

Reactivity of M/TiN/SiC systems (M = W and Mo) at high temperature

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Received: 18 September 2009 / Accepted: 10 February 2010 / Published online: 23 February 2010
  Springer Science+Business Media, LLC 2010

Abstract Owing to the development of high temperature applications using SiC, this study examines the effect of TiN coatings against Si and C atoms diffusion in presence of two refractory metals (W or Mo). Indeed, SiC reacts rapidly with these metals at elevated temperatures generating unacceptable reaction zones and a mechanical embrittlement. Samples used during this work were prepared on wire and planar metallic substrates, SiC and TiN being deposited by CVD. The effect given by TiN interlayers with thicknesses between 10 and 20 μm was considered at 1773 K. From our results, TiN can be considered as an effective diffusion barrier in presence of W, whereas it ensures no real protection in the case of Mo-containing samples.

Introduction

High temperature applications such as fast neutron fission gas reactors or fusion technologies induce the use of refractory compounds as SiC. Indeed, this carbide has many advantages; we can quote its high melting point, low density, good mechanical behaviour, resistance to oxidation at high temperatures and chemical inertness to corrosive media [1–5]. In many occasions, silicon carbide can be in contact with metals. It is now well established that SiC

reacts rapidly with most of them from 1273 K [6–12]. In order to ensure life-time of the components (SiC and metals), the development of protective coatings is necessary. During a previous work, we examined the stability given by a TiC interlayer [13]; it appears that TiC is able to provide a notable reduction of the reaction zone at high temperature. The effect is satisfactory in the case of Si atoms diffusion, nevertheless carbon atoms succeed in diffusing through TiC. This last point can be explained by the fact that TiC is a carbide with an intrinsic diffusion mechanism of carbon atoms [14]. Starting from this situation, it appears that the simplest way to improve the protection is to use a compound derivative of TiC without carbon. Amongst several compounds presenting comparable properties, we focus our attention on TiN. This gold-like nitride is well known for its hardness properties. It is generally used as reinforcing coating on drilling or cutting tools. Since many years, TiN is used successfully in multilayers with SiC or Si to obtain superhard coatings [15–17]. TiN is also applied as diffusion barrier to protect multi-components systems. Indeed, during studies concerning the development of new electronic interconnecting materials (Al or Cu) with silicon, it appears that TiN and (Ti, Zr) N_x interlayers give a notable thermal protection preventing reaction between Si and metals [18]. Nevertheless, high temperature thermodynamic calculations in the Ti–Si–N system reveal that a reaction occurs at 1373 K between TiN and Si with formation of Si_3N_4 and TiSi_2 [19]. Other studies report the possibility to apply a diffusion barrier based on the Mo–Si–C–N quaternary system [20, 21]. RF magnetron sputtering in an argon–nitrogen atmosphere leads to the formation of an amorphous layer able to prevent the diffusion of silicon and carbon atoms in the system Mo/SiC up to 1533 K. In the present case, we consider the interaction between W or Mo with SiC at

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elevated temperatures and we present the results obtained during our investigations concerning the effect of an intermediate TiN layer in the systems W/TiN/SiC and Mo/TiN/SiC at 1773 K. This temperature was selected in this study owing to the high values of diffusion kinetics that we had previously measured for W/SiC and Mo/SiC systems [1, 2].

