Possible role of oxygen impurities in degradation of *nc*-TiN/a-Si_3N_4 nanocomposites

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The recently reported strong effect of minor oxygen impurities on the degradation of mechanical properties of superhard *nc*-TiN/a-Si_3N_4 can be, by analogy with similar effects known in metallic alloys, understood on the basis of a simple size effect of large O^{2-} impurity species incorporated into the Si_3N_4 interface. The electronic effect of the O^{2-} sites within the Si_3N_4 interface is also likely to play an important role in weakening the Si–N and, possibly to a lesser extent, also Ti–N bonds. A simple model which assumes that the strength (and hardness) of these materials is approximately proportional to the reciprocal surface coverage of the TiN nanocrystals by oxygen impurities shows a surprisingly good agreement with the measured data. *© 2005 American Vacuum Society.*
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I. INTRODUCTION

During the ongoing discussion regarding the poor reproducibility of the high values of hardness reported earlier by Veprek *et al.* it was suggested that the values reported by these researchers were incorrect (e.g., Ref. 1). This has been disputed in Refs. 2–4. More recently, Fischer-Cripps *et al.* have shown that, in spite of some methodological criticism regarding the evaluation procedure used by the indentometer of Veprek *et al.*, the hardness values reported by them seem to be correct.[5]

Based on an analysis of recently published papers where, upon the addition of silicon to TiN during the deposition, either little or no hardness enhancement was found, Veprek *et al.* identified three possible reasons for the lack of reproducibility of their data by other workers.[6] Besides a too low temperature and too low nitrogen pressure during the deposition, oxygen impurities were identified as the most serious obstacle. At an oxygen impurity content as low as 0.4 at. %, the maximum achievable hardness in these coatings is less than 40 GPa.[6,7] Furthermore, when the oxygen impurity exceeds about 1 at. %, no hardness maximum of $\geqslant 50$ GPa was observed at a silicon content of about 7 to 9 at. %. This corresponds to silicon content where the maximum hardness was previously reported for this and similar systems deposited by plasma chemical vapor deposition (CVD) (Refs. 8–10) and by reactive sputtering.[11] This may explain the results reported by other workers who did not find any hardness enhancement when increasing the silicon content from zero (i.e., from TiN) to that of Si_3N_4.[12]

With these examples in mind, and considering the large differences in the results published on the "Ti–Si–N" coatings in a number of recent papers by different groups (for more examples, see Refs. 6 and 13), many questions arise. Here we consider only two:

1. In which of the published coatings was the reported hardness enhancement due to the formation of a stable nanostructure by self-organization upon spinodal decomposition,[14] and which were hardened by energetic bombardment during their deposition when their oxygen content was obviously large?
2. Why are the nanocomposites, which are deposited according to the generic design principle[8] and, therefore, have a high thermal stability, so much sensitive to minor oxygen impurities?

In order to answer the first question, one has to perform annealing experiments in nitrogen at elevated temperature to verify if the hardness, measured at room temperature after the annealing, remains constant up to about 1100 °C. Such a high thermal stability was reported for *nc*-TiN/a-Si_3N_4 and other superhard nanocomposites.[11,13,15] In contrast, the hardness strongly decreased upon annealing to $\geqslant 500$ °C when its enhancement was due to energetic ion bombardment during the deposition.[16] The lack of relevant data in the published papers allows us only to speculate about the possible answers to this question.[13] Therefore, we leave it to future work and, instead, shall concentrate on the second question regarding the large effect of small quantities of oxygen impurities.

There are many well-known examples which show that minor impurities may degrade the properties of a variety of materials (e.g., Refs. 17 and 18), in particular of nanosized ones (e.g., Ref. 19). For example, very low concentration of Li, Na, and Mg of <20 parts per million(ppm) in bulk alu-

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minum is sufficient to lead, upon annealing to 280–350 °C, to a large enrichment of these elements within the 2–3 nm thin protective oxide layer on commercial aluminium foils. This may result in severe corrosion of the metal leading to a catastrophic failure, and a loss of the adherence of applied lacquers.[20] The annealing is done in order to remove hydrocarbon residue.

There are many examples of how minor impurities content, which segregated into the grain boundaries of a commercial alloy during the service time of the machine, caused their embrittlement and finally a failure of a machine part due to catastrophic crack growth. One such example, often quoted in the literature and textbooks, is the fracture of the axis of a steam turbine power generator resulting in the catastrophic failure of the whole unit.[21,22] An analysis of the fractured surface has shown that this was caused by a brittle fracture due to segregation of minor impurities to the grain boundaries during the long-term operation of the generator. These impurities were introduced into the steel alloy during fabrication in an amount of the order of 100 ppm that exceeded their solubility in the bulk.

