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Conductive nanocomposite ceramics as tribological and electrical contact materials

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Abstract. Conductive ceramics have widespread use in many industrial applications. One important application for such materials is electrical contact technology. Over the last few years, a new class of nanocomposite ceramic thin film materials has been developed with contact coatings as one key objective. This family of materials has proven to combine the favorable contact properties of metals, such as low electrical and thermal resistivity, and high ductility, with those of ceramics such as low friction and wear rate, high chemical integrity and good high-temperature properties. Furthermore, it is also found that the tribological properties of such materials can be tailored by alloying thus creating a triboactive system. The technology is now industrialized, and a practical example of a contact system utilizing a nanocomposite coating for improved performance is given.

PACS. 81.15.Cd Deposition by sputtering – 84.70.+p High-current and high-voltage technology – 84.32.Dd Connectors, relays, and switches

1 Conductive ceramics – an introduction

The traditional materials used in electrical contacts are metals, mainly due to their high electrical and thermal conductivity in combination with a ductile behavior that promotes the formation of large and stable a-spots (the contact spots in an electrical junction, passed through by the bundled electrical current flow lines [5]) and thus low contact resistance. However, metallic contact materials have a number of drawbacks, such as:

- Sensitivity to corrosion.
- High friction coefficient (non-lubricated).
- High wear rate (soft metals).
- High wear rate (soft metals).
- Poor high-temperature properties.

By using conductive ceramics, both as bulk and as thin films, some of these disadvantages may be overcome. For a long time, non-metals have been used in contact applications, e.g. graphite brushes in sliding contacts [1]. Graphite and transition/refractory metal carbides, nitrides, oxides, etc., have also been used in different switching applications for reduction of arc erosion and high-temperature degradation [2–5]. In these applications,

ceramic materials were always part of a composite with a matrix consisting of a noble and/or low-resistivity metal. An alternative way of utilizing ceramic materials in electrical contacts, is in the form of thin films deposited on a metallic substrate/conductor. In the 1980's and 1990's, several studies were made on TiN and TiC and similar types of thin film coatings as electrical contact materials [6–9]. The R&D efforts did not yield any industrial usage at that time, mainly due to the mechanical and oxidation properties of the stoichiometric or near-stoichiometric coating materials that could not meet the demands of electrical contact applications. The class of ceramic materials covers a wide range of electrical properties from pure insulators to highly conductive compounds [10,11]. Both ionic and electronic conduction are found, and the electronic mode involves semiconductors as well as semimetals and metallic conduction. Presently, there exist a considerable number of conductive ceramic materials which are utilized in a broad variety of commercial applications [11]. Table 1 gives a brief overview of the different conductive ceramics and their use.

In the mid 1990's, Barsoum and co-workers [12,13] discovered that so-called MAX materials, such as Ti_3SiC_2 and Ti_2AlN , could be synthesized with partly metallic properties such as high thermal and electrical conductivity and high ductility, while retaining typical

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Table 1. Examples of commercially available conductive ceramics.

Application	Materials
Ohmic resistors	SnO_2 , In_2O_3 , ITO*, PdO , RuO_2 , $\text{Bi}_2\text{Ru}_2\text{O}_7$, $\text{Bi}_2\text{Ir}_2\text{O}_7$
Voltage-dependent resistors (varistors)	ZnO , SiC
Temperature-sensitive resistors	Fe_3O_4 - ZnCr_2O_4 **, Mn_3O_4 **, BaTiO_3 ***,
Heating elements	SiC , MoSi_2 , LaCrO_3 , SnO_2 , ZrO_2
Batteries and fuel cells	ZrO_2 ****
Gas sensors	ZrO_2 ****, SnO_2 , WO_3 , Fe_2O_3
High- T_c superconductors	$\text{YBa}_2\text{Cu}_3\text{O}_7$

* ITO = Indium Tin Oxide; ** NTC = negative temperature coefficient of resistivity; *** PTC = positive temperature coefficient of resistivity; **** = Yttria Stabilized Zirconia.

ceramic properties such as high hardness, low friction coefficient and high corrosion resistance. This class of ceramics, which today consists of more than 60 different materials, has many properties that makes it suitable for use in electrical contact applications [14]. Consequently, a thin-film technology has been developed, based on PVD magnetron sputtering utilizing Ti_3SiC_2 as sputter target. It was then found, that two types of coating materials could be synthesized from the same source [15]:

- A high-temperature ($>800^\circ\text{C}$) phase consisting of a retained MAX structure.
- A low-temperature ($<300^\circ\text{C}$) nanostructured phase.