Experimental methods

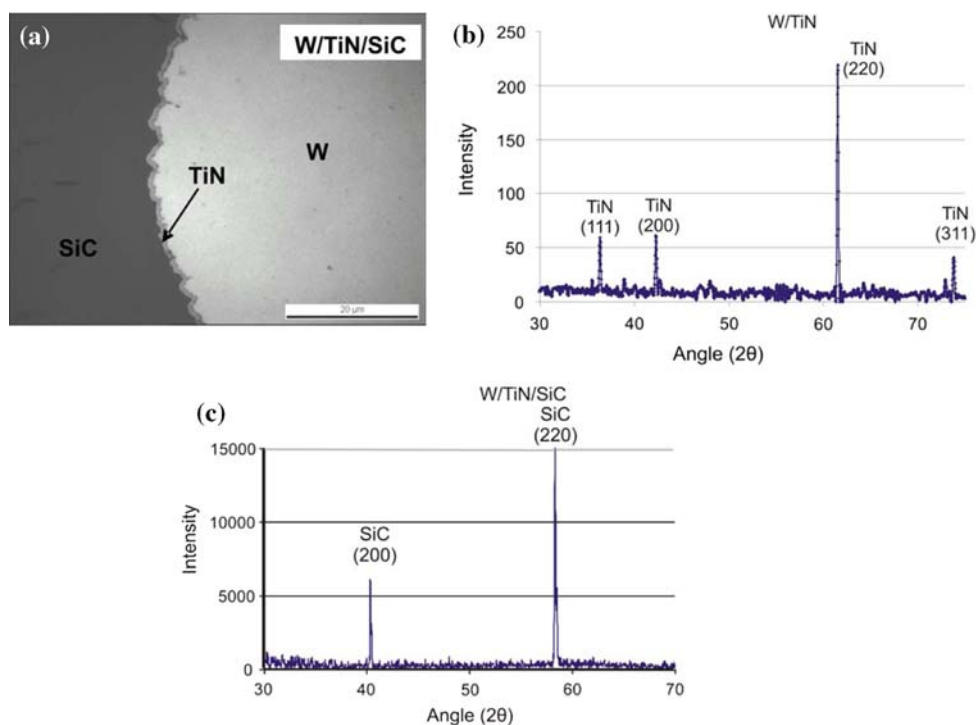
A conventional cold-wall CVD system was used during this study. The diffusion couples were prepared by successive deposition of TiN and SiC layers on 100 or 125 μm diameter wire and planar substrates of pure W (99.95% purity) and Mo (99.9% purity) supplied by Goodfellow company. In order to eliminate impurities, a thermal pre-treatment at 1273 K for 10 min was applied to all substrates in a 250 sccm pure H_2 flow. A pure titanium wire heated at 1500 K for 10 min was also used as an oxygen getter. Well crystallized TiN layers were easily obtained at 1273 K from gas mixture composed of TiCl_4 and N_2 in presence of H_2 as transport gas [22, 23]. Owing to the low vapour pressure at room temperature, it was necessary to heat the chloride at 333 K with the help of thermostated bath. SiC layers growth was carried out at 1373 K from tetramethylsilane (TMS) as precursor in presence of hydrogen as the dilution and reducing gas [24–27]. TMS gas which decomposes at 1073 K is well known to form adherent SiC films on metallic substrate

materials [28]. The deposition experiments were performed under normal pressure at constant flows of TMS (10 sccm) and H_2 (150 sccm) for SiC, substrate temperature being controlled by an optical pyrometer supplied by Mirage Company. The so-obtained TiN and SiC layers were homogeneously deposited on W substrates and well crystallized, the same results were obtained on Mo substrates (Fig. 1). The stabilities at high temperature of the M/TiN/SiC ($M = \text{W}$ and Mo) systems were examined with the help of annealings at 1773 K for durations of 8 or 16 h. In this context, the samples introduced into a graphite crucible were then heated with a high frequency furnace flushed with Ar. In order to profile the atomic composition, annealed samples were analysed on polished section with an electron probe microanalyzer (EPMA, Cameca SX-100) with wavelength-dispersive spectrometer (WDS) operated with an acceleration voltage of 20 kV, and a 1 μm probe size of. Prior to those analyses, the couples were embedded in epoxy resin and polished with diamond suspension size down to 1 μm .

