Irradiation damages in Ti3SiC2: formation and characterisation of the oxide layer

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Abstract

The concept of the fuel for the IVth generation reactors should consist of fuel pellets surrounded with a matrix that must contain fission products. Thanks to their interesting thermo-mechanical properties, carbides are sensed to become this matrix. Among the studied carbides, Ti_3SiC_2 can be distinguished; actually, its nano-laminated structure confers to it some softness as well as a better toughness than classical carbides like SiC or TiC. However, before to use this remarkable carbide, a study of its behaviour under irradiation must be led. Thus, some characterisations were performed on 75 MeV Kr irradiated specimens. They allowed to underline that TiO_2 (formed on the surface of Ti_3SiC_2 during the surface preparation) seems to be sputtered by irradiation, and that the unit cell of Ti_3SiC_2 is dilated along c axis.

Keywords:

Ti_3SiC_2 ; irradiation ; heavy ions ; krypton ; Scanning Electron Microscopy ; Atomic Force Microscopy ; Low-Incidence X-Ray Diffraction

I Introduction:

Within the framework of Generation IV International Forum, new nuclear power plants are studied, as well from the reactor point of view as from the fuel cycle one. They are characterised by an increased security level, a better economic competitiveness, and an ability to recycle all the fuel in order to upgrade fissionable material, and to minimize the long-lived wastes production by the transmutation process. Among the six systems considered, the Gas Fast Reactor (GFR) is studied in France; it is designed for an under helium-pressure, and high-temperature nominal working.

The concept of the fuel for this kind of reactor consists of fuel pellets surrounded with a matrix that must contain the fission products. Taking into account the working conditions of the GFR, carbides are sensed to become this matrix; actually, they have remarkable thermo-mechanical properties, and are neutrons transparent (contrary to metals). However, their behaviour under irradiation is little known nowadays.

Ternary Ti_3SiC_2 seems to get away from other studied carbides. Actually, in 1972 Nickl *et al.* [1] noted that this material, which was synthesised for the first time in 1967 [2], is abnormally soft for a carbide. At the beginning of the 90's, Pampuch, Lis and co-workers [3-8] led works on synthesis of pure bulk Ti_3SiC_2. Their best samples were 80-90 % pure, the residue being TiC. During their works, they showed that Ti_3SiC_2 is elastically quite stiff (Young's modulus of

325 GPa) and confirmed its softness (Vickers hardness of 6 GPa). So they labelled Ti_3SiC_2 as a "ductile ceramic".

At the end of the 90's, Barsoum *et al.* understood that Ti_3SiC_2 forms part of a family of ternary layered compounds with the general formula: $M_{n+1}AX_n$, where n is 1, 2 or 3, M is an early transition metal, A is an A-group element, and X is C and/or N [9, 10]. Compounds of this family are all elastically stiff, thermally and electrically conductive, readily machinable, relatively soft, thermal shock resistant and unusually damage tolerant. More specifically, pure Ti_3SiC_2 seems to be stable to at least 1,700 °C in inert atmospheres [11, 12], and can be quenched from 1,200 °C to room temperature and remained intact [10]. Some others properties of Ti_3SiC_2 are gathered in table 1.

Table 1: Properties of Ti_3SiC_2

Properties		References
Density	4.5	[9, 13]
Molar mass	195.71 g mol^{-1}	
Young's Modulus	325 GPa	[13, 14]
Hardness	6 GPa	[9]
Toughness	8 MPa $m^{1/2}$	[14]
Thermal conductivity	37 W m^{-1} K^{-1}	[15]
Heat capacity	110 J mol^{-1} K^{-1}	[15]
Thermal expansion	9.2x10^{-6} K^{-1}	[15, 16]

Therefore, the aim of this study is to better grasp the behaviour under irradiation of Ti_3SiC_2, of which the mechanical properties offer a real alternative to brittle carbides.

II Experimental:

II 1 Samples preparation

First, samples are polished in order to obtain a smooth surface. Then, they are annealed at 800 °C for 4 hours under argon atmosphere in order to release internal stresses due to polishing. Eventually, specimens are irradiated with heavy ions in order to simulate the impacts of fission products, of recoil atoms of alpha decays, and to a lesser extend of neutrons. In first approximation, we can consider that the stresses observed are only due to irradiation.

