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An evaluation of potential material–coolant compatibility for applications in advanced fusion reactors

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Abstract

In assessing possible potential issues for fusion applications, the compatibility of several metallic structural materials was examined using high temperature/pressure steam as test environment. High corrosion resistance associated with protective oxide film formation was regarded as essential for the function of protecting from tritium permeation and corrosion damage. A Ti–Al-based intermetallic compound with V addition, recently developed, showed excellent performance. A low-activation ferritic/martensitic steel, F82-H, was comparable with the current advanced materials for modern supercritical fossil boilers, while some potential vanadium alloys, although not intended for use in steam, were found less compatible.

1. Introduction

1.1. Background

Materials programs in the basic research phase are not always aware of the issues in ultimate service requirements. Before evolving into an engineering phase, specific reactor design windows must be referred to. For a reactor designer, the current choice of a material-coolant system is confined in the following sets of combinations [1]:

Materials	Coolant
• Austenitic steels,	
• Ferritic/martensitic (F/M) steels,	• Liquid (Water, liquid metal/e.g., lithium)
• Vanadium (V) alloys,	
• Ceramics and their composites,	• Gas (helium)
• Intermetallic compounds	

Common issues in energy systems design are the needs of higher service temperatures and lower failure risks. These requirements are generally contradictory to each other, unless either the material, coolant or their combined behavior are improved. Then what option can really be potential at the moment?

Engineering experience indicates that the issues of chemical compatibility as well as mechanical strength are among the most critical. Radiation effects are connected with those properties, but the effects themselves are generally less strictly handicapped by temperature shift. In the chemical compatibility aspect, ferritic/martensitic steels can be compatible with water at light water reactor operating temperatures. However, at temperatures above 647 K (374°C), the critical point for liquid water, one can pick only helium, unless superheated steam is considered. Vanadium alloys have potential for higher operating temperatures in conjunction with liquid metal coolants. For materials in the pre-engineering stage, such as SiC composites and Ti–Al, coolant selection is still premature.

1.2. Objectives

An experimental evaluation was carried out of the compatibility of some candidate fusion structural

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materials using high pressure superheated steam as test environment. Testing the materials in steam has dual incentives. Firstly, tritium oxide vapor is expected to affect structural materials when helium is used to sweep solid breeders in the blanket. Effects expected are corrosion, tritium trapping and permeation. Secondly, it is interesting to explore the potential applicability of superheated steam as coolant at least in the side of transmitting heat to the power generating system of an advanced fusion reactor.

The technology basis for super critical steam is well established. Its attractive features relative to other coolants are, a higher heat capacity than helium, greater flexibility in temperature/pressure combination, and less complex corrosivity than liquid water. There is also a lower hazard potential than with liquid metals. Further, heat-resisting steels used in the advanced fossil boilers have a common origin with the low activation ferritic/martensitic steels for fusion. The performance of Ti–Al-based intermetallic compounds is especially of interest as there is a theoretical expectation of good resistance to oxidation by the formation of protective Ti–Al spinel oxide film in high temperature steam. Such film can also be a good barrier to tritium permeation [2].

2. Experimental

2.1. Materials

Oxidation resistance in high pressure superheated steam was investigated for three types of candidate materials for fusion first wall application, a low-activation steel F82H, vanadium alloys, and TiAl-based intermetallic compounds. The excellent high-temperature strength of TiAl is well known, and in addition to that, an interesting response of a TiAl alloy to irradiation, an increased ductility due to irradiation, has recently been found [3]. It is further of interest that V addition to a TiAl improves its strength and also ductility over wide range of temperatures [4]. The TiAl–V alloy used in this study has an yield strength of 950 MPa and about 50% of elongation at 600°C. One version of this material shows more than 7% elongation even at room temperature with 800 MPa of yield strength. Table 1 shows the chemical compositions of the materials used in this study. For comparison, several heat-resisting steels for main steam pipes and heat exchanger tubes in modern fossil power generation plants were also tested [5]. STBA 24 has been used most widely as heat exchanger tubes in a conventional boiler and its service temperature is typically around 560°C. HCM12A, NF616, and HCM2S are the current candidate materials for advanced boilers. Expected service temperature is 600°C to 610°C for HCM12A and NF616. Both HCM12A and NF616 have a ferritic/martensitic microstructure and chemical compositions again similar to F82H.

