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ORIGINAL RESEARCH

Vapor phase codeposition of Cr and Si on Nb-base in situ composites by pack cementation process

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Abstract In order to identify suitable halide activators and pack compositions for codepositing Cr and Si to form diffusion coatings on Nb-base in situ composites by the pack cementation process, thermochemical calculation was taken to analyze the vapor pressure of halide species generated at high temperatures. NH_4Cl , NaF and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were selected as the halide salts. The results of thermochemical calculations suggested that the pack powder mixtures, which contained Cr, Si, halide salts and Al_2O_3 , may be activated by NH_4Cl and NaF. According to the thermochemical calculations, the pack powder mixture of 12Cr–6Si–5 NH_4Cl –77 Al_2O_3 (wt%) activated by NH_4Cl was formulated and coating deposition experiments were carried out at 1200 and 1300 °C. With adequate control of pack compositions and deposition conditions, it was found that codeposition of Cr and Si could indeed be achieved at these temperatures. The coating has a three-layer structure, of which was mainly composed of $\text{Cr}_2(\text{Nb},\text{X})$ (X represents Ti and Hf elements), Nb_5Si_3 and $(\text{Nb},\text{Cr})_3\text{Si}$. Then the kinetics of coating growth process affected by temperature was studied. The experimental results of the oxidation showed that the coating can efficiently prevent substrate from oxidizing.

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1. Introduction

The improvement of aircraft engines and gas turbines requires advanced high temperature structural materials, for operation at temperatures above 1100 °C. However, Nickel-base superalloy airfoils presently have maximum surface operating temperature of approximately 1150 °C [1–3], which is close to the temperature limit for Ni-base superalloys. Thus, high temperature structural materials have been required to break through the applicability limit. As the candidates of the important high-temperature structure materials, Nb-based in situ composites have been widely attracted owing to their high melting point,

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low density and high strengths at elevated temperatures and moderate room temperature fracture toughness. However, their oxidation behavior at high temperatures is poor, severely restricting their application and development at high temperature [4–6]. Research has shown that the oxidation resistance of Nb-based in situ composites can be enhanced significantly by adding some elements such as Cr, Si, Al, Ti and Hf [4–6]. Further alloying with especially beneficial elements like Cr and Si often leads to deterioration of mechanical properties [7]. In other words, the amount of alloying elements is limited by this compromise between mechanical and oxidation properties. It is now generally recognized that deposition of coatings can form dense, adherent and slow-growing oxide scales. The coatings not only retain the fine mechanical properties but also offer the most promising approach to improving long-term environmental stability at high-temperatures [8,9].

The pack cementation process is a coating–deposition process normally used in coating industry [10–14], and it is an in situ chemical vapor deposition (CVD) process activated by halide salts such as NH_4Cl , NaF or AlCl_3 [10,14–18]. Compared to other techniques for depositing coatings on metal alloy substrates, it has a plenty of distinctive advantages, such as low cost, controllable thickness up to 200 μm , simultaneous deposition of multiple elements and ability to be applied to complex shapes and various sizes.

Guo et al. have studied the Cr-modified silicide coatings prepared by pack cementation on Nb–Si based alloy. The pack mixtures composed of 12Si–12Cr–5NaF–71Al₂O₃ (wt%) were used in this paper. Then the coating deposited at 1350 °C for 10 h was used for an oxidation test, and it was found that the Si–Cr codeposition coating can provide effective protection against oxidation in the air at 1250 °C for 10 h, owing to the formation of SiO₂ and Nb, Cr-doped TiO₂ scale [19]. In the previous paper, Zhou et al. have reported the Cr-modified silicide coatings on Nb–Si system intermetallics deposited by molten salt combined with pack cementation [20].

However, due to lack of data of the partial pressures of halide vapor species, processing parameters for the coatings were determined based on extensive experiments. Xiang et al. [21–23] has made use of the ChemSage computer program in combination with the SGTE database to carry out thermochemical analyses. Based on the calculations obtained, experiments for codepositing Al and Si on γ -TiAl and nickel base superalloys by the pack cementation were undertaken.

