

# On the interdiffusion in multilayered silicide coatings for the vanadium-based alloy V-4Cr-4Ti



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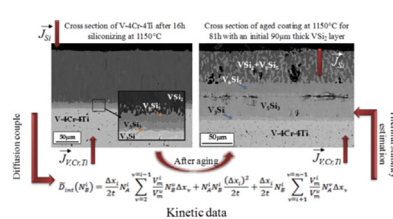
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## HIGHLIGHTS

- The pack cementation technique is implemented to study interdiffusion in V/Si and V-4Cr-4Ti/Si couples.
- Interdiffusion coefficients of vanadium silicides were experimentally determined within the range 1100–1250 °C.
- For either V/Si or V-4Cr-4Ti/Si couples, the VSi<sub>2</sub> layer has the highest growth rate.
- The Cr and Ti alloying elements mainly modified the V<sub>5</sub>Si<sub>3</sub> and V<sub>6</sub>Si<sub>5</sub> growth rate.
- Numerical simulation allows for a confident assessment of the VSi<sub>2</sub> coating lifetime on V-4Cr-4Ti.

## GRAPHICAL ABSTRACT



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## ABSTRACT

To provide protection against corrosion at high temperatures, silicide diffusion coatings were developed for the V-4Cr-4Ti alloy, which can be used as the fuel cladding in next-generation sodium-cooled fast breeder reactors. The multilayered coatings were prepared by halide-activated pack cementation using MgF<sub>2</sub> as the transport agent and pure silicon (high activity) as the master alloy. Coated pure vanadium and coated V-4Cr-4Ti alloy were studied and compared as substrates. In both cases, the growth of the silicide layers (V<sub>3</sub>Si, V<sub>5</sub>Si<sub>3</sub>, V<sub>6</sub>Si<sub>5</sub> and VSi<sub>2</sub>) was controlled exclusively by solid-state diffusion, and the growth kinetics followed a parabolic law. Wagner's analysis was adopted to calculate the integrated diffusion coefficients for all silicides. The estimated values of the integrated diffusion coefficients range from approximately 10<sup>-9</sup> to 10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup>. Then, a diffusion-based numerical approach was used to evaluate the growth and consumption of the layers when the coated substrates were exposed at critical temperatures. The estimated lifetimes of the upper VSi<sub>2</sub> layer were 400 h and 280 h for pure vanadium and the V-4Cr-4Ti alloy, respectively. The result from the numerical simulation was in good agreement with the layer thicknesses measured after aging the coated samples at 1150 °C under vacuum.

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## 1. Introduction

In the past, vanadium-based alloys were widely studied in the scope of fusion applications [1–5]. Currently, vanadium alloys have

experienced a revival in interest and are considered promising candidates as structural materials for future nuclear systems known as generation IV nuclear systems. Recently, the French agency CEA (Commissariat à l'Énergie Atomique) conducted a research program to evaluate the potential of V-4Cr-4Ti as a fuel cladding in the Sodium Cooled Fast Reactors (SFRs) [6,7]. Vanadium provides good mechanical properties at high temperatures, and environmental and safety advantages associated with its low activation characteristics [8]. It is also characterized by a favorable behavior under irradiation (inducing swelling and embrittlement of many metallic materials) over a wide temperatures range [9]. However, vanadium and its alloys suffer from a poor oxidation resistance at high temperatures even in oxygen-rarefied environments. The oxidation of vanadium results in the formation of a porous and unprotected oxide layer with high oxidation rates [10–12]. Furthermore, the mechanical properties of vanadium alloys vanish because of the high solubility of oxygen in vanadium at elevated temperatures (max. solubility ~10% at.), which induces embrittlement [13,14].

The oxidation resistance of V-4Cr-4Ti at moderate temperatures (up to 700 °C) can be slightly enhanced by optimizing the composition with small additions (~0.5% wt.) of Si, Al or Y [15]. Recently, a solution for protecting the V-4Cr-4Ti alloy, which consists in four-layered silicide coatings, was developed using a pack cementation process [16,17]. The silicide layers that constitute the coating are described in the V-Si binary phase diagram and designated as follows: VSi<sub>2</sub>, V<sub>6</sub>Si<sub>5</sub>, V<sub>5</sub>Si<sub>3</sub> and V<sub>3</sub>Si. It was also showed that vanadium coated by silicides is a viable approach to prevent contamination by oxygen in several environments [18,19] (impure He, liquid Na and air). The coated V-4Cr-4Ti exhibits a very low oxidation rate up to 1100 °C in isothermal and cyclic conditions as a result of the formation of a protective SiO<sub>2</sub> layer. Such high temperatures are not encountered in normal operating conditions in the 4th generation reactor using Na coolant but could be reached in case of incident occurrence on the reactor cooling system. Because previous observations [19] have revealed important thickness changes and microstructural evolutions at temperatures above 1000 °C, it was of interest to quantify the interdiffusion between the silicide layers as a result of the chemical potential gradient between the coating and substrate. The objectives of this study are as follows: i) to determine the growth kinetics and interdiffusion coefficients for the silicide layers in the V/Si and V-4Cr-4Ti/Si systems and ii) to evaluate the thermodynamic stability of the coating/substrate system at 1150 °C using a diffusion-based approach to calculate the coating lifetimes on both substrates (pure V and the V-4Cr-4Ti alloy).

