Effect of processing parameters on *in situ* screen printing-assisted synthesis and electrical properties of Ti_3SiC_2 -based structures

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Abstract: This work reports on the development of pastes containing Ti, TiC, Si, and C elementary powders for *in situ* synthesis of Ti_3SiC_2 via screen printing. Four paste compositions were manufactured using two powder mixtures (Ti/Si/C and Ti/TiC/Si/C) with different stoichiometry. The pastes were screen printed onto Al_2O_3 substrates and sintered at 1400 °C in argon varying the dwell time from 1 to 5 h. The printed pastes containing TiC and excess of Si exhibited the lowest surface roughness and after 5 h sintering comprised of Ti_3SiC_2 as the majority phase. The electrical conductivity of this sample was found to range from 4.63×10^4 to $2.57 \times 10^5 \text{ S} \cdot \text{m}^{-1}$ in a temperature range of 25–400 °C.

Keywords: MAX phases; Ti_3SiC_2 ; screen printing; *in situ* synthesis; electrical conductivity

1 Introduction

Titanium silicon carbide (Ti_3SiC_2) is a versatile and remarkable ceramic, which over the past years has been gaining attention. It provides the high electrical and thermal conductivity characteristics of metals and the mechanical and chemical stability over a wide range of temperature characteristics of ceramics, making it a material with pronounced potential for a wide field of application including electrical and electronics [1]. Additionally, Ti_3SiC_2 is well-known for its unique combination of mechanical, electrical, and thermal properties of both metal and ceramic materials. It exhibits high electrical and thermal conductivity,

excellent thermal shock resistance, oxidation resistance, thermal and chemical resistance, easy machinability, high rigidity, high hardness, and high elastic modulus [2]. The reported electrical conductivity of this material ranges from 4.5×10^6 to $9.6 \times 10^6 \text{ } \Omega^{-1} \cdot \text{m}^{-1}$, which is considerably high for ceramics, and makes it a potential candidate for applications as electrical contacts, in high-power electronics, corrosion protective coatings, and heat exchangers [3,4]. Different technologies have been used for the synthesis and processing of bulk and Ti_3SiC_2 films, such as temperature fluctuation synthesis [5,6], reactive HIP [7], spark plasma sintering [8], ink-jet printing [9], preceramic paper fabrication [10], DC magnetron sputtering [11], 3D-printing [12], and mechanical alloying [13]. Additionally, Dcosta *et al.* [14] fabricated Ti_3SiC_2 powder-based structures through 3D printing combined with cold isostatic pressurizing and sintering.

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In electronics, ink-jet printing and screen printing have gained attention due to their low cost, speed velocity, and simplicity. Screen printing is one of the printing techniques currently used for the fabrication of conductive lines and films. This technique is gradually replacing the conventional methods for production of small and medium scale-integrated electronic devices. It is a cost-effective high-performance and high-processing-speed technique, which is environmentally friendly, has high reliability, and allows the use of different printing substrates [15]. Phair *et al.* [16] reported that the composition and rheological properties of the required paste and the screen printing parameters are directly related to the performance of this process and the quality of the screen printed ceramic films. The screen printing process itself consists in the deposition of a ceramic paste through a screen mesh and under a determined pressure applied by a squeegee allowing the fabrication of thick films. The printing geometry is drawn onto the screen mesh and thus, it uses only the sufficient quantity of the pastes thereby reducing waste [17]. This process has been used successfully for the fabrication of several electronic devices. Faddoul *et al.* [15] reported the screen printing of silver pastes on low temperature co-fired ceramic (LTCC) substrates for microelectronic applications. Goldberg *et al.* [18] showed that screen printing can be applied for batch fabrication of integrated chemical-sensor arrays. Phair [19] reported the screen printing of oxide layers in solid oxide fuel cells (SOFC). The processing of Ti_3SiC_2 -based pastes via screen printing has been already investigated by Carrijo *et al.* [20]. However, as of yet there is no report on *in situ* synthesis of Ti_3SiC_2 from its elemental powder via screen printing, in which the main advantage is to save processing steps.

Additionally, the use of alumina as substrate enables the preparation of $\text{Ti}_3\text{SiC}_2\text{--Al}_2\text{O}_3$ layered composites for applications that require high temperatures due to their comparable thermal expansion coefficients [21].

