Isothermal Calorimetric Observations of the Effect of Welding on Compatibility of Stainless Steels with High-Test Hydrogen Peroxide Propellant

Rudy Gostowski, PhD.

Marshall Space Flight Center, National Aeronautical and Space Administration, TD40,

Huntsville, AL

Introduction

High-Test Hydrogen Peroxide (HTP) is receiving renewed interest as a monopropellant and as the oxidizer for bipropellant systems. HTP is hydrogen peroxide having concentrations ranging from 70 to 98%. In these applications the energy and oxygen released during decomposition of HTP is used for propulsion.

$$2\,H_2O_2\,(l) \rightarrow 2\,H_2O\,(g) + O_2(g) \qquad \Delta H_r = 2887.0\ \mathrm{J\ g^{-1}}\ \text{anhydrous HTP [1]} \qquad (1)$$

However, incompatibility with structural materials will lead to decomposition of HTP in areas of the propulsion system that does not result in useful energy production. In addition, incompatibility may cause undesirable pressure and temperature rises and loss of capacity. Compatibility is generally thought to be controlled by complex interactions of the surface area, the chemical constituency and the surface finish of the material. Therefore, implementation of HTP as a propellant requires testing to determine the compatibility of structural materials for fabrication of the propulsion system. Compatibility has been expressed functionally with a series of classes ranging from one to four with one being preferred [2]. Percent Active Oxygen Loss per Week (%AOL/wk) has been used to quantitatively express compatibility.

$$\%AOL/wk = 100\,(W_1 C_1 - W_2 C_2) / W_1 C_1 \qquad (2)$$

W_1 and W_2 represent the initial and final masses of HTP solution respectively. C_1 and C_2 are the initial and final HTP mass fractions. To relate these quantitative measurements to the functional compatibility designations, metal samples having a %AOL/wk of ≤5 are assigned [3] to Class 1, while those having a value between 5 and 80 are considered Class 2. Class 3 materials have a %AOL/wk >80.

Isothermal heat-conduction microcalorimetry (IMC) permits measurement of the energy released when HTP decomposes which indirectly provides %AOL/wk data for the sample and facilitates class ranking.

In propulsion systems components must be fabricated and connected using available joining processes. Welding is a common joining method for metallic components. The goal of this study was to compare the HTP compatibility of welded vs. unwelded stainless steel.

Experimental

Propulsion grade high-test hydrogen peroxide (90%, FMC, Inc), reagent hydrogen peroxide (35%, Spectrum), nitric acid (70%, trace metal grade, Fisher Scientific) and sodium hydroxide solution (50%, Fisher Scientific) were used as received. Stainless steel sheet (0.15 cm thickness, CRES 316L and CRES 304L, Penn Stainless Products, Inc.) was cut into panels (10.2 x 10.2 cm). One panel of each alloy was Tungsten Inert Gas (TIG) welded with purge gas (Helium), one welded without purge gas and one was not welded. The panels were milled into coupons (3.8 x 1.0 cm). The dimensions of the coupons including the weld bead were determined using calipers and the surface area estimated (Table 1). The samples were then evaluated with a Surface Roughness Tester (Surftest 402 Series 178, Mitutoyo) yielding the root mean square of the deviations of the surface profile from the mean line (Rq) and the maximum peak to valley height (Rmax). Results are also listed in Table 1. The coupons were cleaned in acetone and detergent and rinsed with deionized water. Coupons were passivated by soaking in 70% nitric acid for five hours, rinsed, soaked in 35% hydrogen peroxide for four hours, rinsed in deionized water and air-dried. Molded borosilicate serum bottles (30ml, Wheaton Science Products) were passivated by soaking in sodium hydroxide (10%) for one hour, rinsed, soaked in nitric acid (35%) for one hour, soaked in 35% hydrogen peroxide for twenty four hours, rinsed in deionized water and air dried.