The following chapter will deal with the latter material and materials with similar structure and properties. The thickness of the films studied in the present work, is in the range of 0.5 to 2 μm .

2 Nanocomposite contact materials

2.1 Structural and mechanical properties

The material systems applied as thin-film nanocomposite contact materials in this study consist of either two, (Ti and C), three (Ti, Si and C) or four elements (Ti, Si, C, and Ag). The addition of further elements will intuitively increase the degree of complexity seen for these material systems. This will complicate the task of finding proper growth-structure-property relationships to suit an application such as in an electrical contact. However, it will also provide improved design opportunities to grow a material in which different properties can be combined thereby forming a multifunctional material. The materials investigated in this study are truly multifunctional in the sense that they combine properties that are considered to be contradictory, for instance, hardness and ductility. For the studied systems this is achieved by a design of the microstructure at the nanometer level to form a nanocomposite thin film. This is accomplished by combining the inherent properties of the chosen materials systems that

Fig. 1. Principle sketch of nanostructured contact coating. A = amorphous matrix, B = nanocrystalline TiC, C = Ag particle. **Fig. 2.** Nanocomposite structures, HRTEM micrographs. nc-TiC/a-SiC left, nc-TiC/a-C right. A = amorphous SiC (left) and C (right) matrices respectively; B = nanocrystalline TiC.**Table 2.** Mechanical properties of nanocomposites.

Material	Hardness [GPa]	E-modulus [GPa]
TiC	30	390
nc-TiC/a-C	9–12	120–170
nc-TiC/a-SiC	17–23	220–260
nc-TiC/a-SiC+Ag	13–16	140–210

are characterized by a strong segregation tendency between phases with none or very low miscibility with the precise (atom-by-atom) and non-equilibrium growth conditions found in thin film vapor-phase growth techniques such as magnetron sputtering.

For the Ti-C as well as the Ti-Si-C system this approach will result in a two-phase system in which 10–20 nm nanocrystals (nc) of TiC are embedded in a thin few nanometer thick tissue of amorphous carbon or SiC [16–18]. A principle sketch of the material systems is given in Figure 1. TEM micrographs of nc-TiC/a-SiC and nc-TiC/a-C films are shown in Figure 2.

The addition of Ag will give rise to a three-phase system as nanocrystallites of Ag or possible Ag alloyed with Si will be dispersed in the nanocomposite structure [18].

In Table 2, the mechanical properties of the different nanocomposite concepts are given. The mechanical properties were obtained using a nanoindentation technique, a Nanoindenter XP utilizing the Oliver Pharr method for estimation of the mechanical properties. To avoid influence

from the substrate, the indent depths did not exceed 10% of the coating thickness.

The properties of the phases as well as the interfaces present between them will be highly decisive for the overall properties of the material. For instance, with respect to mechanical properties the Ti-Si-C system is characterized by a high hardness and a reduced elastic modulus, yet the material shows pronounced ductility upon indentation [17]. The same applies for Ti-C with even more pronounced effects. The first attribute stem from the presence of TiC in the structure whereas the ductility is suggested to originate from TiC grain rotation in the softer amorphous SiC or C matrices. The seemingly opposing mechanical properties are not the only noteworthy characteristics of these thin-film materials as it also combines other properties that show similar opposing trends such as the electrical properties.

2.2 Oxidation and corrosion properties

The stability of the nanocomposites towards oxidation has not yet been systematically studied. However, preliminary results suggest that both the nc-TiC/a-SiC and nc-TiC/a-C films form rather thin surface oxides in ambient atmosphere, X-ray photoelectron (XPS) spectra typically show small amounts of Ti-O and Si-O (when Si is present in the films) suggesting that a mixture of these oxides are formed. The peaks are removed after a few seconds of sputtering. It should be noted, however, that the surface oxidation is related to the grain size of TiC. For example, in nc-TiC/a-C nanocomposites, the grain size of TiC can be reduced by increasing the relative amount of carbon during film growth. XPS analysis of these carbon-rich films shows more surface oxides which can be attributed to the fact that a smaller grain size will lead to a larger surface area exposed to air and therefore a higher oxidation rate.

