OXIDATION OF V-4Cr-4Ti ALLOYS CONTAINING Al, Si, and Y*

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OBJECTIVE

The objectives of this task are to (a) evaluate the oxygen uptake of several V-4Cr-4Ti alloys with additions of 0.5 wt.% Si, or Al, or Y as a function of temperature and oxygen partial pressure in the exposure environment and compare the uptake with that of the base alloy without alloying additions; (b) examine the microstructural characteristics of oxide scales and oxygen trapped at the grain boundaries in the substrate alloys; and (c) evaluate the influence of alloy composition on oxygen uptake and develop correlation(s) between alloy composition, exposure environment, and temperature.

SUMMARY

A systematic study has been conducted to determine the effects of time and temperature on the oxidation behavior of Si-, Al-, and Y-modified V-4Cr-4Ti alloys. All samples were from 0.80-mm-thick cold-rolled sheets, and each was annealed in vacuum at 1000°C for 1 h prior to high-temperature exposure. Different samples from each alloy were heated in air between 400 and 620°C for times up to a few hundred hours. Weight change data were used to evaluate the kinetics of oxidation process in the modified alloys, and the rate constants were compared with data developed earlier on base alloy.

INTRODUCTION

Refractory alloys based on V-Cr-Ti are being considered for use in first-wall structures in advanced blanket concepts that employ liquid Li as a coolant and breeding material. Further, advanced concepts that use He as a coolant also require structural alloys such as V-Cr-Ti alloys that can withstand the thermal loading at high temperature. Interstitial impurity atoms such as oxygen can affect both irradiation behavior and baseline properties of the alloys. Therefore, oxidation performance of V-4Cr-4Ti alloy with simultaneous additions of Si, Al, and Y has been examined in air at 300-700°C. Alloying additions of 0.1, 0.3, and 0.5 wt.% of each of the three elements have been included in the study [1]. The base and modified alloy specimens of 0.22-mm thickness exhibited negligible weight changes after 1 h oxidation at 300°C. The change in Vickers microhardness number was ≈5. After oxidation at 500°C, the specimens exhibited some increase in weight, and the hardness number increased by ≈60 and was similar for both the base and the modified alloys. After oxidation at 700°C for 1 h, all alloys exhibited significant weight increase, and the modified alloys showed more uptake of oxygen than the base alloy. Furthermore, the results showed that oxygen uptake increased as the concentration of the alloying elements increased from 0.1 to 0.5 wt.%, but the difference was small when compared with the total weight change. The Vickers hardness number

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increased by ≈325 for the base alloy after oxidation and it was reported that the modified alloy surfaces were too rough to allow reliable measurement [1].

The purpose of the present work is to evaluate the oxidation behavior of V-4Cr-4Ti alloys with individual additions of Si or Al or Y over longer time periods and to compare their performance with that of the large heat of V-4Cr-4Ti alloy fabricated by Argonne National Laboratory.

EXPERIMENTAL PROGRAM

The alloys selected for evaluation included V-4Cr-4Ti alloy from Heat #832665 (from ANL) and V-4Cr-4Ti alloys with additions of 0.5 wt.% Si, or Al, or Y (from Tohoku University, Japan). The modified alloys were obtained in ≈0.8-mm-thick sheets. Samples measuring about 0.8 x 10 x 10 mm were cut from each alloy. Before any further treatment or testing, all samples were annealed for 1 h at 1000°C in vacuum at $<10^{-6}$ torr. The samples were wrapped in titanium foil to protect them from contamination during this heat treatment process. Samples from each alloy were heated in a thermogravimetric test apparatus (TGA) in air at different temperatures to determine oxidation kinetics as a function of temperature. The TGA experiments were carried out at 400, 500, and 620°C. Weight gain was recorded continuously on a strip chart throughout each experiment [2,3]. All samples were also weighed separately before and after any high-temperature exposure to determine the resulting total weight change. We plan to measure the hardness variation in the thickness direction in several of the oxidized specimens. Also, metallographic examination of the exposed specimens and X-ray diffraction analysis of the oxide scales on several of the specimens are planned.