An Isothermal Microcalorimeter (Model 4400, Water Bath Model 7238, Calorimetry Sciences Corp, Provo, UT) was used to obtain heat flow measurements at 60 °C. The unit was permitted to thermally equilibrate at the set temperature for 24 hours and then calibrated against an internal resistance heater standard. Three measurement cells were evaluated against a reference cell holding a sealed vial containing deionized water (20mL). Aluminum closures were used with trifluoroethylene (TFE)-faced silicone liners for the reference and sample vials. Background heat flows (P_B, $\mu W\ g^{-1}$ anhydrous HTP) were measured for three vials containing only hydrogen peroxide (90%, 20mL). The anhydrous HTP mass was taken as 90% of the total fluid mass. Heat flows were constant over the 50-hour observation interval.

Vials were opened, metal sample coupons added and recapped. In all cases the heat flow quickly attained a thermal equilibrium state (<15 hours) followed by a slow rise to a peak value (P_{S+B}, $\mu W\ g^{-1}$ anhydrous HTP) within 70 to 320 hours and subsequently diminished. The background value (P_B) representing a sum of the homogeneous HTP decomposition and the heterogeneous HTP decomposition on the surface of the vial was subtracted from the peak heat flow (P_{S+B}). The resulting value (P_S, μW g^{-1} anhydrous HTP) corresponded to the maximum heterogeneous HTP decomposition on the surface of the coupon.

As shown in Equation 2, P_S was converted to a first order rate constant (k, s^{-1}) by division with the heat of reaction for the decomposition of hydrogen peroxide ($\Delta H_r = 2887.0 \times 10^6$ μW s g^{-1}) [1]. Using Equation 3 the resulting first order rate constant was converted from reciprocal seconds to %AOL/wk with the results listed in Table 1.

$$k = \frac{P_S}{\Delta H_r} \tag{2}$$

$$\%AOL/wk = \left(6.048\times10^{7}\right) k \tag{3}$$

Results

Table 1

Surface area, finish of samples and percent active oxygen loss per week[a, b]

Material	Joining Method	Area (cm^2)	Surface Roughness		Maximum %AOL/wk
			Rmax (μm)[c]	Rq (μm)[d]	
CRES 316L	No weld	10.31±0.02	0.97±0.25	0.30±0.09	5.9±0.5
CRES 304L	No weld	10.30±0.04	1.14±0.18	0.33±0.15	27.9±1.6
CRES 316L	TIG, He purge	9.36±0.14	3.66±1.02	1.07±0.19	34.0±10.0
CRES 304L	TIG, He purge	9.43±0.04	2.29±1.02	1.83±1.11	68.2±11.5
CRES 316L	TIG, No purge	9.40±0.11	32.26±14.02	15.42±2.39	36.1±4.1

CRES 304L	TIG, No purge	9.46±0.11	106.93±61.21	17.81±2.32	94.5±3.1

[a] Average of three coupons.

[b] 90% confidence level.

[c] Maximum peak to valley height.

[d] Root mean square of the deviations of the surface profile from the mean line.

Unwelded CRES 316L shows good compatibility and by the rating system is nearly Class 1. CRES 304L is a Class 2 material. Welded CRES 316L and welded CRES 304L have significantly less compatibility than their unwelded counterparts with the CRES 304L falling beyond the upward limit of Class 2 materials. When welded without purge gas the CRES 316L is not significantly different from the metal welded with the gas. However, CRES 304L welded without purge gas has a much higher %AOL/wk and would be considered a Class 3 material.

Discussion

As mentioned previously, compatibility is determined by the surface area, the chemical constituency and the surface finish of a material. In this investigation exposed area is obviously not at factor as the welded samples had a slightly smaller surface than the unwelded, but were more reactive. The chemical makeup of welded CRES 316L and welded CRES 304L have been observed in the literature to change from the parent material as chromium and iron are segregated in zones [4-6]. In particular, the ratio of chromium to iron [6] in CRES 316L increased from 0.26 to 0.79 in the heat affected zone (HAZ) of the weld and to 1.52 in the weld bead itself. In CRES 304L the ratio of chromium to iron increased from 0.28 to 0.44 in the HAZ and to 0.33 in the weld bead. It is possible that the increased reactivity of the welded samples and of those welded without purge gas is due to this segregation phenomenon. Likewise the reactivity increased in keeping with the greater roughness of the welded and welded without purge gas samples. Therefore enhanced roughness may also be responsible for the increased reactivity.