Results

The main aim of those investigations was the thermal stability given by TiN interlayers in the systems M/TiN/SiC ($M = \text{W}$ and Mo). The two different metals considered here were chosen because of their very high melting points. Two types of substrate were considered in each case, cylindrical wires and planar wafers. The reason of

Fig. 1 TiN coatings: **a** optical image of a W/TiN/SiC couple, **b** X-ray diagram realised on W/TiN wires and **c** X-ray diagram realised on W/TiN/SiC wires



these double examinations is to reveal a possible effect induced by the geometry. Indeed, owing to the relative high dilation coefficient of TiN comparing to the ones of SiC and metals (W or Mo), the apparition at elevated temperatures of mechanical constraints could modified the results. Moreover, it is important to note that SiC layer is not well adherent on TiN. As a consequence, this can also have an effect on the results. On the micrographs presented herein, the major part of the SiC layer is absent on planar samples. The annealing temperature of 1773 K with durations of a few hours was considered as sufficient to reveal the presence or the lack of reaction.

TiN effect in the system W/TiN/SiC

In a first study, the stability of $W_{1-x}Re_x$ /SiC couples was considered and especially the diffusion kinetics of Si and C atoms in pure W and $W_{1-x}Re_x$ ($x = 5$ and 25 at.% Re) alloys [1]. It appears that SiC reacts with W-based alloys with formation of W_5Si_3 and WC, the temperature range considered in this case was 1673–1873 K (Fig. 2a). Our investigation on the W/TiC/SiC system revealed a notable protection against silicon atoms but a low effect against carbon atoms diffusion, what could probably be increased by using another compound as protection [13]. At the starting point of the present work, we tried to determine if nitrogen atoms were able to avoid residual diffusion of carbon atoms, what seems very difficult with TiC, especially at high temperature (Fig. 2b). In the case of W cylindrical or planar substrates, even after an annealing treatment at 1773 K during 8 or 16 h, no reaction zone involving tungsten could be observed (Figs. 2c, 3, 4). In any cases, we can only note a reaction between TiN and SiC leading to the formation of the solid solution $TiN_{1-x}C_x$ [29]. The formation of this phase is highlighted by a slightly discoloration of TiN, this last one becoming gold-like to grey in presence of carbon (Fig. 3). Despite the TiN layer of 15 μm thick and a thermal treatment of 16 h at 1773 K, WDS microanalysis realized on the wire sample reveal neither the presence of silicon nor carbon (Fig. 5). We can only note the formation of $TiN_{1-x}C_x$ on a zone smaller than 5 μm . Considering the planar geometry sample, the reduced TiN coating thickness of about 10 μm appears sufficient to protect the metal. Nevertheless, it is

Fig. 2 Optical images revealing reaction zone dimensions at 1773 K: **a** W/SiC treated for 8 h, **b** W/TiC/SiC treated for 8 h, **c** W/TiN/SiC annealed for 16 h

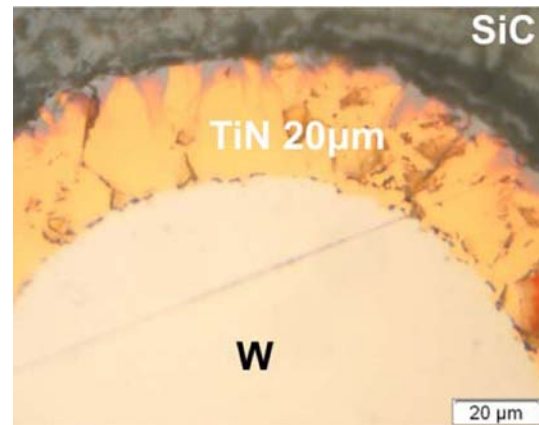
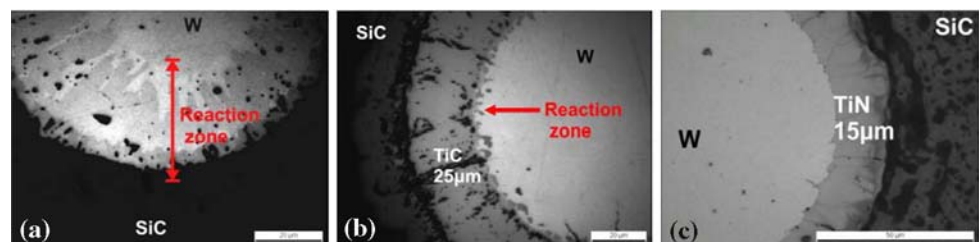


