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N.B.: When citing this work, cite the original article.

Original Publication:

Jonas Lauridsen, Per Eklund, Jens Jensen, H Ljungcrantz, A Oberg, E Lewin, U Jansson, A Flink, H Hogberg and Lars Hultman, Microstructure evolution of Ti-Si-C-Ag nanocomposite coatings deposited by DC magnetron sputtering, 2010, ACTA MATERIALIA, (58), 20, 6592-6599.

<http://dx.doi.org/10.1016/j.actamat.2010.08.018>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-63405>

Microstructure evolution of Ti-Si-C-Ag nanocomposite coatings deposited by dc magnetron sputtering

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Abstract

Nanocomposite coatings consisting of Ag and TiC_x (x<1) crystallites in a matrix of amorphous SiC were deposited by high-rate magnetron sputtering from Ti-Si-C-Ag compound targets. Different target compositions were used to achieve coatings with a Si content of ~13 at%, while varying the C/Ti ratio and Ag content. Electron microscopy, helium ion microscopy, x-ray photoelectron spectroscopy, and x-ray diffraction were employed to trace the Ag segregation during deposition and possible decomposition of the amorphous SiC. Eutectic interaction between Ag and Si is observed and the Ag forms threading grains that coarsen with increased coating thickness. The coatings can be tailored for conductivity horizontally or vertically, by controlling the shape and

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distribution of the Ag precipitates. Coatings were fabricated with hardness in the range 10-18 GPa and resistivity in the range 77-142 $\mu\Omega\text{cm}$.

Keywords: nanocomposite; analytical electron microscopy; helium ion microscopy (HIM); x-ray photoelectron spectroscopy (XPS); eutectic solidification.

1. Introduction

TiC-based nanocomposites have been studied intensively during the last decade and are well known as tribological coatings [1,2,3,4,5,6]. They have recently also been adopted in electrical applications [7, 8, 9, 10]. These nanocomposites typically consist of nanocrystalline TiC embedded in an amorphous matrix, which in the binary Ti-C system is amorphous C [4,5,11,12]. If a third element like Si is added to TiC, the phase formation complexity increases, but with that also the flexibility to tailor multifunctional materials. In our previous works, we investigated Ti-Si-C based nanocomposites deposited by dc magnetron sputtering and showed that they combine mechanical strength, and low coefficient of friction [13], with high conductivity and low contact resistance [7,10,14]. The addition of a noble metal like Ag to ceramic nanocomposites is in general interesting in a variety of fields such as tribological coatings [15], and antibacterial coatings [16,17].

Our focus is set on studying the Ti-Si-C-Ag system for improving the electrical properties of such coatings by reducing the resistivity with retained mechanical properties. This should be possible to achieve by controlling the nucleation and growth of TiC nanocrystallites in a dense matrix of segregating Si and Ag at the percolation limit, while

avoiding the formation of thick C or SiC tissue phases around the TiC as they are poor conductors.

We have previously investigated Ti-Si-C-Ag nanocomposite coatings deposited by dual dc magnetron sputtering from a Ti_3SiC_2 compound target and an Ag elemental target, with a relatively low deposition rate (1.2-2.0 $\mu\text{m/h}$) [8]. While the details of the phases present and their structure require more investigation, it is clear that the Ag segregation tendency is strong, leading to μm -large precipitates. An increased deposition rate may effectively quench the Ag surface diffusion and enable a desirable homogenous distribution of the element around the TiC crystallites.

Here, we study the phases formed in Ti-Si-C-Ag coatings deposited in a high-rate dc magnetron sputtering system using a single compound target in face-on geometry at high deposition rate (up to 11 $\mu\text{m/h}$) and investigate the effect of Ag and C content on the coating microstructure, electrical, and mechanical properties.

2. Experimental details

Ti-Si-C-Ag coatings were deposited by dc magnetron sputtering in a high vacuum industrial deposition system from a Ti-Si-C-Ag compound target. Table 1 presents the experimental conditions for the coatings. Four Ti-Si-C-Ag compound targets were chosen with different composition to achieve coating compositions with a similar Si content, but varying C/Ti ratio and different Ag content. Substrates of Si(100) and SiO_2 (100) wafers (both 15x10x0.5 mm) were placed on a fixed substrate holder facing the target. Prior to growth, the substrates were plasma etched for 5 minutes, with a pulsed dc bias of -440 V at 250 kHz. During deposition, a constant dc bias of -30, -50, or -80 V was applied. Ambient substrate temperature was used.

