited variable oxidizing behavior and therefore high chromium containing alloys such as HASTELLOY alloy G-30 consistently show the lowest corrosion rates.[2]

It is well known that wet process phosphoric acid contains a number of impurities such as sulfuric and hydrofluoric acids, chlorides, silicon, aluminum, iron, magnesium, calcium and sodium compounds. It is these impurities which dramatically affect the active/passive behavior of alloys in WPA production. Table 1 shows the variability of contaminants in wet process acids in the concentration range of 52-56 percent as supplied by several production facilities or source of acid. As a result of this variability it is essential to test alloys for potential use in these production facilities in producers actual process acids and to treat each facility on a case-by-case basis.

Traditionally, non-metallic materials, i.e., impervious graphite, have been used for process equipment such as evaporators or heat exchangers for WPA production due to the severe corrosivity of these process streams. However, issues such as breakage/reliability, maintenance (unscheduled downtime, replacement time, boil-out frequency and time) and hence ultimately production throughput have made alloyed-materials the most cost effective route in these facilities. Table 2 lists the nominal chemical compositions of several alloys for which data is presented. The factors affecting corrosion and corrosion/erosion such as concentration, temperature, impurity levels, and velocity are discussed. Laboratory corrosion data in producers' acids are presented specifically on HASTELLOY alloy G-30, now used for 5 years in the industry, and ULTIMET alloy, a newly-developed alloy for resisting both corrosion and wear phenomena.

HASTELLOY alloy G-30

Even though many variables play a role in the corrosiveness of wet-process phosphoric acids, years of experience with metallic materials have helped to establish trends which identify the beneficial effects of certain alloying elements. When compared to lower alloys such as 300 series stainless, duplex stainless, "20-type" alloys, and other nickel-base alloys, the high chromium-containing HASTELLOY alloy G-30 consistently shows the lowest corrosion rate in wet process acids. As shown in Table 3, not only does G-30 alloy exhibit the lowest corrosion rate but that the corrosion rate decreases significantly over time. This is true particularly of high chromium-containing alloys as the passive film appears to become more impervious to corrosive attack due to the oxidizing nature of the process acid. In fact, it has been commented by one WPA production facility that the corrosion rate of HASTELLOY alloy G-30 heat exchanger tubes in the field have experienced as much as seven times lower corrosion rates than that reported from testing performed in the same acid for a 96-hour test period under laboratory autoclave conditions (standard test conditions).

Numerous laboratory results in a variety of producers' acids have been conducted in the past and previously reported showing the superiority of HASTELLOY alloy G-30.[3, 4] Since the severity of corrosive conditions change within each facility and from facility-to-facility, it is prudent to compare the highest corrosion rate observed on several alloys tested as shown in Table 4. HASTELLOY alloy G-30 offers the best corrosion resistance even under the worst conditions. Similarly, test data generated from several different plants continues to show consistently the superior corrosion protection offered by G-30 alloy (Table 5).

Due to the levels of chloride and fluoride compounds in most WPA process streams, the selection of an alloy which can resist pitting corrosion is a necessity, particularly for weld metal and heat-affected zone corrosion resistance. Table 6 lists the critical pitting temperature for a number of alloys in a high-chloride (24,300 ppm), oxidizing environment for unwelded specimens. Again, HASTELLOY alloy G-30 displays superior resistance to localized corrosion phenomenon. It should be noted that for the NiCrMo alloy systems, the critical pitting temperature of the welds in the as-welded condition has been documented to be 15-20° C lower than that of the wrought material.[5] In fact, this is true of lower alloys as well and laboratory tests indicate that even with duplex stainless steels, the critical pitting temperature of the weld zone in the as-welded condition is lowered by 20° C (as tested in 10% $FeCl_3$). Certainly, it has been experienced in the process industries for years that the weld metal typically is the first to corrode in most applications.