In the majority of the cases, the exact mechanism of the weakening of the grain boundaries is not understood. For example, it has been known for more than 100 years that bismuth impurity in copper causes its embrittlement at a concentration smaller than 100 ppm, but it was not clear if it is a size[23,24] or electronic[25,26] effect or both. Recent studies revealed that this embrittlement arises mainly due to the segregation of bismuth atoms into the grain boundaries of copper, where they may form a regular coincidence site lattice arrangement, as shown by high resolution electron microscopy.[27] In a coarse grain copper, an average concentration of bismuth of about 100 ppm results in its relatively high concentration in the grain boundaries. In a bicrystal of copper doped with Bi the Bi/Cu atomic ratio within the "monolayer" interface of about 2/3 is close to the reciprocal value of the ratio of their atomic radii.[27] The recent work of Schweinfest *et al.* brought strong arguments suggesting that the embrittlement arises due to a simple size effect of the larger bismuth atoms,[28] in agreement with the earlier suggestions of Sutton and Vitek[23] and Vitek *et al.*[24] On the other hand, Duscher *et al.* have provided convincing results that the electronic effect is predominant in this case.[29] Thus, in spite of a long time since this effect is known and in view of the excellent work which has been done,[27–29] the fundamental understanding of this relatively simple system remains open to a debate. However, one should keep in mind that there is neither solely "size" nor solely "electronic" effect, because a change of a bond distance results in a redistribution of charge and vice versa. This is illustrated by the well-known example of relatively small fluctuations of bond distances and angles in amorphous hydrogenated silicon,[30] which result in a local fluctuation of charges with δ^- and δ^+ of the order of 0.2 elementary charge being localized on the shorten and elongated bonds, respectively.[31] These changes of local charges result in significant changes of optoelectronic properties of *a*-Si:H as compared to bulk silicon crystal.

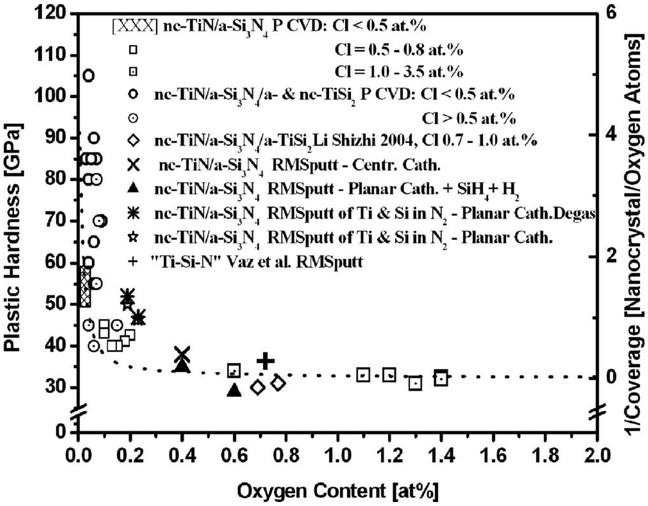

FIG. 1. Effect of oxygen on the degradation of hardness in *nc*-TiN/*a*-Si_3N_4 nanocomposites deposited by plasma CVD and by reactive magnetron sputtering in five different apparatuses from three different countries: "P CVD"—nanocomposites deposited by means of plasma chemical vapor deposition as described in Ref. 10 with chlorine content as indicated; "Li Shizhi"—P CVD as described in Ref. 32; "RMSputt—Planar Cathode"—reactive magnetron sputtering of either Ti and Si target or Ti target combined with PCVD of Si from SiH_4+H_2 (see Ref. 11); "RMSputt—Centr. Cathode"—a prototype of an industrial-like coating equipment with a central cathode (Ref. 33); "Ti–Si–N" Vaz *et al.*" (see Ref. 34). The dotted line corresponds to the reciprocal coverage of the nanocrystals with oxygen atoms (see text).

In the present article, we shall show that the strong decrease of the hardness of the superhard *nc*-TiN/*a*-Si_3N_4 nanocomposites caused by a small amount of oxygen impurities can be explained, in a similar manner, by a weakening of the Si_3N_4 interface which acts as a "glue" between the TiN nanocrystals. In pure nanocomposites, this interface gives rise to their extraordinary mechanical properties and high tensile strength of 10 to 40 GPa, which is approaching the ideal strength of flaw-free material.[3] Therefore, a relatively small degree of contamination results in a large effect as compared to the pure material. One has to keep in mind the fact that even the highly degraded coatings, with oxygen content of about 1 at. % and hardness decreased to about 30 to 35 GPa (see Fig. 1), are still strong materials.

