



Article Effect of the Deposition Time and Heating Temperature on the Structure of Chromium Silicides Synthesized by Pack Cementation Process

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Abstract: Transition metal silicides have attracted great interest for their potential use in optoelectronic devices, photovoltaic cells, and thermoelectric conversion elements because of their high melting point, high oxidation resistance, and satisfactory thermoelectric properties. This study focuses on the effect of the deposition time and the heating temperature on the morphology and structure of the chromium silicides synthesized by the pack cementation method. A series of experiments were carried out at various temperatures (1000–1150 °C) with different deposition times (15–120 min). The morphology and the chemical composition of the samples were determined using SEM with an EDS analyzer. The structure determination and phase identification were performed by XRD analysis. The examination of the as-formed materials was completed by performing thermal stability tests. The most suitable conditions for producing $CrSi_2$ sample with satisfactory properties and simultaneously minimizing the cost and production time are listed. It was found that the sample synthesized at 1000 °C for 15 min during the chromizing step, in combination with the siliconizing step at 1000 °C for 60 min, presents the best thermal stability and these selected temperatures offer appropriate, economical, and repeatable results.

Keywords: chromium silicides; pack cementation; heating temperature; deposition time; thermal stability

1. Introduction

Transition metal silicides have long been promising materials in microelectronic devices, photovoltaic cells, and thermoelectric conversion elements operating at high temperature under ambient atmosphere because of their low electrical resistivity, excellent chemical stability, high melting point, and satisfactory thermoelectric properties [1]. Metal silicides have been used in high-temperature structural applications because of their advantages such as high-temperature strength and oxidation resistance, among others. Additionally, metal silicides can be used as protective coatings on engineering materials to protect them from corrosion in harsh environments [2–4].

The chromium–silicon (Cr–Si) system is technologically interesting, as several chromium silicides phases exist in the binary phase diagram, such as the cubic intermediate phase Cr₃Si (cubic Pm3n), the tetragonal intermediate phase Cr₅Si₃ (W₅Si₃ type-tetragonal I₄/mcm), the cubic intermediate phase CrSi (cubic P2₁3) and the hexagonal phase CrSi₂ (hexagonal P6₂22) [5]. The Cr₅Si₃ and CrSi silicides have high hardness, very strong atomic bonds, and high-temperature yield strength [6].

Chromium disilicide (CrSi₂) crystallizes in the hexagonal C40 structure with space group P6₂22 [1]. It is an indirect narrow-gap (Eg = 0.35 eV) semiconductor with carrier concentration, 1020 cm⁻³, that has been targeted and used for robust, stable, photovoltaic



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). applications and inexpensive thermoelectric (TE) materials [7]. At room temperature $CrSi_2$ has a high Seebeck 90–120 mV/K and a specific electrical resistance of the order of $10^{-3} \Omega cm$ [1]. The thermal conductivity at room temperature is 10 W/mK, with phonons being the major factor [8]. Additionally, it is reported that the $CrSi_2$, the compound with the highest silicon content among the Cr–Si phases, has the highest oxidation resistance [1,5].

Ball milling, solid-phase reaction, reactive deposition epitaxy, and reactive co-deposition of Cr and Si are just a few of the techniques used to form chromium silicides [1,8–10]. Additionally, the Czochralski method, floating-zone technique, and solution-melt method can be also used to grow CrSi₂ single crystals [11–13]. Zhang et al. [14] showed that mechanical alloying of elemental chromium and silicon powders can produce all four equilibrium phases in the Cr–Si system. Fernandes et al. [15], as well as Dasgupta et al. [8], prepared CrSi₂ by mechanical alloying with stainless steel milling balls. Colgan et al. [16] have shown that, during the interaction in the Cr–Si system, CrSi₂ is always the first phase formed. They have also shown that after consuming all the available silicon, CrSi₂ can react with unconsumed chromium to form Cr₅Si₃. According to the starting Si/Cr atomic ratio, Cr₅Si₃ can react either with CrSi₂ or Cr to form CrSi or Cr₃Si, respectively. Many of these techniques require lengthy and energy-consuming processes, expensive equipment, and often fail to produce high-quality materials.

Chemical vapor deposition (CVD) by pack cementation has been widely used because of its simplicity, practicality, and low cost of production [17–19]. It can be used on substrates with complex geometry and is an environmentally friendly method since no toxic fumes are released during the formation of the films. Pack Cementation is a deposition process comprised of two steps. The first step is the chemical reactions, which transform and deposit the material in a more reactive form on the substrate, and the second is the solid-state diffusion. In detail, the chemical products from the decomposition of the halide salt activator react with the thermodynamically preferred metal material, creating gaseous halides, which decompose on the surface of the other component (substrate). The byproducts of the chemical reaction react again with the metal to form new volatile metal halides until the donor is fully consumed. Then, the thermal diffusion occurs either inward or outward between the metals, resulting in the formation of the deposited material [20]. Many silicide materials have been successfully formed by the pack cementation process [21–24].