Welded tubing in the wet process phosphoric acid industry is normally procured to ASTM B626 Class II or Class III for heat exchanger applications. Most welded high-molybdenum nickel-base alloy welded tubing, such as HASTELLOY alloy G-30, is procured to Class III. The Class III designation covers cold-worked and solution-annealed product; however, the method of cold working the seam weld prior to annealing is left up to the procuring personnel. Therefore, the tubing can be procured as either "bead worked" (rolling only the seam weld to introduce cold work of the weld) or as cold reduced/cold pilgered (the tube is welded-up oversized and then drawn down to size uniformly at the seam weld and tube wall). The significant difference metallurgically between the products can be substantial with regard to full recrystallization and homogenization of the weld. [6]

Since the high performance NiCrMo alloy systems show greater resistance to deformation than lower alloyed materials, minimum cold deformation of the weld zone will not always offer the ideal microstructure in the weld zone upon final annealing. This typically results in compromised corrosion resistance in the weld and heat-affected zones of the welded tubing. It has been shown that welded tubing of HASTELLOY alloy C-276 with 3% cold reduction exhibits a 20% higher corrosion rate in the weld zone than tubing which received 30% cold reduction as tested in boiling H_2SO_4 (276 mils per year versus 222 mils per year, respectively).[7] Scanning electron microscopy showed that the mode of attack in the weld zone of the 3% cold-reduced tube was uniform corrosion attack of the unrecrystalized dendritic areas while the mode of corrosive attack on the 30% cold-reduced tube was less severe and was limited to the grain boundaries of the larger recrystallized grains.

Velocity Effects

The industry standard velocity of the process stream, about 7 feet/second, may decrease as carbate tubing begins to foul, until boil-out is performed. Preliminary laboratory testing using a rotating cylinder electrode geometry shows that the corrosion rate of HASTELLOY alloy G-30 does not increase when peripheral velocity is increased from 1.5 feet/second up to 6.2 feet/second (Table 7). This would suggest that velocity, at least up to about 6 feet/second, shoud not contribute to excess corrosion on G-30 alloy tubes. It has been noted by at least one commercial wet process phosphoric acid production facility that the period of time between boil-out is approximately 4 times longer with G-30 alloy heat exchanger tubes than that experienced with graphite.

ULTIMET alloy

There are many instances, especially upstream in the process flow, where the need for corrosion and wear resistance is required. This is particularly true for components such as agitators, valves and pump parts. ULTIMET alloy, a newly developed cobalt-based alloy, has recently shown promise for applications in WPA manufacturing.

Preliminary corrosion data in several producers' acids as compared to HASTELLOY alloys G-30 and G-3, along with alloy 625, show that the general corrosion rate of ULTIMET alloy is second only to G-30 alloy (Table 8). While no data has been accumulated yet from field trials, ULTIMET alloy is in test at five P_2O_5 production facilities.

In addition to its promising general corrosion resistance in strong oxidizing environments such as wet process phosphoric acid, ULTIMET alloy has exceptional pitting corrosion resistance in the presence of chlorides as shown in Table 9 and Figure 1. The pitting corrosion resistance of ULTIMET alloy even surpasses that of alloy 625 and HASTELLOY alloy C-276.

While there exists a variety of wear phenomena, data is presented in Figures 2 through 6 which display superior cavitation erosion, low and high stress abrasion and galling resistance of ULTIMET alloy. This coupled with its high strength properties, much like that of Ferralium alloy 255 (see Table 10) and its corrosion resistant properties makes ULTIMET alloy a viable candidate for WPA production.

Conclusions

- HASTELLOY alloy G-30 has the lowest corrosion rate over all nickel and iron-base alloys tested in various commercial wet grades of phosphoric acid.
- For nickel-base alloys "cold reduced/cold pilgered" welded tubing procured to ASTM B626 Class III should offer good corrosion protection at the weld and the base metal. "Bead-worked" welded tubes as procured to ASTM B626 Class II or III may be vulnerable to deterioration of the weld zone due to imperfect recrystallization and homogenization.
- Velocity increases from 1.5 feet/second to 6.2 feet/second in WPA does not result in increased corrosion on HASTELLOY alloy G-30.
- Test results show that ULTIMET alloy has excellent corrosion resistance in WPA and wear resistance (as measured in the laboratory) and should be considered a viable candidate for components in WPA production which experience corrosion and wear.