The present study is designed to identify the pack compositions and coating conditions suitable for codepositing Cr and Si using elemental Cr and Si as the source to form diffusion coating, by means of thermochemical analysis in combination of experimental studies on the substrate of Nb-base in situ composites.

2. Thermochemical analyses

Pack cementation is an in situ chemical vapor deposition process where the substrates to be coated are buried in a mixed powder pack in a sealed refractory container [24]. The pack powder is composed of pure or alloyed depositing elements, halide salt activator and inert filler (usually Al₂O₃).

At high temperatures, a series of halide vapor species containing the depositing elements will generate within the pack. The coating forms via decomposition of these halide

vapors on the substrate surface and subsequent solid-state diffusion between the deposited elements and the substrate. The partial pressures of these halide vapors are determined by the pack composition and coating temperature.

In order to achieve the intended codeposition, the partial pressures of halide vapor species of the two depositing elements should be ideally controlled in a comparable range [12–14]. This may be achieved by adjusting the concentration or activity of the depositing elements in the pack powder mixture and by carefully selecting a suitable halide salt as an activator.

In this study, the Thermo-Calc computer program combined with the SSUB3 database system was applied to calculate these partial pressures for a range of pack powder compositions.

The results obtained were used to identify most possible coating conditions and pack powder mixtures for depositing Cr and Si coatings on Nb–Si in situ composites with a coherent structure, comparing the vapor pressures of chromium halides with those of silicon halides.

The calculations were based on the Gibbs energy minimization technique and the mass conservation rule. For all the calculations undertaken in this study, the total pressure within the packs was assumed to be one atmosphere.

2.1. Pack mixtures activated by NH_4Cl

The calculations were carried out for the composition series of 12Cr– x Si–5NH₄Cl–(83– x)Al₂O₃ (wt%) with Si content (x) varying from 12 to 6 wt%, and the initial pack composition was based on the previous experiments taken by Guo et al. [19]. Fig. 1 shows the partial pressure of SiCl₄ in these packs constitute of 12Si–12Cr–5NH₄Cl–71Al₂O₃ (wt.%) is at least three orders of magnitude higher than even the highest partial pressure of the vapor species containing Cr. At about 1200 °C, the partial pressure of SiCl₄ is almost four orders of magnitude higher than CrCl₃. However, when the temperature exceeds 1500 °C, a transformation of the highest partial

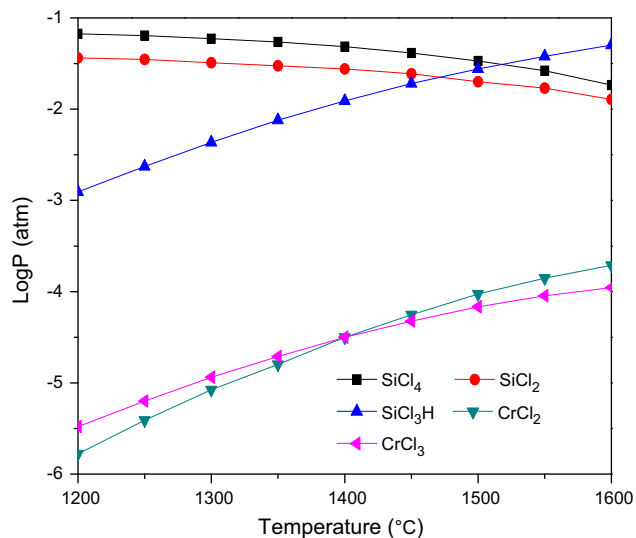


Fig. 1 Equilibrium partial pressures of Cr and Si chloride vapor species as a function of temperature in a NH_4Cl activated pack containing 12 wt% of Si.

pressure occurred from Si-chloride to Cr-chloride, which is mainly responsible for transporting and depositing Si and Cr in the pack respectively. Thus, these packs have a stronger tendency of depositing Si than depositing Cr. Then the Si concentration was reduced to as low as 6 wt% while keeping Cr and NH_4Cl concentrations constant. From Fig. 2, it is seen that the modification of concentration has significantly impact on these results. The partial pressure of Cr-chlorides significantly increased because of the decrease in partial pressure of Si-chloride resulting from the reduction of Si content. When Si content is 6 wt%, the partial pressure of SiCl_2 became within two orders of magnitude with the Cr-chlorides, suggesting that it is possible to codeposit Cr and Si.