II 2 Specimens and irradiations

Samples were obtained by pressure sintering of Ti_3SiC_2 powder. This material is rarely pure: indeed synthesis of Ti_3SiC_2 implies a non-negligible proportion of powder that is not transformed. Thus, our samples are made of about 75 % of Ti_3SiC_2, 20 % of TiC and 5 % of $TiSi_2$.

Specimens were irradiated with ^{86}Kr ions at "Grand Accélérateur National d'Ions Lourds" (GANIL) Caen, France.

The energy of ions was of 75 MeV, and the average flux of 9x10^9 cm^{-2} s^{-1}. Two parameters varied for irradiations: dose and temperature. Thus, three different irradiations were performed; table 2 recapitulates these parameters.

Table 2: Irradiation parameters of specimens

Temperature of irradiation /°C	Dose /cm^{-2}
25	10^{14}
25	10^{15}
500	10^{15}

SRIM software allows to evaluate some parameters relative to this irradiation. Thus, the projected range is 7.9 µm, the electronic stopping power is 1.6×10^4 keV µm^{-1}, and the nuclear stopping power is 66 keV µm^{-1}.

II 3 Characterization techniques

In order to understand the noticed phenomenon, the characterisations of the samples are compared with the ones performed on a control sample; it is prepared in the same conditions, and no irradiated.

The surface of the materials was observed through Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). SEM is a Jeol JSM 6400 used with an acceleration voltage of 15 kV and with a secondary electrons detector. AFM is a Nanoscope III A used in contact mode with a 0.12 N m^{-1} stiffness-constant probe made in silicon nitride.

The structure in the irradiated area of Ti_3SiC_2 was analysed by Low-Incidence X-Ray Diffractometry (LI-XRD). The diffractometer is a Siemens D5000 with a copper anticathode.

III RESULTS and DISCUSSION

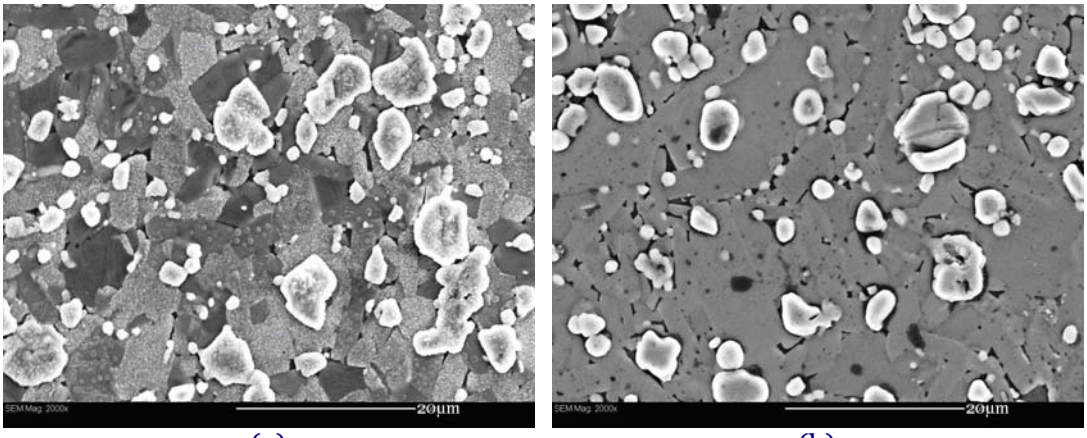
During the post-polishing annealing, a white layer has formed on the surface of our samples; this layer could be due to oxidation of Ti_3SiC_2. Actually, this material is easily oxidable and it is likely that an oxide would be forming despite argon atmosphere. Moreover, according to literature [17], oxidation of Ti_3SiC_2 is beginning by a TiO_2 layer formation before the formation of a TiO_2+SiO_2 layer at the Ti_3SiC_2/TiO_2 interface; so, the white colour of the surface can lead to suppose the TiO_2 presence.

Therefore, materials were irradiated in the presence of an oxide layer on their surface. Thereof, characterisation of irradiation damages will have to take into account this oxide presence.