X-ray diffraction (XRD) in grating incidence (GI) mode with an incidence angle of 4° was performed in a Philips diffractometer equipped with a Cu $K\alpha$ x-ray source operating at 45 kV and 40 mA.

Time-of-flight energy elastic recoil detection analysis (ToF-E ERDA) at the Uppsala Tandem Laboratory was employed to measure the elemental composition of the coatings using 40 MeV $^{127}\text{I}^{9+}$ projectile ions at 22.5° incident angle and a detector placed at a recoil scattering angle of 45° [18]. The composition results were evaluated with the CONTES code [19].

X-ray photoelectron spectroscopy (XPS) measurements were performed in a Physical Electronics Quantum 2000 spectrometer using monochromatic Al $K\alpha$ radiation, and the binding energy was calibrated against Ag, Cu, and Au [20]. High resolution XPS spectra were recorded over an area of 2 x 2 mm, after 90 seconds of sputter etching with 4 kV Ar^+ ions. The normally studied Si2p spectrum is overlapped with a broad Ag4s peak; therefore, we show the Si2s spectra.

Scanning electron microscopy (SEM) was performed in a LEO 1550 microscope. Plan-view and cross-sectional images were obtained using accelerating voltages of 5-20 kV and by secondary electron imaging. Thickness measurements of the coatings were performed on the coatings deposited onto Si(100) substrates.

Helium ion microscopy (HIM) was performed with an ORION PLUS microscope from Carl Zeiss SMT [21,22]. Plan-view images were obtained by using 30 keV He^+ ions. The imaging was performed in two modes by looking; 1) at emitted secondary electrons using an Everhart-Thornley detector and 2) at backscattered He ions from the same area using an annular micro channel plate. Prior to observation, the sample was plasma cleaned.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained in a Tecnai G² 20 U-Twin 200 kV FEGTEM. Analytical TEM was performed using energy-dispersive x-ray spectroscopy (EDX) in scanning TEM (STEM) mode. Cross-section samples were mechanically polished to a thickness of ~50 μm , and a Gatan Precision Ion Polishing System (PIPS) ion miller thinned the sample to electron transparency.

Nanoindentation was done in an Umis 2000 instrument equipped with a Berkovich indenter. The hardness was calculated according to the Oliver-Pharr method [23], as an average from 49 indents performed at loads of 3 mN. Hardness maps were determined, where the indents were 8 μm from each other in a 56 x 56 μm array.

Room temperature four-point-probe measurements were performed using a Model 280C (Four Dimensions) instrument. The obtained sheet resistance was then multiplied with the coating thickness to obtain the resistivity.

3. Results and discussion

Table 1 lists the composition and the thickness of Coatings 1-12. The thickness varies between 0.7-1.3 μm . The corresponding deposition rates of 6-11 $\mu\text{m/h}$ is ~6 times higher than in our earlier study [8]. The O content in Coatings 1-12 is lower than 3 at.%, the C content increases from Coating 1 to Coating 9, and Coatings 10-12 have the highest Ag content. The substrate bias has no significant effect on the composition or the deposition rate.

Figure 1 shows the x-ray diffractograms from Coatings 1-12. TiC and Ag are the only observed crystalline phases in these coatings. In general, the TiC peak intensity increases for coatings with high C content (cf., ERDA results), indicating a higher crystallinity of

TiC. Coatings 1-6, with low C content, have no TiC 111 and TiC 311 peaks. Coatings 4-6 have overall low peak intensity, indicating low crystallinity. The TiC and Ag average grain sizes for Coatings 1-12 are estimated to be in the range 5-13 nm and 9-15 nm, respectively, using Scherrer's formula. Here, the TiC grain size increases with increased C content. Table 1 also shows that the TiC cell parameter decreases with increased C content.

Figure 1. X-ray diffractograms in grazing incidence geometry of the Ti-Si-C-Ag Coatings 1-12 deposited on Si(100) substrates.