In our previous work [22], CrSi₂ was formed from a Si wafer by the use of a twostep pack cementation chemical diffusion method. Several deposition experiments were performed by using 20 wt.%, 30 wt.%, and 40 wt.% Cr in the pack mixture. A full transformation of the Si wafer into chromium silicide compounds was found for the sample with 40 wt.% Cr in the pack mixture due to the very fast Si diffusion in Cr–Si compounds; bulk Si substrate is no longer available. Additionally, nanocrystalline CrSi₂ powder was successfully prepared by the pack cementation process [21]. Non-isothermal oxidation tests indicate that the CrSi₂ powder, formed by the pack cementation process, was stable due to the formation of chromium and silicon oxides, which further impede the inward diffusion of oxygen [21].

In this work, an attempt was made to search for the optimum heating temperature and deposition time of the bulk chromium silicides synthesized by the pack cementation process. Theoretical thermodynamic calculations were performed to predict the equilibrium Cr–Si phases which can be formed during the pack cementation process. A two-step pack cementation chemical diffusion method was applied. In the chromizing step, several experiments were carried out at temperatures from 1000 to 1150 °C with different deposition times ranging between 15 and 120 min. The effect of the deposition time t and the heating temperature T on the morphology and structure of the as-formed material was studied. The morphology and the chemical composition of the samples were determined using Scanning Electron Microscopy (SEM). The structure determination and phase identification were performed by X-ray Diffraction (XRD) analysis. In the second siliconizing step, the as-formed Cr–Si compounds were enriched to form pure CrSi₂. The second part of this

work aims to expose the as-formed $CrSi_2$ to air at 1000 °C to ensure good thermal stability against high-temperature oxidation.

2. Materials and Methods

The purpose of this work is the determination of the most suitable conditions for producing samples with satisfactory properties and simultaneously minimizing the cost and production time. For the deposition process, a two-step pack cementation process consisting of a chromizing (first step-several chromium silicides phases) and a siliconizing step (second step—CrSi₂ phase) was applied. In detail, (100) oriented Si substrate was cut into pieces and then carefully cleaned with alcohol. During the chromizing step, the prepared substrates were placed in porcelain crucibles, filled with a powder mixture composed of chromium (99.9%, ~325 mesh), which is the donor material, a halide activator (NH_4Cl) , and an inert filler (Al_2O_3) . It should be noticed that the inert filler was not mixed with the rest of the powders. The alumina was placed at the top and bottom of the crucible to fill the empty space. The crucibles were sealed with ceramic lids and placed in a tubular electric furnace, which was argon-purged (99.998% Ar gas; Figure 1). After the heat treatment period, the crucibles were left in the furnace to cool down to ambient temperature without interrupting the Ar flow. All of the formed samples were cleaned with an ultrasonic bath machine to enhance the removal of foreign substances from the surface of the samples submerged in an ultrasonically activated liquid.



Figure 1. A schematic of the experimental growth procedure.

Several experiments were performed at various heating temperatures from 800 $^{\circ}$ C to 1150 $^{\circ}$ C for 120 min and different deposition times, 15, 30, 60, 120 min at a constant temperature of 1000 $^{\circ}$ C in the chromizing step (Table 1). In all cases, a pack mixture with a Cr content of 40 wt.% Cr was used. The Cr concentration was selected due to the successful formation of Cr–Si compounds in our previous work [22]. The treatment time did not include the time it took for the specimens to cool from the deposition temperature to room temperature.

Table 1. Two sub-series of experiments took place during the chromizing step.

	1st Set	2nd Set		
Sample Name	Heating Temperature (°C)	Sample Name	Deposition Time (min)	
1000_120 min	1000	1000_120 min	120	
1050_120 min	1050	1000_60 min	60	
1100_120 min	1100	1000_30 min	30	
1150_120 min	1150	1000_15 min	15	

The higher chromium silicide was the subject of numerous investigations, mainly because of its good oxidation resistance, semiconducting properties at elevated temperatures, and thermoelectric properties. For this reason, a second step of the pack cementation process (siliconizing step) was performed for selective samples synthesized under various heating temperatures and deposition times in the chromizing step. In this case, the pack mixture includes 15 wt.% Si (donor material), 3 wt.% NH₄Cl (activator) and 82 wt. % inert Al_2O_3 (filler). The depositions were performed at 1050 °C for 60 min.

