Fe-Cr-Si Codeposition on Nb-Si based Alloys via Halide Activated Pack Cementation to Improve Oxidation Resistance

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The coating formation by Fe-Cr-Si codeposition was done in a single step via Halide Activated Pack Cementation (HAPC) on Nb-Si alloy with the aim of improving the oxidation resistance. The activator salt and temperature selections for HAPC process were obtained by thermodynamic analysis. The isothermal oxidation test results for the coated alloy at 1200 °C for 62 h showed good oxidation resistance. The mass gain was 17.5 mg/cm². Furthermore, no cracks and spallation on the oxide layers were observed for the coated alloy after the oxidation test, being that the oxidative kinetics curve is in accordance with the parabolic rate law. On the other hand, total oxidation was observed for the uncoated alloy after 12 h at 1200 °C in the isothermal oxidation test. The mass gain was 49.27 mg/cm² and several cracks and spallation on the oxide layers led to a severe oxidation process.

**Keywords:** Nb-Si based alloys, Halide Activated Pack Cementation (HAPC process), Fe-Cr-Si Codeposition, Thermodynamic Analysis, Oxidation Resistance.

1. Introduction

Refractory alloys of Nb-Si system have high melting points (1934 °C for αNb₃Si₂), low densities (7.2 g/cm³ for Nb₃Si) and good mechanical properties at high-temperature. Because of these characteristics, the Nb-Si based alloys have great potential for application in the segments of aeroengines/aerospace being that they can operate between 1100-1200 °C. Furthermore, these alloys are good candidates to substitute Ni-based superalloys currently operating at a maximum temperature of about 1150 °C and a density of about 20% higher than the Nb-Si based alloys.

Considering the microstructural formation of Nb-Si based alloys, Nb₃ (Niobium Solid Solution) and Nb-silicide (Nb₅Si₃ and/or Nb₆Si₅), the intermetallic phases are responsible for improving the oxidation and creep resistance. Although silicide phases allow improving the oxidation resistance of the Nb-Si based alloys, their oxidation resistance is not enough when long-term application at ultrahigh-temperature (>1200 °C) are considered. The development of Nb-Si based alloys, with the addition of certain alloying elements such as Cr, Al, Ti, Sn and Ge improves the oxidation resistance. On the other hand, in order to establish a protective oxide layer, high contents of these elements are introduced in the alloy which can irreversibly alter its mechanical properties. In this way, surface coating is an effective way to improve the oxidation resistance of these alloys while maintaining their mechanical properties.

The surface coatings by HAPC process has been widely applied in different types of materials. In this technique, the substrate (alloy to be coated) is introduced into a powder mixture formed by masteralloy (coating elements to be deposited on the surface), activator salt, and inert material (usually Al₂O₃ or SiO₂). In high-temperature conditions, several halide gaseous species are formed due to the reaction between the masteralloy and activator salt. The coating is formed by decomposition of these gaseous species on the substrate surface followed by solid-state diffusion of the coating elements into the substrate. Different types of activating salts can be used in the HAPC process, such as NH₄Cl, NaF, KBr and many others. The selection of an activator type can be done by thermodynamic analysis that allow for the evaluation of the conditions conducive to the coating formation.

An improvement in the oxidation resistance of Nb-Si based alloys has been performed via HAPC process by deposition and codeposition of elements such as Si, Al, Mo, B, Cr, Ti and Fe. In spite of efforts to develop modified aluminide coating, the silicate-based coatings have greater potential for protection at high-temperatures. In this case, when modified with Fe and Cr, it is possible to obtain coatings with better oxidation resistance and the coated formed does not affect the strength at temperatures above 1100 °C.
The Fe-Cr-Si codeposition via HAPC process in a single step was successfully performed on Nb-alloys with the formation of complex coatings in multiphase microstructures\textsuperscript{18,24}. Oxidative protection is the result of the formation of oxide barriers such as Cr$_2$O$_3$ and SiO$_2$ on the surface, when thermally oxidized in the presence of atmospheric air that prevents oxygen from penetrating the substrate\textsuperscript{27}.