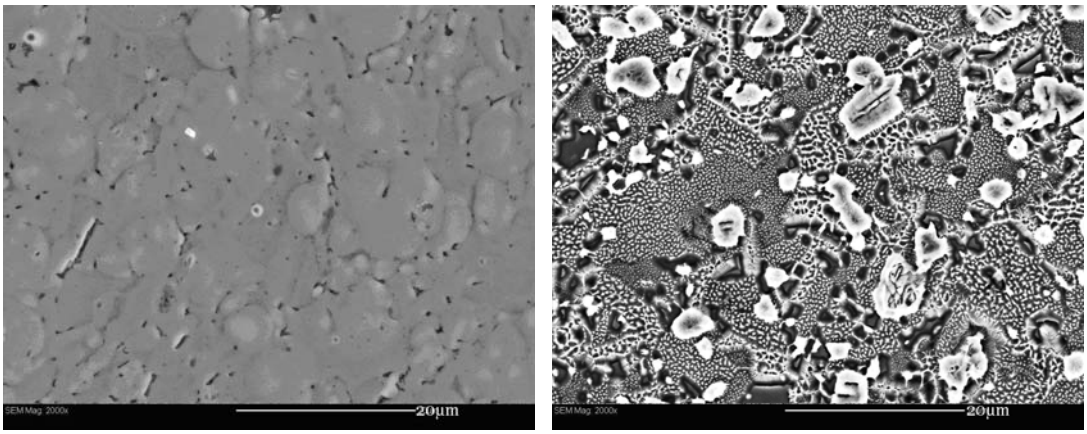
III 1 Scanning Electron Microscopy

The images obtained by SEM for the four samples are gathered in figure 1. We can notice the control sample is made of relieves on a smooth surface. EDX analysis allowed to detect oxygen presence on the whole surface of the sample, as well on the smooth area as on relieves; this confirms the oxide presence.

Irradiation of the surface of Ti_3SiC_2 wasn't null and void. Actually, the higher the dose, the lower the relief; oxide seems to be sputtered by a room temperature irradiation. On the other hand, the high temperature irradiation led to a different behaviour: relieves stay intact whereas the smooth area seems to be damaged. So, oxide would stand up more to a high temperature irradiation than to a room temperature one.



(a) (b)



(c) (d)

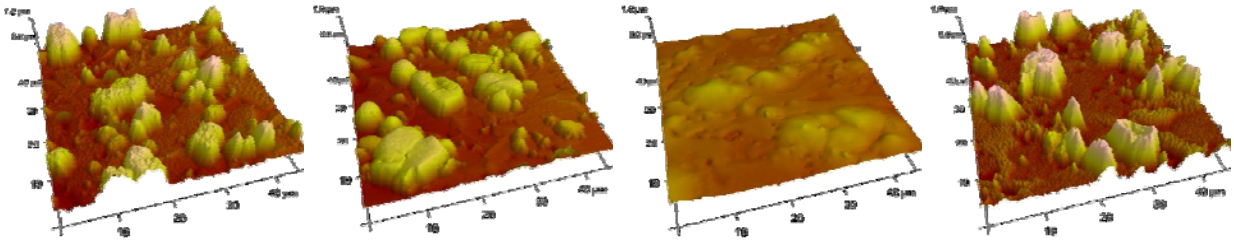
Figure 1: SEM images, x2000 magnification: (a) control sample, (b) 10^{14} cm^{-2} and room temperature irradiation, (c) 10^{15} cm^{-2} and room temperature irradiation, (d) 10^{15} cm^{-2} and 500 °C irradiation

III 2 Atomic Force Microscopy

Firstly, AFM (cf. figure2) allows to confirm the observations made by SEM regarding the behaviour of the oxide under irradiation.
Secondly, this microscopy allows to evaluate the roughness of the specimens thanks to a calibration of the height (z axis). Thus, roughness is estimated by the R_a parameter, defined by the ISO 4287 norm:

$$R_a = \frac{1}{\ell}\int_0^{\ell} |z(x)|.dx \qquad (1)$$

where ℓ is the length on which z(x) is measured.



(a) (b) (c) (d)

Figure 2: AFM images, scan of 45x45 µm²: (a) control sample, (b) 10^{14} cm^{-2} and room temperature irradiation, (c) 10^{15} cm^{-2} and room temperature irradiation, (d) 10^{15} cm^{-2} and 500°C irradiation

The table 3 presents the average roughness of each sample.