Thermodynamic predictions were performed using the Thermocalc computer program with SSUB4 database Scientific Group Thermodata Europe to present some preliminary results about the Cr–Si compounds formed during the pack cementation process. It was assumed that the pack cementation process occurred at atmospheric pressure and the temperature was homogenous throughout. An inert Ar atmosphere was also assumed. Since Al_2O_3 is not expected to react or decompose, the existence of the inert filler will not be considered in the calculations. No oxygen-containing solid or gaseous phases were included in the calculations. For the calculation, the presence of the Si substrate was taken into consideration, while the input parameters for the program were fixed based on 10 gr of a pack containing 40 wt.% Cr, 57 wt.% filler (Al_2O_3), and 3 wt.% halide activator salt (NH₄Cl). It should be noticed that these thermodynamic approximations are for an equilibrium state, and thus, the experimental results may vary, and different phases may be formed.

Scanning Electron Microscopy (SEM) was used to examine the morphology and the chemical composition of the samples using a 20 kV JEOL 840A SEM equipped with an OXFORD INCA 300 Energy Dispersive X-ray Spectroscopy (EDS) analyzer (Jeol Ltd., Akishima, Tokyo, Japan). X-ray powder diffraction graphs (XRD) were recorded at Bragg-Brentano (BB) geometry using a two-cycle Rigaku Ultima+ powder X-ray diffractometer (Rigaku Corporation, Shibuya-Ku, Tokyo, Japan) with a Cu Ka radiation operating at 40 kV/30 mA). Finally, thermogravimetric (TGA) measurements were used to examine the thermal stability of CrSi₂ samples, which were performed with a TG-DTA SETARAM SETSYS 16/18 (Setaram Instrumentation, Caluire, France). The samples were heated from room temperature up to 1000 °C at a heating rate of 10 °C/min and air flow about 50 mL/min. The samples were cut to a suitable size to fit inside the crucible, polished, and then cleaned. The surface area was calculated in each case (mm²). The mass samples were in the range of 20–35 mg. The samples in bulk form (expressed in mg/mm^2) were put in alumina crucibles, with an empty alumina crucible used as a reference; sample temperature and weight were continuously recorded to obtain in situ quantitative data relating to the rate of oxidation of the samples.

3. Results and Discussion

3.1. Thermodynamic Prediction of Pack Compounds Formed

Pack Cementation is an in situ chemical vapor deposition process that comprises two steps, the thermochemical reactions, and the solid-state diffusion. In the case of the Cr–Si system, during the first part, the Cr donor powder reacts with the activator (NH₄Cl), which primarily is transformed from α -NH₄Cl phase to β -NH₄Cl [21]. Then, it decomposes above 200 °C [21,22,25], forming HCl vapors that react with the Cr powder. The as-formed gaseous chlorides decompose on the substrate (vapor transport to the substrate surface occurs because of the high thermodynamic activity in the powder mixture and the low activity at the substrate surface [26]), resulting in the deposition of the donor material in a highly reactive form (via the formation of chlorides) that promotes metal–metal interaction. According to the literature [26], at the surface, the transportation of the desired element occurs via several possible deposition reactions such as the disproportionation, displacement reaction with the substrate, and reaction with the environment. Additionally, the byproducts of the reaction react again with the donor material and the process is repeated until the donor is fully consumed. This method has also been reported in the literature and it happens without requiring high vacuum conditions, unlike other methods [26–28]. Eremenko et al. [14] have studied the Cr–Si system and measured the Gibbs energies of Cr silicides as a function of temperature at various temperatures from 700 to 850 °C. They found that the gas partial pressure of Cr chlorides is sufficiently high to transfer a part via the gas phase to the silicon surface. Therefore, the deposition of Cr in a more reactive form is mainly attributed to the decomposition of the activator and the reaction of the products with the Cr powder and the Si substrate. From this stage, a thermal diffusion process occurs by Si atoms to be the predominant species. Several marker techniques were developed during the past few years to determine the dominant diffusing species during the solid-state interaction between thin metal films and Si to form silicides. For the deposition of Cr on Si substrate, several marker studies were performed by using Xe and radioactive ³¹Si. It was found that the diffused species are the Si atoms [5,25,29]. Additionally, Si atoms are the element with the lowest melting point and the bigger total interfacial area, which will diffuse faster in order to reduce the free energy of the system [30–32].

The Thermocalc computing program was used to present some preliminary results about the Cr–Si phases that are thermodynamical to be formed under the pack cementation process. Figure 2 shows the phases that are thermodynamically stable and hence are likely to be formed for a pack containing 40 wt.% Cr and 3 wt.% NH₄Cl activator at 1000 °C as a function of the Si amount. Since the amount of Si increases, new phases will appear. Therefore, the Cr₃Si is the first thermodynamically phase formed, followed by the Cr₅Si₃, CrSi, and CrSi₂. The CrSi₂ phase becomes increasingly stable as the amount of Si increases. According to the phase diagram of the Cr–Si system [5] and knowing that the elemental ratio of CrSi₂ is 1:2, this phase may appear as we move away from the surface of the coating. Therefore, moving from the surface inwards, the stable phases appear to be: Cr₃Si, Cr₅Si₃, CrSi, and CrSi₂. As mentioned above, this trend is expected because Si atoms disperse more quickly [25,29]. However, it should be noticed that the phases on the substrate will be determined by the element deposited, phase diagram, and interdiffusion kinetics.



