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Materials Considerations for the Coupling of Thermochemical Hydrogen Cycles to Tandem Mirror Reactors

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MATERIALS CONSIDERATIONS FOR THE COUPLING OF THERMOCHEMICAL HYDROGEN CYCLES TO TANDEM MIRROR REACTORS*

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Abstract

Candidate materials are discussed and initial choices made for the critical elements in a liquid Li-Na Cauldron Tandem Mirror blanket and the General Atomic Sulfur-Iodine Cycle for thermochemical hydrogen production. V and Ti alloys provide low neutron activation, good radiation damage resistance, and good chemical compatibility for the Cauldron design. Aluminide coated In-800H and siliconized SiC are materials choices for heat exchanger components in the thermochemical cycle interface.

Introduction

This paper describes the initial considerations for some of the main materials and high temperature chemistry related problems associated with utilizing a Tandem Mirror Reactor as the heat source for thermochemical production of hydrogen from water. The rationale for future hydrogen needs in this Country, and an overview of the overall study are provided by R. Werner in a companion paper[1] at this Conference. Werner also describes two reactor blanket concepts for process heat production: (1) a binary liquid Li-Na Cauldron design where heat is removed by boiling of Na, and (2) a moving bed design that uses Li_2O microspheres. He also points out that the main thrust of the study at this time is to investigate the problems of coupling the Li-Na Cauldron to the General Atomic Sulfur-Iodine Thermochemical Cycle. T. Galloway, in another companion paper[2], discusses the chemical engineering considerations in interfacing the Li-Na Cauldron to the Sulfur-Iodine Cycle. In this paper, I will discuss the initial materials selections for critical elements of the Cauldron design and for those elements that interface with the thermochemical cycle.

Materials Requirements

Cauldron

A [illegible] unit of the Cauldron design is schematically illustrated in Fig. 1 and described in greater detail by Werner.[1] It is a low stress design that utilizes a cooled structural wall and limits fluid pressures to ~1.5 atm. The structural wall also serves as the first wall surrounding the plasma. A separate inner wall is used to contain the liquid Li-Na at the full temperature (~1200K) of the Cauldron. The important elements of the Cauldron from a materials standpoint are the following:

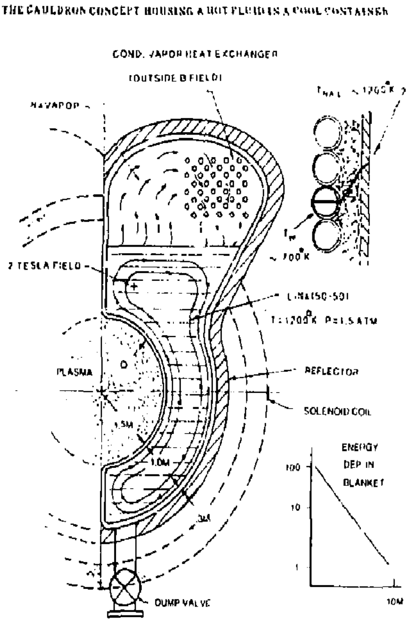

Fig. 1. Schematic view of the Li-Na Cauldron design.

- First wall (structural wall)
- "Feltmetal" insulator**
- Cauldron wall
- Heat exchangers (heat pipes)
- Tritium permeation membranes

We conceive of the structural wall to be made of tubular cooling channels, cooled with a high boiling point organic liquid (e.g., a polyphenyl compound) to avoid MHD effects (see inset, Fig. 1). Materials requirements for this structural wall are most severe in the first wall region where radiation damage and activation effects resulting from the plasma are major considerations. The selection of materials is much greater for the structural wall in the outer regions of the Cauldron, where conventional low-cost alloys (e.g., Fe-Ni based alloys) can be readily used. Hence, materials for that portion of the strucural wall will not be discussed

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further here.