Fig. 3 shows the plot of vapor pressures of Cr-chloride, Si-chloride and SiCl_3H generated within the pack at 1300°C as a function of Si content ($x=6-12$) for a pack series of $x\text{Si}-12\text{Cr}-5\text{NH}_4\text{Cl}-(83-x)\text{Al}_2\text{O}_3$ (wt%). It can be seen that in order to codeposit Cr and Si, the Si content in the pack should not be much higher than about 6.5 wt%, for the partial pressure of Si-chloride and Cr-chloride in a comparable range. Ideally, the Si content should be controlled in the vicinity of 6.5 wt%, where the vapor pressure curve of Cr approach to those of silicon chlorides, indicating codeposition of Cr and Si may be possible.

2.2. Pack mixtures activated by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

The vapor phases composition in the packs activated by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is extremely similar to these activated by NH_4Cl , containing CrCl_x ($x=1-2$) and many other hydrogen containing Si-chloride species, which were calculated for the pack composition series $m\text{Si}-12\text{Cr}-5\text{CrCl}_3 \cdot 6\text{H}_2\text{O}-(83-m)\text{Al}_2\text{O}_3$ (wt.%) with Si content varying from 6 to 12 wt%.

Fig. 4 presents partial pressures as a function of Si content activated by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at a deposition temperature of 1300°C . It can be observed that the partial pressures of SiCl_4 , SiCl_2 , SiCl_3H , CrCl_3 , CrCl_2 fundamentally remain constant and the partial pressure of SiCl_4 is at least four orders of

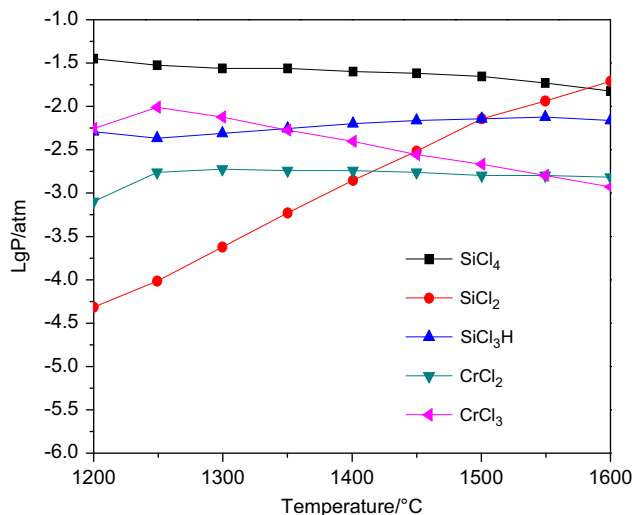


Fig. 2 Equilibrium partial pressures of Cr and Si chloride vapor species as a function of temperature in a NH_4Cl activated pack containing 6 wt% of Si.

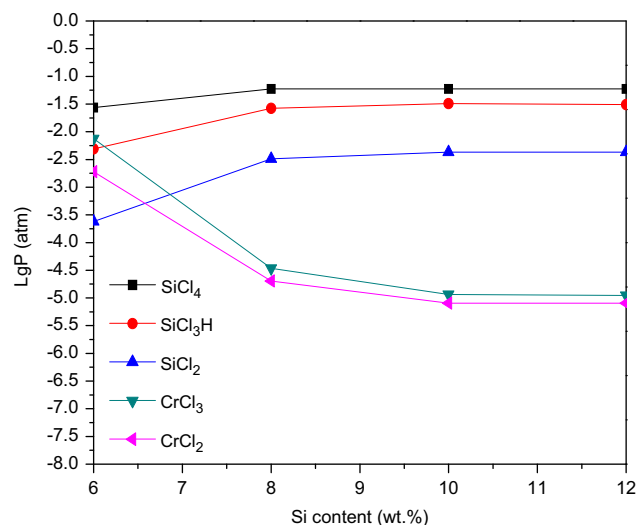


Fig. 3 Equilibrium partial pressures of Cr and Si chloride vapor species as a function of Si content at 1300°C in a pack series activated by NH_4Cl .