Fig. 3 Real-colour optical image of the W/TiN/SiC diffusion couple annealed at 1773 K for 8 h

worth noting that for this geometry SiC is no more adhesive on TiN after annealing this is the only difference observed between cylindrical and planar samples (Fig. 4). Nevertheless, the results are quite similar in both cases. When comparing three different systems: W/SiC, W/TiC(25 μm)/SiC and W/TiN(15 μm)/SiC after heat treatment at 1773 K, very different behaviours are observed (Fig. 2). In the case of unprotected couple W/SiC, a reaction zone of about 40 μm is obtained after only 8 h at 1773 K. After the same duration, the reaction zone for W/TiC/SiC couple is equal to 10 μm . With a TiN layer, no reaction zone can be observed as previously mentioned despite an annealing duration two times longer. Here is put in evidence the strong efficiency of TiN in comparison with TiC. In the case of TiC containing system, a reaction between W and TiC leads to the formation of the solid solution $(Ti,W)C_{1-x}$ creating a chemical instability [13]. Then, C atoms can diffuse easily into TiC layers because of an intrinsic diffusion of C atoms in this compound. For TiN, the situation seems different owing to three main factors: (1) no chemical reaction occurs between W and TiN, (2) its cubic unit cell parameters are smaller than TiC ($a_{TiN} = 4.239 \text{ \AA}$, $a_{TiC} = 4.317 \text{ \AA}$) and (3) the thermal expansion coefficient of TiN is higher than TiC, i.e. $\alpha_{TiN} = 9.4 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{TiC} = 8.5 \times 10^{-6} \text{ K}^{-1}$. Those two last characteristics are unfavourable to the diffusion of carbon and silicon atoms because they reduce the

Fig. 4 Planar W/TiN/SiC diffusion couple annealed at 1773 K for 16 h: **a** contrast image, **b** real colours image

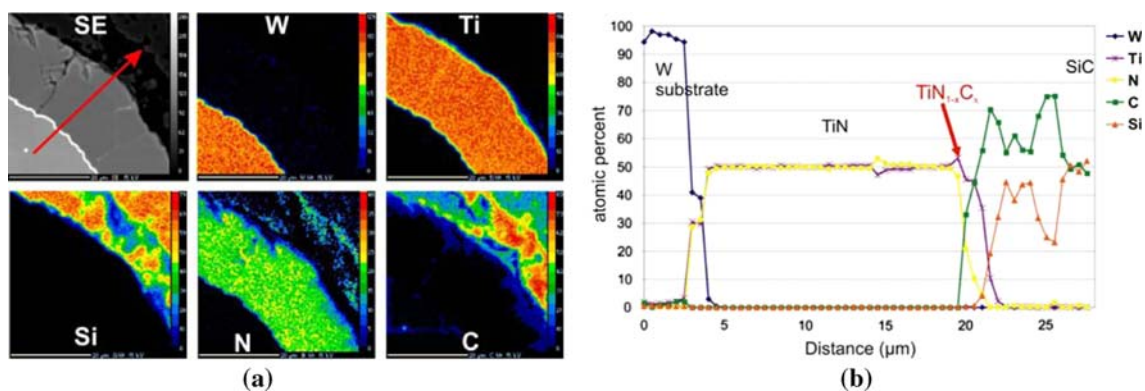
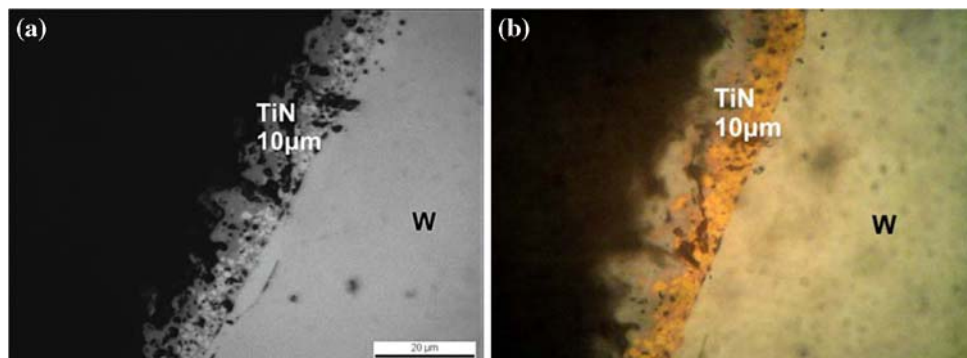
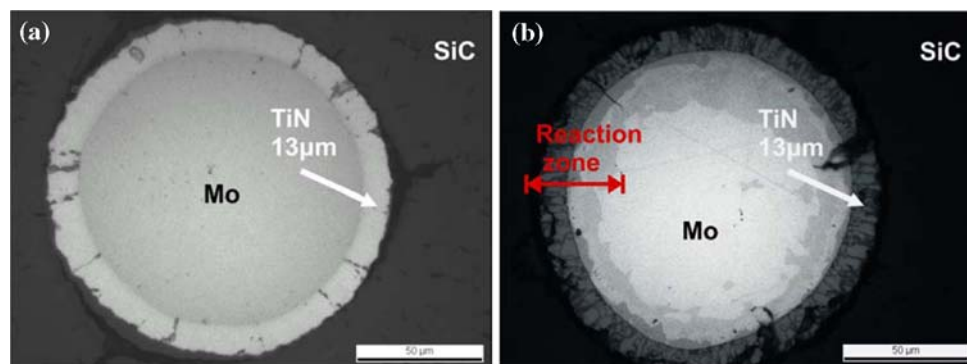