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References

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2. P.E. Manning, J.D. Smith and J.L. Nickerson, "New Versatile HASTELLOY Alloys for the Chemical Process Industry", Materials Performance, Vol. 27, No. 6, p. 67, June 1988.

3. A.I. Asphahani, D.C. Agarwal and P.E. Manning, "HASTELLOY alloy G:30: A Specialty Alloy for Applications in the Fertilizer Industry," ACS 194th National Meeting, New Orleans, LA, September, 1987.

4. A.I. Asphahani and J.L. Nickerson, "HASTELLOY alloy G-30 - A Specialty Alloy for Applications in the Process Industries," Haynes International, Inc., Technical Information No. H-2050.

5. L.E. Flasche, "Corrosion Resistance of High Performance NiCrMo Alloy Weldments," AWS, publication pending.

6. "For Better Corrosion-Resistant Welded Tubing: A Distinction Between 'Bead Worked' and 'Cold Reduced' Tubular Products," Haynes International, Inc., Technical Information No. H-2074.

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Table 1: Chemical Analysis of Wet-Process Phosphoric Acid (as supplied by the production source)

	Source				
	A	B	C	D	E
% P_2O_5	54.7	55.5	54.3	51.9	55.7
%H_2SO_4	4.5	5.3	5.1	3.0	4.2
%F^-	0.33	0.29	0.49	0.63	0.66
%Fe_2O_3	2.1	1.5	0.79	0.84	1.45
%SiO_2	NA	NA	NA	0.15	NA
ppm Cl^-	90	3900	NA	3500	50

NA = not analyzed

Table 2: Nominal Chemical Compositions (weight percent)

Alloy	Fe	Ni	Cr	Mo	W	Cu	Co
316L	Balance	12	18	2.0	-	-	-
alloy 904-L	Balance	25	20	4.5	-	1.5	-
Ferralium alloy 255	Balance	5.5	26	3.0	-	2.0	-
SAN 28	Balance	31	28	3.5	-	1.0	-
20Cb-3 alloy	Balance	34	20	3.0	-	3.5	-
825	Balance	42	21	3.0	-	1.8	-
G-3	20	Balance	22	7.0	-	1.5	-
625	3.0	Balance	21	9.0	-	-	-
C-22 alloy	3.0	Balance	22	13	3.0	-	2.5*
G-30 alloy	15	Balance	30	5.0	2.5	1.5	5.0*
ULTIMET alloy	3.0	9.0	26	5.0	2.0	-	Balance

*Max.

Table 3: Corrosion in 54% P_2O_5 at 300°F, Mill Annealed Condition Corrosion Rate (mpy)

Alloy	Test Duration 96 Hrs.	288 Hrs.	576 Hrs.	864 Hrs.
20Cb-3 alloy	303	99.8	30.7	55.7
alloy 904-L	62.0	54.0	44.6	34.6
Ferralium alloy 255	34.2	36.9	31.7	-
SAN 28	33.4	31.0	25.4	21.4
C-22 alloy	37.6	34.3	31.6	25.9
G-30 alloy	25.2	22.0	20.1	13.4

Table 4: Highest Corrosion Rate (mpy) Recorded from Several Tests, Mill Annealed Condition

Alloy	54% P_2O_5 116°C(241°F)	54% P_2O_5 149°C(300°F)	70% P_2O_5 204°C(400°F)
SAN 28	63	3236	53
alloy 825	553	1331	18
alloy G-3	41	1246	28
alloy 625	36	803	22
G-30 alloy	7	317	10

Table 5: Average Corrosion Rates (mpy) in Acids from Several Plants

Media	°C (°F)	G-30 alloy	G-3	625	SAN28
52% P_2O_5	116 (241)	4	11	12	48
52% P_2O_5	149 (300)	28	64	79	248
54% P_2O_5	116 (241)	8	16	16	55
54% P_2O_5+2000 ppm Cl^-	116 (241)	7	16	15	92

Table 6: Critical Pitting Temperature
(4% NaCl + 0.1% $Fe_2(SO_4)_3$ +0.01M HCl)

