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Hydride-based cold-start heater for automotive catalyst

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Abstract

A novel, closed-cycle, hydride-based cold-start heater for automotive catalysts is described. The device consists of coupled AB_5 and β-Ti alloy beds and is designed to store a small part of the automotive exhaust heat for later release during cold-start. Without the significant use of electric power, it can heat the catalyst bed to operating temperature in a few seconds thereby greatly reducing cold-start hydrocarbon emissions. A full-sized prototype was built and tested both on the bench and in an FTP automobile. ULEV performance was achieved with a 2.2 L, 4-cylinder vehicle.

Keywords: Hydride; Hydrogen; Heat storage; Automotive catalyst; Hydrocarbons

1. Introduction

It is well known that much of the pollution produced by an automobile occurs during the first few minutes after cold-start, before the catalyst bed has reached effective operating temperature. A number of techniques to minimize this problem have been proposed: electrical heating of the catalyst [1], vacuum insulation of the converter to keep the catalyst hot during non-use [2], hydrocarbon traps [3], exhaust gas igniters [4], and higher temperature catalysts that can be placed closer to the engine [5]. This paper discusses another option, namely the very rapid heating of the cold exhaust gas immediately upstream of the catalyst bed by using the exothermic heat of hydriding and an efficient heat exchanger [6].

2. The hydride cold-start heater

The hydride cold-start heater (HCSH) is schematically shown in Fig. 1. Its configuration is similar to the well-known hydride heat pump, but it is really a heat storage device with occasional operation. A heater bed and a source bed are separated by a solenoid valve (S) and a one-way (check) valve. The heater bed contains a low pressure (high temperature) hydriding alloy and the source bed contains a near-ambient (room temperature) hydriding alloy. The heater alloy is contained in a heat exchanger located in the automobile exhaust pipe immediately upstream of the catalytic converter. The source bed is located separately under the auto. Also contained in the sealed system is an initial inventory of hydrogen necessary to fill only the source alloy to the hydride end of its plateau.

The operation of the HCSH is conceptually and practically quite simple. As a starting point, most of the H_2 is in the source bed at an equilibrium pressure somewhat above atmospheric. The heater alloy is largely dehydrided. The starting of the car automatically activates the opening of the valve S which allows H_2 to desorb from the source bed and rush to the heater bed. The heater bed is then rapidly and exothermically hydrided, resulting in heat exchange to the cold exhaust gas and then to the downstream catalyst. The result is heating of the upstream end of the catalyst to its ‘‘light-off’’ temperature (typically 300 °C) in a few seconds, after which the normal exothermic catalyst operation takes over. After about a minute, a timer closes valve S. Within a few more minutes the engine reaches its normal operating temperature with an exhaust temperature typically above 500 °C. The heater bed then endothermically dehydrides, with the H_2 being driven through the check valve back into the source bed, effectively storing

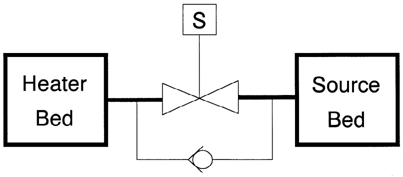

Fig. 1. Schematic diagram of hydride cold-start heater (HCSH).

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some of the exhaust heat. The cycle is now complete and the HCSH is ready for the next cold-start.

3. Prototype heater bed

A full-scale prototype heater, shown in Fig. 2, was constructed using 1.0 kg of powdered heater alloy contained in a series of looped, 3.2 mm stainless steel tubes and activated in situ. The tubes were attached to gas distribution manifolds in a series of ‘‘daisy-wheels’’. Each tube contained an internal proprietary gas distribution method to prevent both pressure drop and expansion effects. The entire heat exchanger was 8.9 cm diameter, 25.4 cm long and had about 2500 cm^2 of active surface area. The maximum reaction heat generated during a heating half-cycle was about 460 kJ (128 Whr). After considering sensible heat losses, about 50% of this heat content ends up in the hot air leaving the heater. This is enough to bring the upstream end of the catalyst up to ‘‘light-off’’ temperature.

The heater alloy used was a specially developed Nb-stabilized β-Ti alloy. Most β-Ti alloys are subject to either metallurgical decomposition into α-Ti+intermetallics or H-induced disproportionation. Ti–Nb seemed to have considerable stability over the temperature range of operation for the HCSH. The hydrogen pressure–composition isotherms for the heater alloy used are shown in Fig. 3.

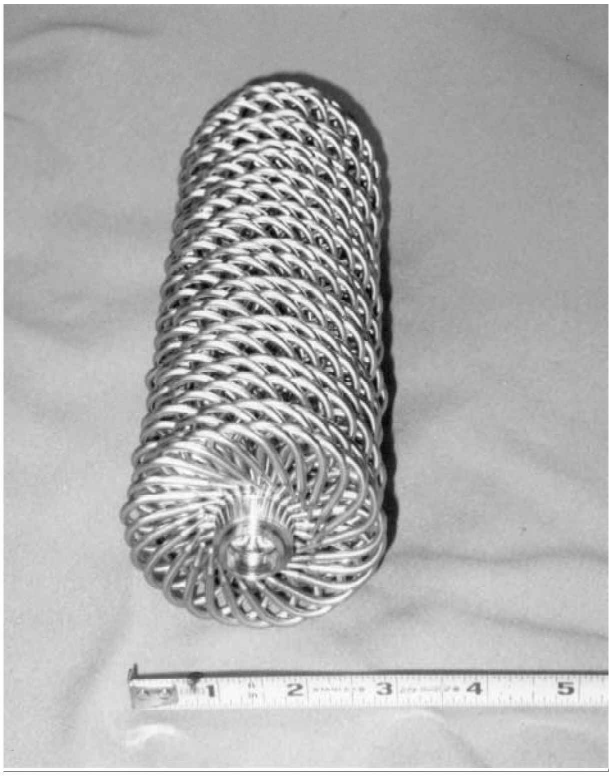

Fig. 2. Prototype HCSH heater section. Scale is in inches.