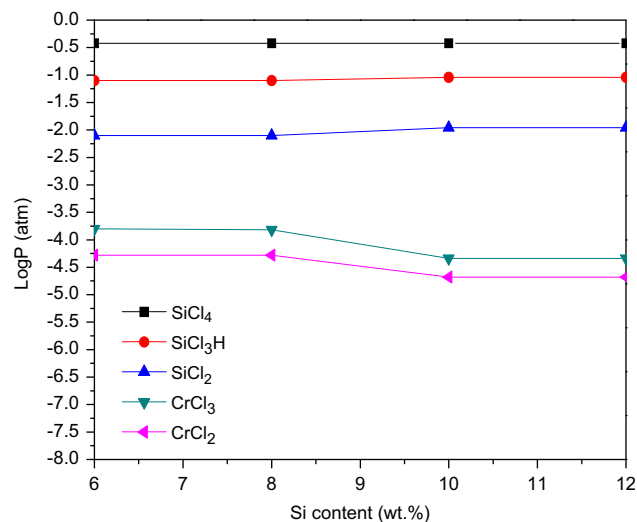


Fig. 4 Effect of Si content on the equilibrium vapor pressures of Cr and Si chloride species formed at 1300°C in a pack series activated by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

magnitude higher than these Cr-chlorides when Si content varies from 6 wt% to 12 wt%, indicating that codepositing Cr and Si cannot be achieved by the use of these compositions.

Fig. 5 illustrates the temperature dependence of the partial pressures of these vapor species in the range $1300-2000^\circ\text{C}$ for a pack containing 6 wt% Si. It can be seen that when the temperature is higher than 1600°C , the partial pressures of Si-chlorides and Cr-chlorides are within two orders of magnitude, and it has a possibility to achieve codeposition. However, it cannot be taken into account owing to the quite high request of technique because of the so high temperature.

2.3. Pack mixtures activated by NaF

The initial pack composition was $12\text{Cr}-12\text{Si}-5\text{NaF}-71\text{Al}_2\text{O}_3$ (wt%). The calculated partial pressures of these vapor species

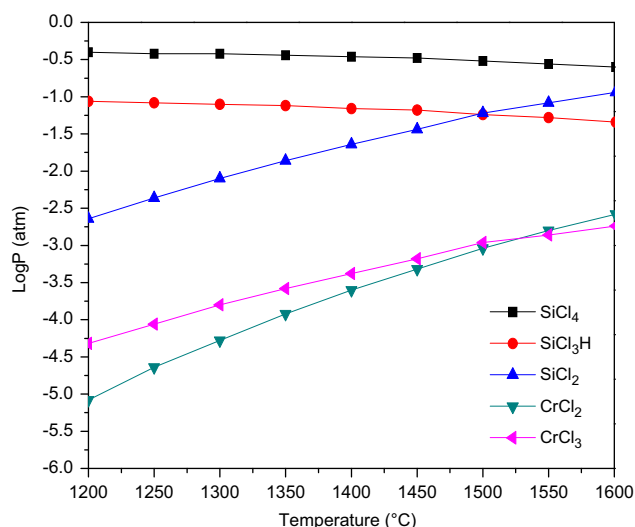


Fig. 5 Equilibrium vapor pressures of Cr and Si chloride species as a function of temperature in a pack activated by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