Although Fe-Cr-Si codeposition has been performed for Nb-based alloys\textsuperscript{18,24}, the literature lacks a discussion about thermodynamic analysis of the HAPC process. Thus, in the present study, a thermodynamic analysis was performed to select the activator salt type and temperature in the HAPC process that provides the best coating. For this, an alloy of Nb-Si with a high volume fraction of Nb$_5$Si$_3$ phase was coated by Fe-Cr-Si codeposition via HAPC process. The evaluation of the protective coating was performed by isothermal oxidation test at 1200 °C.

2. Experimental Procedures

2.1. Thermodynamic analysis

The objective of the thermodynamic analysis is to select the activator salt and temperature in the HAPC process that provides conditions for the codeposition of Fe-Cr-Si on substrate. For this, the thermodynamic analysis was performed using HSC Chemistry 6.0 software based on Gibbs Energy Minimization (GEM) to calculate heterogeneous equilibria occurring during the HAPC process and some activating salts based on chlorides, fluorides, and bromides as NH$_4$Cl, NaF and KBr, respectively.

The deposition of the gaseous species for the coating formation is directly related to the partial pressures formed during the reaction between the activator and masteralloy. The codeposition is achieved when the partial pressures of different halide gaseous species formed are the highest possible and close to each other\textsuperscript{16,26}. High partial pressures indicate high stability of the gaseous species, which can induce important fluxes between the substrate and the gaseous phase and consequently result in the fast kinetic growth of the coating layers\textsuperscript{27}. For the thermodynamic analysis in the present study, the composition of the masteralloy was in the ratio 30:20:50 of Fe, Cr and Si, respectively\textsuperscript{18}.

2.2. Specimen preparation

An Nb-Si alloy with microstructure formed of high volume Nb$_5$Si$_3$ phase was obtained by the nominal composition 62.5Nb-37.5Si (at. %). The Nb-Si alloy was produced from high-purity materials, Nb (min. 99.99 wt. %) and Si (min. 99.99 wt. %), by arc-melting with argon atmosphere (min. 99.995%) and using a non-consumable tungsten electrode. The as-cast alloy was heat-treated at 1450 °C for 48 h with (min. 99.995%) and using a non-consumable tungsten electrode. Si (min. 99.99 wt. %), by arc-melting with argon atmosphere from high-purity materials, Nb (min. 99.99 wt. %) and 62.5Nb-37.5Si (at. %). The Nb-Si alloy was produced.

2.3. Coating process

The masteralloy was produced with a nominal composition of 30Fe-20Cr-50Si (wt. %) by arc-melting and using high-purity elements Fe (min. 99.99 wt. %), Cr (min. 99.99 wt. %) and Si (min. 99.99 wt. %). Posteriorly, the masteralloy was reduced into a fine powder to optimize its chemical reactivity using agate mortar and pestle. The composition in the pack mixture was 60 wt. % of Fe-Cr-Si masteralloy, 40 wt. % of Al$_2$O$_3$ and 15 mg of activator salt, all placed in a 15 cm$^3$ quartz tube sealed under primary vacuum. The codeposition via HAPC process was carried out in a single step at 1200 °C for 12 h according to thermodynamic analysis.

2.4. Oxidation test

In order to evaluate the protective effects of the coating formation via HAPC process, oxidation tests were performed for the uncoated and coated alloys. The isothermal oxidation tests were carried out under atmospheric air at 1200 °C for 62 h. The mass change of the samples was measured by placing them in an alumina crucible and using NETZSCH thermal analysis (STA449F3) with an accuracy of 1 µg.

2.5. Analyzing methods

The microstructural characterization of the substrate, coating and the oxide formation on surface were performed using Scanning Electron Microscopy via Back-Scattered Electron images (SEM/BSE) and Secondary Electron images (SEM/SE) through ZEISS-EVO MA15 equipment. The phases formed in the Nb$_5$Si$_3$ alloy before and after heat treatment and the oxide formation on surface were identified by X-Ray Diffraction (XRD) through XPert Pro (Panalytical) diffractometer, using Cu-K$_\alpha$ radiation, an angular interval 20 from 20 to 80, an angular step of 0.05 and 1.0 s counting time. Energy Dispersive X-Ray Analysis (EDXA) was used to evaluate the composition of the coating and oxide formation.

