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

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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.

$$2\ H_2O_2\ (l) \rightarrow 2\ H_2O\ (g) + O_2(g) \qquad \Delta H_r = 2887.0\ \text{J/g} \qquad (1)$$

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 [1]. Percent Active Oxygen Loss per Week (%AOL/wk) has been used to quantitatively express compatibility.

$$\%\text{AOL/wk} = 100(W_1C_1 - W_2C_2)/W_1C_1 \qquad (2)$$

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 five or less are assigned [2] to Class 1, while those having a value greater than five and equal to or less than eighty are considered Class 2. Class 3 materials have a %AOL/wk greater than eighty.

Isothermal microcalorimetry (IMC) permits measurement of the energy released when HTP decomposes which indirectly provides %AOL/wk data for the sample and facilitates ranking in the aforementioned classes. In this instrument the sample is held at a constant temperature by a water bath. A Peltier device within the sample cavity detects heat flow to or from the sample. In the case of HTP decomposition the flux is exothermic. IMC provides a sensitive and relatively reproducible evaluation of compatibility pertinent to this study [3].

In propulsion systems components must be fabricated and connected using the 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.

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 from suppliers. Stainless steel sheet (0.06 inch, CRES 316L and CRES 304L, Penn Stainless Products, Inc.) was cut into panels (4 x 4 inch). 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 (1.5 x 0.4 inch). 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). Results are also listed in Table 1. The coupons were cleaned in acetone and detergent and rinsed with dionized water. Coupons were passivated by soaking in 70% nitric acid for five hours, rinsed, soaked in 35% hydrogen peroxide for four hours, rinsed in dionized 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 dionized 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, μW/g) were measured for three vials containing only hydrogen peroxide (90%, 20mL). The HTP mass was taken as 90% of the total fluid mass. Vials were opened, metal sample coupons added and recapped. The maximum observed heat flow (P_{S+B}, μW/g) was then recorded. The equilibrium 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 (Equation 2) from the peak observed heat flow (P_{S+B}). The resulting value (P_S, μW/g) corresponded to the maximum heterogeneous HTP decomposition on the surface of the coupon.

$$P_S = P_{S+B} - P_B \qquad (2)$$

sample observed background

As shown in Equation 3, P_S is converted to a first order rate constant (k, 1/s) by division with the heat of reaction for the decomposition of hydrogen peroxide (ΔH_r = 2887.0 J/g) [1]. Using Equation 4 the resulting first order rate constant was converted from reciprocal seconds to %AOL/wk with the results listed in Table 1.

$$k = P_S\,(1\text{e-}6)/\,\Delta H_r \tag{3}$$

$$\%\text{AOL/wk} = k\,(60480000) \tag{4}$$

Results

Table 1

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

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

[a] Average of three coupons.

[b] 90% confidence level.

Unwelded CRES 316L shows good compatibility and by the rating system is between Class 1 and Class 2. CRES 304L would be considered a Class 2 material. Welded CRES 316L and welded CRES 304L have significantly less compatibility than their unwelded counterparts with the CRES 304L falling near 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 [4,5,6]. In particular, the ratio of chromium to iron [6] in CRES 316L increased from 0.260 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 0.280 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.

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