## 2. Materials and methods

Coatings were manufactured by chemical vapor deposition using the halide-activated pack cementation technique. A full description of the chemical reactions that occur is given in Ref. [17]. The gas phase containing the element(s) to deposit and the substrate can be compared to terminal phases of a semi-infinite diffusion couple. Before coating, parallelepiped samples (10 × 10 × 1.5 mm<sup>3</sup>) were cut from a pure vanadium foil (V 99.8% wt.; Fe 280; Al 165; O and Si 220; N 90; C 21; Cr, Hf, Nb, P, Ta, Zr, Ti, Ni, Mo < 50; B < 25; S < 10; H < 3; U < 1 all data in ppm (reference Alpha Aesar #11097)) and a V-4Cr-4Ti ingot [7] manufactured by GfE Metalle und Materialien GmbH. Prior to the pack cementation process, the samples were prepared by grinding the surface with silicon carbide abrasive papers down to 2400 grits, rounding the corners, cleaning ultrasonically in acetone then in ethanol and drying the samples with hot air. The samples were introduced in silica tubes sealed under vacuum (~5 10<sup>-6</sup> mbar) with a pack

powder mixture containing the high-activity master alloy (pure silicon). The coating deposition process was undertaken for three durations (9, 16 and 25 h) at 1100 °C, 1150 °C, 1200 °C and 1250 °C for both substrates.

The coated samples were then cleaned, cross-sectioned, cold mounted in epoxy resin and prepared with conventional methods for metallographic examination by optical and electronic microscopy. The chemical identification of the phases was performed by EDS and EPMA using appropriate standards for calibration. Thicknesses were measured by using SEM for a precise determination of the layer growth rates.

## 3. Results

### 3.1. Microstructure of the diffusion couples

Fig. 1a and b shows the cross sections of the coatings obtained on pure vanadium and V-4Cr-4Ti, respectively, after a siliconizing treatment performed at 1150 °C for 25 h. In the temperature range of 1100 °C–1250 °C, all vanadium silicides described by the V-Si binary phase diagram were observed ([29] for more detailed about characterization of silicide layers). The outer VSi<sub>2</sub> phase is the thickest layer while the inner layers grow much more slowly. The main difference between the two diffusion couples (V/Si and V-4Cr-4Ti/Si) is related to the thickness of the inner V<sub>6</sub>Si<sub>5</sub> and V<sub>5</sub>Si<sub>3</sub> layers. Specifically, it is observed that the thickness of the V<sub>5</sub>Si<sub>3</sub> layer decreases while that of V<sub>6</sub>Si<sub>5</sub> significantly increases during the growth of the silicides on the V-4Cr-4Ti substrate.

The interface between the V<sub>6</sub>Si<sub>5</sub> and VSi<sub>2</sub> layers in the coating formed on the V-4Cr-4Ti substrate is strongly perturbed in comparison to that on the pure vanadium substrate, where interfaces parallel to the initial one were observed. It is also important to note that on pure vanadium, a very thin and discontinuous layer of V<sub>6</sub>Si<sub>5</sub> forms at 1100 °C along the V<sub>5</sub>Si<sub>3</sub>/VSi<sub>2</sub> interface. Thus no thickness measurement was carried out for this layer at this temperature.

### 3.2. Growth kinetics

The thicknesses of the silicide layers are directly measured on cross sections of the diffusion couples V/Si and V-4Cr-4Ti/Si.

Assuming that the deposition process is governed by the solid-state diffusion, the thickness variation ( $\Delta x$ ) of each layer should follow Equation (1):

$$\frac{d\Delta x}{dt} = \frac{k_p}{\Delta x} \quad (1)$$

The integration of this equation gives:

$$\Delta x^2 = 2k_p t \quad (2)$$

where  $k_p$  is the apparent parabolic constant (called also the rate constant of the first type [20]) and  $t$  is the annealing time at a given temperature  $T$ . Rate constants for each layer are directly deduced from the linear regression of the plot of the thickness variation versus the square root of the annealing time. An example is given in Fig. 2 for pure vanadium (a) and the V-4Cr-4Ti alloy (b) at 1150 °C. The points represent an arithmetic mean of the thicknesses measured at different zones for samples obtained, respectively, after 9, 16 and 25 h of siliconizing. The rate constants were similarly deduced from the plot of the thickness variation vs. the square root of the annealing time at 1100, 1200 and 1250 °C. The data are presented in an Arrhenius plot in Fig. 3.

The values of the parabolic constants range approximately between 10<sup>-13</sup> and 10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup> from 1100 to 1250 °C. The data

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