The nanocomposite films also seem to exhibit excellent corrosion properties. For example, tests of nc-TiC/a-SiC coatings in a Batelle chamber showed excellent results with only small amounts of N and Cl in the surface after 21 days testing [17]. No S was observed in these films. In contact resistance measurements (coating on crossed rod, $\varnothing 10$ mm), no significant change was observed. The addition of Ag in the surface will, of course, change the chemical stability since Ag is well known to interact with sulphur-containing compounds. The corrosion behavior of these materials is currently investigated in more detail and further results will be presented elsewhere.

2.3 Resistivity and contact resistance

Resistivity and contact resistance were measured by the four-terminal method, with an applied current of 5 A while recording the voltage drop over the contact. For low contact resistance values, measurements were performed with switched polarity and the mean value of the two measurements was given.

Table 3. Resistivity of nanocomposites. Four-terminal measurements.

Material	Resistivity [$\mu\Omega\text{cm}$]
TiC	60–80
nc-TiC/a-C	1200–1600
nc-TiC/a-SiC	250–350
nc-TiC/a-SiC + Ag	40

Fig. 3. (Color online) Contact resistance vs. contact force for nanostructured thin film materials and Ag (reference). The coatings are deposited on a Pd-plated Al plate which is pressed against an Ag-plated Cu plate. The dimension of the plates are 10×10 mm, with a thickness of 1 mm.

The electrical conduction properties of the nanocomposite thin films (Tab. 3) are poor compared to those of the noble metals typically applied as contact materials. Measurements of the resistivity of the nanocomposites give resistivity values in the region of 10^2 – 10^3 $\mu\Omega\text{cm}$ [16–18]. These values are higher compared to for instance near-stoichiometric bulk TiC [19]; noting that thin films with their limited thickness in general show higher resistivity values compared to bulk materials due to a more pronounced surface scattering. Addition of Ag to Ti-Si-C system will lower the resistivity one order of magnitude for films containing approximately 17 at.% of Ag [18]. Further addition of Ag would certainly lower the resistivity, but also compromise the hardness, friction and wear as well as the corrosion properties, i.e. the multifunctionality of the films.

In spite of the less good electrical conductivity encountered for the nanostructured films, they have shown to be good contact materials particularly at higher loads [16–18], see Figure 3.

For example, at 800 N these films will exhibit a contact resistance against Ag of 6 $\mu\Omega$. This is a magnitude lower than TiC against Ag and only slightly higher than Ag against Ag at the applied force [16]. The behavior of the nanocomposite films in comparison to TiC films is attributed to the higher ductility of this material, which facilitates the breaking-up of surface oxides and sulphides and hence the formation of interfacial conducting bridges. However, at much lower loads these films will show significantly higher values with 50–100 $\mu\Omega$ against

Fig. 4. Coefficient of friction vs. time for a number of different contact coating materials [20]. Parameters: contact force 10 N, contact geometry: crossed cylinders ($\emptyset 10$ mm), vibration stroke 20 μ m, Frequency 100 Hz.

Fig. 5. The principle for triboactive TiC. Grey atoms: Ti; black atoms: C; white atoms: Al. (A) Original TiC structure. (B) Some Ti substituted by Al. (C) Triboactivated structure with superficial C.

Ag at an applied load of 100 N. This relatively high value is due to the surface properties of these films, where the penetration of hard oxides such as TiO_x and SiO_x limits the ability of forming well-defined contact spots at low loads. This inherent property of the material will severely hamper the use of Ti-Si-C films in contact applications characterized by low contact force, such as consumer electronics. Today, this problem is solved by the addition of Ag, but for future demands the surface properties of the films need to be further tailored without compromising other properties such as low friction and wear, etc.

2.4 Friction and wear properties

The nanocomposites have favorable dry friction properties compared to Ag as well as conventional TiC, see Figure 4. In this case, a number of nanocomposite coatings and references (Ag, TiN, and Ni) were subjected to non-lubricated fretting testing (low amplitude, oscillating movement) against Ag coating [20]. The nanocomposites showed substantially lower friction coefficients as compared to the reference materials.

The Ti-C coatings can be made triboactive [21,22] if some of the Ti atoms have been substituted for Al atoms, see Figure 5, creating a metastable material. Aluminium is a so called weak carbide former, meaning it reluctantly form bonds to carbon. This weakens the bonds in the structure, thereby increasing the mobility of the C atoms.

Fig. 6. Friction coefficient vs. no. of passings for TiC and TiAlC respectively. Ball-on-disc geometry. Steel ball $\emptyset 6$ mm; sliding velocity 0.1 m/s; radius of rotation 2.5 mm; normal load 5 N. The balls were sliding in the same track, and were replaced every 3000 passing.