Figure 2. Amount of equilibrium phases formed during pack cementation process as a function of the Si amount.

3.2. Effect of Deposition Temperature

Chromium silicides compounds were synthesized by pack cementation process for 40 wt.% Cr, 3 wt.% NH₄Cl, and 57 wt.% Al₂O₃ in the pack mixture at various temperatures. The coating quality formed at temperatures below 1000 °C is very poor. The coating thickness is inhomogeneous, large areas of the silicon substrate are exposed and there are many cracks and cavities. Additionally, inclusions of alumina were being observed in the coating originating from the powders of the pack mixture due to the outward diffusion [30,31]. For this reason, the inert filler was not mixed with the Cr powder and NH₄Cl activator; it was placed at the top and bottom of the crucible to fill the space, as described in the experimental section. Since coatings of that quality are useless for

any kind of application, we will focus on the samples formed at 1000 °C to 1150 °C. Figure 3 shows some typical SEM cross-section micrographs (at different magnifications) of the samples formed during the chromizing step at various temperatures. According to the cross-sectional SEM micrographs, the micrograph is "divided" into two parts. This is because a full transformation of the Si substrate into various chromium silicide compounds occurs, forming cracks and holes. The consumption of Si substrate for the formation of Cr–Si compounds, and the faster diffusion of Si leads to cracks and voids, which are formed due to the difference in intrinsic diffusivities of chemical constituents (higher Si diffusion rate compared to Cr) named the Kirkendall effect [32]. The cracks might have also been caused by the thermal expansion coefficient mismatch between the formed compounds and the substrate.

Table 2. EDS scannings of the chromized samples obtained by 40 wt.% Cr in the pack mixture for 120 min at various temperatures.

A/A	1000_120 min		1050_120 min		1100_120 min		1150_120 min	
	Si (at.%)	Cr (at.%)						
1	34.74 ± 2.24	65.26 ± 2.67	38.67 ± 2.54	61.33 ± 3.01	31.23 ± 3.01	68.77 ± 2.56	32.63 ± 2.45	67.37 ± 2.78
2	50.75 ± 1.84	49.25 ± 1.96	36.01 ± 2.45	63.99 ± 2.67	52.14 ± 1.69	47.86 ± 1.82	33.16 ± 2.22	66.84 ± 2.67
3	44.77 ± 1.95	55.23 ± 1.71	47.56 ± 2.55	52.44 ± 2.15	66.62 ± 1.45	33.38 ± 1.23	49.53 ± 1.97	50.47 ± 1.61
4	62.44 ± 2.34	37.56 ± 1.98	61.22 ± 2.84	38.78 ± 1.95	66.54 ± 1.11	33.46 ± 1.23	63.81 ± 1.95	36.19 ± 1.71
5	66.78 ± 1.56	33.22 ± 1.26	65.23 ± 2.02	34.77 ± 1.94	66.38 ± 1.21	33.62 ± 1.10	49.91 ± 2.05	50.09 ± 1.69
6	62.72 ± 2.84	37.28 ± 1.94	66.80 ± 1.34	33.20 ± 1.54	65.75 ± 1.87	34.25 ± 1.76	66.75 ± 1.03	33.25 ± 1.33



Figure 3. The cross-sectional morphologies at 400 μ m and 100 μ m (shown inset) of the chromized samples obtained by using 40 wt.% Cr in the pack mixture for 120 min at (**a**) 1000 °C; (**b**) 1050 °C; (**c**) 1100 °C; (**d**) 1150 °C. The areas denoted as #1, #2, #3, #4, #5, and #6 correspond to the EDS analysis presented in Table 2.

EDS analysis was performed on several regions of the samples to identify the asformed structure. Table 2 presents the cross-sectional EDS analysis of the chromized samples obtained by use of 40 wt.% Cr in the pack mixture for 120 min at 1000 °C, 1050 °C, 1100 °C, and 1150 °C. In Figure 3, areas denoted as #1 and #2 were found to contain Cr-rich compounds, while the EDS analysis of #4, #5, and #6 shows compounds that are rich in Si. This is expected from the Thermocalc calculations about equilibrium phases formed during pack cementation. It seems that Si-rich and Cr-rich phases were formed near the consumed substrate and the surface, respectively, during the chromizing step.