Figure 2 shows high resolution XPS spectra for selected coatings deposited at a substrate bias of -80 V. XPS showed that the positions of Ag3d peaks (not shown) were identical for all the coatings. The peaks at 374.2 eV (Ag3d_{3/2}), and 368.2 eV (Ag3d_{1/2}) correspond to Ag-Ag bonds. No Ag-Ti intermetallic bonds were observed. It cannot be determined from the Ag3d spectra if there are Ag-Si bonds in the coating, since the transition from Ag-Ag bonds to Ag-Si bonds causes no significant peak shift or broadening [24]. Nevertheless, mixing is known to be very limited in the Ag-Si system and there is no formation of metastable phases at temperatures up to 400 °C [24,25]. Furthermore, our XRD results indicate that there are no crystalline silver silicides in the as-deposited coatings, in agreement with the phase diagram of this eutectic system [26]. Figure 2a shows the Ti2p spectra, where it is observed that Coatings 3, 6, 9, and 12 have their Ti2p peaks at 454.6 eV (Ti2p_{3/2}) and 460.5 eV (Ti2p_{1/2}), corresponding to Ti-C bonds [27,28], and that Coating 3 has additional peaks at 454.1 eV (Ti2p_{3/2}) and 459.7 eV (Ti2p_{1/2}), corresponding to Ti-Si bonds. The Ti-C peaks intensity increases with increased C content. Figure 2b shows the Si2s spectra, where it is observed that Coatings 3, 6, 9, and 12 have their Si2s peaks at 150.4 eV, 151.6 eV, and 153.5 eV, corresponding to Si-Si, Si-C, and Si-O bonds, respectively. Coating 3 also shows an additional peak at 149.8 eV, corresponding to Si-Ti. The Si2s peak for Coating 6 is slightly shifted compared with Coatings 9, and 12 to lower binding energy, which means that Coating 6 has a larger contribution of Si-Si bonds than Coatings 9 and 12. Figure 2c shows the C1s spectra, where Coatings 3, 6, 9, and 12 have their peaks at 281.8 eV, 282.4 eV, and that Coating 6, 9 and 12 have an additional peak at 284.6 eV, which corresponds to C-Ti, C-Si, and C-C bonds [29], respectively. With increased C content, the C-Si and the C-C peaks intensity

Figure 2. XPS spectra from selected coatings, a) Ti2p, b) Si2p, and c) C1s.

increases. From XPS and XRD results we infer that Si takes the place of C in the NaCl structure and bond to Ti. The formation of Si-Ti bonds instead of Si-C with an increased cell parameter, c.f. Table 1, is thus a substitute for understoichiometric TiC_x in Coating 3. The amorphous matrix (cf., TEM results below), consists of Si, SiC, and C, depending on the C content. A low C content in the coating corresponds to a matrix that consists mainly of a-Si, while increasing C content promotes a-Si, a-SiC, and a-C, in that order. From the XPS results, a small increased contribution of Si-O bonds with increased negative substrate bias was observed (not shown). Fitting of the C1s spectrum shows that the contribution to the peak at 282.4 eV, denoted C-Si, is not only from C-Si bonds, but probably also from sputtering damage and an interfacial state. The latter has been observed in nanocomposite TiC coatings and is known as TiC^* [29,30,31].

Figure 3a-d shows plan view SEM images of Coatings 3, 6, 9, and 12, respectively. The four coatings have a nodular morphology with precipitates. Coatings 9 and 12 with the highest C and Ag content, exhibits the largest precipitates on the surface.

Figure 4a-c shows plan-view HIM images of Coating 3. Figure 4a, taken with secondary electrons, shows small spherical precipitates on the surface. This is probably Ag that has diffused to the surface during the shut-down phase of the deposition process when the coating is still at elevated temperature. Figure 4b is a larger overview image taken with secondary electrons, where spherical precipitates with sizes in the interval 20-150 nm are clearly observed on the surface. The same area is imaged in Figure 4c, with backscattered He ions to achieve Z-contrast. The secondary electrons come from a few nanometers below the surface, whereas the information from the backscattered He ions comes from several tens of nanometers. Hence, Figures 4b-c indicate that the spherical precipitates on

Figure 3. Plan view SEM images of a) Coating 3, b) Coating 6, c) Coating 9, and d) Coating 12.

Figure 4. Plan view HIM images of Coating 3.

the surface contain Ag. It is also evident from the backscattered He ions contrast that there are large Ag agglomerates distributed further down in the bulk, which is confirmed (below) by TEM observations.