In this work, we propose the production of pastes containing commercial Ti, TiC, SiC, and graphite powders to synthesize Ti_3SiC_2 thick films via screen printing onto paper derived Al_2O_3 substrates. The rheological properties of the pastes produced for screen printing, as well as the microstructure and electrical properties of the printed structures were also investigated.

2 Experimental

For the production of pastes, Ti (25 μm , ABCR GmbH & Co. KG, Karlsruhe, Germany), TiC (2.5 μm , H.C.Starck, Laufenberg, Germany), Si (3 μm , Siligrain, Kristiansand, Norway), and graphite (4 μm , Lehmann und Voss Co. KG, Hamburg, Germany) powders were used.

For the synthesis of Ti_3SiC_2 , two different powder mixtures were used: (1) Ti/Si/C and (2) Ti/TiC/Si/C. For each mixture, two different stoichiometries were prepared (Table 1). Ethyl cellulose (EC) and terpineol (Fluka Chemie GmbH, Switzerland) were used as binder and solvent, respectively. The amount of carbon provided from binder and solvent was also taken into account. The binder was first dissolved in terpineol using mechanical stirring at 80 °C and subsequently elementary powders were added using a three-roll mill (Exakt Advanced Technologies GmbH, Germany).

The numbers in the nomenclature of the samples specify the composition and stoichiometry of the pastes. The first number corresponds to the composition (mixture type) and the second is related to the amount

Table 1 Composition of pastes

	P1.1		P1.2		P2.1		P2.2	
	(vol%)	(wt%)	(vol%)	(wt%)	(vol%)	(wt%)	(vol%)	(wt%)
Terpineol	65.5	41.6	67.3	42.1	61.1	33.1	61.6	34.5
EC	7.2	19.8	4.5	12.1	3.4	7.8	2.9	7.0
Ti	10.5	26.2	13.0	32.0	9.6	20.6	8.4	18.5
Si	7.9	10.2	9.7	12.5	10.8	12.0	14.1	16.1
Graphite	8.9	2.2	5.5	1.3	4.1	0.9	3.5	0.8
TiC	—	—	—	—	11.0	25.7	9.5	23.1
Stoich.	3Ti/2Si/2C		3Ti/2Si/C		3Ti/3TiC/3Si/C		3Ti/3TiC/4.5Si/C	
Mixture	Ti/Si/C				Ti/TiC/Si/C			

of precursors. For example, P1.1 corresponds to the paste produced with Ti, Si, and C powders with 3Ti/2Si/2C powder composition, whereas P2.2 corresponds to the paste produced with Ti, TiC, Si, C powders but with stoichiometry of 3Ti/3TiC/4.5/Si/C.

For the printing process, a screen printer (ELA, DEK - ASM Assembly Systems GmbH, Germany) was used. The pastes containing the elemental powders were deposited onto paper-derived Al_2O_3 substrates. The preparation of printing substrates was previously reported in Ref. [22]. The screen used was made of polyester (Koenen GmbH, Germany) with a Mesh opening of 333 μm , an open screen surface of 49%, and a Mesh count of 21 cm^{-1} . The printing process was carried out with a squeegee pressure of 100 N and a print speed of 150 mm/s. The one-layer printed structures were left drying for 24 h at room temperature ($\sim 20^\circ\text{C}$) and then dried for 24 h at 80°C . Afterwards, the green screen printed samples were sintered at 1400°C for 1, 3, and 5 h in a flowing argon atmosphere with heating and cooling rates of 180 K/h.

The print design is shown in Fig. 1(a). It was divided in two parts: (1) corresponding to the thinner line and superior part of the design and (2) to the larger and lower part. This classification was made in order to obtain more accurate measurements for the characterization of the printed structures. Figure 1(b) shows a representative photograph of a screen-printed sample with the P2.2 formulation.