Inside the structural wall is a layer of fibrous metallic insulator in the form of a commercial product called "Feltmetal". Requirements of this material are that it provide the necessary thermal insulation, and to have good compressive strength and low shear strength (to provide for differential expansion of the inner and outer walls). The Feltmetal further serves the function of providing an inner channel for removal of tritium that diffuses through the walls. It should be possible to fabricate Feltmetal from any of the ductile metals. We anticipate that a bulk material density of about 20-40% of theoretical density for the Feltmetal will provide the necessary properties for this application.

For the Cauldron wall, the main materials considerations are: radiation damage and activation in the region near the plasma, and corrosion and long-term creep strength for the entire wall region.

The condensing Na vapor heat exchanger at the top of the dome can be accomodated in two ways: (1) using heat exchanger tubes containing liquid Na or K heat exchanger fluids, or (2) using heat pipes with Na working fluid. If heat pipes are used, a secondary circulating Na, K or possibly He loop would be required to carry the heat to the thermochemical process. A high thermal conductivity and good corrosion resistance are important considerations for the heat exchanger materials.

Tritium released from the boiling Li-Na pool will need to be recovered through several paths. A portion can be recovered from the Feltmetal channel, a portion will pass into the heat pipes or the heat exchange loop, and a portion can be intentionally removed through permeation membranes in the vapor dome. Without pursuing design specifics, it should be clear that materials that have a high permeation rate for tritium and that will withstand corrosion by the liquid metal environment, will be needed for tritium recovery in this system.

Thermochemical Cycle Interface

Interfacing the heat output of the Cauldron with the General Atomic Sulfur-Iodine Cycle involves the two following design elements:

- Transport Piping
- Heat Exchangers

Good creep strength and corrosion resistance are the main considerations for the transport piping required to carry heat from the Cauldron to the various components of the thermochemical process. If liquid Na or K are used for the transport fluids, the creep problems are reduced because of the low pressure in the system, but corrosion becomes an important consideration. If high pressure He is used for heat transport, creep becomes a major consideration. An additional consideration for the transport piping is the removal of any residual tritium to prevent it from entering the thermochemical cycle. Tritium permeation membranes, such as discussed in the Cauldron section above, would also be applicable for tritium removal here.

Before discussing next the materials requirements for heat exchangers at the thermochemical cycle interface, I will briefly describe the main areas of the General Atomic Cycle where heat input is required. Additional details can be found in Galloway's paper.[2] The cycle is represented by the following reactions:[3]

$$2\,H_2O + SO_2 + xI_2 \xrightarrow{\text{aqueous}} H_2SO_4 + 2HI_x \quad (1)$$

$$2\,HI_x \xrightarrow{\leq 573K} xI_2 + H_2 \quad (2)$$

$$H_2SO_4 \xrightarrow{\leq 1144K} H_2O + SO_2 + 1/2\,O_2 \quad (3)$$

Reactions (1) and (3) are the ones of concern for heat requirements. In reaction (1), aqueous H_2SO_4 at about 50 wt % is produced near room temperature and needs to be concentrated to about 97 wt % H_2SO_4 by evaporating off excess water to form an azeotropic boiling solution. The 98 wt % azeotrope is then boiled at ~673K and 10 atm pressure to form a vapor consisting primarily of gaseous SO_3 and H_2O. This sequence of H_2SO_4 concentration and boiling of the azeotrope is one of the primary heat consuming steps of the cycle. Subsequent to boiling the H_2SO_4, the gaseous SO_3/H_2O mixture is heated to ~1150K where most of the SO_3 decomposes to form SO_2 and O_2. This then constitutes the second major heat consuming step in the cycle and also the step that requires the highest temperature input. Significant amounts of high temperature heat are also needed for shaft and electrical power in the cycle. Our main concerns here will be to identify materials for the H_2SO_4 boiler and the SO_3 decomposer heat exchangers. These processes both present highly corrosive conditions for heat exchanger materials. Hence, corrosion resistance is one of our main considerations in selection of heat exchanger materials. Other considerations are interfacing with the transport loop fluid (e.g., Na), and creep in the case of the SO_3 decomposer.