Fig. 5 WDS experimental analysis on W/TiN/SiC couple heat treated at 1773 K for 16 h, **a** secondary electron image, weight concentration cartographies of W, Ti, Si, N, C, **b** concentration

profiles of W, Ti, Si, N, C by EPMA. The path of the profiles analysis is indicated by an arrow on the secondary electron image

Fig. 6 Contrast image of Mo/TiN/SiC diffusion couple: **a** before annealing, **b** annealed at 1773 K for 8 h



distances between metallic atoms and the dimensions of the grain boundaries. A reduced layer of 5 or 10 μm could be sufficient to provide a satisfactory protection at high temperature.

TiN effect in the system Mo/TiN/SiC

One of the other metals interesting for high temperature applications is molybdenum. It is known that Mo reacts strongly with SiC [2]. In order to ensure the integrity of the system, the intercalation of TiN as protective layer was

examined at 1773 K. Figure 6a shows the appearance of the sample with a TiN layer of about 13 μm before the thermal treatment. Figure 6b shows that after an annealing of 8 h at 1773 K, a reaction zone of about 39 μm is observed. To check that this reaction zone is not induced by mechanical constraints and cracks correlated to the cylindrical geometry; an experiment was also realized on Mo planar substrate (Fig. 7). After annealing at 1773 K for 16 h, a reaction zone of about 44 μm is obtained despite the 20 μm TiN coating. This indicates that a diffusion mechanism takes place without any dependence with the

Fig. 7 Planar Mo/TiN/SiC diffusion couple annealed at 1773 K for 16 h: **a** contrast image, **b** real colours image