We skip the experimental section in this article because the preparation and investigation into the properties of the *nc*-TiN/*a*-Si_3N_4 nanocomposites, to be discussed here, were described in many earlier papers. We refer to the recent review,[13] earlier papers,[7–11] and to references therein.

II. RESULTS AND DISCUSSION

The hardness of the superhard nanocomposites prepared by plasma CVD according to the generic design principle[8,9] reaches typical values of 50–60 GPa in a quasibinary system, such as *nc*-TiN/*a*-Si_3N_4 and up to 105 GPa in the quasiternary *nc*-TiN/*a*-Si_3N_4/*a*- and *nc*-$TiSi_2$ (see, e.g., Ref. 13

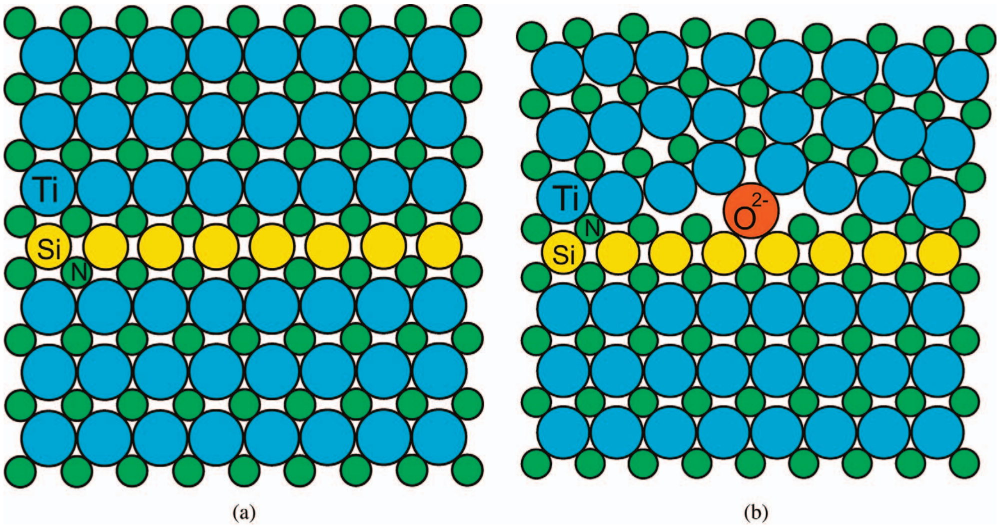

FIG. 2. Simple illustration of a planar TiN/Si_3N_4 interface in a pure (a) and oxygen contaminated (b) system. Considering the size of Ti atom of 0.13 nm one sees that the size of the O^{2-}-related defects of about ⩾0.7–0.9 nm is comparable with the size of the TiN nanocrystals of 3–4 nm.

and references therein). Argon estimated the tensile strength of these materials and has shown that it approaches the ideal strength of flaw-free strong ceramic materials.[35,36] This was confirmed by a number of experimental data in Ref. 3. Therefore it is logical to expect that already a small concentration of oxygen, which in its typical O^{2-} oxidation state has a large radius, may cause a large effect on the properties of such materials, as shown in Fig. 1. This figure is a compilation of more recent data in addition to those published in our earlier papers.[7,6] One notices that already at oxygen impurity concentrations of about ⩾0.1 at. % the hardness is strongly degraded. When the content exceeds about 0.5 to 0.7 at. %, the hardness remains below 35 GPa, and is nearly constant. We emphasize again, that these are still hard and strong materials when compared to conventional ceramics and metallic alloys whose hardness is below 10–15 GPa.

It is well known that few nanomenters small crystals are free of defects, because any defect, such as an impurity atom, vacancy, dislocations, and others, represents a large increase of the Gibbs free energy of such nanocrystal. Therefore, during the deposition of the nanocomposites at a relatively high temperature of 550 °C,[8–11] the diffusion is sufficiently fast to enable the defect to segregate into the grain boundaries which have an excess specific volume, and therefore, can more easily accommodate such a defect. For these reasons, it is physically correct to consider all oxygen impurity atoms being segregated into the grain boundaries of the *nc*-TiN/*a*-Si_3N_4 nanocomposites. Figure 2(a) shows a cross-sectional view of the structure of the planar interface between nitrogen terminated TiN surfaces and a SiN_x monolayer inserted so that the silicon atoms are bonded only to nitrogen. This reflects the fact that in the stoichiometric *nc*-TiN/*a*-Si_3N_4 nanocomposite deposited at a sufficiently high temperature, nitrogen pressure and in an intense glow discharge plasma, the Si $2p$ binding energy measured by means of x-ray photoelectron spectroscopy (XPS) corresponds to that of stoichiometric Si_3N_4.[8,11,13] This means that silicon is covalently bonded to nitrogen only. Let us recall, that the maximum hardness in these systems is achieved when the thickness of the Si_3N_4 interface is about one monolayer as estimated already in Ref. 8 and substantiated in more detail later in Refs. 10 and 13.