3. Results and Discussion

3.1. Thermodynamic analysis

Figure 1 shows the formation of different activators considering one mol of Cl$_2$, F$_2$ and Br$_2$ from 0 to 1500 °C. It is observed that the thermal decomposition (Gibbs free energy more positive) of chlorides occurs more easily when compared to the decomposition of fluorides and bromides, noting too the wide difference between them. Above 200 °C NH$_4$Cl activator is more unstable than CrCl$_3$ activator and, as temperature increases, this instability becomes more evident, justifying the previous choice of NH$_4$Cl as the HAPC process activator because of its ability to decompose more easily and generate the species required for the coating formation reaction.

Figure 2 shows the partial pressure profile of different halide gaseous species formed in the reaction between activating salt with the Fe-Cr-Si masteralloy. The use of NH$_4$Cl as activator provides a gaseous phase containing mainly the species of FeCl$_3$, CrCl$_3$, CrCl$_3$, SiCl$_3$, SiCl$_4$ and SiCl$_4$, these gaseous species can be considered as vectors of Fe, Cr and Si from the gas phase to the substrate. It is important to note that the higher the partial pressure of
gaseous species the greater the activity of these species in the coating formation. Furthermore, it is observed that from 1200 °C most of these species have a steeper decline in their partial pressures, so this would be the maximum temperature for the HAPC process and maximum activity in its process.

The halide gaseous species with partial pressures less than $10^{-5}$ bar has no significant influence on the deposition process and those with values below $10^{-6}$ bar were excluded from the plot because the deposition is made difficult by the low partial pressure. Another important detail is the proximity of the partial pressure profiles of the gaseous species, being that the codeposition of Fe, Cr, and Si can occur at the same time.

In the case of using any other activator for the deposition of gaseous species, the gas phase generated may be very different, as observed in Figure 2 for activating salts such as NaF and KBr. For the HAPC process activated by NaF, at temperature range of 1000 to 1500 °C, there are only the formations of the silicon gaseous species (SiF$_4$, SiF$_3$, SiF$_2$, and SiF), therefore there would only be Si deposition on the substrate. For the HAPC process activated by KBr, the partial pressures of gaseous species are very low (below $10^{-6}$ bar) and there are only the formations of Fe and Si halide gaseous species at 1200 °C. Thus, Cr deposition would not occur and there would probably be only a minimum Fe-Si codeposition.

Therefore, considering the analysis of the Gibbs free energy of formation in Figure 1 and the studies of the halide gas phases in Figure 2, the codeposition of Fe, Cr, and Si would have better conditions in a process activated by NH$_4$Cl at 1200 °C.

### 3.2. Uncoated alloy characterization

Figure 3 shows microstructural characterization of the uncoated alloy in the as-cast condition and after being heat treated at 1450 °C for 48 h. In Figure 3A it can be seen that in the as-cast condition, the alloy is constituted by $\beta$Nb$_5$Si$_3$ phase, a situation of non-thermodynamic equilibrium. After the heat treatment, the alloy is constituted by $\alpha$Nb$_5$Si$_3$ and...
Nb\textsubscript{ss} phases, indicating thermodynamic equilibrium as showed in Figure 3B by SEM/BSE image. In this case, the Nb\textsubscript{ss} phase does not appear in the diffractogram (Figure 3A) due to the fact that the most intense peak of Nb\textsubscript{ss} phase coincides with the peak of the αNb\textsubscript{5}Si\textsubscript{3} phase at 2θ=38.507°. Taking into account that the alloy with nominal composition 62.5Nb-37.5Si (at. %) is in the single phase field (Nb\textsubscript{5}Si\textsubscript{3}), the presence of the Nb\textsubscript{ss} phase is associated with a possible loss of Si during the arc melting stage.