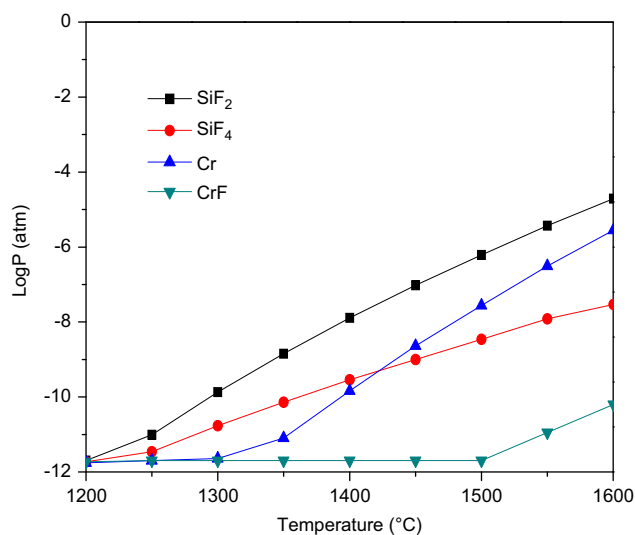


Fig. 6 Equilibrium vapor pressures of Cr, CrF and SiF_x ($x=2,4$) as a function of temperature in a pack activated by NaF.

are compared in Fig. 6. It shows that the partial pressure of SiF_2 is two orders of magnitude higher than the vapor pressure of Cr. The vapor pressure of Si-fluoride is higher than the partial pressure of Cr-fluoride, which controls the deposition tendency of Si rather than Cr in the codeposition process.

The partial pressure of SiF_2 is within two orders of magnitude with Cr and CrF in the temperature range of 1200–1400 °C, indicating that codeposition of Si and Cr may be possible at these temperatures. However, the vapor pressure of the pack activated by NaF is relatively lower than other activators.

2.4. Selection of activators

The thermochemical calculations presented in the preceding sections revealed that the type of halide salts selected as

activators is especially important in determining the partial pressure distribution of halide vapors and hence the depositing tendency of the pack compositions.

Among the halide salts studied, NH_4Cl and NaF are the most suitable activators for codepositing Cr and Si. Compared with NaF, NH_4Cl , a salt commonly used for studying the pack cementation process [10,11,16,17], appears to be a better activator for generating the required conditions for codepositing Cr and Si. It also can be seen that the vapor pressure of the pack activated by NaF was obviously lower than others compared Figs. 6 and 2, which affect the process of depositing. Thus, NH_4Cl is selected as the activator in the subsequent coating deposition experiments to verify the conditions predicted by the thermochemical analysis for codepositing Cr and Si.

3. Experimental procedures

The substrate used in this study is a Nb–Si in situ composites with a nominal composition of 59.5%Nb–6.2Si–22.7Ti–2.3Al–4.3Cr–5Hf (wt%).

The alloy specimens were sliced into buttons of about 10 mm in diameter with a thickness 3 mm. The button surfaces were ground and polished to an 800 grit finish, and then degreased by industrial alcohol before placing them in pack powers. Powders of Al_2O_3 , Cr, Si and halide salts were used to prepare the pack powder mixtures, and the average particle sizes of Al_2O_3 , Cr, Si and NH_4Cl powders were 100 mesh, 100 mesh and 200 mesh, respectively. The powder mixtures were precisely weighed out and manually mixed by hand with an agate mortar and pestle. Packs were prepared by burying the substrates in a well-mixed pack powder mixture in a cylindrical alumina retort of 22 mm diameter and 28 mm height. Then the furnace was heated to codeposition temperature at a rate of 5 K min^{-1} , held on a required period with constant temperature and naturally cooled to room temperature. In this process the gas-argon was kept flowing.

The techniques of X-ray diffraction (XRD, Model D/Max 2500PC Rigaku, Japan) and scanning electron microscopy (SEM, Model Quanta600, USA) with energy dispersive spectroscopy (EDS) and back-scattered electron imaging were used to characterize the coatings produced. The coating thickness was estimated from the EDS data by plotting the element concentrations against the depth at which the concentrations were measured.

4. Results and discussion

4.1. Microstructure of coating

According to the analyses of thermochemical of calculations, the pack powder mixtures, which contain Cr 12 wt%, Si varying from 7 to 6 wt%, NH_4Cl 5 wt%, 77 wt% Al_2O_3 for balancing, were formulated and prepared. Specimens were all coated for 10 h at 1200 °C and 1300 °C. Coating deposition experiments were then carried out to demonstrate the suitability of these compositions for codepositing Cr and Si on Nb–Si in situ composites.