Conclusions

In summary, HTP reactivity increased due to welding concurrently with formation of segregation zones and increased roughness. These effects were even greater when purge gas was not used. Causality between these factors while reasonable was not established and their fractional contributions to reactivity were not determined.

Acknowledgments

The author is grateful to Bill Stanton (Marshall Space Flight Center, Metallic Materials Group) for welding the various specimens and to Yvonne Villegas (NASA-Undergraduate Student Research Program), Genne Nwosisi (NASA-Minority Programs) and Jennifer Baldridge (NASA-Undergraduate Student Research Program) for their help in preparation and execution of the IMC analysis.

References

[1] W.C. Schumb, C.N. Satterfield and R.L. Wentworth, Hydrogen Peroxide, Reinhold, Baltimore, 1955, p. 249.

[2] W.C. Schumb, C.N. Satterfield and R.L. Wentworth, Hydrogen Peroxide, Reinhold, Baltimore, 1955, p. 163.

[3] Bulletin #104: Materials of Construction for Equipment in Use with Hydrogen Peroxide, FMC, 1966, p. 48.

[4] T. Takalo, N. Suutala and T. Moisio, Metall. Trans A. 10A (1979) 1173.

[5] J. Foulds and J. Moteff, Metall. Trans. A. 13A (1982) 173.

[6] M. Ahmad, K.A. Shoaib, M.A. Shaikh and J.I. Akhtar, J. Mat. Sci. 29 (1994) 1169.

Isothermal Calorimetric Observations of the Effect of Welding on Compatibility of Stainless Steels with High-Test Hydrogen Peroxide Propellant

Rudy Gostowski, PhD.
Chemical Propulsion Group
Propulsion Research Lab
TD40-MSFC-NASA

Background

- High-Test Hydrogen Peroxide (HTP) as a monopropellant and as the oxidizer for bipropellant systems
- Concentrations ranging from 70 to 98%.

$$2\,H_2O_2\,(l) \rightarrow 2\,H_2O\,(g) + O_2(g) \qquad \Delta H_r = 2887.0\ \mathrm{J\ g^{-1}}$$

anhydrous HTP

Compatibility

- Incompatibility with structural materials will lead to decomposition of HTP in areas of the propulsion system that does not result in useful energy production.
- Incompatibility may cause undesirable pressure and temperature rises and loss of capacity.
- Compatibility is generally thought to be controlled by complex interactions of the surface area, the chemical constituency and the surface finish of the material.
- Implementation of HTP as a propellant requires testing to determine the compatibility of structural materials for fabrication of the propulsion system.

Measures of Compatibility

- Qualitative: Series of classes ranging from one to four with one being preferred
- Quantitative: Percent Active Oxygen Loss per Week (%AOL/wk)
- Relationship
  - %AOL/wk ≤5 Class 1
  - %AOL/wk 5 to 80 Class 2
  - %AOL/wk >80 Class 3

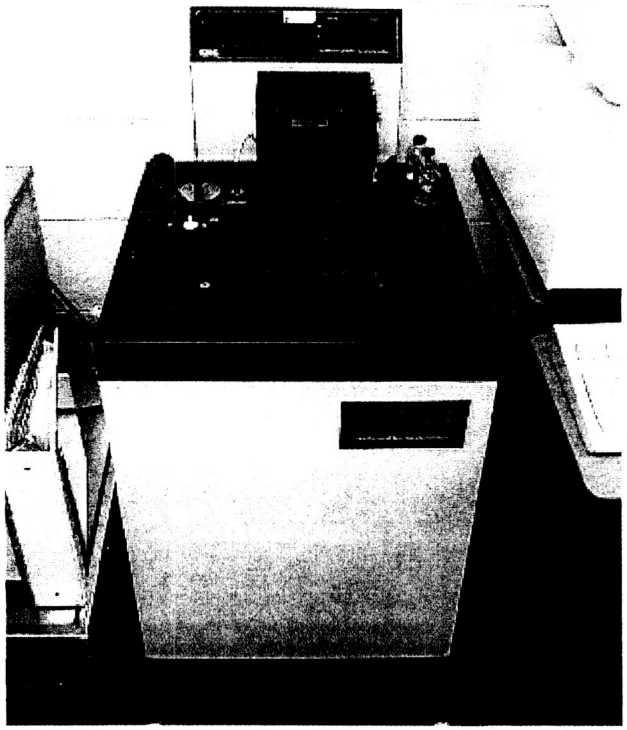
Percent Active Oxygen Loss per Week (%AOL/wk)

