Investigation of phases and textures of binary V-Si coating deposited on vanadium-based alloy (V-4Cr-4Ti) using electron backscatter diffraction

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Abstract. Barrier coating consisting of binary silicide compounds Si₅V₆ were deposited on a V-4Cr-4Ti vanadium alloy substrate. Samples were cycled in a furnace for 122h at 650°C and 1100°C. The electron backscattered (EBSD) combine with X-ray energy dispersive spectrometry (EDS) techniques were employed to identify the phases in the multi-layered coating and to determine growth texture for each phase. The microstructure evolutions occurring during cycling at 1100°C in the protective coating and the crystal orientation relationships between Si₅V₆ were determined.

1. Introduction
The low capture cross-section for thermal neutrons and the capability of vanadium to withstand high temperatures makes vanadium attractive as structural material for fuel cladding either in gas- or sodium-cooled fast reactors in generation IV nuclear systems. However, an oxygen concentration as low as 1 ppm in Na [1] at 550°C is required to avoid oxygen embrittlement of vanadium. Thus, a diffusion barrier for oxygen based on a multilayered silicide coating was developed [2]. It was demonstrated [3] by oxidation tests in air and low-O₂ environments that this type of coating is very efficient in preventing embrittlement by oxygen in the expected operating temperature range of 550 to 750°C. Moreover, it was compatible with liquid Na (10 ppm O₂) during 1000h at 550°C. To further validate the capability of this system for cladding application, its behaviour was also evaluated under severe conditions that could arise in case of accidental overheating [4]. In these cases temperatures as high as 1000°C in liquid Na can be reached. The microstructure evolution and origin of failure in these conditions has to be fully analysed and understood.

The electron backscattered technique (EBSD) combined with electron dispersive spectroscopy (EDS) was employed to characterize the multilayered silicide coating, in terms of phase distribution, growth texture for each phase as well as orientation relationships between the silicide layers. The present communication reports this microstructure characterisation work on two coated specimens after cyclic oxidation tests: 1) After 122 1h-cycle at 650°C in air. This specimen did not undergo much change from the “as deposit” state, 2) After 430 1h-cycle at 1100°C which corresponds to severe accidental overheating conditions.

2. Material and methods
V-4Cr-4Ti substrate was provided by GfE Metalle und Materialien GmbH, Nuremberg, Germany; the manufacturing process is detailed elsewhere [5]. Coupons 10 mm × 10 mm × 1 mm were cut from a rolled plate and recrystallised at 1000°C. Then polished down to 1200 grit SiC paper and their corners rounded. The silicide coating was deposited onto the coupons by halide-activated pack cementation [2].

Cyclic oxidation tests were performed on the coated samples in a tubular furnace in air for a 1-h cycle at 650°C and at 1100°C. The specimens were then removed from the furnace, between
each cycle, cooled for 10 min at room temperature and weighed. Cyclic oxidation conditions allowed for the evaluation, in a single experiment, of both the oxidation resistance of the coating and the effect of thermo-mechanical stresses applied to the coating-substrate system. The 650°C sample was cycled 122 times, while the 1100°C sample was cycled 430 times. After the test, the oxidized samples were cut transversally, embedded in epoxy resin, manually ground using wet SiC paper down to 4000 grit. Then the samples were polished to 0.4 µm silica colloidal solution and cleaned with warm water. In the last step of polishing, H₂O₂ was added to the colloidal silica. The polished samples were cleaned with warm water, acetone, ethanol, dried in air and then coated with carbon.

The Oxford Instruments NordlysNano EBSD detector combined with an X-Max80 EDS detector coupled with Oxford Instruments AZtec software, attached to a FEG-SEM was employed for phase identification and microstructural characterization. The FEG-SEM was operated at 20kV acceleration voltage.

3. Results and discussion

3.1 Phase Identification
Figure 1 shows a calculated Si-V phase equilibrium diagram, using MTDATA [6] and the Scientific Group Thermodata Europe (SGTE) Solution Database. This indicates the existence of the following: Si₂V, Si₅V₆, Si₃V₅ and SiV₃ phases. A phase database was created for these phases using TWIST in CHANNEL5 and used for phase search and indexing the EBSD Kikuchi patterns obtained from the various phases found in the coating. PhaseID module from AZtec software was used for phases identification. Crystal structure details for these phases were taken from Pearson’s Handbook [7]. The similar diagram was also proposed by C. Zhang et al. [8].

![Figure 1: Si-V equilibrium phase diagram, calculated using MTDATA [6] and the Scientific Group Thermodata Europe (SGTE) Solution Database](image)

Figure 2 shows a SEM image from a section of the coating. EDS quantitative results from the points shown in Figure 2 are summarized in Tables 1. It is clear from these results that all the four phases predicted in the phase diagram were found to exist in the coating. The EDS quantitative results show that low levels of Ti and Cr have partitioned into these phases and the atomic ratios of V to Si are close to the theoretical values, despite the data being acquired at 70 degree tilt angle used for EBSD. A summary of the phases identified is given in Table 1.
Figure 2: SEM images from analyzed samples: a) after 122 cycles (1h-cycle) at 650°C, b) after 430 cycles (1h-cycle) at 1100°C. Analysed area is defined by the red marked rectangle.