Fig. 7 shows a cross-sectional SEM image and concentration profiles of Si, Cr, Ti, Nb and Hf in the coating layer as

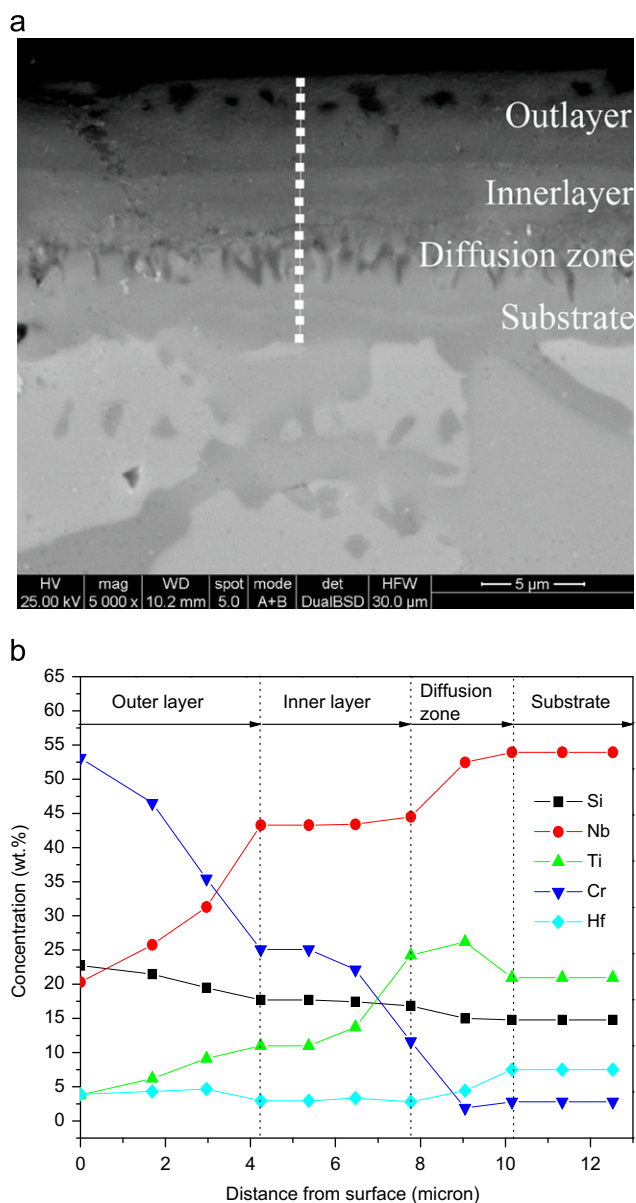


Fig. 7 Cross-sectional SEM image (a) and concentration profile of major elements (b) in the Cr and Si codeposition coating layers heated at 1300 °C for 10 h.

measured by EDS for a specimen coated at 1300 °C for 10 h and the pack mixture compose of 6 wt% Si. The sample positions for EDS point analysis were shown by a series of white spots along a line roughly perpendicular to the coating surface in Fig. 7(a). It can be seen from the SEM image [Fig. 7(a)] that the coating consisted of three uniform layers with a total thickness of about 11 μm. The outer layer with a thickness of about 4 μm contains mostly Cr, Si, Nb and a little of Ti and Hf. The constituent of the inner layer is similar to outer layer with different concentrations. And the thickness of the inner layer is approximately 7 μm. Underneath the inner layer there exists a diffusion zone, which can be visually recognizable in the SEM photograph and from concentration profiles [Fig. 7(b)]. In the diffusion zone, the concentration of Nb was apparently decreased; on the contrary, the concentrations of Cr and Si distinctly increased and Ti and Hf were

remained constant compared with the constituent of substrate. It also can be seen that across the depth of the coating, the Nb content increases gradually. However, the concentrations of Cr and Si across the depth of the outer layer vary sequentially.