Table 3: Average roughness measured by AFM

Temperature of irradiation /°C	Dose /cm^{-2}	Roughness: R_a /nm
Control sample		360
25	10^{14}	310
25	10^{15}	130
500	10^{15}	360

These measures quantitatively confirm the changes noticed by the microscopies. Thus, at room temperature the higher the dose, the lower the roughness; relieves are sputtered up to obtain an almost smooth surface. On the other hand, an irradiation at 500 °C doesn't lead to a

decrease of the roughness even though the surface state is slightly different than the control sample one.

III 3 Low-Incidence X-Ray Diffraction

First LI-XRD should allow to resolve the doubt about the nature of the white layer formed after annealing. Second it should allow to characterise the structural changes in the irradiated area. Figure 3 presents the diffractograms performed at 1° and 3° incidence angles. The penetration depth of X-rays in Ti_3SiC_2 is estimated at 230 nm for $\alpha = 1°$, and at 720 nm for $\alpha = 3°$; as the projected range is of 7.9 µm, the analysed zone for both angles is a damaged zone.

The first remark is about the oxide: it's TiO_2, in its rutile form, which was formed on the specimens before irradiation.

Then, we can notice the sputtering of the oxide layer at room temperature: this one is wearing off with the dose increase, like observed with microscopies. We can conclude that the formed rutile doesn't stand up at this irradiation, especially for high doses.

Behaviour under irradiation of our sample at 500 °C is also interesting. Microscopies showed a no-sputtered oxide layer. LI-XRD on the one hand confirms this observation, on the other hand gives information about this oxide composition: it isn't only composed of rutile. Actually, anatase, the low temperature stable phase of TiO_2, is also present.

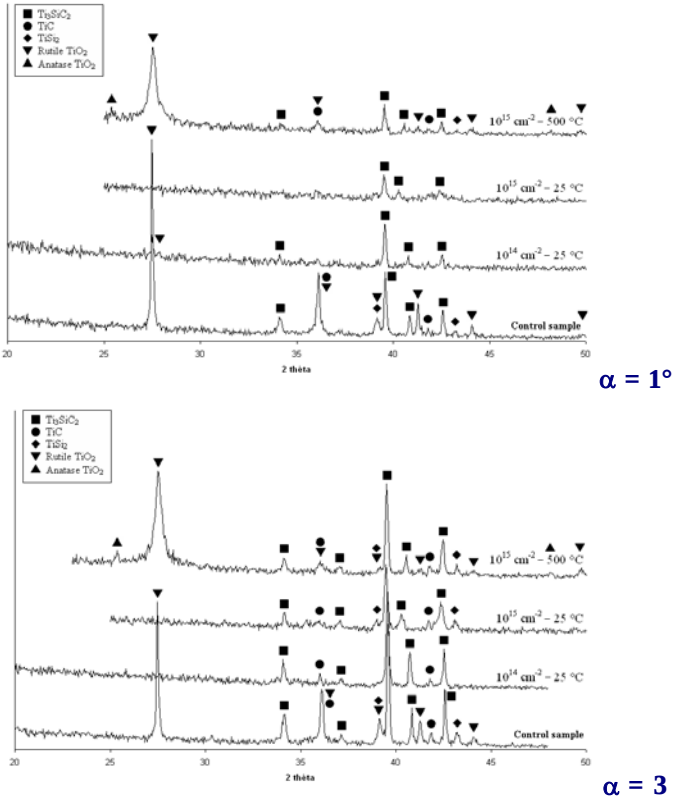


Figure 3: Diffractograms for $\alpha = 1°$ and $\alpha = 3°$

Anatase to rutile transformation occurs at about 600-700 °C but the rutile to anatase transformation is not spontaneous. So, temperature doesn't seem to be the reason of anatase formation. There isn't a lot of paper about the behaviour of TiO_2 under irradiation. Furthermore, the anatase to rutile transition is more often observed: after having irradiated then annealed some anatase specimens, Sumita *et al.* then Nakao *et al.* [18, 19] noticed a rutile formation. This would be due to the formation of Ti^{3+} and Ti^{2+} in anatase lattice; the unstable state of Ti^{3+} and/or Ti^{2+} would probably act as "seeds" for rutile in anatase, and so would lower the crystallisation temperature of rutile to anatase.