RESULTS

Extensive studies were conducted on the oxidation kinetics of V-4Cr-4Ti and V-5Cr-5Ti alloys over a temperature range of 300-650°C; the results were reported earlier [2-4]. The current oxidation study on the modified V-Cr-Ti alloys supplements the data developed earlier on those two alloys. Figure 1 shows normalized weight changes (in mg/mm^2), obtained by TGA, of the modified V-Cr-Ti alloys in air at temperatures of 400-620°C. Data obtained earlier on V-4Cr-4Ti base alloy are also shown in this figure for comparison [3]. The curves show that oxidation follows parabolic kinetics at all temperatures. The data also show that Al and Y additions seem to decrease the oxidation rate of the alloy when compared with that of base alloy. The effect of Si addition on oxidation is negligible at 400°C, probably because Si is present in both the base alloy (≈750 wppm Si) and modified alloy (≈5000 wt.%). However, at 500 and 620°C, the modified alloy showed significant reduction in rate when compared with those of base alloy. The results also showed that additions of any of the three elements improved oxidation resistance in air.

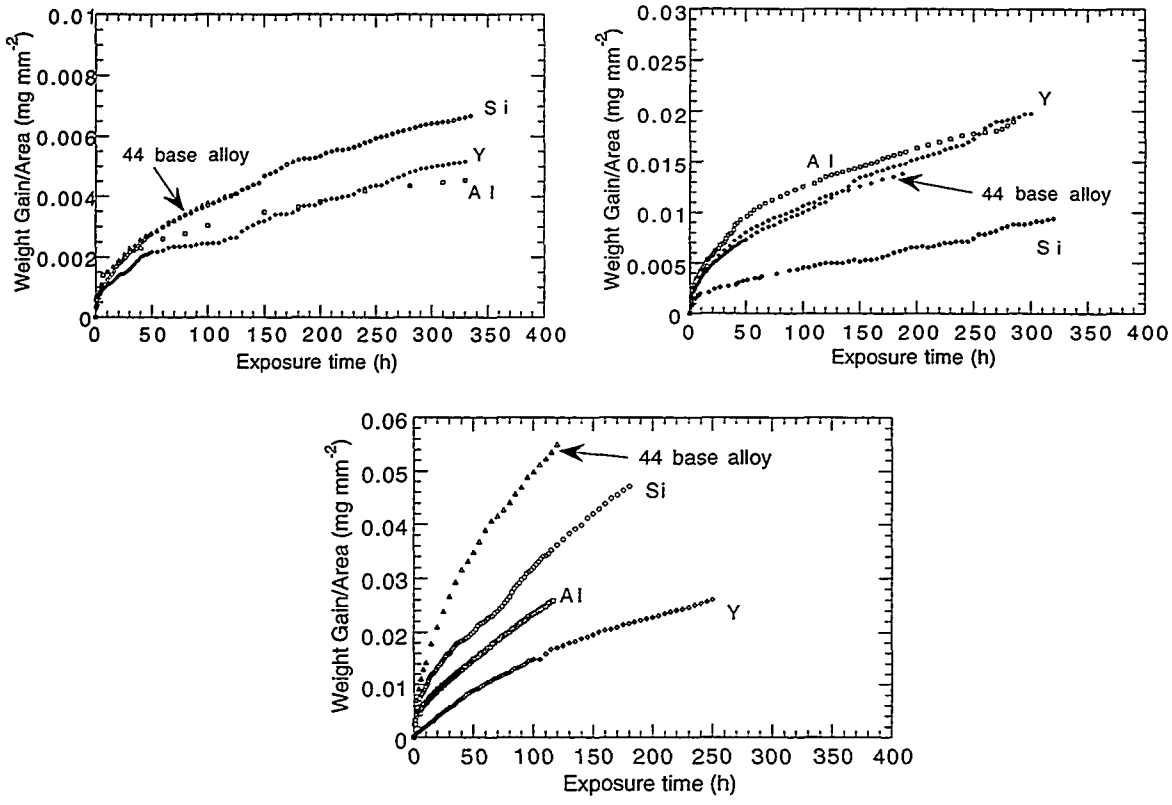

Figure 1. Thermogravimetric weight change data for Si-, Al-, and Y-modified V-Cr-Ti alloys exposed to air at 400 (top left), 500 (top right), and 620°C (bottom).