Figure 4 shows the XRD pattern of the samples synthesized with 40 wt.% Cr in the pack mixture at various heating temperatures. In Figure 3, areas #1-#2 and #4-#6 correspond to Cr₅Si₃ and CrSi₂ phases, respectively, based on the results of EDS analysis in Table 2 and XRD characterization. The areas denoted as #2, #3 in the 1000_120 min, #3 in 1050_120 min, #2 in 1100_120 min and #3, #5 in 1150_120 min samples correspond to the CrSi phase. The results of EDS analysis for all samples agree with the identification of the XRD patterns, indicating that the same compounds were found in the diffraction patterns of all samples synthesized between 1000 and 1150 °C. Once again, it is apparent that phases 'rich' in Cr appear near the surface of the samples, while phases 'rich' in Si are in the center of samples. This is also confirmed by the thermodynamic calculations in Figure 2 and the literature results [22].

Figure 5 shows the lattice parameters (a and c) and the cell volume (v) versus temperature for CrSi₂, Cr₃Si, and Cr₅Si₃ calculated by the Rietveld refinement. The errors are estimated to be generally lower than 9×10^{-5} and 3×10^{-5} for the α and c lattice parameters, respectively. The lattice parameters (a and c) and the cell volume (v) versus temperature for CrSi₂, Cr₃Si, and Cr₅Si₃ slightly increase with increasing the heating temperature. After the formation of a silicide compound, the layer grows either by metal atom motion at the silicon–silicide interface or by silicon atom motion at the silicide–metal interface. As discussed above, the diffusion process of Si on the silicide compounds of Cr is very fast under these conditions. Although the movement of Si atoms does not cause significant stresses, once they have arrived at their respective interfaces, the Si atoms will react with chromium to form Cr–Si silicides. This process causes an increase in volume. Additionally, the c/a ratio for CrSi₂ was found to be ~1.43 deviating from the ideal value of 1.5 [33]. Dasgupta et al. [8] have found a value of 1.438 for the c/a ratio of CrSi₂ supporting that this deviation results in smaller interlayer bond distances.



Figure 4. XRD pattern of the chromized sample obtained by 40 wt.% Cr in the pack mixture for 120 min at (a) 1000 °C; (b) 1050 °C; (c) 1100 °C; (d) 1150 °C. The peaks were indexed by use of PDF #75-2250 (Cr₃Si), #51-1357 (Cr₅Si₃), #35-0781 (CrSi₂), and #51-1356 (CrSi) [34].



Figure 5. (a,b) Refined lattice parameters; (c) cell volume of CrSi₂, Cr₃Si, and Cr₅Si₃ as a function of temperature.

The thermal expansion coefficients (α) were calculated by using the data of the lattice parameters [35,36]. In the temperature range studied (1000–1150 °C), the thermal expansion coefficients were found to be $\alpha_{\alpha} = 9.64 \times 10^{-6} \circ C^{-1}$ and $\alpha_{v} = 28.93 \times 10^{-6} \circ C^{-1}$ for Cr₃Si; $\alpha_{\alpha} = 6.41 \times 10^{-6} \circ C^{-1}$, $\alpha_{c} = 14.07 \times 10^{-6} \circ C^{-1}$ and $\alpha_{v} = 26.89 \times 10^{-6} \circ C^{-1}$ for Cr₅Si₃ and $\alpha_{\alpha} = 11.77 \times 10^{-6} \circ C^{-1}$, $\alpha_{c} = 17.72 \times 10^{-6} \circ C^{-1}$ and $\alpha_{v} = 36.30 \times 10^{-6} \circ C^{-1}$ for CrSi₂. These results confirm the relationship between linear and volumetric thermal expansion coefficients ($\alpha_v = 3\alpha_1$) for the Cr₃Si cubic system and are in good agreement with the literature results [36]. The thermal expansion coefficients of Cr_5Si_3 and $CrSi_2$ present anisotropy between the two crystallographic axes. The results for the thermal expansion coefficients of Cr₅Si₃ and CrSi₂ were compared with the literature and were found to be in good agreement [8,36–38]. According to the literature [37,39], the thermal expansion coefficients are isotropic for cubic materials, but it is expected to be anisotropic in non-cubic material such as orthorhombic disilicides and hexagonal 5-3 silicides. Additionally, it is known that the thermal expansion coefficient in the c-direction is larger than that in α -direction for most compounds due to the complex crystal structure and the different bond strength along with different crystal orientations [40]. The different values of thermal expansion coefficients between the formed compounds and the substrate (the coefficient of expansion for Si is $2.6 \times 10^{-6} \circ C^{-1}$) lead to anisotropy which can cause micro-cracks during the procedure.