Figure 5 shows cross-sectional TEM and HRTEM images with corresponding SAED patterns from a) Coating 3 (12 at% Ag and a C/Ti ratio of 0.50) and b) Coating 12 (21 at% Ag and a C/Ti ratio of 1.03). Coating 3 exhibits widely separated plate-to-lens-like precipitates, which from HIM, the SAED analysis and STEM/EDX (see below) are identified as Ag. The SAED patterns in Figure 5 also show that TiC is the other crystalline phases in the coatings. The Ag precipitates are 3-100 nm wide, 10-300 nm long, and inclined by $\sim 30^\circ$ to the substrate surface. They are widely separated and form larger and coarser shapes closer towards the surface. However, the higher C content in Coating 12 yields a much higher density of Ag precipitates that are distributed more homogeneously with sizes ranging from a few nanometers near the substrate to some tens of nanometers closer to the coating top surface. TEM images (not shown) of Coating 6 (with 10 at% Ag similar to Coating 3, but with a C/Ti ratio of 0.76) showed a similar microstructure as Coating 3, but with smaller Ag precipitates. TEM images (not shown) of Coating 9 (with 14 at% Ag similar to Coating 3, but with a C/Ti ratio of 1.05, like Coating 12) showed similar microstructure as Coating 12. We infer from the above results that a high C content hinders the growth of the Ag precipitates.

Further insight into the plate-like nature of the Ag precipitates can be gained from HRTEM imaging obtained from the bottom of the coating. Figure 5a shows for Coating 3, plate-like Ag precipitates with a width of ~ 5 nm and a length of ~ 20 nm in an otherwise amorphous and nanocrystalline matrix. A closer inspection of the inclined plate-like Ag

Figure 5. TEM images, a) overview, high resolution images and SAED pattern of Coating 3, b) overview, high resolution images and SAED pattern of Coating 12.

precipitates in Figure 5a reveal that they are projected in the [110] zone axis, hence have the (220) surface parallel to their long sides in macroscopic scale and perpendicular (002) planes (see HREM and FFT insets in Figure 5a). The long (220) sides are in their turn faceted by low-energy {111}-planes. In contrast, the HRTEM image insets in Figure 5b show the Ag precipitates in Coating 12. Here, Ag crystallites are equiaxed and either single crystals or multiple-twinned precipitates in the size of ~4 nm.

The phenomenon of Ag segregation in Ti-Si-C-Ag coatings was also observed in our study based on magnetron sputtering from one Ti-Si-C compound target, and one Ag elemental target [8]. To explain this phenomenon, we first note that there is essentially no solid solubility for Ag in Si, Ti, and C, and either of their compounds. Thus, there should be a strong tendency for segregation of Ag to the coating surface during deposition. The difference in growth behavior between the coatings of the present study can be explained from the difference in the C/Ti ratio. At ambient substrate temperature both Ag and TiC phases can grow (unless hindered) by virtue of the element's surface diffusivity (c.f. Figure 5a, and reference 32). With increased C content for a given Ti content, the maximum C fraction in the TiC_x phase ($x \sim 0.47\text{-}0.97$) [32,33] is exceeded, which triggers a phase separation into TiC and C, in the case of no Si [4,5,11] or SiC (in the present case). The observation from Figure 5 and XPS indicates that the amorphous SiC phase has a much more limited diffusivity of Ag and TiC than amorphous Si and C. Thus, the emerging TiC and Ag crystallites may become covered by the amorphous matrix more frequently.

Following above, the coating microstructure is the result of a competition between Ag, TiC, and SiC segregation. Once a growing Ag crystallite becomes buried under SiC, it

stops growing since the bulk diffusion of Ag is limited at the present substrate temperature [34]. New Ag grains then renucleate on the surface. This competitive growth combined with coalescence of Ag grains on the surface, and self-shadowing of the deposition flux explains the observed coarsening closer to the coating surface.

Figure 6 shows a STEM image of Coating 3 and the intensities from Ti, Si, and Ag obtained from an EDX line scan acquired from start (S) to finish (F) in the STEM image. In the matrix, the Ti and the Si signal are high and no Ag signal is observed. Over the precipitates the Ti and Si signal intensity drops and the Ag signal intensity increases. This and the XPS results above verify that the large precipitates consist of Ag.