However, a paper mentions a rutile to anatase transformation after an ions irradiation [20]; this phenomenon would be explained by a partial relaxation of the internal stress and strain caused by collision events with implanted atoms. But these irradiations were performed at room temperature, and our result is only for the high temperature irradiation. Another track comes from Dalmasso works about Al_2O_3, MgO and $MgAl_2O_4$ oxides [21, 22]. Actually, these materials were irradiated almost at the same experimental conditions, and it results that a partial amorphisation was remarked.
Moreover, Kim *et al.* [23] noted an amorphous to anatase phase transition due to an ion beam. Actually, they made TiO_2 amorphous thin films by a reactive DC magnetron sputtering method, with and without Argon ion-beam assistance. Then, after annealing at 400 °C, they noticed that anatase is formed only for films deposited with ion-beam assistance, others staying amorphous. Therefore, our hypothesis is that irradiation may have caused a rutile to amorphous phase transformation. Then, either the high temperature or the internal stress and strain caused by collision events or both have allowed an amorphous to anatase transformation. Anyway, according to microscopies, it seems that either the temperature avoids the TiO_2 sputtering or anatase protects rutile against sputtering.
A last remark is about the $2\theta = 40.9°$ line of Ti_3SiC_2. Indeed, this one, which characterises the diffraction of the 008-plan, is highly shifted as a function of irradiation parameters. This shift is due to a lattice parameter change. Table 4 presents an assessment of the Ti_3SiC_2 lattice parameter for each specimen and each incidence angle.

Table 4: Lattice parameters of Ti_3SiC_2 as a function of irradiation parameters

Incidence angle	Dose /cm^{-2}	Irradiation temperature /°C	Lattice a /Å	c /Å
1°	Control sample		3.065	17.65
	10^{14}	25	3.065	17.68
	10^{15}	25	3.058	17.89
	10^{15}	500	3.061	17.76
3°	Control sample		3.065	17.66
	10^{14}	25	3.065	17.71
	10^{15}	25	3.061	17.89
	10^{15}	500	3.064	17.78

Thus, we can notice that the c parameter is highly changing. This can be explain by the fact that Ti_3SiC_2 has a hexagonal structure, and so a strong sensibility along the c axis. Thus, we can assume that the insertion of krypton atoms (and perhaps oxygen atoms from TiO_2) in this material is preferentially carried out along this axis. Eventually, we can notice that the higher the temperature, the smaller the change in c parameter. A diffusion of inserted atoms or an annealing of the defects can explain this phenomenon. But these hypotheses are to be confirmed.

IV Conclusion:

This study about the irradiation damages in Ti_3SiC_2 is beginning and characterisations are mostly about the TiO_2 oxide that had been formed after an annealing of the samples. However, these first results are interesting.
First of all, rutile seems not to stand up to a 75 MeV Kr room temperature irradiation; it is indeed sputtered by the ion beam.
On the other hand, a 500 °C irradiation would allow the formation of anatase. This irradiation led to a no-sputtered oxide; this phenomenon is due to either the temperature or anatase that would protect oxide layer.
Eventually, about Ti_3SiC_2, its unit cell is dilating along the c axis, certainly because of insertion of krypton, verily oxygen, atoms, and of the moving of atoms in the damaged zone.