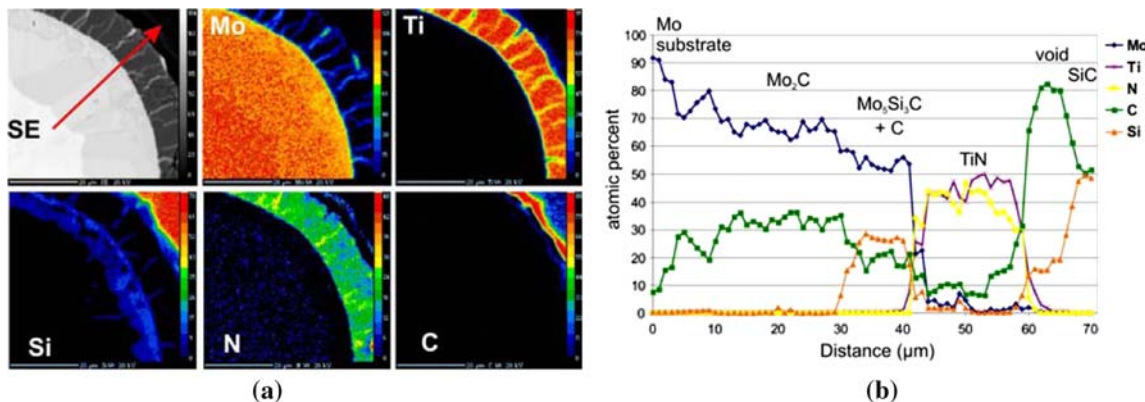
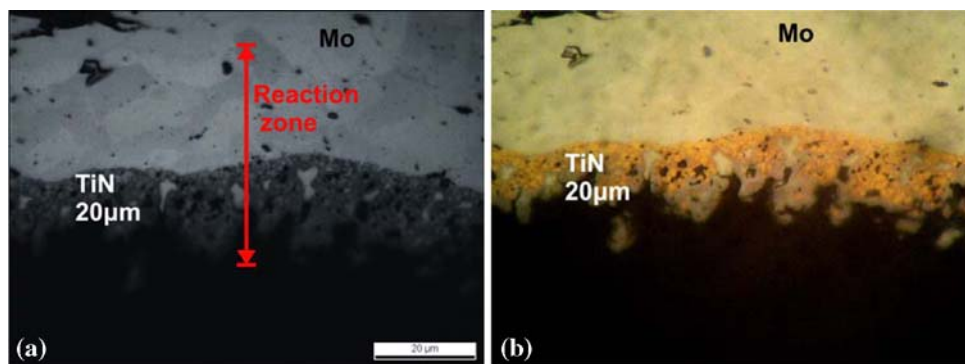


Fig. 8 WDS experimental analysis on Mo/TiN/SiC couple heat treated at 1773 K for 16 h, **a** secondary electron image, weight concentration cartographies of Mo, Ti, Si, N, C, **b** concentration

profiles of Mo, Ti, Si, N, C by EPMA. The path of the profiles analysis is indicated by an arrow on the secondary electron image

Table 1 Atomic concentrations and errors of Mo, Ti, Si, N, C by EPMA on Mo/TiN/SiC couple heat treated at 1773 K for 16 h

	Mo	Ti	Si	N	C
Mo ₂ C (15)	65.8 ± 2.9	0.1 ± 0.1	0.7 ± 1.6	0.0 ± 0.0	33.3 ± 1.9
Mo ₅ Si ₃ C + C (8)	53.3 ± 1.9	0.0 ± 0.0	26.7 ± 0.9	0.0 ± 0.0	19.4 ± 2.7
Ti(N,C) (11)	3.0 ± 2.2	44.6 ± 3.5	1.6 ± 1.2	42.5 ± 2.8	8.3 ± 1.7
SiC (3)	0.0 ± 0.0	0.1 ± 0.1	48.4 ± 1.2	0.0 ± 0.0	51.5 ± 1.2

Four phases are evidenced: Mo₂C, Mo₅Si₃C with carbon traces, Ti(N,C) and SiC. In each case, the number of points used for the average is indicated between the brackets

substrate symmetry. The concentration cartographies on the Fig. 8a confirm the composition of the reaction zone and reveal the presence of Mo channels going through the TiN layer. The WDS analysis realized on this cylindrical sample shows that two phases are obtained: the ternary Mo₅Si₃C and Mo₂C (Fig. 8b; Table 1). The corresponding diffusion path can be written: Mo/Mo₂C/Mo₅Si₃C/(TiN)/SiC (Figs. 8a, 9). This result is the same than the one obtained with the Mo/SiC and Mo/TiC/SiC systems [2, 30]. The secondary electron micrograph by SEM presented on this sample confirms the diffusion of Mo into TiN without any evidence of reaction between the metal and the nitride (Fig. 10). The vertical section of TiN–Mo ternary phase