3.3. Fe-Cr-Si codeposition on Nb-Si alloy via HAPC process

Figure 4A shows the cross-section by SEM/BSE image after Fe-Cr-Si codeposition on Nb-Si alloy (substrate) via HAPC process. For the conditions indicated by the thermodynamic analysis, a successful coating was obtained for practical application. The coating formation showed a good chemical homogeneity, uniform thickness and a complete covering on the surface of substrate. In addition, the results showed a coating formed by multiphase microstructure consisting of four layers to be referred to as: outer layer, intermediate layer, inner layer and diffusion zone. The average thickness of the diffusion zone, inner and intermediate layer was 26.1 µm and the outer layer was 10.5 µm, resulting in a coating thickness of 36.6 µm. Moreover, the layers of the diffusion zone, inner and intermediate showed a uniform and homogeneous formation. The absence of pores and voids near the interface implies good adherence between the coating and substrate\textsuperscript{28}. On the other hand, it is observed that the outer layer showed the formation of pores and voids, which do not decrease the oxidation resistance of the coating, but only of the outer layer.

Figure 4B show the concentrations profiles of Fe, Cr, Si e Nb elements along the coating thickness. The exact position of the measurement points can be seen in Figure 4A. It can be observed that the chromium concentration starts at 50.27 at. % in the outer layer (point 1) and progressively decreases in the adjacent coating layers (points 2-7). The silicon concentration starts at 36 at. % in the outer layer (point 2) and continuously increased to about 42 at. % in the intermediate layer (point 2), then remained constant along the intermediate layer and in part of the inner layer (points 3-4, respectively). At points 5-7 the silicon concentration is close to the alloy composition, about 37.5 at. %. The iron concentration starts at 26 at. % in the outer layer (point 1) and declines to 18 at. % in the intermediate layer (points 2-3).
Then iron concentration increased in the inner layer, to about 24.5 at.% at point 4 and finally decrease to minimum levels in the points 5 to 7. The presence of chromium and silicon content along the coating thickness improves the oxidation resistance of the alloy through oxide formation on the surface after oxidation at high temperatures. This variation in the concentration profiles can be also visualized in Figure 4C, which shows the mapping of the coating layer by EDXA.

EDS analysis showed that the coating layer is formed by phases with compositions close to NbFe₅Cr₅Si₈ (outer...
layer), Nb₂Fe₂CrSi₅ (middle layer), Nb₂Fe₅CrSi₆ (inner layer), NbFeSi and Nb₂FeSi₂ (diffusion) zone, according to the Vilasi et al.²⁴.

3.4. Isothermal oxidation tests

Figure 5A show the results for the oxidation tests at 1200 °C for 62 h involving the uncoated and coated alloys. For the uncoated alloy, the sample undergoes high oxidation with a mass gain of 49.27 mg/cm² after 12 h at 1200 °C in air being completely oxidized. In contrast, the coated alloy showed good oxidation resistance with a mass gain of 17.5 mg/cm² after 62 h at 1200 °C. The total oxidation for the uncoated alloy suggests the formation of cracks and spallation on the oxide layers during exposure at high temperature. Hence, the oxygen penetrates into the substrate leading to rapid continuous oxidation reaction at the metal/oxide interface. In opposition, the coated alloy did not undergo severe oxidation since this later maintained its integrity after the oxidation test, as illustrated in Figure 5A. For the coated alloy, the oxidation kinetic curve followed a parabolic-like law during the isothermal oxidation test. The parabolic rate constant calculated from plot of mass change versus the square root of time for the coated alloy is approximately 2.64 mg²/cm⁴h, as shown in Figure 5B.

Figure 6A shows the surface of the coated sample after the oxidation test by SEM/SE image. Again, no cracks and spallation on the surface oxide layers were observed. Figure 6B shows the presence of elements of Fe, Cr, Si, and Nb on the oxidized surface by EDXA mapping. It is observed that the chromium (blue color) is the major element followed by minor proportions of silicon (red color) and iron (green color)/niobium (yellow color), respectively.

Figure 5. A Oxidation kinetics at 1200 °C for 62 h in the air for uncoated and coated alloys and B linear plot for the coated alloy.