Before Ti_3SiC_2 synthesis, investigation of the rheological behavior of the pastes was carried out at 20°C using a modular compact rheometer (MCR 302, Anton Paar GmbH, Germany). For high viscosity samples the parallel-plate geometry with diameter of 50 mm and gap of 1 mm was required. For low viscosity samples a cone and plate set up with diameter

of 17 mm and gap of 1 mm was used. The flow behavior measurements were performed with shear rates ranging from 1 to 100 s^{-1} . Measurements at higher shear rates were not performed once all pastes presented a shear thinning behavior. Storage modulus (G') and loss modulus (G'') were measured using a sweep measurement at a frequency of 1.0 Hz and shear stresses ranging from 0.01 to 1000 Pa. The 3-step recovery analysis was used to simulate the behavior of the pastes during screen printing. In the first and third steps, an oscillatory shear stress of 1 Pa at 1.0 Hz was applied for 600 s. In the second step during 180 s a high rotational shear rate of 100 s^{-1} was applied. The recovery ratio (%) was calculated from the measurement on the first and third steps using Eq. (1) [23]:

$$\text{Recovery ratio} = \frac{G' \text{ at 1680 s in third step}}{G' \text{ at 900 s in the first step}} \times 100 \quad (1)$$

After screen printing, the surface properties of the green and sintered screen printed layers in order were evaluated by confocal microscopy (NanoFocus AG, Oberhausen, Germany). For the line profile, topography images and measurement of thickness and roughness values (a scan image surface $\approx 1.0\text{ mm} \times 3.0\text{ mm}$) of part 1 of the print design (Fig. 1(a)) was used. For data calculation the WinSam 2.6.08 software (Department of Manufacturing Technology – LFT, University of Erlangen-Nuremberg) was used. The software enables a three-dimensional surface area scan of the sample. The quality of the images was optimized using a leveling method called line to line. The line-to-line leveling method comprises the adjustment of an image profile line with a polynomial equation, which is then subtracted from that image line. The average height of each line is set equal to the previous corrected line as proposed by Méndez-Vilas and Diaz [24]. The calculation of surface roughness parameters such as average surface roughness (R_a) and root mean square deviation (R_q) was performed by drawing ten section lines of $\sim 2\text{ mm}$ over each screen-printed layer. For the calculation along a measured line ($Z(x)$), Eqs. (2) and (3) were needed [25]:

$$R_a = \frac{1}{l} \int_0^l |Z(x)| dx \quad (2)$$

$$R_q = \sqrt{\frac{1}{l} \int_0^l Z^2(x) dx} \quad (3)$$

Solid area films of all paste compositions were prepared manually and sintered with the same sintering

Fig. 1 (a) Printing design and (b) screen-printed P2.2 sample.

profile as the screen-printed samples and used for X-ray diffraction analysis (D8 Advance, Bruker Corporation, USA). The solid area films were prepared in order to avoid interference from the substrates during analysis. The samples were exposed to monochromatic Cu K α radiation with a scanning rate of 0.01 (°)/s over 2θ between 25° and 95°. The microstructure of the sintered samples was evaluated using scanning electron microscopy (SEM, Quanta 200, FEI, Czech Republic) coupled with energy-dispersive X-ray spectroscopy (EDX, INCA x-sight TVA3, Oxford Instruments, UK) for compositional analysis.

Part 2 of the print design (Fig. 1(a)) was used for electrical measurements of the sintered screen printed layers. A heating apparatus (PE95/T95 System Controller, Linkam Scientific Instrument, UK) was used for the measurements at temperatures ranging between 25 and 400 °C. The electrical resistivity was evaluated using a DC four-point probe method (Keithley 2450 source Metter, Tektronix Inc., USA) and the values were obtained through Eqs. (4) and (5):

$$\rho_m = 2 \pi s R \quad (4)$$

$$\rho = 0.73 \left[\frac{th}{s} \right] \rho_m \quad (5)$$

where ρ_m = measured resistivity ($\Omega \cdot m$); ρ = resistivity ($\Omega \cdot m$); R = resistance (Ω); th = thickness (m); s = probe distance (m).

A correction factor (0.73) is required when a conductive film is deposited onto an insulating surface, once the ratio between sample thickness and distance of probes (th/s) is smaller than 1. The samples' thicknesses were measured using a confocal microscope and all samples were analyzed in triplicate.

3 Results and discussion

Figure 2 shows the flow data (Fig. 2(a)) and viscoelastic properties (Fig. 2(b)) of the pastes.

All compositions presented a shear thinning behavior. The highest viscosity value was found for P1.1 despite having the lowest solid content among all pastes. This suggests that the EC content is the main factor influencing paste viscosity. For all compositions, the values of G'' were higher than G' suggesting liquid-like behavior (Fig. 2(b)). These values increased with the increase in the viscosity. All samples present a LVER (linear viscoelastic region) and absence of cross

Fig. 2 (a) Viscosity vs. shear rate curves and (b) storage (G') and loss (G'') modulus in function of the shear stress for the different paste compositions.

over point prior to a shear stress of 100 Pa.