Table 1: EDS quantification results and phases identification results from points 1-4 (Figure 2)

| Element | Si at.% | Ti at.% | V at.% | Cr at.% | Phase   | Space Group | Crystal System |
|---------|---------|---------|--------|---------|---------|-------------|---------------|
| Point 1 | 65.41   | 1.81    | 31.61  | 1.17    | SiV     | 180         | hexagonal     |
| Point 2 | 41.88   | 3.89    | 52.32  | 1.91    | Si₅V₆   | 72          | orthorhombic  |
| Point 3 | 35.89   | 3.62    | 58.61  | 1.88    | Si₃V₅   | 140         | tetragonal    |
| Point 4 | 19.48   | 1.97    | 75.10  | 3.46    | Si₃V₃   | 223         | cubic         |

3.2 EBSD mapping
The EBSD maps were acquired following phase identification, using the phases information determined and listed in Table 1. The EBSD phases distribution and Inverse Pole Figure (IPF) color coded maps are shown in Figures 3 (a, b) and Figure 3 (c, d) respectively. These clearly show that all the phases in the coating have been successfully identified and mapped and that each layer has a distinctive grain shape and size. The average grain sizes, aspect ratio (GAR) and thickness for each of the phases are shown in Table 2. A significant change of microstructure and layers thickness is observed between the two annealing temperatures (Figure 3, Table 2). For both temperature of cycling the Si₅V grains are relatively coarse and elongated with the highest aspect ratio, while the Si₃V₆ phase is characterized by smaller and more regular shape grains. However, one can notice the increasing of grain aspect ratio in the case of SiV-1100 sample. The Si₅V₆ phase has more regular shape of grain for SiV-650 sample, but with the increased annealing temperature of 1100°C, two types of grain populations are observed: small and regular shape grains closed to Si₅V₆ layer and bigger and elongated shape (with higher GAR) grains closed to Si₃V₅ layer (Figure 3, Table 2). This microstructure and thickness changes can be explained by the high diffusion rate of vanadium and its alloying elements (Cr and Ti) at 1100°C (Figure 3). Figure 3 also shows the orientation inverse poles figure (IPF) for the color code EBSD map. It is clear that the Si₃V₅ and Si₃V₆ layer grains have the same [001] orientation.

Contoured EBSD pole figures from each of the phases in the coating are shown in Figures 4 for SiV-1100 samples. It is clear from the Figure 4 a), b), c) that the external layers are strongly textured with a {0001} and {11-20} fiber in the SiV₂ and {001} fibers in the Si₃V₆ and Si₃V₅ phases. There also exists the following orientation relationship between the Si₃V₅ / Si₅V₆ and SiV₂ / Si₃V₆ phases: {001} Si₃V₅ // {001} Si₃V₆ and {11-20} SiV₂ // {001} Si₃V₆. The same fiber textures and crystallographic relationships were observed for the sample SiV-650. Figure 4 d) shows the pole figures for the SiV₃ layer, close to the substrate. This layer has the lowest thickness, only few grains are present in the analyzed area (Table 2, Figure 3). For that reason one could notice that the statistics are poor for this data set, which also shows that the SiV₃ layer is not strongly textured. The random texture of SiV₃ layer could also be observed on IPF color maps for both samples (Figure 3 c, d).
Table 2: Average grain sizes for Si-V sample annealed at 1100°C

| Phase     | SiV-650 |            |            | SIV-1100 |            |            |
|-----------|---------|------------|------------|----------|------------|------------|
|           | Thickness | Grains Size | Aspect ratio | Thickness | Grains Size | Aspect ratio |
| Si₂V₅     | 80 µm    | 16 µm      | 4          | 80 µm    | 15 µm      | 3.5         |
| Si₂V₆     | 6 µm     | 4 µm       | 2          | 20 µm    | 12 µm      | 2.5         |
| Si₂V₅     | 4 µm     | 3 µm       | 2          | 35 µm    | 6 : 17 µm  | 2 ; 3 µm    |
| SiV₃      | 3 µm     | 2 µm       | 2          | 10 µm    | 7 µm       | 2.5         |

Figure 3: EBSD phases distribution maps: a) after 122 cycles (1h-cycle) at 650°C, b) after 430 cycles (1h-cycle) at 1100°C and IPF color coded map in layer growth direction: c) after 122 cycles (1h-cycle) at 650°C, d) after 430 cycles (1h-cycle) at 1100°C from Si-V samples.

Figure 4: Set of pole figures from the data in Figure 3 for SiV-1100 sample: a) SiV₂ phase with {0001} and {11-20} fiber texture, b) Si₃V₆ phase with {001} fiber texture, c) Si₂V₅ phase with {001} fiber texture, d) SiV₃ with random texture.
4. Conclusions

With the combination of EDS/EBSD and phase diagrams for the Si-V system, all the phases present in the multilayered silicide coating have been accurately identified. Additionally the full microstructural characterization of the phases nature and distribution, of the grains sizes and textures was made using EBSD. It was shown that the fiber texture is generally the dominating texture for the Si-V multilayer. The crystallographic orientation relationships were found between the V-Si coating phases: \{11-20\} Si$_2$V // \{001\} Si$_5$V$_6$ and \{001\} Si$_3$V$_5$ // \{001\} Si$_6$V$_6$. Microstructural changes in the coating due to a severe accidental increase of temperature in Sodium Fast Reactor were clearly identified.

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