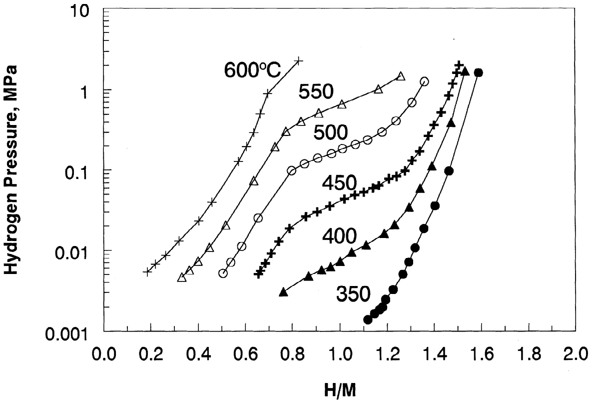

Fig. 3. Pressure–composition isotherms for Nb-stabilized β-Ti heater alloy.

4. Source bed

The source bed was a relatively conventional container of $MmNi_{4.5}Al_{0.5}$ (HY-STOR^{TM} 208 alloy) [7]. Extra source alloy was used relative to the amount of heater alloy in order to serve as a thermal ballast to allow essentially adiabatic source operation during the brief heating half-cycle [8]. Also some extra hydrogen must be available because there is some diffusional loss of H_2 through the heater tubes during hot operation. Approximately 100% extra source alloy was used relative to what would be required for matching the heater. This would allow the HCSH system to operate for the typical 4000–5000 life of an automobile without the necessity of adding any H_2.

5. Test runs

5.1. Bench test

The prototype HCSH described above (Fig. 1) was mounted in a steel tube simulating an automotive exhaust pipe. The heater bed had been previously desorbed below the β-alloy plateau at 550–600 °C. Room temperature (25 °C) air was passed through the tube at the rate of 1100 $L\ m^{-1}$ and a thin, rapid response thermocouple placed in the downstream air within a few mm of the end of the HCSH. Valve S was actuated at time zero and the temperature of the downstream thermocouple monitored. The resultant temperature–time profile of the exit air is shown in Fig. 4. Air temperature reached 300 °C within about 2 s and 400 °C at about 4 s. This test was followed by a simulated hot exhaust regeneration of the heater bed by blowing 600 °C air through the pipe, thus driving H_2 from the heater bed back to the AB_5 bed. The regeneration was successful because a subsequent self-heating run gave essentially the same results as Fig. 4. The HCSH was then cycled a few more times in the same manner.

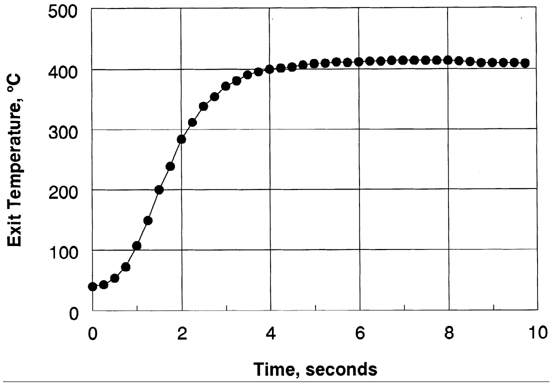

Fig. 4. Temperature of air downstream of HCSH after actuation. Inlet air: 1100 L m^{-1} at 25 °C.

The bench tests were considered completely successful. In particular they demonstrated the following: (1) the heater and source alloys behaved in tandem as the individual thermodynamics predicted; (2) the activated β-Ti alloy reacted with H_2 immediately from a room temperature start, without any delay or incubation time; (3) the system behaved reproducibly over a few cycles; and (4) the hydride–air heat exchanger efficiency was more that adequate.

5.2. On-vehicle tests

After the above bench tests, the prototype HCSH was fitted to a 1993 Honda Accord (4-cylinder, 2.2 L engine) for dynamometer testing according to the standard U.S. Federal Test Procedure (FTP) for emissions testing (a detailed 45 min sequence). An additional small ‘‘light-off’’ catalyst was placed between the HCSH and main catalyst bed, as is the case for electrical exhaust heaters [1]. The non-methane hydrocarbons (NMHC) were monitored during the procedure and integrated to give an average for the cycle which must be viewed in relation to the proposed California standards. As a reference point, the vehicle without the use of any cold-start heater (but including the supplementary ‘‘light-off’’ catalyst) showed an average of 0.075 g NMHC/mile (0.047 g/km) over the FTP. Using the prototype HCSH, the vehicle emitted only 0.023–0.026 g NMHC/mile (0.014–0.016 g/km), which is actually below the 0.04 g/mile (0.025 g/km) California standard for the Ultra Low Emission Vehicle (ULEV). After 20 cyclings of the HCSH, ULEV emissions were still being achieved over the FTP cycle.

6. Conclusions

A novel hydride cold-start heater for automotive catalysts has been successfully designed and tested. It is clearly capable of dramatically reducing cold hydrocarbon emission and even achieving ULEV performance from a conventional catalyzed automobile. The HCSH has certain advantages over alternative emissions control systems. It is passive, automatic and requires no significant electrical input (except for solenoid valve control). However, for this hydride based device to be shown as fully competitive, particularly with hydrocarbon traps and electrical heating, further work on minimizing production cost and confirming good cycle life must be carefully done. In conclusion, we think the potential exists for a new and near-term hydride application in the automotive catalyst industry. In addition, there are other potential applications that may benefit from ‘‘instant preheating’’.

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