The 3-step recovery analysis (Fig. 3) revealed a time-dependent viscosity in all samples. This behavior was probable due to the high particle content, which leads to a progressive breakdown of the network during shearing as also observed by Inukai *et al.* [23].

The main influence can be attributed to the EC content of the pastes. P2.1 and P2.2 exhibited the lowest recovery ratios of $25 \pm 8.9\%$ and $26 \pm 8.9\%$, respectively, and also the lowest viscosity values. The opposite was observed for P1.1 and P1.2, which presented the highest recovery ratios ($68 \pm 1.6\%$ and $96 \pm 4.7\%$, respectively) and the highest viscosities. Phair *et al.* [16] observed the same behavior for screen printed zirconia films. In their study, the content of ethyl cellulose in the pastes directly influenced the recovery ratio of the pastes, which increased with increasing EC content.

Figure 4 shows the topography images of the green screen printed parts and the sintered P2.1 and P2.2 samples at 1400 °C for 5 h in argon.

Table 2 shows the R_a and R_q values of the green and sintered samples, where the influence of the powder

Fig. 3 3-step recovery measurement. Storage (G') modulus and viscosity as a function of elapsed time for all paste compositions.

Fig. 4 Topography of green screen printed layers of all paste compositions and pastes P2.1 and P2.2 after 5 h sintering at 1400 °C in argon.

Table 2 R_a and R_q values of the green and sintered screen-printed layers during different time at 1400 °C

Paste	Green	Sintering time		
		1 h	3 h	5 h
	R_a (μm)/ R_q (μm)	R_a (μm)/ R_q (μm)	R_a (μm)/ R_q (μm)	R_a (μm)/ R_q (μm)
P1.1	$5.7 \pm 1.1/6.9 \pm 1.1$	$9.7 \pm 1.1/12.9 \pm 1.1$	$9.5 \pm 2.7/13.2 \pm 0.6$	$13.0 \pm 1.8/16.4 \pm 2.7$
P1.2	$5.7 \pm 0.6/7.2 \pm 0.7$	$9.8 \pm 0.9/11.9 \pm 1.1$	$10.7 \pm 1.3/13.4 \pm 1.4$	$11.8 \pm 1.6/15.3 \pm 3.0$
P2.1	$6.5 \pm 0.5/8.0 \pm 0.7$	$5.2 \pm 0.4/6.5 \pm 0.5$	$5.1 \pm 0.8/6.4 \pm 1.0$	$6.1 \pm 1.0/7.7 \pm 1.1$
P2.2	$4.7 \pm 0.7/6.0 \pm 0.9$	$5.7 \pm 0.6/7.2 \pm 0.8$	$5.0 \pm 0.6/6.2 \pm 0.8$	$6.3 \pm 0.5/8.1 \pm 0.8$

composition on the roughness can be observed. After sintering, films formed from pastes P2.1 and P2.2 exhibited lower R_a and R_q values and were smoother than the films formed from pastes P1.1 and P1.2 regardless of the sintering time. P1.1 and P1.2 have the highest EC content, which resulted in higher height variation on sample's surface after sintering due to decomposition of EC and hence formation of defects, as already reported in Refs. [26,27]. The mass loss on the surface of the screen-printed films after sintering can be noticed as alterations in the topography images. However, the influence of the powder composition on the surface roughness is evident after sintering. The increase in thickness and surface roughness can be attributed to the reaction and products formed during

sintering.

Figure 5 shows the X-ray diffraction patterns for the films formed from all pastes after different sintering time at 1400 °C. Ti_3SiC_2 was obtained for all paste compositions in the sintering time range of 1–5 h. However, almost all films exhibited the presence of other minority phases. Layers from pastes P1.1 and P1.2, which have no TiC in their initial composition, contain TiSi_2 and Ti_5Si_3 as secondary phases. Layers from P2.1 and P2.2, which contained both TiC and excess Si, exhibit SiC as an additional phase. Furthermore, layers formed from pastes with TiC in their initial composition regardless of the stoichiometry, are composed by Ti_3SiC_2 after 3 and 5 h sintering, precisely the layers formed from paste P2.1 after 3 and

Fig. 5 X-ray diffraction patterns of films formed from all paste compositions after sintering at 1400 °C for 1, 3, and 5 h.