Alloy	Temperature °C (°F)
G-30 alloy	75 (167)
alloy G-3	75 (167)
SAN 28	60 (140)
Ferralium alloy 255	50 (122)
alloy 904-L	45 (113)
Type 317L	25 (77)
alloy 825	25 (77)
20Cb-3 alloy	20 (68)
Type 316	20 (68)

Table 7: Effect of Velocity on Corrosion Rate; Rotating Cylinder Electrode Test
(Hastelloy alloy G-30 in 52% P_2O_5, 116°C, 24 hours)

RPM	Peripheral Velocity (Ft./Sec.)	Corrosion Rate (mpy)
0	0	0.9
500	1.5	6.8
2000	6.2	6.3

Table 8: Corrosion Rates (mpy) in Several Plant Acids
(96 hour testing, average of 2 tests)

Alloy	40% P_2O_5 116°C	40% P_2O_5 149°C	40% P_2O_5 149°C	54% P_2O_5 149°C
alloy 625	7.8	72.2	81.8	69.0
alloy G-3	33.4	104.6	76.0	-
Ultimet alloy	3.8	47.4	53.7	38.0
G-30 alloy	Nil	36.2	43.8	33.3

Table 9: Critical Pitting Temperature
(11.5% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$)

Alloy	Temperature °C (°F)
Ultimet alloy	115 (239)
alloy C-276	110 (230)
alloy 625	75 (167)
G-30 alloy	45 (113)
20Cb-3 alloy	30 (86)
Type 316L	25 (77)

Table 10: Room Temperature Tensile Data (Plate)

Alloy	Yield Strength (KSI)	Ultimate Tensile Strength (KSI)	Elongation (in 2 In.)
Ultimet alloy	80	150	35%
Ferralium alloy 255	98	126	30%