2.2. Experiments

Oxidation tests were performed in high-pressure superheated steam on the five kinds of structural candidate materials. The tests were performed for up to 300 h at 650°C (923 K) and 85 atm (8.6 MPa) using a specially designed static autoclave made of Type 316 stainless steel. The tests were interrupted several times for gravimetric measurements. The specimens, after removal from the test rig, were dried in an evacuated desiccator,

Table 1
Chemical compositions of materials used in this study (wt%)

		Al	Fe	Si	O	N	V	Ti		
Intermetallic compounds	TiAl	33.7	0.02	0.02	0.48	0.30		Balance		
	TiAl–V	23.64			0.042		13.3	Balance		
		Ti	Cr	Fe	Si	V				
Vanadium alloys	VM9401	4.32	4.33		0.12	Balance				
	VM9502	3.96		2.92	0.04	Balance				
		C	Mn	Si	Cr	Mo	W	Ta	V	Fe
Low activation f/m steel	F82H	0.09	0.49	<0.1	7.65	<0.01	2.00	0.04	0.18	Balance
		C	Si	Mn	Ni	Cr	Mo	W	V	Nb
Heat resisting steels for advanced fossil boilers	HCM12A	0.10	0.09	0.57	0.31	10.65	0.37	2.0	0.20	0.05
	NF616	0.12	0.25	0.42		9.02	0.38	1.80	0.18	0.06
	HCM2S	0.05	0.21	0.49		2.17	0.11	1.59	0.23	0.05
	STBA24 [a]	0.12	0.3	0.45		2.25	1.0			

[a] Conventional boiler steel.

weighed by a micro-balance, and put back in the autoclave again.

After the oxidation tests, the surface and cross section of the specimens were examined using scanning electron microscope (SEM) equipped with a field emission gun and an energy dispersive X-ray micro-analyzer (EDX). Oxides formed on the surface were also analyzed for a few selected samples using micro-probe Raman spectroscope and X-ray diffraction (XRD) technique.

3. Results and discussion

3.1. Oxidation kinetics

Mass gains due to oxygen pick-up of the intermetallic compounds, TiAl, TiAl–V and the low-activation steel, F82H in the superheated steam condition are plotted as a function of exposure time in Fig. 1. The results on F82H followed the parabolic rate law similarly to the typical oxidation behavior of the boiler tubing materials. Although TiAl and TiAl–V showed a much lower mass gain and rate than that of F82H in the 300 h test, the addition of V to TiAl resulted in an improved oxidation resistance. Although TiAl–V followed the parabolic low, the oxidation rate of TiAl seemed to break-away after 170 h, suggesting loss of the protective function of the oxide film. Both V-alloys were disintegrated at very early stage of the oxidation test. To examine the oxidation kinetics more quantitatively, the square of mass gains was plotted as a function of exposure time for F82H and TiAl–V in Fig. 2. Good linearity in the plot confirms the parabolic nature of the oxidation rate of both materials, and the slopes of the plot give the parabolic rate constant, K_p. K_p for F82H and TiAl–V were compared with those of the boiler tubing materials obtained in the authors' laboratory [5] in Fig. 3. K_p of heat-resisting steels

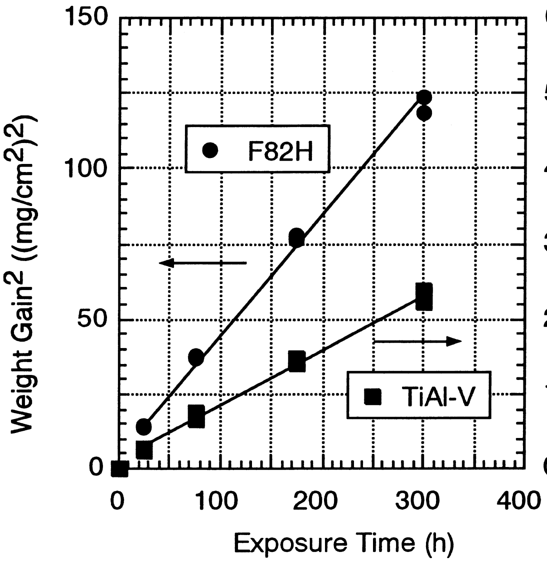

Fig. 2. Parabolic plot of mass gain of candidate materials.

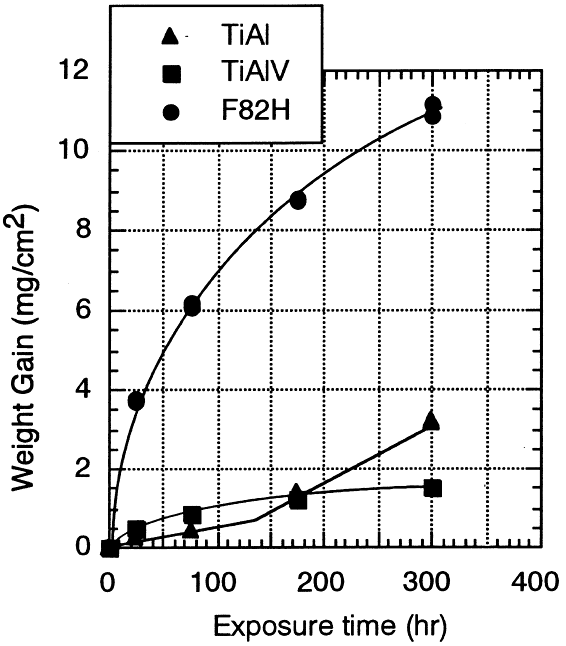

Fig. 1. Mass gain of candidate materials as a function of time in a superheated steam.