3.3. Effect of Deposition Time

Then, experiments for chromium silicides were performed at 1000 °C for various deposition times ranging from 15 to 120 min. Figure 6 shows cross-sectional SEM micrographs (at different magnifications) of chromizing samples for various times. On the one hand, the four samples do not present considerable differences in the silicides formed because both the longer and shorter heating times have led to the formation of all chromium silicide compounds. It should be mentioned again that a full transformation of the Si substrate into chromium silicide compounds can be seen in Figure 6. Table 3 presents the cross-sectional EDS analysis of the chromized samples obtained by use of 40 wt.% Cr in the pack mixture for 120 min, 60 min, 30 min, and 15 min at 1000 °C. Once again, from the results of EDS analysis, it seems that Cr-rich and Si-rich phases were formed near the surface and consumed substrate of samples, respectively. On the other hand, the heating time variations seem to affect the thickness of the samples, which increases with the increase in the deposition time. The cross-sectional SEM micrographs of the samples synthesized at shorter times appear to be more homogeneous compared to the longer ones without presenting large cracks and cavities. For longer deposition time (120 min), the CrSi₂ and CrSi compounds, that are formed first after the transformation of Si substrate into chromium silicides, are consumed to form Cr-rich phases due to the fast Si diffusion leading to a large density of cracks and holes. According to the literature [16], after consuming all the available silicon, CrSi₂ can react with unconsumed chromium to form Cr₅Si₃ or Cr₃Si.









Figure 6. The cross-sectional SEM micrographs at 300 µm and 100 µm (shown inset) of the chromized samples, obtained by use of 40 wt.% Cr, deposited at 1000 °C for (**a**) 120 min; (**b**) 60 min; (**c**) 30 min; (**d**) 15 min. The areas denoted as #1, #2, #3, #4, and #5 correspond to the EDS analysis presented in Table 3.

	1000_120 min		1000_60 min		1000_30 min		1000_15 min	
A/A	Si (at.%)	Cr (at.%)	Si (at.%)	Cr (at.%)	Si (at.%)	Cr (at.%)	Si (at.%)	Cr (at.%)
1	22.62 ± 2.45	77.38 ± 2.56	36.41 ± 2.33	63.59 ± 2.11	31.89 ± 2.86	68.11 ± 2.45	31.25 ± 2.76	68.75 ± 2.44
2	48.67 ± 1.97	51.33 ± 1.44	62.87 ± 2.89	37.13 ± 1.84	47.65 ± 1.78	52.35 ± 1.43	45.26 ± 1.87	54.74 ± 1.35
3	54.60 ± 1.01	45.40 ± 2.33	51.22 ± 1.21	48.78 ± 1.67	67.43 ± 1.53	32.57 ± 1.64	62.33 ± 1.78	37.67 ± 1.34
4	65.40 ± 2.02	34.60 ± 1.44	61.37 ± 2.54	38.63 ± 1.73	61.09 ± 2.76	38.91 ± 1.80	61.89 ± 2.98	38.11 ± 1.71
5	64.21 ± 2.56	35.79 ± 1.65	65.45 ± 1.67	33.55 ± 1.21	66.64 ± 1.12	33.36 ± 1.21	65.88 ± 1.45	34.12 ± 1.34

Table 3. EDS scannings of the chromized samples obtained by using 40 wt.% Cr in the pack mixture at 1000 °C for 120 min, 60 min, 30 min, and 15 min.

Figure 7 shows the typical XRD diagrams of the chromizing samples for various deposition times. According to the XRD characterization and cross-sectional SEM micrographs, various chromium silicide phases such as CrSi₂, CrSi, CrSi₃, and Cr₅Si₃ are formed for all the synthesized samples. Therefore, even at the lowest deposition time of 15 min, a full transformation of the Si wafer into chromium silicide compounds occurs (Figure 6d) because of the very rapid diffusion of silicon in the Cr–Si compounds.



Figure 7. XRD pattern of the chromized sample obtained by use of 40 wt.% Cr in the pack mixture at 1000 °C for (**a**) 120 min; (**b**) 60 min; (**c**) 30 min; (**d**) 15 min. The peaks were indexed by use of PDF #75-2250 (Cr₃Si), #51-1357 (Cr₅Si₃), #35-0781 (CrSi₂) and #51-1356 (CrSi) [34].

According to SEM micrographs, it is obvious that the thickness increases with time. Figure 8 shows the dependence of the thickness as a function of time. There is a nearly parabolic relationship between the thickness of the silicides formed and the deposition time in agreement with the literature results [41]. The growth of chromium silicides follows a uniform process with the layer-by-layer diffusion of silicon in the early stages. The Si diffusion becomes easier from the substrate through the first formed chromium silicide phase in the regions where Cr has not yet reacted. However, cracks and porosity are formed due to the fast diffusion of Si atoms and the different values of thermal expansion coefficients between the Si substrate and the formed Cr–Si compounds leading to strong morphological abnormalities. As mentioned earlier, a larger number of cracks and holes appeared in the sample synthesized at 1000_120 min compared to that synthesized at a shorter deposition time. It should be noted that an increase in the sample thickness is not always the result of growth under isothermal conditions (deposition time selected). Some layers may be developed during cooling from elevated temperatures to room temperature.



Figure 8. Time dependence of the thickness of the chromized samples deposited at 1000 °C for different deposition times.