The high mechanical strength of the interfacial "SiN_x" monolayer is further supported by the recent work of Odén Söderberg *et al.*[37] who succeeded in depositing high quality heterostructures consisting of epitaxial TiN layers with heteroepitaxial "SiN_x" in between. The maximum hardness enhancement of about 33 GPa was achieved when the thickness of the "SiN_x interlayer was equal to one monolayer,[37,38] in agreement with the results reported by Veprek and Reiprich[8] for the *nc*-TiN/*a*-Si_3N_4 and other *nc*-Me_nN/*a*-Si_3N_4 (Refs. 9 and 10) nanocomposites. Similar results were recently published also by Hu *et al.*[39] The somewhat broader maximum of hardness with a maximum at a thickness of about two monolayers of Si_3N_4 is due, most probably, to the lower quality of the heteroepitaxial layers in the paper of Hu *et al.* as compared to the work of Odén. This can be seen by a comparison of the transmission electron micrographs in these two reports. This finding also explains why some workers claim an optimum thickness to be of two monolayers for the "Ti–Si–N" coatings deposited at a relatively low temperature[40] where the interface remains rough due to an incomplete phase segregation.[6,13]

These results are further supported by first-principles theoretical calculations of Hao *et al.*[41] who have shown that the value of the decohesion energy of such a "sandwich" consisting of a layer of "SiN_x" inserted between the TiN lattice planes reaches maximum for one monolayer of β-silicon nitride. In that case, the decohesion energy of such a "sandwich" lies between the ideal decohesion energy of [111] and [110] TiN lattice planes, and it is higher than that of bulk Si_3N_4.[41] Therefore, there is hardly any doubt that the original prediction of Veprek and Reiprich[8] and Veprek *et al.*[9] was correct.

Summarizing all these results we conclude that only one monolayer of a flaw-free SiN_x interlayer, where all Si atoms are covalently bonded to nitrogen as in Si_3N_4, provides the nanocomposites with their high strength and hardness. The oxygen impurities incorporated into this interfacial SiN_x monolayer cause defects similar to nanocracks, as schematically illustrated in Fig. 2(b). Their lateral size is comparable to the average size of the TiN nanocrystals of about 3–4 nm.[8,9,13]

Let us now estimate the average density of such flaws in the nanocomposites with an oxygen impurity content of about 0.1 at. %. For simplicity we assume nanocrystals of a cubic shape and edge size $d \approx 4\ \text{nm} = 4 \cdot 10^{-7}$ cm, as found for the quasibinary *nc*-TiN/*a*-Si_3N_4 nanocomposites with the maximum hardness of 50–60 GPa.[8–10] The number of such nanocrystals per 1 cm^3 of the material is $N_d = d^{-3} \approx 1.56 \cdot 10^{19}$ nanocrystals/$cm^3 \approx 1.64 \cdot 10^{20}$ crystals/mol when taking the molar volume of the *nc*-TiN/*a*-Si_3N_4 nanocomposites with the maximum hardness to be about 10 to 11 cm^3. The impurity content of 0.1 at. % of oxygen corresponds to $6.02 \cdot 10^{20}$ O-atoms per mol. Thus, there are on average about 3.7 defects associated with oxygen impurities, such as shown in Fig. 2, per one TiN nanocrystal in the interface.

Let us now define the surface coverage as the number of oxygen atoms per one TiN nanocrystal. Because the strength (and hardness) of the nanocomposites is expected to increase with decreasing density of flaws in the material, i.e., with decrease of the surface coverage by oxygen, we plotted in Fig. 1 the reciprocal value of the coverage versus the oxygen impurity concentration (see dotted line in Fig. 1). The close similarity with the experimental data is surprisingly good, particularly if one takes into account the fact that the ultrahard nanocomposites had somewhat larger crystallite size,[45] and therefore a larger reciprocal coverage for given oxygen content. Based on this simple estimate it is also easy to understand why the dependence of hardness on oxygen impurity content shows a plateau for oxygen content of ≥ 0.5 at. %, and why it strongly increases when the oxygen impurity content decreases below about 0.1 at. % (see Fig. 1). Obviously, the strength (and hardness) of the nanocomposites with oxygen content of ≥ 0.5 at. % is limited by the strength of that contaminated interface. Therefore, the strength approaches the ideal one[3] only for nanocomposites with a very low concentration of the defects of < 0.25 oxygen atoms per one nanocrystal corresponding to oxygen impurity of < 70 ppm. For an oxygen impurity content of ≥ 0.5 at. %, which corresponds to surface coverage of ≥ 19 defects per one nanocrystal, the hardness of the coatings is determined by the strength of the oxygen-related bonds.