diagram confirms that no reaction can occur in this composition range (Fig. 11). Moreover, the interface Mo/TiN does not show any reaction front. Those results reveal a particular interaction between Mo and TiN. From the results obtained herein, we can conclude that Mo atoms diffuse into the TiN layer by the grain boundaries leading to the TiN grains dissociation and finally to the integrity destruction of the nitride layer. The average thickness of the reaction zones was measured for comparison with Mo/SiC growth kinetic. In order to evaluate the growth rate constant, we used the following Eq. 1:

$$x^2 = 2k_p \times t \tag{1}$$

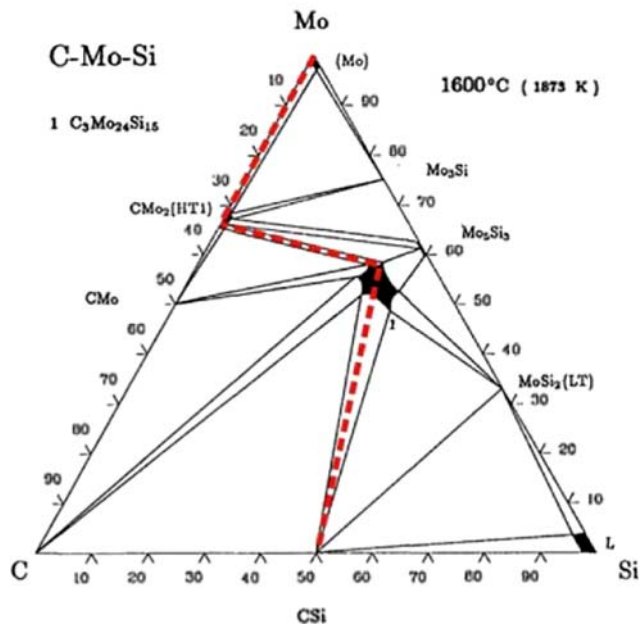


Fig. 9 Isothermal section of Mo–Si–C phase diagram at 1873 K with diffusion scheme in the system Mo/TiN/SiC [31, 32]

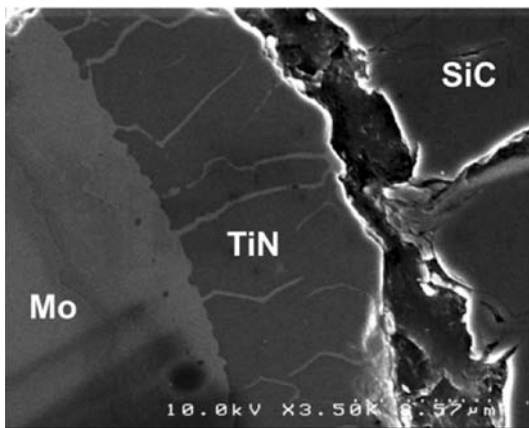


Fig. 10 Secondary electron images of Mo/TiN/SiC couple heat-treated at 1773 K for 16 h

where x and k_p are, respectively, the thickness and parabolic growth rate constant of reaction layer and t is the annealing time equal to 16 h. The parabolic growth rate at 1773 K for the cylindrical Mo/TiN/SiC system is found to be equal to $1.39 \times 10^{-10} \text{ cm}^2/\text{s}$. The corresponding value for the planar system is equal to $1.68 \times 10^{-10} \text{ cm}^2/\text{s}$. Those values are lower than the expected value for the system Mo/SiC, i.e. $1.78 \times 10^{-10} \text{ cm}^2/\text{s}$. The presence of the TiN layer reduces noticeable the diffusion kinetic. Nevertheless, this nitride cannot supply a sufficient protection on molybdenum. Indeed, Si and C atoms are free to diffuse through TiN layer using Mo channels.