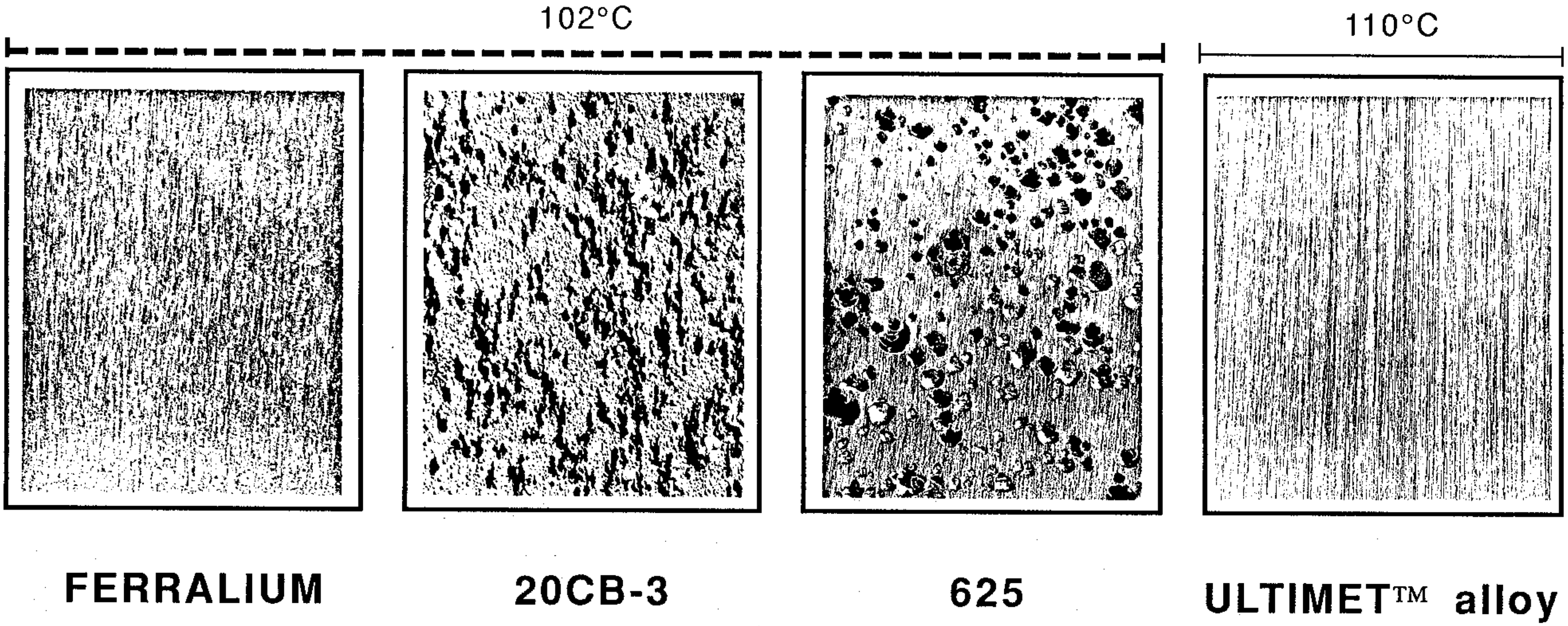

Figure 1. Pitting test samples; 11.5% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$ (24-Hour Exposure)

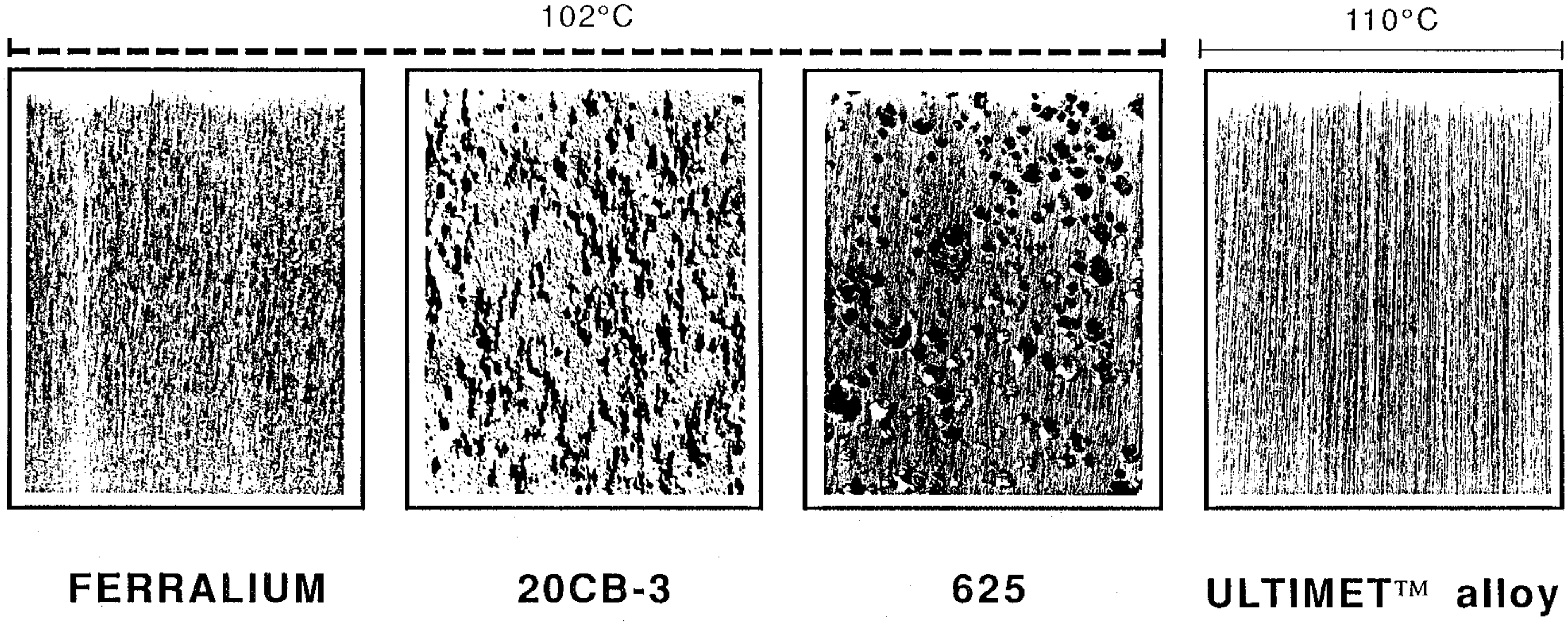

Figure 1. Pitting test samples; 11.5% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$ (24-Hour Exposure)