The now metastable material will try to transform to stabilize. This occurs as enough energy is transferred from friction heating or mechanical work in e.g. a dry or starve lubricated sliding contact situation. Since the activation energy for interstitial diffusion of carbon is lower than vacancy diffusion of e.g. aluminium, the material transformation ejects carbon. The local heating and mechanical work creates an easily sheared superficial carbon layer on top of the initial hard coating material. The coating takes an active part in the contact and acts self lubricating on the atomic scale, as schematically shown in Figure 5.

A practical demonstration of the triboactive effect is given in Figure 6. Whereas the friction coefficient of TiC remains at the same level throughout the entire test, the triboactive TiAlC lowers its friction coefficient to a substantially lower level after an initial running-in period [22].

2.5 Industrial application

Nanocomposites of commercial Ti-Si-C mixtures with additives, such as Ag, that yield good conductive coatings are an attractive alternative for gold in electronics. In e.g. handsets, matings of connector puts high requirements on wear resistance together with low contact resistance. This is today mostly solved with plated gold on top of nickel. The gold is expensive and has poor wear resistance to dust and dirt, therefore low cost and better wear resistant coating like Ti-Si-C is an interesting alternative. A study on nanocomposites of Ti-Si-C (MaxFas^{TM} supplied by Impact Coatings AB) coatings with additives, such as Ag, were evaluated in terms of contact resistance before and after a mating/unmating wear test in dust atmosphere followed by condensation test in humid air. The condensation was controlled by cycling ambient temperature from 25–55 °C at a fixed humidity of 95% RH. The connector is industrially manufactured and used in a handset with a contact force of 1 N each pin.

From the SEM micrograph (Fig. 7) it can be seen how the male Au connector is worn severely and how the Ni

Fig. 7. Au against Au connector worn with dust 3000 matings/unmatings. Male connector.

surface is exposed to a large extent. At some parts even the Cu is exposed as measured with EDX-mapping, not showed here.

We have found that Au connectors yield high resistance values after 3000 mating cycles, approximately 4 pins out of twelve have a value higher than 400 mΩ (virgin value: 130 mΩ), the high values remain throughout the wear tests.

The nanocomposite coated connectors (Fig. 8a) show the resistance before mating and unmating at an even level at approximately 130 mΩ. The measured values include both internal serial resistance and contact resistance. After the 3000 mating and unmating operations the resistance is still low with one spike at 400 mΩ. After condensation the contact resistance is at the same level as virgin. It should be pointed out that the resistance values before mating and after mating and unmating will be affected by any residual dust, however this will be an inherent property of the material in real application. Figure 8b shows 3000 mating and unmating operations for the Au female connectors, the virgin resistance is in the same level as the nanocomposites: 130 mΩ. However, the resistance of the worn connectors showed more spikes for Au compared to the nanocomposite coated connectors. The higher resistance values for Au is measured both as the connectors are mated and after condensations. The increase in resistance might be related to the fact that residual dust is present in the wear zone during the measurement and the corrosion of exposed copper from the substrate in the condensation test.

The findings during the initial study show that Au as a contact material is more worn in a dust environment compared to nanocomposites. Moreover, Au experience spikes in the resistance, as measured during mating and unmating and after condensation. Nanocomposites withstand the dust environment and condensation and show stable values even after condensation, hence nanocomposites are preferable contact coatings in wear applications.

(a)

(b)

Fig. 8. Contact resistance measurements after 3000 mating and unmating cycles performed with dust applied in the connector. Totally 36 pins in sets of 12 were tested. (a) nanocomposite female connector mated against Au male. (b) Au female connector mated against Au male.

3 Conclusions

The findings of the present work are the following:

- Nanocomposite thin films of conductive ceramic materials have been synthesized by magnetron sputtering at temperatures below 300 °C.
- This family of materials has proven to combine the favorable contact properties of metals, such as low electrical and thermal resistivity and high ductility, with

those of ceramics such as low friction and wear rate and high chemical integrity.

- The tribological properties of this type of materials can be tailored by alloying with a weak carbide former (Al) which creates a triboactive system.
- A substantial improvement in performance of a real-life contact system can be achieved by utilizing a nanocomposite coating.

The basic research on nanocomposites is very dynamic and it is expected that new material and system concepts will further improve functionality and performance of electrical contact systems.

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