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References

[1] J.J. Nickl, K.K. Schweitzer, P. Luxenberg: Gasphasenabscheidung im Systeme Ti-C-Si. J. Less Common Metals **26** (1972) 283.
[2] W. Jeitschko, H. Nowotny: Die Kristallstruktur von Ti_3SiC_2 - ein neuer Komplexcarbid-Typ. Monatsh. Chem. **98** (1967) 329-337.
[3] R. Pampuch, J. Lis, L. Stobierski, M. Tymkiewicz: Solid Combustion Synthesis of Ti_3SiC_2. J. Eur. Ceram. Soc. **5** (1989) 283.
[4]. J. Lis, R. Pampuch, L. Stobierski: Reactions during SHS in a Ti-Si-C system. Int. J. Self-Propag. High-Temp. Synth. **1** (1992) 401.
[5] R. Pampuch, J. Lis, J. Piekarczyk, L. Stobierski: Ti_3SiC_2-based materials produced by self-propagating high temperature synthesis and ceramic processing. J. Mater. Synth. Process. **1** (1993) 93.
[6] J. Lis, R. Pampuch, J. Piekarczyk, L. Stobierski: New ceramics based on Ti_3SiC_2. Ceram. Int. **19** (1993) 219.
[7] J. Lis, Y. Miyamoto, R. Pampuch, K. Tanihata: Ti_3SiC_2-Based Materials Prepared by HIP-SHS Techniques. Mater Lett **22** (1995) 163-168.
[8] J. Morgiel, J. Lis, R. Pampuch: Microstructure of Ti_3SiC_2-based ceramics. Mater Lett **27** (1996) 85-89.
[9] M.W. Barsoum: The $M_{N+1}AX_N$ Phases: A New Class of Solids; Thermodynamically Stable Nanolaminates. Prog. Solid St. Chem. **28** (2000) 201-281.
[10] M.W. Barsoum, T. El-Raghy: The MAX phases: Unique new carbide and nitride materials - Ternary ceramics turn out to be surprisingly soft and machinable, yet also heat-tolerant, strong and lightweight. Am. Sci. **89** (2001) 334-343.
[11] M.W. Barsoum, T. ElRaghy: Synthesis and characterization of a remarkable ceramic: Ti_3SiC_2. J Am Ceram Soc **79** (1996) 1953-1956.
[12] M.W. Barsoum, T. El-Raghy: A progress report on Ti_3SiC_2, Ti_3GeC_2, and the H-phases, M_2BX. J. Mater. Synth. Process. **5** (1997) 197-216.
[13] J. Travaglini, M.W. Barsoum, V. Jovic, T. El-Raghy: The corrosion behavior of Ti_3SiC_2 in common acids and dilute NaOH. Corros. Sci. **45** (2003) 1313-1327.
[14] C.J. Gilbert, D.R. Bloyer, M.W. Barsoum, T. El-Raghy, A.P. Tomsia, R.O. Ritchie: Fatigue-crack growth and fracture properties of coarse and fine-grained Ti_3SiC_2. Scr. Mater. **42** (2000) 761-767.
[15] M.W. Barsoum, T. El-Raghy, C.J. Rawn, W.D. Porter, H. Wang, E.A. Payzant, C.R. Hubbard: Thermal properties of Ti_3SiC_2. J. Phys. Chem. Solids **60** (1999) 429-439.
[16] T. Iseki, T. Yano, Y.S. Chung: Wetting and properties of reaction products in active metal brazing of SiC. J. Ceram. Soc. Jpn. (Inter. Ed.) **97** (1990) 47.
[17] N.F. Gao, Y. Miyamoto, D. Zhang: On physical and thermochemical properties of high-purity Ti_3SiC_2. Mater Lett **55** (2002) 61-66.
[18] T. Sumita, H. Otsuka, H. Kubota, M. Nagata, Y. Honda, R. Miyagawa, T. Tsurushima, T. Sadoh: Ion-beam modification of TiO_2 film to multilayered photocatalyst. Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **148** (1999) 758-761.
[19] S. Nakao, T. Nonami, P. Jin, Y. Miyagawa, S. Miyagawa: High-energy metal ion implantation into titanium dioxide films. Surf. Coat. Technol. **128** (2000) 446-449.
[20] K. Fukushima, I. Yamada: N+ ion implantation effects on microhardness and adhesion in TiO_2 films. Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **112** (1996) 116-119.

[21] C. Dalmasso: Caractérisation des défauts ponctuels induits par l'irradiation des les céramiques : Exemple des oxydes alph-Al_2O_3, MgO et $MgAl_2O_4$. Thesis (France) (2005).

[22] M. Beauvy, C. Dalmasso, C. Thiriet-Dodane, D. Simeone, D. Gosset: Damages in ceramics for nuclear waste transmutation by irradiation with swift heavy ions. Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms **242** (2006) 557-561.

[23] S.H. Kim, C.K. Hwangbo: Influence of Ar ion-beam assistance and annealing temperatures on properties of TiO_2 thin films deposited by reactive DC magnetron sputtering. Thin Solid Films **475** (2005) 155-159.