CAVITATION EROSION DATA

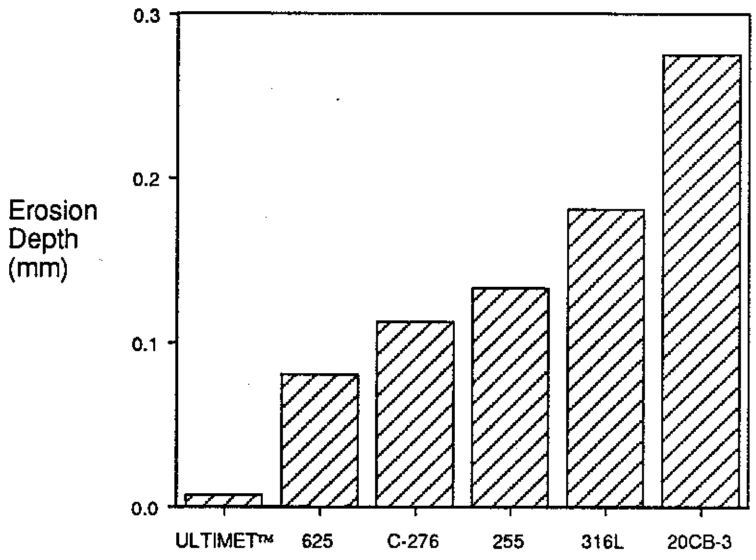

Figure 2. Cavitation erosion resistance, ASTM G-32, 24 hours in distilled water, 20 kHz frequency, 0.05 mm amplitude.

Low Stress Abrasion Data - ASTM G65 Test

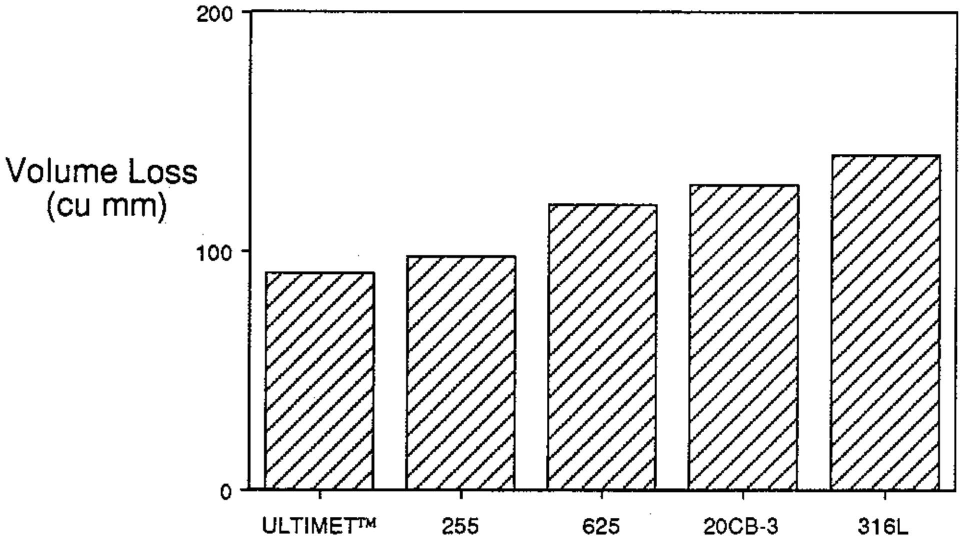

Figure 3. Low stress abrasion resistance, ASTM G-65, 2000 revolutions, 13.6kg load.