So far, we considered only a simple size effect. However, the strong electron affinity of oxygen is also likely to cause electronic weakening of the Si–N bonds in the vicinity of O^{2-} impurities by attracting electron density from these neighbors. Such effects, albeit somewhat more complicated, are known, e.g., from the chemistry of complex compounds as the "trans-effect" (see, e.g., Ref. 42). It is further known that silicon oxynitride, SiO_xN_y, which plays an important role as a binder in high-tech silicon nitride ceramics, has a much lower melting and evaporation temperature than pure Si_3N_4.[43] For these reasons the electronic effect should be important in this case. The oxygen impurities may, in principle, also influence the Ti–N bonds in a similar way. However, because of the metallic nature of TiN we suggest that this effect will be much smaller because of the screening of the O^{2-} charge by the delocalized electrons in the conduction band of TiN.

We cannot fully exclude the possibility of clustering of the oxygen-containing defects. However, because silicon suboxide deposited e.g. by means of plasma CVD at low temperature as a fairly homogeneous layer shows disproportionalization ("clustering") $SiO_x \rightarrow nc\text{-Si} + SiO_2$ only upon annealing to much higher temperatures than the deposition temperature of 500–600 °C used in our studies, we consider such clustering of the impurities in our nanocomposites as unlikely. Nevertheless, even if such clustering should occur, it would result in a smaller number of larger defects which are much more sensitive to external, applied stress. Furthermore, because the practically achievable strength of ceramic materials is determined by the probability of the occurrence of a critical flaw within the volume being tested, the impurities clustering would not change the overall effect on the degradation of the hardness. In order to elaborate a more quantitative picture we would need a precise statistical study of such flaws. However, because we have never observed any sign of such "defect clusters" in a large number of available high resolution transmission electron micrographs,[44] we consider the possibility of any substantial clustering of the oxygen impurities as unlikely.

III. CONCLUSIONS

The experimentally found, strong degradation of the hardness of *nc*-TiN/*a*-Si_3N_4 nanocomposites by oxygen impurities can be understood in terms of the size effect of this impurity by analogy with similar, well-known effects of minor impurities of other elements which cause embrittlement of grain boundaries and catastrophic failure of many metals and alloys (e.g., Bi in Cu). Moreover, within one monolayer of the Si_3N_4 interface between the TiN nanocrystals, which is needed to achieve the maximum hardness, electronic effects of the O^{2-} impurities are likely to play also a role by weakening the Si–N (and probably to a lesser extent also Ti–N) bonds in the vicinity of such impurities. Only first-principles calculations may provide a deeper insight into the question, whether the size or the electronic effect play the dominant role in the degradation of the mechanical properties of superhard *nc*-TiN/*a*-Si_3N_4 nanocomposites. Such calculations should also provide a more exact configuration of the O^{2-} impurities sites within the interface than the simplified, but physically very probable configuration shown in Fig. 2(b).

A simple model which assumes that the strength (and hardness) of these materials is approximately proportional to the reciprocal surface coverage of the TiN nanocrystals by oxygen impurities shows a surprisingly good agreement with the measured data (see dotted line in Fig. 1).

It is worth noticing that at the lowest oxygen concentration of 0.01 at. % (100 ppm) measured by Veprek *et al.* in their nanocomposites,[45] there is still on average one flaw, as shown in Fig. 2(b), per about 3 TiN nanocrystals in these materials. Moreover, the highest hardness of 80 to $\geqslant 100$ GPa was achieved in the quasiternary *nc*-TiN/*a*-Si$_3$N$_4$/*a*- and *nc*-TiSi$_2$ systems where the TiSi$_2$ phase is likely to acts as an oxygen scavenger thus removing it from the TiN/Si$_3$N$_4$ interface. Therefore, a further improvement of the mechanical properties of the quasibinary *nc*-TiN/*a*-Si$_3$N$_4$ nanocomposites should be possible by decreasing the impurity content below this level. This would be important because the quasibinary nanocomposites retain their hardness over a period of more than four years (the longest period over which we have measured it on a series of samples) whereas the quasiternary show softening due to the instability of the TiS$_2$ C-49 phase after several months.[13]

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