$$\%\mathrm{AOL/wk} = 100\,(W_1 C_1 - W_2 C_2) / W_1 C_1$$

- W_1 and W_2 represent the initial and final masses of HTP solution
- C_1 and C_2 are the initial and final HTP mass fractions

Isothermal Microcalorimetry (IMC)

- Isothermal heat-conduction microcalorimetry (IMC) permits measurement of the energy released when HTP decomposes which indirectly provides %AOL/wk data for the sample and facilitates class ranking.



joining method for metallic components.

- The goal of this study was to compare the HTP compatibility of welded vs. unwelded stainless steel.

  - Reagent hydrogen peroxide (35%, Spectrum)
  - Nitric acid (70%, trace metal grade, Fisher Scientific)
  - Sodium hydroxide solution (50%, Fisher Scientific)
- CRES 316L and CRES 304L Stainless steel sheet (0.15 cm thickness, Penn Stainless Products, Inc.)

Coupon Preparation

- Cut into panels (10.2 x 10.2 cm).
- Welding Conditions
  - Tungsten Inert Gas (TIG) welded with purge gas (Helium)
  - Tungsten Inert Gas (TIG) welded without purge gas
  - Not welded.
- Milled into coupons (3.8 x 1.0 cm).
- Dimensions including the weld bead
- Surface area calculated
- Surface roughness evaluated

Surface Roughness Evaluation

- Surface Roughness Tester (Surftest 402 Series 178, Mitutoyo)
- Root mean square of the deviations of the surface profile from the mean line (Rq)
- Maximum peak to valley height (Rmax).

Cleaning and Passivation

- Cleaning
  - Acetone degrease
  - Detergent wash
  - Rinsed with deionized water.
- Passivation
  - 70% nitric acid for five hours
  - Rinsed
  - 35% hydrogen peroxide for four hours
  - Rinsed in deionized water
  - Air-dried

Sample Vial Preparation

- Used as supplied: molded borosilicate serum bottles (30ml, Wheaton Science Products)
- Passivation
  - Sodium hydroxide (10%) for one hour
  - Rinsed
  - nitric acid (35%) for one hour
  - 35% hydrogen peroxide for twenty four hours
  - Rinsed in deionized water
  - air dried

Calorimetry Procedure: Pre-Test

- Isothermal Microcalorimeter: Model 4400, Water Bath Model 7238
- Calorimetry Sciences Corp, Provo, UT)
- Measurement temperature: 60 °C.
- Thermal equilibration at the set temperature for 24 hours
- Calibrated against an internal resistance heater standard.

Calorimetry Procedure: Background (P_B)

- Evaluated against a reference cell holding a sealed vial containing deionized water (20mL)
- Aluminum closures were used with trifluoroethylene (TFE)-faced silicone liners for the reference and sample vials.
- Background heat flows (P_B, μW g^{-1} anhydrous HTP) were measured for three vials containing only hydrogen peroxide (90%, 20mL)
- The anhydrous HTP mass was taken as 90% of the total fluid mass
- Heat flows were constant over the 50-hour observation interval.

Calorimetry Procedure: Sample (P_{S+B})

- Coupon Addition
  - Vials opened
  - Metal sample coupons added
  - Recapped
- Heat flow quickly attained a thermal equilibrium state (<15 hours) followed by a slow rise to a peak value (P_{S+B}, μW g $^{-1}$ anhydrous HTP) within 70 to 320 hours and subsequently diminished.