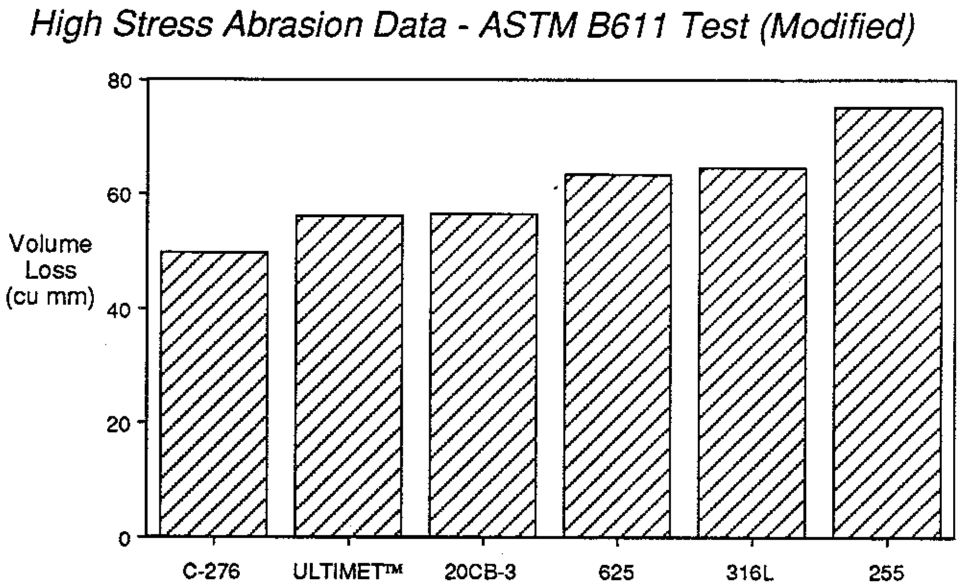
High Stress Abrasion Data - ASTM B611 Test (Modified)

Figure 4. High stress abrasion resistance, ASTM B611 modified, 250 revolutions, 22.7 kg. load.

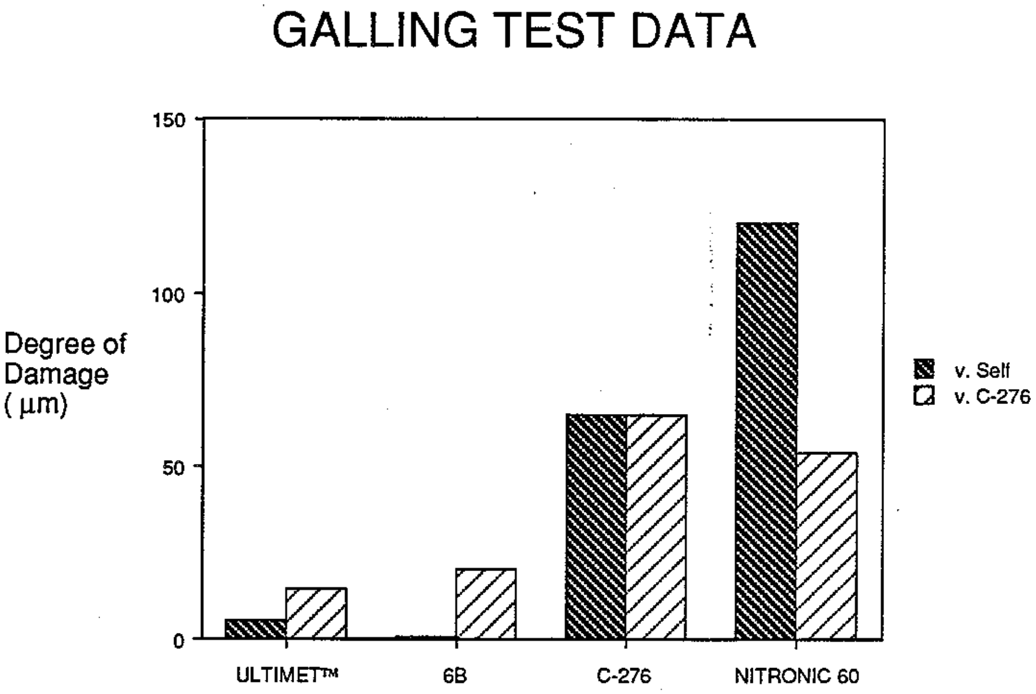
GALLING TEST DATA

Figure 5: Galling resistance, 10 stroke test, load 2722 kg.