Figure 6. Line scan of Coating 3, from start (S) to finish (F), left) STEM images over the scanned area, and right) EDX spectra.

Figure 7 shows a STEM image and an EDX mapping of Coating 9. The coating has homogenous (featureless) structure over the first ~200 nm thickness followed by a granular structure defined by the Ag. The result for Ag is expected, based on the structure identification above (c.f., Figure 5 b) and is the result of segregation together with

gradual coarsening. Ti and C are evenly distributed over the coating thickness, except where there are Ag grains. Ag and Si, however, increase in concentration at the transition from homogenous to granular coating growth. The growth of crystalline Ag thus appears to exert a drag on the Si. Si migration through Ag layers has been reported to occur starting at 200 °C and more readily at above 300 °C [35]. The above observations can be explained by considering the nature of the Ag-Si phase diagram in which the liquid alloy exists down to the eutectic temperature of 845 °C and is deep to the Ag side (at 89 at.% Ag). For solid-state reactions, we note that Ag-induced crystallization of amorphous Si takes place in isothermal experiments at 525 °C [36,37] with possible metastable Ag-Si silicides forming [37] in particular Ag₃Si [38]. While we employed ambient substrate temperature, there are significant contributions to the adatom mobility from energetic particle bombardment. Thus, we propose that an Ag-Si alloy segregates on the growing coating surface during the co-deposition of all four elements until TiC and Ag precipitates and grows as described above. At that stage, solidification of Si starts and forms a SiC phase (as for Coating 9, which has a relatively high C/Ti ratio). This model corresponds to constitutional undercooling [39], by which a domain of eutectic composition forms between the two phases (Ag and Si(C) here) during cellular transformation.

For coatings with a lower C/Ti ratio in which C preferentially bonds with Ti and the matrix mainly exist of a-Si, the Ag precipitates grow longer and larger, and thus become more separated for a given concentration. This can be understood because of the underlying eutectic phase transformation between Ag and Si, and that there is SiC that hinders the Ag grains from growing. One can speculate that Si can form tissue layers on

Figure 7. STEM image of Coating 9 and an EDX mapping.

an emerging Ag (111) surface, but that it would be highly permeable to Ag [40] and that adding C to the structure impede the Ag diffusion by forming a SiC layer. Ag would then tend to renucleate on top of the SiC. In this general description, we have neglected the

TiC precipitation, but acknowledge that it is a parallel process, which is well described for the Ti-C [11,12] and Ti-Si-C [7,14] systems.

Table 1 also shows the resistivity and mechanical properties of Coatings 1-12. The resistivity values are in the range 77-142 $\mu\Omega\text{cm}$, which is a substantial reduction compared to $\sim 250 \mu\Omega\text{cm}$ for Ti-Si-C coatings [14], or 1200-5000 $\mu\Omega\text{cm}$ for nc-TiC/a-C coatings [11,12]. Coatings 10-12 with the highest Ag content has the lowest resistivity ($\sim 77 \mu\Omega\text{cm}$), and Coatings 7-9 with relative high carbon content and low Ag content has the highest resistivity ($\sim 142 \mu\Omega\text{cm}$). Comparing the resistivity between coatings, with a similar Ag content, shows that Coatings 1-3 with the lowest C content have the lowest resistivity, and Coatings 7-9 with the highest C content have the highest resistivity. The decrease in the resistivity with increased Ag content is expected, since Ag is a better conductor than TiC and a-SiC [32,41,42]. Likewise, a reduced C content yields a lower resistivity due to that the volume fraction of the less conducting SiC decreases. The electrical properties can be explained with percolation models. The required Ag volume fraction to achieve conduction through percolation in an insulating matrix has been estimated to an Ag fraction of ~ 0.35 [43]. Here, the percolation is not in an insulating matrix, but in a low-conductivity one; hence, the model cannot be used completely. Figure 8a shows a XSEM image from Coating 3, where the bright large elongated spots are Ag precipitates. From this image, we speculate that in Coating 3 with large Ag precipitates close to the coating surface, percolation occurs easily horizontally by the large Ag precipitates, but less so vertically due to that the Ag precipitates are isolated from each other. Correspondingly, from Figure 8b showing a XSEM image where the small equiaxed bright spots are Ag, we draw the conclusion that Coating 12 with its more

Figure 8. Cross sectional SEM images of a) Coating 3 and, b) Coating 12.

homogenous microstructure consisting of small and contacting Ag grains exhibits percolation through the coating in all directions.