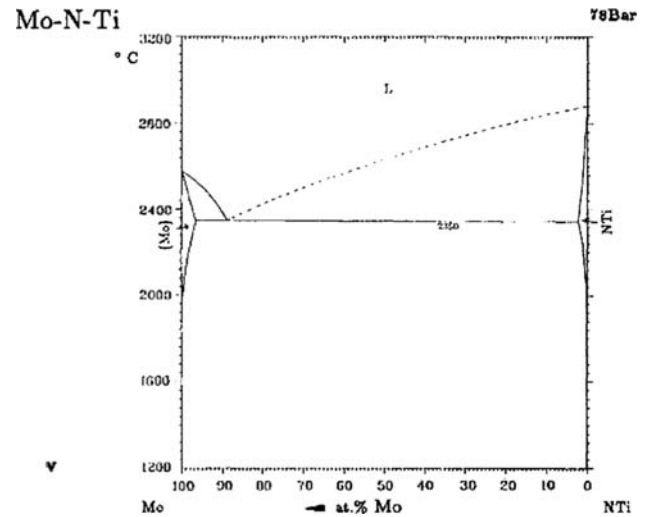


Fig. 11 Vertical section of TiN–Mo ternary phase diagram [33]

Discussion

Despite similar coefficients of thermal expansion and Young's modulus values, W and Mo have very different stabilities in presence of TiN. Indeed, the TiN layer is stable on W whereas it is destroyed on Mo. This difference of behaviour is probably induced by a strong difference of W and Mo atoms nobilities. It is well-known that the atomic diffusion coefficients are correlated to the melting temperature. When regarding the melting points of W (3683 K) and Mo (2883 K), we can deduce that those two metals have very different mobility levels. Mo having the lower melting point, then it may be more mobile. Tungsten interacts probably with TiN following the same mechanism but with such a low rate that it is impossible to observe. Moreover, during our previous studies on W/SiC and Mo/SiC systems between 1573 and 1873 K we noticed a far higher diffusion kinetic on the Mo substrate. This could also justified a fewer effect when TiN is intercalate between Mo and SiC.

During this work, two kinds of geometry were examined: cylindrical and planar. The reason of these double examinations is coming from the fact that the synthesis of cylindrical samples is simplest and ensure the adherence of SiC on TiN. In this geometry, a stress appears at high temperature because of the strong difference between the thermal expansion coefficients of the metals ($\alpha_W = 4.5 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{\text{Mo}} = 5.2 \times 10^{-6} \text{ K}^{-1}$) and SiC ($\alpha_{\text{SiC}} = 4.5 \times 10^{-6} \text{ K}^{-1}$) in comparison to the high thermal expansion coefficient of TiN ($\alpha_{\text{TiN}} = 9.4 \times 10^{-6} \text{ K}^{-1}$). Nevertheless, the reaction zone dimension on the molybdenum cylindrical substrate is less important comparing to the planar one. In the case of the cylindrical sample, the highest strength inside the TiN layer induced by the

geometry is less favourable to the diffusion of Mo, Si and C atoms. A higher grain boundaries reduction is probably the reason why the corresponding parabolic growth rate is less elevated, despite a thinner TiN layer than on the planar substrate. Concerning tungsten substrates, the results are the same for the both geometries essentially because this metal does not interact noticeably with TiN.

Conclusion

The main objective of this work was to examine the effect of an additional TiN interlayer between SiC and metallic substrates of W or Mo. Indeed, important reactions leading to the formation of silicides and carbides occur at 1773 K in the systems W/SiC and Mo/SiC. Samples were prepared by chemical vapour deposition. TiN layers thicknesses were between 10 and 20 μm . After thermal treatments at 1773 K during 8 or 16 h, samples were characterised and revealed two kinds of situations:

- (1) an effective protection is obtained on tungsten substrates with a 10 μm thick TiN layer despite a annealing duration equal to 16 h at 1773 K.
- (2) TiN is not efficient as a protective coating on molybdenum at 1773 K. Whatever TiN thicknesses considered, important reaction zones are obtained for all annealing durations.

The hypothesis of the Mo diffusion mechanism at the TiN grain boundaries should be examined during an upcoming study. Nevertheless, the interdiffusion of Mo and TiN remains of interest to increase the mechanical behaviour of applications implementing Mo-containing pieces.

Acknowledgement The authors wish to thank M. Lahaye (CeCaMA, Bordeaux) for his assistance in SEM and EPMA studies.

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