The phase constituent of as-coated surface was determined mainly through XRD analysis results, combined with the above EDS analyses. Fig. 8 shows the XRD patterns of the Cr–Si coating codeposited at 1300 °C for 10 h. It can be determined that the coating was mainly composed of $\text{Cr}_2(\text{Nb},\text{X})$ (X represents Ti and Hf elements), Nb_5Si_3 and $(\text{Nb},\text{Cr})_3\text{Si}$ phases from the results of XRD and EDS analyses. These analyses demonstrated the feasibility of depositing Cr and Si. And the Cr–Si codeposited coating formed on Nb–Si in situ composites was evidently by the inward diffusion of Cr and Si. As shown in Fig. 8, the Al_2O_3 phase is not present in the coating revealed by the XRD spectrum and SEM image, which was known to be contained in the coatings that formed by the outward growth mechanism and demonstrates that the activated Cr and Si atoms were diffused into the coating layer during the coating formation process. The inward growth mechanism of the coatings was in accordance with the results of Van Loo and Rieck [25,26]. The high temperature oxidation resistance and corrosion resistance of the coating need to be investigated in the future study.

4.2. Effect of temperature

In order to verify the temperature effect on coating, coating deposition experiments were carried out at the temperatures ranging from 1200 to 1300 °C by using pack power mixtures containing 12 wt%Cr, 6 wt%Si, 5 wt% NH_4Cl and 77 wt% Al_2O_3 . The deposition duration was 10 h at all temperatures. And the structures of the coatings were the same as those previously mentioned.

As already stated, the experimental process is diffusion controlled, so the relation of the coating growth rate (k) and

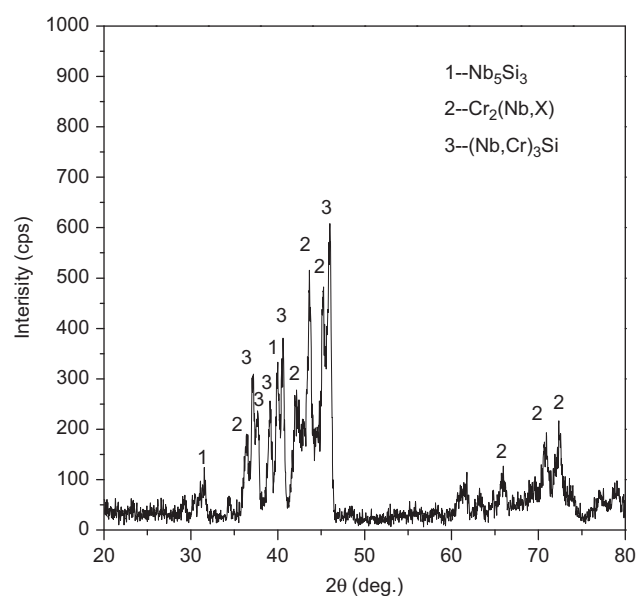


Fig. 8 XRD spectrum for a sample coated by codeposition at 1300 °C for 10 h.

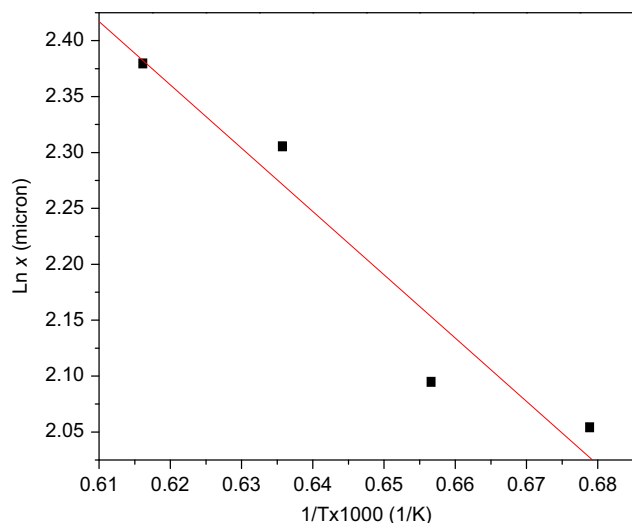


Fig. 9 Dependence of \ln coating thickness on deposition temperature.

the coating thickness (x) can be described as the following equation:

$$k = x/t^{0.5} \quad (1)$$

where t is the codeposition time. It was known that the relation of the growth rate of coating and the temperature followed Arrhenius relationship [27]:

$$\ln k = -Q/(RT) + C \quad (2)$$

where Q is the activation energy, R is the gas constant and C is a constant.