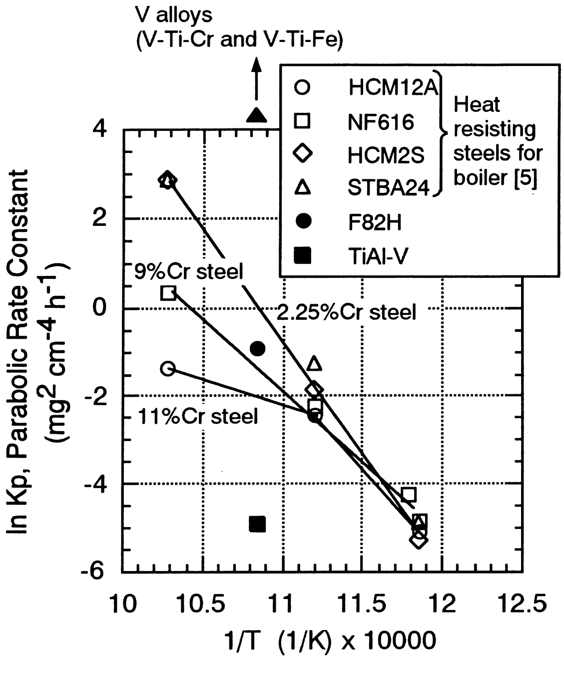

Fig. 3. Comparison of parabolic rate constants of candidate materials with those of heat-resisting steels.

are known to mainly depend on Cr content [6]. F82H which contains 7.65% Cr showed K_p values similar to the series of boiler tubing materials consistent with Cr-content. The present results suggest that the oxidation resistance of F82H in superheated steam can be equivalent to the boiler tubing materials for the advanced fossil power plant. K_p was much smaller for TiAl–V.

3.2. Composition and structure of oxide layer

Double-layered oxide films with an Fe-rich outer layer and Cr enrichment in the inner layer were formed on F82H. This is again very similar to the boiler tubing steels. It is known that the separation of Fe-rich outer layer and Cr-rich inner layer is due to higher diffusion rate of Fe ions over Cr ions and that the inner layer is a better diffusion barrier, and it mainly contributes to the oxidation resistance of the steels.

Fig. 4 shows SEM micrographs of cross sectional surface regions of TiAl and TiAl–V after 300 h exposure to the superheated steam and the composition profiles. For TiAl, two or possibly three layers of oxide film formed. SEM/EDX analysis showed that Al was enriched in the inner layer, and the outer layer was a Ti-rich oxide containing an extremely low concentration of Al. These compositional characteristics of the oxide films are similar to those formed in air [7]. The oxide film formed on TiAl–V was thinner compared with TiAl case. This observation is consistent with the mass gain results. In the case of TiAl–V, no clear separation of layers was observed with SEM. The compositional profile also suggested mono-layer structure of the oxide film, namely, all the three elements, Ti, Al, and V, were detected in the proportion without significant change from the original metal throughout the thickness of the oxide layer. Outer layers of TiAl and TiAl–V were analyzed using Raman spectroscope and XRD for better resolution of the effects of V-addition on oxidation. From the analysis, two distinct differences in surface oxide structures were found between the two TiAl-based alloys. First, the outer layer oxide on TiAl was identified to be TiO_2 (Rutile type), while the TiO_2 (Anatase type) formed on TiAl–V was of a somewhat different in crystal type. Second, the XRD analysis showed the presence of