5 h of sintering and paste P2.2 after sintering for 5 h, except for the presence of small peaks of Al_2O_3 in the later.

Figure 6 shows the microstructure of the layers after different sintering time. A highly porous structure is noticed from the layers formed from pastes P1.1 and P1.2 in comparison to those formed from pastes P2.1 and P2.2. Moreover, an increase in the density of the printed films is evident for layers formed from pastes P2.1 and P2.2 with increasing sintering time. Corroborating with XRD results, all samples exhibited Ti_3SiC_2 after sintering at different time. Although none of the samples presented a reaction zone at the interface between the substrate and the printed layers (Fig. 6, third column), samples produced from pastes P1.1 and P1.2 exhibit Al_2O_3 inclusions and samples sintered for 1 and 3 h contained TiO_2 within their structures. Samples P1.1 and P1.2 exhibit a very porous structure, with phase discontinuity and inhomogeneous phase profile.

The EDX mapping around the interface between the Al_2O_3 substrate and the screen printed films produced from pastes P1.1, P1.2, P2.1, and P2.2 after 5 h sintering is shown in Fig. 7. TiO_2 was not found after 5

h sintering on P2.1 and P2.2 screen printed films. The possible reason for the formation of TiO_2 is the native oxide layer present on the surface of Ti particles. The films produced from pastes P2.1 and P2.2 exhibit a higher content of Si than P1.1 and P1.2. Hence, full formation of Ti_3SiC_2 is expected. Moreover, a non-homogeneous distribution of Si in the P1.1 and P1.2 screen printed films can be seen, which suggests that the initial content of Si in the reactants was insufficient to ensure synthesis of pure Ti_3SiC_2 .

Few works have reported the formation of unwanted impurity phases, such as TiC, Ti_5Si_3 , and TiSi_2 during the synthesis of Ti_3SiC_2 . Sato *et al.* [28] reported the formation of Ti_5Si_3 as secondary phase after synthesis of Ti_3SiC_2 from elementary powders of Ti, Si, and C. Racault *et al.* [29] reported a solid-state synthesis route, which resulted in Ti_3SiC_2 with less than 5 at% of TiC. Arunajatesan and Carim [30] proposed an arc-melting and annealing route for Ti_3SiC_2 synthesis, where the highest purity sample contained 2 vol% TiC as second phase. Several attempts have been suggested for the synthesis of Ti_3SiC_2 using different starting compositions, such as Ti/Si/C [31], Ti/SiC/C [32], Ti/Si/TiC [33], and Ti/Si/C/SiC [34]. Depending on the chosen starting

Fig. 6 SEM micrographs of the sintered screen printed layers of all paste compositions at 1400 °C in argon.

Fig. 7 EDX mapping of screen printed films after 5 h sintering at 1400 °C in argon. The highlighted colored regions denote for different detected elements.

reactants, different reaction paths were obtained [35]. In studies where Ti/Si/C were used as reactant powders, it was reported that the Si loss was the most likely reason for the difficulty of forming a Ti_3SiC_2 single phase [36] and therefore, the thermal stability can be increased by inhibiting Si removal from the surface [4]. With excess of both TiC and Si, Lorenz *et al.* [37] successfully synthesized paper-derived Ti_3SiC_2 by adjusting the starting stoichiometry to 3Ti/3TiC/3Si/C. Therefore, for this work the starting compositions Ti/Si/C and Ti/Si/TiC/C were selected. Here, although the presence of TiSi_2 and Ti_5Si_3 in the sintered screen-printed films formed from pastes P1.1 and P1.2 were not detected, the Ti_3SiC_2 content in layers formed from pastes P2.1 and P2.2 was noticed to be higher than those formed from P1.1 and P1.2. Furthermore, increasing the sintering time led to an increase in the Ti_3SiC_2 content formed from paste P2.2 and after 5 h sintering increased densification of the films formed from both P2.1 and P2.2 occurred. The increased yield and densification is attributed to the replacement of the carbon source to carbides in the starting reactants, which are known to reduce the amount of secondary phases formed. The Si loss is the most likely reason for the difficulty of forming Ti_3SiC_2 single phase, as reported by Radhakrishnan *et al.* [38].