3.4. Siliconizing Step

The higher chromium silicide (CrSi₂ phase) was the subject of numerous investigations, mainly because of its good oxidation resistance, semiconducting properties at elevated temperatures, and thermoelectric properties [22,41–44]. According to the pack chromizing results, several Cr the sample synthesized at 1000_120 min Si compounds were formed, the majority of which are rich in Cr. To enrich the Cr-Si compounds with Si, the second step of pack cementation process was performed by using Si powder as the donor material. Figure 9 shows the typical cross-sectional and plan-view SEM micrographs (shown inset) of selective siliconized CrSi₂ samples. EDS analyses at several areas of cross-sectional and plan-view micrographs revealed that the elemental ratio of Cr: Si was 1:2 (34 ± 3 at.% Cr and 63 ± 3 at.% Si). No other chromium silicide phases or impurities were found. The cross-sectional SEM micrographs of selective samples present gaps and holes that pre-existed in the first chromizing step (Figures 3 and 6). However, the 1000_15 min sample in Figure 9d, synthesized at 1000 °C for 15 min during the chromizing step, seems to be more homogeneous with smaller cracks and holes compared with those synthesized at higher temperatures and longer times. Additionally, for the plan-view SEM micrographs, the surface morphology of 1000_15 min is quite homogeneous with some porosities in places, as shown inset in Figure 9d. For the same temperature but after 120 min, the surface morphology is dense and present elevated roughness with distinguishable low depth craters, while the morphology of the higher heating temperature samples also looks more uniform, and smoother compared to that of 1000_120 min sample. The atoms obtain higher energy decreasing the crystalline defects densities and forming smooth surfaces [45,46].

The XRD results in Figure 10a show the presence of the $CrSi_2$ compound indicating that the previously Cr phases were successfully enriched with Si. It should be mentioned that very sharp and high peaks of the $CrSi_2$ phase appear for all the examined samples. The various chromium silicide phases could not prevent the fast Si diffusion into the substrate (now, the substrate is the various chromium compounds synthesized in the chromizing step), and thus, the $CrSi_2$ phase is formed. Table 4 presents the thickness of the samples synthesized at 1000_120 min, 1150_120 min, and 1000_15 min, which gradually increases from approximately 540 µm to 620 µm and 611 µm, respectively. The thickness increases with increasing the heating temperature and decreasing the deposition time in the chromizing step. Therefore, the most noticeable evolution in thickness is observed for 1150_120 min and 1000_15 min samples. However, as discussed above, the deposition time of 120 min is long enough to consume all the Si substrate due to the fast Si diffusion, leading to the formation of a large number of cracks.



Figure 9. Cross-sectional at 400 μ m and the corresponding plan-view SEM micrographs at 100 μ m (shown inset) of the siliconized samples obtained by use of 15 wt.% Si in the pack mixture for the sample synthesized during the chromizing step at (a) 1150_120 min; (b) 1000_120 min; (c) 1000_30 min; (d) 1000_15 min.



Figure 10. (a) XRD pattern of the siliconized samples; (b) crystallite size calculated by the WH analysis. The peaks were indexed by use of PDF #35-0781 (CrSi₂) [34].

A/A	Sample Name	Thickness (µm)	Critical Temperature of Oxidation (°C)
1	1150_120 min	620.5	504.9
2	1100_120 min	547.9	358.9
3	1000_120 min	540.4	331.1
4	1000_60 min	567.3	344.1
5	1000_30 min	589.4	514.4
6	1000_15 min	611.6	609.0

Table 4. Calculated parameters from the synthesis of CrSi₂ samples at various temperatures and times.

The crystallite size was calculated by using Williamson–Hall (W–H) analysis [47]. The crystalline size was estimated from the y-intercept of the linear fit to the data of a plot of $4\sin\theta$ along the x-axis and wcos θ along the y-axis. Figure 10b shows the crystalline size of the synthesized CrSi₂ samples in the siliconizing step. It was found to change from 43.14 nm to 76.62 nm and 26.24 nm for 1150_120 min, 1000_120 min, and 1000_15 min, respectively, in agreement with the literature results for the crystallite size of the CrSi₂ samples [21,42].

For the examination of the thermal stability of the CrSi₂ samples, TGA experiments were performed in an air environment by heating the samples under non-isothermal conditions from room temperature up to 1000 °C. These experiments look at whether the materials could work properly without being degraded by oxides. The main emphasis is given on how the different synthesis conditions have influenced the material's thermal stability. Figure 11 shows the mass gain per unit area curves for CrSi₂ samples synthesized at various temperatures and times. The samples present high thermal stability because the increase in mass up to 1000 °C is insignificant compared with the total mass before oxidation. It can be seen that the mass gain per unit area is even lower than 0.006 mg/mm². This can be explained by the high diffusivity of Cr in the nanostructure and the active formation of a Cr-rich oxide layer [48,49]. According to the literature [50], the oxidation rate of CrSi₂ is determined by the diffusion of all the reaction components at lower temperatures (700–900 °C), whereas it is mainly controlled by the diffusion of chromium over cationic vacancies in the p-type Cr₂O₃ lattice at higher temperatures.