Because the k of Eq. (1) is identical to Eq. (2), and here t is a constant, Eq. (1) can be expressed by

$$\ln x = A - B/T \quad (3)$$

where $A = C + 0.5 \ln t$ and $B = Q/R$.

Fig. 9 demonstrates the $\ln x$ (the coating thickness) as a function of $1/T$ (T is the absolute temperature). It clearly shows a linear relationship which provides strong experimental evidence supporting Eq. (3). The least squares fit of the data in Fig. 9 obtained a slope of -5.66 . Then according to Eq. (3), the activation energy of forming the codepositing coatings in these temperature is calculated to be 40.04 kJ/mol.

4.3. Oxidation resistance

Fig. 10 shows the variation of weight gain per unit area, ΔW , of the bare and Cr–Si coated Nbss/Nb₅Si₃ in situ composites due to oxidation at 1250 °C with time. After oxidation for 100 h at 1250 °C, the weight gain per unit area for the Cr–Si coated Nbss/Nb₅Si₃ in situ composite is 14.2 mg/cm², which is dramatically reduced as compared to the bare alloy. Oxidation mechanism of the coated Nbss/Nb₅Si₃ in situ composites needs to be investigated in the future study.

5. Conclusions

Thermochemical calculations indicated that codeposition of Cr and Si on Nb–Si in situ composites by the pack cementation process is possible using NH₄Cl activated packs,

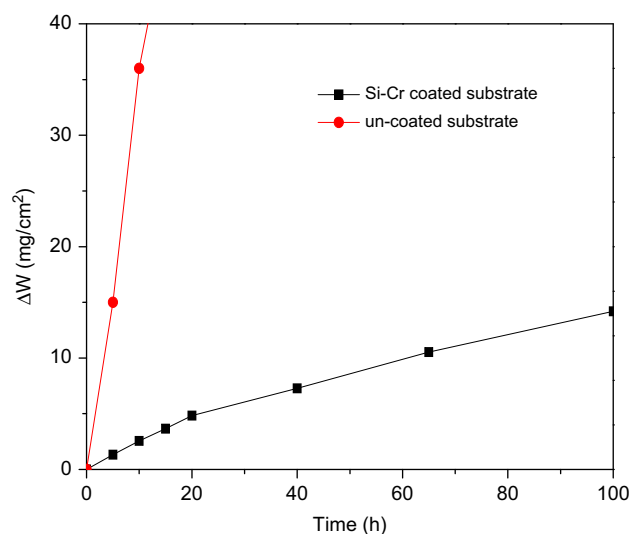


Fig. 10 The oxidation mass gain curves of Cr–Si coating and substrate at 1250 °C.

containing 12 wt%Cr and 6 wt%Si as the deposition source. These calculations suggested that pack powder mixtures activated by NH₄Cl and NaF can be adjusted to achieve codepositing Cr and Si. The pack powder mixtures activated by CrCl₃·6H₂O may deposit only Si.

The results of coating deposition experiments confirmed that, with careful control of the pack mixtures, the codeposition of Cr and Si could be obtained on Nb–Si in situ composites at 1300 °C for 10 h using the NH₄Cl-activated pack. The coatings deposited consisted of Cr₂(Nb,X) (X represents Ti and Hf elements), Nb₅Si₃ and (Nb,Cr)₃Si phases with a diffusion zone between the coating and the substrate. It suggests that the coatings form via a sequential deposition mechanism through inward diffusion of Cr and Si. It is also known that the thickness of the coating is affected by the codeposition temperature. The resultant coating can prevent efficiently substrate from oxidizing.

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