As the layers produced from pastes P2.1 and P2.2 exhibited the largest amount of Ti_3SiC_2 phase of all tested pastes after 5 h of sintering, their electrical properties were analyzed.

Figure 8 shows the electrical conductivity as a function of temperature for the layers formed from pastes P2.1 and P2.2 after 5 h sintering at 1400 °C.

Fig. 8 Electrical conductivity vs. temperature of films formed from pastes P2.1 and P2.2 after 5 h sintering at 1400 °C.

Both P2.1 and P2.2 structures exhibit a metallic-like behavior, where the resistivity increased with the increasing temperature. These results agree with Yoo *et al.* [39] who studied the electrical behavior of bulk Ti_3SiC_2 in the temperature range from 26 to 576 °C. However, the electrical conductivity at 25 and 400 °C of the screen-printed layers produced from pastes P2.1 and P2.2 after 5 h sintering (Table 3) was two orders of magnitude lower than reported in literature. The sample P2.1 is less conductive than the sample P2.2 regardless of the presence of alumina in the later. Effective conductive paths may differ among samples with similar composition. Although statistically significant especially for lower temperatures, the difference between both samples lies within the same order of magnitude.

Palmquist *et al.* [40] performed a study involving the synthesis of different MAX phases in the Ti–Si–C systems by thin film fabrication via magnetron sputtering of Ti, Si, and C targets. They noticed that resistivity of $\text{M}_{n+1}\text{AX}_n$ phase films were noticeably low (Ti_3SiC_2 in a range of 0.5–0.3 $\mu\Omega\cdot\text{m}$) and TiC_x films returned values one order of magnitude higher. Notably, the presence of silicides in MAX phases is known to decrease the conductance. For mixed phases of Ti_3SiC_2 with Ti_5Si_4 and $\text{Ti}_5\text{Si}_3\text{C}_x$ the resistivity is two times higher (0.4–0.8 $\mu\Omega\cdot\text{m}$) when compared to the single phase. Emmerlich *et al.* [11] produced $\text{Ti}_3\text{SiC}_2/\text{TiC}_x$ thin films deposited via DC magnetron sputtering from three elemental targets of Ti, Si, and C on MgO and Al_2O_3 with an electrical resistivity of 25 $\mu\Omega\cdot\text{m}$. However, the electrical resistivity of a good conductor is well known to be in the order of $10^{-8} \Omega\cdot\text{m}$. This value can be influenced by several factors, such as temperature, impurities, and plastic deformation [41]. As discussed above, the defects on the screen-printed films, such as cracks, porosity, and high roughness may disrupt phase continuity decreasing electrical conductivity. Despite the non optimal results the strategy proposed

Table 3 Electrical conductivity at 25 and 400 °C of layers formed from pastes P2.1 and P2.2 after 5 h sintering at 1400 °C

Sample	Electrical conductivity ($\text{S}\cdot\text{m}^{-1}$)	
	25 °C	400 °C
P2.1	9.99×10^4 ($\pm 6.90 \times 10^3$)	4.63×10^4 ($\pm 9.45 \times 10^3$)
P2.2	2.57×10^5 ($\pm 1.85 \times 10^4$)	7.13×10^4 ($\pm 9.25 \times 10^4$)

here using elemental powders as the starting materials can be potentially applied for the synthesis of other electrically conductive and oxidation resistant MAX phases, including Ti_3AlC_2 and Ti_2AlC [42].

4 Conclusions

Pastes composed of Ti, TiC, Si, and C elementary powders for *in situ* synthesis of Ti_3SiC_2 via screen printing were developed. Pastes containing two powder mixtures (Ti/Si/C and Ti/TiC/Si/C) as reactant powders were produced and observed that the EC content had the greatest influence on the viscosity and all green screen printed films presented a good printing quality. After sintering the screen printed films for 1, 3, and 5 h at 1400 °C in argon, Ti_3SiC_2 was obtained as the majority phase. Pastes with Ti/TiC/Si/C in their initial composition exhibited lower roughness, denser microstructure, and higher adhesion in comparison to pastes without TiC content in their composition. Pastes containing Ti/TiC/Si/C and excess Si in their initial composition exhibited Ti_3SiC_2 as the main phase. Ti_3SiC_2 -based films *in situ* synthesized via screen printing exhibited electrical conductivity ranging from 4.63×10^4 to $2.57 \times 10^5 \text{ S} \cdot \text{m}^{-1}$.

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