Each coating exhibited a variation in hardness, as shown by the map in Figure 9 for Coating 7. If the indent is over an area where the Ag concentration is high, a low hardness down to 1 GPa is obtained, due to that Ag has a low hardness. Vice versa when the indent is over an area where the concentration of TiC is high a hardness up to 23 GPa is obtained, due to that TiC has a hardness of 15-28 GPa [7,32]. An average of 49 indents on each coating gave a hardness of Coatings 1-12 in the range 10-18 GPa.

Figure 9. Hardness map from Coating 7. The scale bar is in GPa.

4. Conclusions

Dense coatings consisting of nanocrystalline Ag and TiC embedded in a matrix of amorphous SiC with variable Si and C content can be deposited at deposition rate up to 11 $\mu\text{m/h}$ by dc magnetron sputtering from a Ti-Si-C-Ag compound target, where the amorphous matrix in the resulting coatings is controlled by the C content of the target. Segregation of Ag during deposition leads to Ag precipitation on the growth surface after a certain thickness depending on the C/Ti ratio. By eutectic interaction between Ag and Si, more or less elongated Ag grains grow in an inclined direction from the substrate surface. The Ag precipitates are coarser higher up into the coating due to coalescence and surface roughening. The TiC crystallites increase in size from 5 nm to 15 nm with increased C content. Increased C content in the coatings gives a transition from Si-Ti bonds to Si-Si bonds and Si-C bonds, which gives an increased volume fraction of SiC matrix, but only a small fraction of free carbon. An increased amount of SiC limits the grain coarsening of Ag and yields a more homogenous microstructure than coatings with lower C content by virtue of overgrowth by SiC on the Ag followed by Ag renucleation. The coating resistivity becomes decreased both by increased Ag content, and with decreased C content, but is in a narrow range of 77-142 $\mu\Omega\text{cm}$. Effectively, the quaternary coatings can be designed for conductivity horizontally or in all direction including vertically by design of the shape and number density of Ag precipitates. This can be achieved by increasing the Ag concentration in the coatings from 10 at.% to 20 at.% and controlling the C/Ti ratio for a given Si content around 13 at.%. The hardness of the coatings is strongly microstructure dependent, with average values in the range of 10-18 GPa.

Acknowledgments

The authors acknowledge Dr. F. Pérez-Willard at Carl Zeiss SMT AG, Germany, for HIM, and the VINN Excellence Centre in Research and Innovation on Functional Nanoscale Materials, *FunMat*, for financial support.

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Table 1. Deposition parameters, electrical, mechanical properties, cell parameter and composition for Coatings 1-12.

Coating	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>	<i>11</i>	<i>12</i>
Target	1	1	1	2	2	2	3	3	3	4	4	4
Bias (V)	-30	-50	-80	-30	-50	-80	-30	-50	-80	-30	-50	-80
Resistivity ($\mu\Omega\text{cm}$)	100	78	113	99	108	114	127	142	116	78	77	79
Hardness (GPa)	14	14	15	18	14	17	10	11	10	10	10	12
Thickness (μm)	0.86	0.72	0.73	1.1	1.26	1.07	0.99	1.24	1	1	1.1	1.09
Dep. rate ($\mu\text{m/h}$)	7.4	6.2	6.3	9.4	10.8	9.2	8.5	10.6	8.6	8.6	9.4	9.3
a_{TiC} ($\text{\AA}$)	4.37	4.36	4.36	4.31	4.32	4.32	4.33	4.32	4.33	4.34	4.33	4.34
Ti (rel. at.%)	47	45	48	41	41	42	34	32	35	33	32	33
Si (rel. at.%)	15	15	14	14	14	13	14	13	12	12	11	11
C (rel. at.%)	24	24	24	32	31	32	37	35	37	34	33	34
Ag (rel. at.%)	12	14	12	11	12	10	14	18	14	20	22	21
O (rel. at.%)	2	2	3	2	2	2	1	2	2	1	2	2
C/Ti	0.51	0.53	0.50	0.78	0.76	0.76	1.09	1.09	1.06	1.03	1.03	1.03