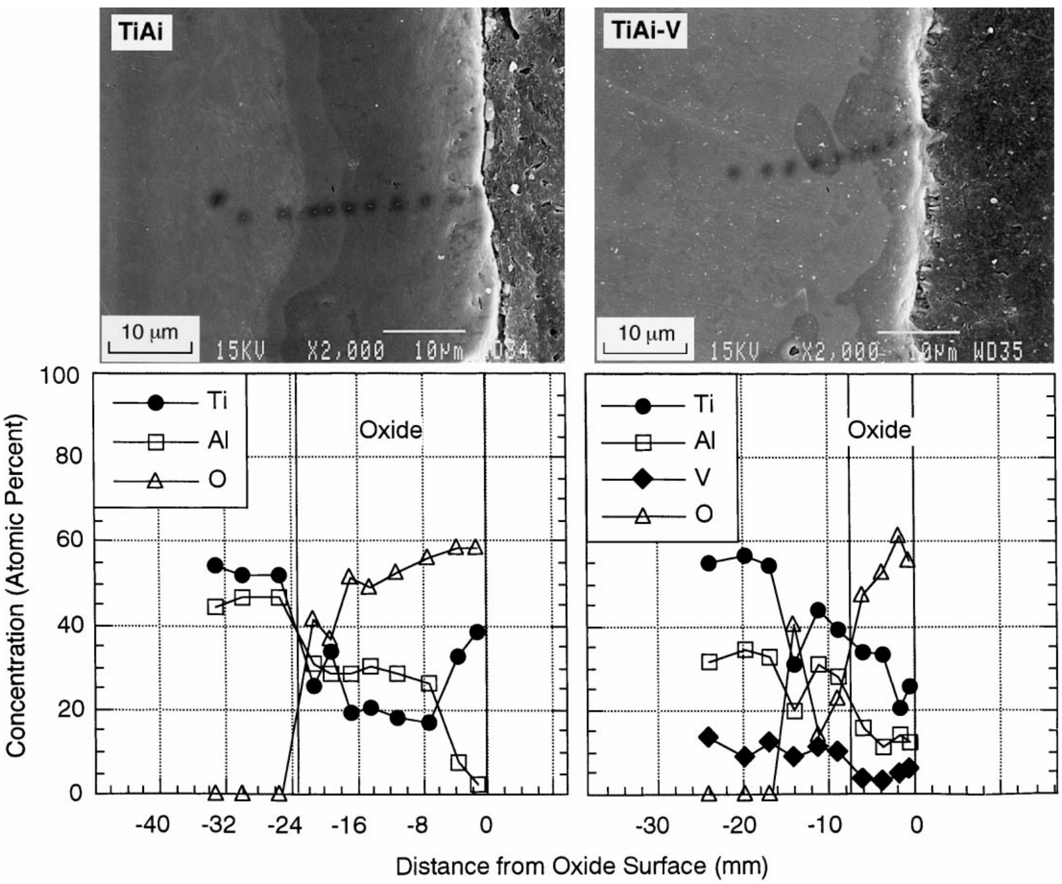

Fig. 4. SEM micrographs and oxide composition profiles of TiAl and TiAl–V.

oxide containing Al and V on TiAl–V, which was also consistent with the SEM/EDX result.

These facts suggest that the V-addition to TiAl modifies the oxide structure in the direction of improving the protective function of ionic transport, and possibly to provide a better diffusion barrier of tritium and hydrogen.

3.3. Compatibility with superheated steam

One of the attractions of using superheated steam as a coolant from the system design point of view is that service temperatures can be higher due to the flexibility in the temperature/pressure combination. To take advantage of this superheated steam, corresponding improvements in both mechanical properties and corrosion resistance of materials at elevated temperature are needed. F82H is expected to perform equivalently to the advanced boiler steels in both mechanical and oxidation properties. F82H, by the way, is almost equivalent to the advanced boiler steels in chemical compositions and in microstructure. A TiAl-based intermetallic compound was reported to have much better potential in high-temperature strength and resistance to irradiation degradation [3] but also for oxidation resistance. TiAl–V possesses an improved corrosion resistance. The excellent corrosion resistance as demonstrated with the rate constant approximately two orders of magnitude less than those for boiler steels, was due to the highly protective oxide layer formed on TiAl–V. The current technology considers the use of protective coatings on some structural metals. Typically, an oxidized aluminide coating as thick as 80 μm was reported to provide a very effective tritium barrier [3]. The oxide film on TiAl–V is inherently self-healing and is expected to provide a more dependable barrier in an oxidizing environment to minimize tritium permeation. Extensive future study is worthwhile to prove this speculation.

There is another question which still remains open at this stage regarding to the possible effects of hydrogen or tritium on the mechanical properties of TiAl–V at the temperatures of interest.

4. Conclusions

The compatibility of candidate materials for first wall applications with superheated steam has been investigated. The following conclusions can be drawn.

1. TiAl has been found highly resistant to oxidation in superheated steam.
2. Improved corrosion resistance was demonstrated with V-modified TiAl.
3. The oxide structure was modified by the addition of V to TiAl.
4. The oxidation rate of F82H was comparable to the advanced fossil boiler materials.
5. V alloys disintegrated in a rather short time.

The results suggest the potential applicability of TiAl–V and superheated steam in a material–coolant system for advanced fusion reactors.

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