Materials Candidates

The materials that we are currently considering for the applications given above are listed in Table 1, together with a summary of pros and cons in regard to their applicability. Further information regarding the listed materials is given below.

V Alloys

Vanadium alloyed with about 10-20 wt % Ti is probably the best choice for a first wall material because of its low activation and its resistance to void formation under neutron activation.[4] Alloying with Ti also suppresses He gas bubble formation.[4] I also expect low tritium retention in V alloys, because recent work by Hisamatsu and Kanno shows hydrogen permeation rates to be very high in V, e. g., about ten times higher than through pure Nb at ~700K, and second only to Pd.[5] A high tritium penetration rate also makes V and its alloys good candidates for tritium permeation membranes. Vanadium shows good resistance to corrosion by liquid lithium at temperatures of ~ 1100K according to a compilation by Cowles and Pasternak,[6] and I anticipate that it will also be resistant to corrosion by liquid sodium and potassium. Fabrication and welding of vanadium and its alloys does not seem to present any problems as long as the interstitial (O, N and H) contents are low.[7]

Nb Alloys

Niobium and its alloys are well known for good corrosion resistance to liquid alkali metals,[8] ease of fabrication, good structural characteristics, and high tritium (hydrogen) permeation rates.[5] Niobium is therefore a good alternate material to vanadium as a tritium permeation membrane. It is also a candidate material for heat pipes and heat exchangers in the Cauldron dome.

β-Ti Alloys

The β-titanium alloys, especially those containing a fair amount of vanadium, provide a possible alternative to vanadium as a low-activation first wall material. There is insufficient information on the neutron radiation damage behavior of β-titanium to make a good judgement. However, it is encouraging that the tritium (hydrogen) diffusivity in β-titanium alloys is substantially higher than in the α-titanium alloys[9] so that hydrogen concentration buildups and degradation of the physical/mechanical properties of β-titanium should be substantially reduced in comparison with α-titanium. Pure titanium metal shows good corrosion resistance to liquid lithium at 1000-1200K,[8] and similar behavior can be expected with liquid sodium or potassium. Alloying additions of V, Cr, Fe, or Mo to stabilize β-titanium (thus avoiding the α-β phase transformation at 1155K) should not affect its corrosion resistance, although Al should be avoided or minimized since it is reactive with alkali metals. Fabrication and welding of both α- and β-titanium alloys in large complex structural units has been amply demonstrated.[10] The above characteristics of β- titanium alloys qualify it as the best current choice for the Cauldron wall material in contact with the liquid Li-Na.

Mo Alloys (TZM)

Molybdenum alloys, particularly TZM, have a distinct advantage in heat pipe and heat exchanger applications where high thermal conductivities are needed to minimize temperature drops. Molybdenum alloys also have high strengths and outstanding resistance to corrosion by liquid alkali metals.[8] Small-scale (up to ~3 cm in dia.) welding of molybdenum heat pipes and laboratory test capsules is well-established, but large component welds are not currently part of our technology. It seems appropriate to consider TZM as the best candidate for heat pipe or heat exchanger applications in the Cauldron dome.

In-800, In-800H

The Fe-Ni-Cr based alloys, In-800 and -800H, are good candidates for transport piping between the Cauldron and the thermochemical process because of their good creep strength in the temperature regime of interest. Also, Navzorov, working on an alloy with a composition of 62 Fe, 14 Ni, 21 Cr, 2.4 Si, 0.9 Mn, 0.16 C, which is roughly similar to In-800, found reasonably low corrosion rates in liquid sodium at temperatures up to 1173K.[11] Compatibility should be good with liquid potassium.

The alloy In-800H has been found by workers at the Ispra and General Atomic laboratories to have fairly good corrosion resistance in the presence of decomposing SO_3 gas and steam at 773-1173K.[12] They have found further that the corrosion resistance is improved markedly by coating the In-800H with aluminide.[12] Thus, use of an In-800H heat exchanger with liquid sodium on one side and decomposing SO_3 gas and steam on the other side is a possibility, but because of the extreme reactivity between sodium and the gas stream constituents, an accidental leak in the system would cause serious problems. Hence, design alternatives still need to be explored to develop a safe system.