Figure 6. Images on the surface oxide layer after the oxidation test for the coated alloy being: A SEM/SE image, B EDXA mapping and C X-Ray Diffraction.
Table 1. Results of several oxidation test reports for Nb-Si based alloys being considered uncoated alloys with alloying elements and coated alloys via HAPC process.

| Alloys (at. %) | Masteralloy | Deposition Condition (°C/h) and Salt Activator | Coating Thickness (µm) | Oxidation Test (°C/h) | Change Mass (mg cm\(^{-2}\)) | \(K_p\) (mg\(^2\) cm\(^{-4}\) h\(^{-1}\)) |
|----------------|-------------|-----------------------------------------------|------------------------|------------------------|-------------------------------|----------------------------------|
| **Present work** |             |                                               |                        |                        |                               |                                  |
| Nb\(_{ss}\)/Nb\(_5\)Si, (62.5Nb-37.5Si) | -           | -                                             | -                      | 1200/12                 | 74                            | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (62.5Nb-37.5Si) | Fe-Cr-Si    | 1200/12 NH\(_4\)Cl                            | 36.6                   | 1200/62                | 21                            | 2.69                            |
| **Coated alloy via HAPC process** |             |                                               |                        |                        |                               |                                  |
| Nb\(_{ss}\)/Nb\(_5\)Si, (62.5Nb-37.5Si) | Si          | 1100/7 MgF\(_2\)                             | 110                    | 1200/50                | 6.67                          | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (62.5Nb-37.5Si) | Nb-Fe-Cr-Si | 1200/24 CrCl\(_3\)                          | 38                     | 1100/90                | 2.1                           | -                                |
| Nb\(_{ss}\), (Nb-8.9Hf-1.2Zr)\(_{30}\) | Si          | 1300/8 NaF                                  | 100                    | 1250/50                | 6.5                           | 0.79                            |
| Nb\(/NbC\(_{3}\), (Nb-35Cr)\(_{30}\) | Si-Y        | 1250/8 NaF                                  | 200                    | 1250/50                | 13.1                          | 5.1                             |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-16Si-22Ti-17Cr-2Al-2Hf)\(_4\) | Si-B-Ti | 1300/10 NaF                                  | 162                    | 1250/100               | 2.39                          | 0.22                            |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-15Si-24Ti-4Cr-2Al-2Hf)\(_4\) | Mo-Si-B | 1000/25 NaF                                  | 50                     | 1300/24                | -0.55                         | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-16Si-25Ti-2Cr-2Al-8Hf)\(_9\) | Nb-Ti-Fe-Cr-Si | 1200/24 CrCl\(_3\) | 50                     | 1200/50                | 1.1                           | 0.019                           |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-16Si-22Ti-17Cr-2Al-8Hf)\(_{10}\) | Si-Ge | 1300/10 NaF                                  | 176                    | 1250/100               | 16.3                          | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-16Si-22Ti-17Cr-2Al-8Hf)\(_{11}\) | Si | -                                          | -                      | 1250/100               | 5.42                          | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-16Si-20Ti-6Cr-4Al-5Hf-2B-0.06Y)\(_{12}\) | Si-Al-Y | 1050/10 NaF                                  | 49                     | 1250/100               | 50                            | 62.6                            |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-14.3Si-39.4Ti-4.9Cr-3Al-2.8Hf)\(_{13}\) | Si-B | 1150/8 NaF                                  | 60                     | 1250/100               | 2.8                           | 5.70 x 10\(^{2}\)               |
| **Uncoated alloy** |             |                                               |                        |                        |                               |                                  |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-16Si-22Ti-17Cr-2Al-2Hf)\(_4\) | - | -                                           | -                      | 1250/100                | 190.08                        | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-15Si-24Ti-4Cr-2Al-2Hf)\(_4\) | - | -                                           | -                      | 1300/24                | 87.6                          | -                                |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-18Si-24Ti-2Cr-2Al-8Hf)\(_4\) | - | -                                           | -                      | 1250/50                | 198.91                        | 1220                            |
| Nb\(_{ss}\)/Nb\(_5\)Si, (Nb-18Si-24Ti-2Cr-2Al-8Hf)\(_4\) | - | -                                           | -                      | 1250/50                | 96.48                         | 220                             |
| Nbss/Nb\(_5\)Si, (Nb-16Si-24Ti-10Cr-2Al-2Hf)\(_5\) | - | -                                           | -                      | 1200/100               | 134                           | -                                |
| Nbss/Nb\(_5\)Si, (Nb-16Si-24Ti-17Cr-6Al-2Hf)\(_5\) | - | -                                           | -                      | 1200/100               | 18.9                          | 1.897                           |
In this case, the presence of the chromium and silicon elements constitute the oxides formed on the oxidized surface, shown in Figure 6C by X-Ray Diffraction. Thus, the formation of oxides of chromium and silicon were responsible for the increasing oxidation resistance of the coated alloy.