Figure 11. TGA non-isothermal curves of the as-formed CrSi₂ samples synthesized at various (**a**) temperatures and (**b**) times during the chromizing step.

Table 4 presents the critical temperature at which the oxidation rate becomes significant. The oxidation starts at about 505 °C and 609 °C for the 1150_120 min and 1000_15 min

samples, respectively. The samples synthesized at a higher temperature and a shorter time appear to increase start-up oxidation temperatures. However, surface roughness was shown to play a role in the oxidation behavior of several materials [51–56]. Platt et al. [54] reported that there is a clear trend towards rougher surfaces generating thicker oxides. Charpentier et al. [53] found that a rougher initial surface favors the hardness of the oxide layer, which could be correlated to a better adherence between the oxide layer and the substrate. In our case, the 1000_15 min sample was found to present the lower surface roughness (Figure 9d) compared with that synthesized at longer deposition times and higher temperatures. It seems that the initial surface roughness affects the oxidation rate; the largest surface roughness provides the largest mass gain per unit area. Additionally, the 1000_15 min CrSi₂ sample has the lowest crystallite size. It was reported that materials with nanocrystalline size affect thermal stability [57–60]. Birbilis et al. [59] showed that nanocrystalline materials with fine grain size and high diffusion coefficients facilitate the formation of protective oxides. In our previous work [21], the crystallite size for $CrSi_2$ in powder form (32.5 nm) was calculated; the compound was found to be stable up to 690 °C, forming a protective layer of chromium and silicon oxides.

Bulk $CrSi_2$ was found to be stable in the air up to 700 °C due to the formation of a protective layer of Cr_2O_3 or SiO_2 , limiting the oxygen diffusion [48]. The XRD patterns of the oxidized samples after TGA tests confirm the presence of a small amount of Cr_2O_3 in Figure 12a. However, it should be mentioned that, in the XRD pattern, the $CrSi_2$ is still the dominant phase after the thermal oxidation tests of all studied materials. No Si oxides can be found in the XRD pattern because of their small amount or concurrence of their most intense peaks with peaks of other present compounds or the presence of amorphous SiO_2 . This result is in good agreement with the literature data [48], showing that Cr_2O_3 is the only oxide phase detected in the diffraction patterns at 1000 °C. It was reported that the Cr_2O_3 is a thermodynamically stable phase up to high temperatures due to its high melting point, forming an adherent layer that reduces oxygen interaction [61].



Figure 12. (a) Bragg–Brentano XRD pattern; (b) SEM micrographs of non-isothermally oxidized $CrSi_2$ samples during non-isothermal oxidation from ambient temperature to 1000 °C. The peaks were indexed by the use of PDF #35-0781 ($CrSi_2$) and #38-1479 (Cr_2O_3) [34].

The non-isothermally oxidized $CrSi_2$ samples were also examined with SEM microscopy and EDS analysis. Figure 12b shows the selected cross-sectional SEM micrograph and the corresponding plan-view image (shown in inset) for the siliconizing sample synthesized at 1000_120 min in the chromizing step. From the EDS analysis, the non-isothermally oxidized $CrSi_2$ samples were found to contain 62.3 (±2.25) at.% Si and 30.9 (±2.30) at.% Cr. Once again, the EDS analyses reveal that the $CrSi_2$ is the dominant phase after thermal

oxidation tests confirming the thermal stability of the synthesized samples. The oxide scale compounds which were formed in the material are at an insignificant concentration.

4. Conclusions

This study reports the synthesis of chromium silicide phases by the pack cementation process studying the effect of the deposition time t and the heating temperature T on the morphology and structure of the synthesized samples. A series of experiments were carried out at temperatures from 1000 to 1150 °C with different deposition times ranging between 15 and 120 min. The effect of different experimental conditions on the structure, composition, and short-term thermal stability in the air was investigated. According to the pack cementation process, the activator is decomposed and reacts with Cr powder and Si substrate. The results of the thermodynamic calculations clearly show that all the equilibrium phases predicted by the Cr–Si phase diagram can be formed during the pack cementation process. XRD patterns revealed the presence of various chromium silicide compounds in all chromizing step cases, without any oxide traces. The deposition temperature and heating time were found to affect the coating thickness and the microstructure of the synthesized samples. All the siliconized samples demonstrated significant thermal stability under non-isothermal measurements in the air. We can conclude that the sample, synthesized at 1000 °C_15 min during the chromizing step in combination with the siliconizing step at 1000 °C for 60 min, presents the best thermal stability. The selected temperatures provide acceptable, economical, and repeatable results. Therefore, pack cementation is a cost-effective and large-scale method to produce chromium silicides.

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