Siliconized SiC

SiC currently presents the best prospect as a heat exchanger material. Siliconized SiC (a two phase composition consisting of a mixture of SiC and Si) is produced at the Norton and Carborundum companies and is especially suited for this type of application. This type of material, which contains about a 10-15 wt % excess of silicon metal, is impervious to gases, has a high thermal conductivity, high strength, good thermal shock resistance, and can be fabricated in complex shapes and bonded together to form heat exchanger assemblies.[12] Corrosion testing of SiC for 1121 h and Si for 592 h in 97 wt % H_2SO_4 at 673K at the Lawrence Livermore Laboratory showed no evidence of corrosion,[12] thus confirming the corrosion resistance of both SiC and Si for the H_2SO_4 boiler application. The corrosion resistance of SiC to liquid sodium and potassium, however, is probably poor, since SiC is reported to have poor corrosion resistance to liquid lithium.[6] Hence liquid sodium should not be used directly in a siliconized SiC heat exchanger for the H_2SO_4 boiler. The organic coolants from the plasma first wall and cooled structural wall regions of the Cauldron should be compatible with siliconized SiC, and are in the right temperature regime ($\geq$673K) for the H_2SO_4 boiler.

Summary

To summarize, a number of candidate materials have been identified for use in the Cauldron blanket design, and for interface components with the General ATomic Sulfur-Iodine Thermochemical Cycle. The best materials choices at present are the following: V alloys for the first wall, β-Ti alloys for the Cauldron wall in contact with liquid Li-Na, TZM Mo alloy for heat pipe and other heat transfer surfaces in the Cauldron dome region, V or Nb for tritium permeation membranes, In-800 for transport piping for liquid Na or K, In-800H with an aluminide coating for the heat exchanger surface in contact with decomposing SO_3 gas, and siliconized SiC for the heat exchanger used to boil concentrated H_2SO_4. A problem remains in the selection of the heat exchanger material in contact with liquid Na or K at the SO_3 decomposer interface. Although In-800H appears suitable, an intermediate heat exchange loop using high pressure He gas may need to be interposed for safety reasons. Although the materials choices given above appear to be the best at this time, changes may occur as our design develops, and as new materials information becomes available.

Table I. Current Materials Considerations for the Cauldron Blanket Design and the Interface with the General Atomic Sulfur-Iodine Cycle

MATERIAL	APPLICATION	PROS AND CONS
V Alloys	o First Wall o Feltmetal Insulator o T Permeation Membrane	o Good Resistance to Radiation Damage o Low Activation o Good Corrosion Resistance to Liquid Li, Na, K o High T Permeation Rates
Nb Alloys	o T Permeation Membrane o Heat Pipes	o Good Corrosion Resistance to Liquid Li, Na, K o High T Permeation Rates o Good Fabricability
β-Ti Alloys	o First Wall o Feltmetal Insulator o Cauldron Wall	o Resistance to Radiation Damage is Probably Good o Low Activation o Good Corrosion Resistance to Liquid Li, Na, K o High T Diffusion Rates
Mo Alloys (TZM)	o Heat Pipes o Heat Exchangers	o Very High Strength o Excellent Heat Conductivity o Excellent Corrosion Resistance to Liquid Li, Na, K o Good Small-Scale Fabricability o Problems in Large-Scale Fabrications
In-800, In-800H	o Transport Piping for Liquid Na, K o Heat Exchangers	o Good Creep Strength to 1150K o Good Corrosion Resistance to Liquid Na, K o Aluminide-coated In-800H Shows Good Corrosion Resistance to SO_3
Siliconized-SiC	o Heat Exchanger for H_2SO_4	o Excellent Compatibility with Boiling H_2SO_4 at 673K o Compatibility with Liquid Na or K is Probably Poor

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