Table 1 lists several studies related to oxidation tests involving Nb-Si based alloys. The Fe-Cr-Si coating applied to the Nb/Nb$_2$Si alloy in this work showed significant improvements in oxidation resistance compared to uncoated alloys from other studies containing various elements in its compositions, such as Al and Cr, which provide this resistance, except for an alloy containing a high concentration of these elements presented by the work of Su et al.$^{32}$. On the other hand, other types of coatings presented in Table 1 have shown to be better in oxidation tests when compared to the coated alloy of this study, showing values below 2.638 mg$^2$/cm$^4$.h, with the exception of two alloys coated with Si-Al-Y$^{35}$ and Si-Y$^{3}$, with values of 62.6 and 5.1 mg$^2$/cm$^4$.h, respectively.

Moreover, the evaluation of the lifetime coatings and their behavior for the oxidation tests involve qualitative parameters of the coating (adhesion, cracks, voids) as well as quantitative aspects of composition of the coatings and phases formed. Thus, in relation to the present study, the presence of cracks in the substrate that extends to the coating might have had a negative effect in reducing its oxidation resistance.

4. Conclusions

Fe-Cr-Si Codeposition via HAPC process in a single step and activated by NH$_4$Cl was performed for the formation of a coating on Nb-Si alloy to improve oxidation resistance. The thermodynamic analysis was successfully used for selection of codeposition parameters; namely, the temperature and the activator nature. The conclusions that were drawn from the present study can be summarized as follows:

- From the thermodynamic analysis performed with different activating salts (NH$_4$Cl, NaF and KBr), the calculations suggested that the NH$_4$Cl activator was better for the codeposition of Fe, Cr and Si elements at 1200 °C. In this case, the formation of gaseous species based on Cr, Si and Fe with high partial pressure and close to each other were crucial to promote the coating growth;
- A multiphase microstructure formed of four layers was obtained on the coated surface of the Nb-Si alloy. The presence of the coating elements (Fe-Cr-Si) was verified in the coating formed by EDXRA results. Thus, the chromium and silicon content along the thickness of the coating improved the oxidation resistance of the alloy through the formation of protective oxides during exposure at high temperatures. The total thickness of the coating was approximately 37 µm. The inner layers of the coating, with a thickness near 26 µm, exhibited a uniform and homogeneous aspect with the absence of pores and voids which is desired for an improved oxidation resistance. The outer layer exhibited the formation of pores and voids with a thickness near 10 µm which may in part explain the relatively lower oxidation resistance compared to other coating from the literature;
- The oxidation tests showed an improvement in the oxidation resistance for the coated alloy as opposed to total oxidation of the uncoated alloy. The coated alloy had a mass gain of 17.5 mg/cm$^2$ after 62 h at 1200 °C, almost three times smaller than the uncoated alloy, which had a mass gain of 49.27 mg/cm$^2$ after 12 h at 1200 °C. The oxidation kinetic curve for the coated alloy followed a parabolic law with a rate constant determined to be 2.638 mg$^2$/cm$^4$.h, approximately. The formation of SiO$_2$ and CrO$_3$ oxide scales on the surface of the coating contributed to enhancing the oxidation resistance of the alloy.

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