Figure 2 shows replots of weight change data as a function of square root of exposure time. In general, the data can be fitted by straight lines, indicating a parabolic kinetics. Table 1 lists the parabolic rate constants derived from the present data for the modified alloys along with data reported earlier for the base alloy. Additional oxidation experiments are in progress in low-pO_2 and in high-purity He environments at 500°C, to evaluate the role of reduced pO_2 in the oxidation process.

Table 1. Parabolic rate constants for base and modified alloys derived from air-oxidation data

Alloy	Parabolic rate constant (mg/mm^2) at		
	400°C	500°C	620°C
V-4Cr-4Ti	3.8×10^{-4}	1.1×10^{-3}	5.0×10^{-3}
V-4Cr-4Ti-0.5 Si	3.8×10^{-4}	4.8×10^{-4}	3.2×10^{-3}
V-4Cr-4Ti-0.5 Al	2.8×10^{-4}	1.2×10^{-3}	2.2×10^{-3}
V-4Cr-4Ti-0.5 Y	2.8×10^{-4}	1.1×10^{-3}	1.5×10^{-3}

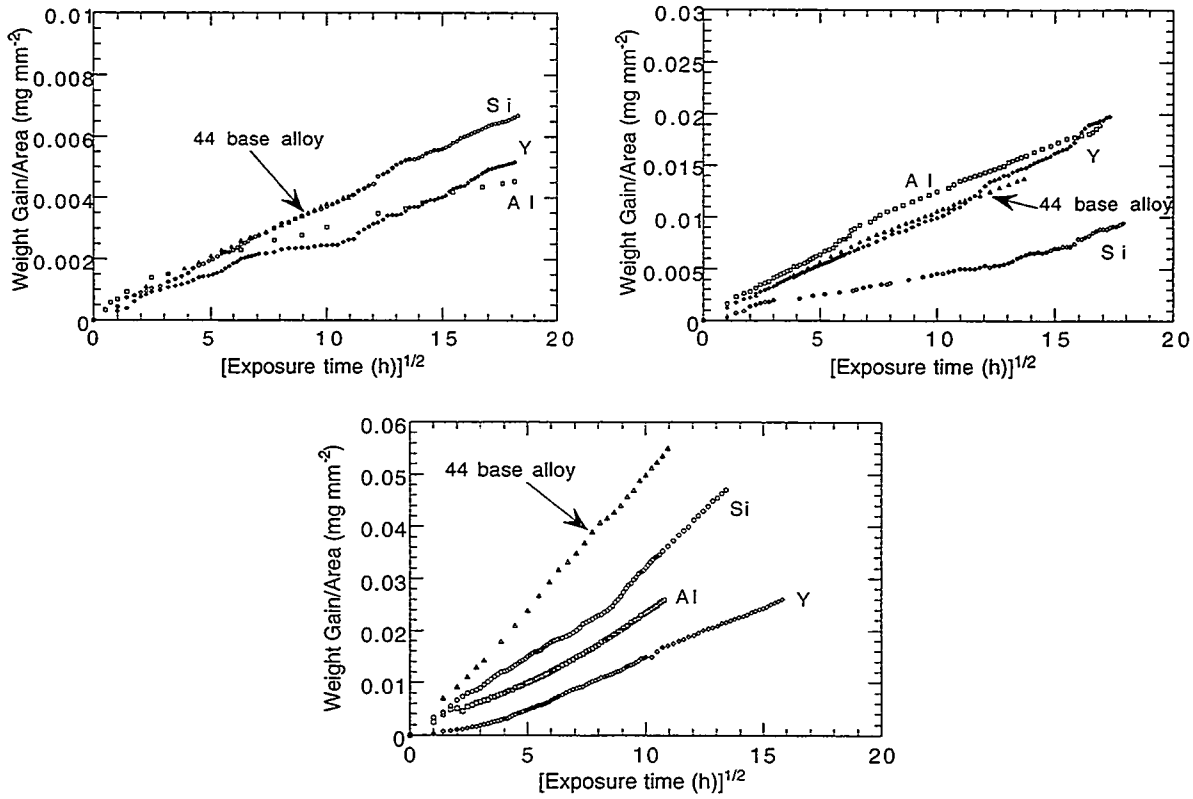

Figure 2. Weight change data plotted against square root of exposure time for Si-, Al-, and Y-modified V-Cr-Ti alloys exposed to air at 400 (top left), 500 (top right), and 620°C (bottom).

REFERENCES

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