Calculaton of %AOL/wk

- Background value (P_B, μW g^{-1}): sum of the homogeneous HTP decomposition and the heterogeneous HTP decomposition on the surface of the vial
- With sample value (P_{S+B}, μW g^{-1}).
- Subtraction: (P_S, μW g^{-1})
  - Maximum heterogeneous HTP decomposition on the surface of the coupon.
- First order rate constant (k, s^{-1})
  - Division by heat of reaction($\Delta H_r = 2887.0 \times 10^6$ μW s g^{-1})
- %AOL/wk
  - Conversion of seconds to weeks

Results (90% confidence level)

Material	Joining Method	Area (in^3)[b]	Rmax (µin)[b]	Rq (µin)[b]	Maximum %AOL/wk[b]
CRES 316L	No weld	1.598 ±0.00307	38.0 ±10.0	12.0 ±3.69	5.87 ±0.52
CRES 304L	No weld	1.597 ±0.00561	45.0 ±7.25	13.0 ±5.75	27.9 ±1.56
CRES 316L	TIG, He purge	1.451 ±0.0224	144 ±40.3	42.3 ±7.60	34.0 ±10.0
CRES 304L	TIG, He purge	1.462 ±0.00674	90.3 ±40.0	72.0 ±43.8	68.2 ±11.5
CRES 316L	TIG, No purge	1.457 ±0.0168	1270 ±552	607 ±94.2	36.1 ±4.08
CRES 304L	TIG, No purge	1.466 ±0.0167	4210 ±2410	701 ±91.2	94.5 ±3.06

Results

- Unwelded CRES 316L shows good compatibility and by the rating system is nearly Class 1. CRES 304L is a Class 2 material
- Welded CRES 316L and welded CRES 304L have significantly less compatibility than their unwelded counterparts with the CRES 304L falling beyond the upward limit of Class 2 materials
- Welded without purge gas the CRES 316L is not significantly different from the metal welded with the gas
- CRES 304L welded without purge gas has a much higher %AOL/wk and would be considered a Class 3 material.

Discussion

- The chemical makeup of welded CRES 316L and welded CRES 304L have been observed in the literature to change from the parent material as chromium and iron are segregated in zones.
- In particular, the ratio of chromium to iron in CRES 316L increased from 0.26 to 0.79 in the heat affected zone (HAZ) of the weld and to 1.52 in the weld bead itself.
- In CRES 304L the ratio of chromium to iron increased from 0.28 to 0.44 in the HAZ and to 0.33 in the weld bead.
- It is possible that the increased reactivity of the welded samples and of those welded without purge gas is due to this segregation phenomenon.
- Reactivity increased in keeping with the greater roughness of the welded and welded without purge gas samples. Therefore enhanced roughness may also be responsible for the increased reactivity.

Conclusions

- HTP reactivity increased due to welding concurrently with formation of segregation zones and increased roughness. These effects were even greater when purge gas was not used. Causality between these factors while reasonable was not established and their fractional contributions to reactivity were not determined.

In Press

- Thermochimica Acta 71282 (2003) 1–3
- doi:10.1016/S0040-6031(03)00121-7

Future Work

- Injector Material Evaluation
  - In-Space Propulsion
  - NASA/Boeing-Rocketdyne
- Damage Effects on Passivation
  - Hillary Huttenhower (NASA-Undergraduate Student Research Program)

Acknowledgments

- Eddie Davis (Chemical Group-ED36-MSFC-NASA)
- Bill Stanton (Metallic Materials Group-ED33-MSFC-NASA)
- Yvonne Villegas (NASA-Undergraduate Student Research Program)
- Genne Nwosisi (NASA-Minority Programs)
- Jennifer Baldridge (NASA-Undergraduate Student Research Program)

References

- W.C. Schumb, C.N. Satterfield and R.L. Wentworth, Hydrogen Peroxide, Reinhold, Baltimore, 1955, p. 249.
- Bulletin #104: Materials of Construction for Equipment in Use with Hydrogen Peroxide, FMC, 1966, p. 48.
- T. Takalo, N. Suutala and T. Moisio, Metall. Trans A. 10A (1979) 1173.
- J. Foulds and J. Moteff, Metall. Trans. A. 13A (1982) 173.
- M. Ahmad, K.A. Shoaib, M.A. Shaikh and J.I. Akhtar, J. Mat. Sci. 29 (1994) 1169