

Wetting and spontaneous infiltration: the case study of TaC/(Au, Al and Cu) compared to TiC/Cu

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Abstract. Spontaneous infiltration of molten metals in to ceramic skeletons, in the course MMCs' production, is related to improved wetting of the ceramic by metals. TiC is considered a "metal-like" carbide and is supposed to be wetted well by metals through metallic bonding mechanism. Nevertheless, TiC/Cu exhibit an unusual behavior since spontaneous infiltration of molten Cu takes place, while TiC is partially wetted by Cu ($\theta=90^\circ$).

In this work we studied the relation between wetting and spontaneous infiltration in the TaC/Au, Al and Cu systems. TaC is also considered a "metal-like" carbide and indeed no chemical interaction was observed at the interfaces of the studied systems.

Sessile drop experiments showed almost perfect wetting in the three system but spontaneous infiltration occurred only in the first two (e.g. TaC/Au or Al). Thermodynamic calculation shows the difference between the systems which also has its' influence on the mechanical properties of the MMCs'. Further calculation clarifies the difference between TaC/Cu and TiC/Cu infiltration behavior, but is unable to explain the wetting results differences.

Correlation between wetting and spontaneous infiltration in some cases is not straight forward and more studies and calculations on the atomistic level should be done in order to clarify this matter.

1. Introduction

Spontaneous production of MMC's (Metal Matrix Composites) in a pressure less atmosphere is very attractive. Nevertheless, external pressure is usually necessary since ceramics are not wetted well by molten metals, therefore spontaneous infiltration doesn't take place [1,2]. Often improved wetting of ceramics is achieved by the addition of a reactive element which interacts with the ceramic and forms a new phase at the interface (e.g. "reactive wetting"). Unfortunately this new phase is brittle and its' width is not controlled. This might lead to production of MMC's with poor properties. It became common knowledge that successful spontaneous infiltration could occur if the contact angle (called "wetting angle"), θ , is lower than 90° . When ideal parallel pore walls of the ceramic are considered, this condition is sufficient [3]. In practice, pore walls are never parallel; they also have a certain roughness which could hinder infiltration and actually successful infiltration requires contact angles bellow 60° [3]. Trumble [4] proposed an analytical model which predicted that infiltration could take place when θ_c is lower than 50.7° . The straight forward link between contact angle and spontaneous infiltration is done since both depend on the same physical phenomenon; both wetting and infiltration are controlled by the energy gain of the system when surfaces of the ceramic and the molten metal are



replace by a solid-liquid interfaces. Lack of infiltration despite improved wetting might occur in systems in which reactive wetting takes place (graphite/Si system for example [5]), in this case the growth of the new interface phase, can block pores and deny further infiltration of the molten metal. Blockage of pores was also observed in the case of $\text{CaF}_2/\text{In-Ti}$. Despite improved wetting ($\theta=30^\circ$), infiltration didn't take place probably due to the high vapor pressure of CaF_2 , which practically blocked the access of the molten alloy into the open pores [6].

In previous results [7], despite the fact that the contact angle in the TiC/Cu was found to be 90° and in other reports even higher [8,9], spontaneous infiltration took place in the frame time of second which clearly suggests that infiltration didn't proceed through a reactive wetting mechanism. Titanium carbide has a high melting point, displays extremely high hardness and shock resistance and its electrical conductivity is comparable to that of metals [10-12]. In the high temperature capillarity community it is considered a "metal-like" material and therefore could be easily wetted by liquid metals, since it is well known that metal wets other metals due to metallic bonding formed at the solid/liquid interface, without the need of chemical reaction (dissolution or new phase formation) [1,13]. The partially wetting and improved infiltration in the TiC/Cu is peculiar, therefore we decided to study the wetting and infiltration behavior in a similar system. For this purpose we chose TaC and Au, Al and Cu as infiltrating metals. Tantalum belong the V group of elements which exhibits, just like the IV group, carbides with a wide composition range. The high density of TaC (14.3 gr/cm^3) limits its use as a structural material, yet it is used in various applications due to its high melting point, chemical inertness and metallic electrical conductivity [10,14]. These properties are related to the mixed covalent-metallic bonds. Nevertheless, TaC is brittle, therefore there is an advantage in producing a MMC based on TaC and a ductile metal. Shanker et al. [15] made an attempt to develop MMCs' based on TaC for use as electrodes in plasma systems and obtained improved mechanical properties. Due to its metallic character, TaC just like TiC is an excellent candidate for production and study spontaneous infiltration processes of MMC's. The high stability of TaC suggests that little if any chemical interaction might occur at the interface, which would not compromise its' integrity. In the current study we intend to investigate the wetting properties of TaC in contact with pure metals (Al, Cu and Au) at 1423 K, followed by spontaneous fabrication of MMCs' and characterization of its' mechanical properties, in order to find more about the relations between wetting, spontaneous infiltration and properties.

2. Materials and Methods

Fully dense TaC samples were fabricated from 99% purity powder using SPS (Spark Plasma Sintering) - apparatus (type HP D5/1, FCT System. Rauenstein, Germany). The SPS consolidation was made using 20KN pressure at 2473K for 30 minutes. The final Ta:C ratio was determined by XRD analysis. The lattice parameter of the rock salt TaC after SPS process was 0.4453 nm. According to Bowman [16], the C:Ta ratio is 0.974. Sessile drop wetting experiments were performed at 1423K, under a dynamic vacuum (10^{-3} Pa). Contact angles were measured using a Nikon 990 Coolpix digital camera and derived from the magnified images using the "Image Pro 4" software. Composites based on TaC were fabricated by free infiltration of TaC preforms obtained by cold compacting under 15MPa (60% porosity) and after densification by SPS at 2073K for 30 min under 60MPa applied pressure (20% porosity). The infiltration process was carried out at 1423K, under a pressure of 10^{-3} Pa , for 30 minutes. Solidified ceramic/drops interfaces were characterized using SEM (Jeol JSM 35C) while ceramic/metal interfaces in the infiltrated composites were characterized using TEM (Jeol 2010F) analysis. Samples for TEM characterization were first sectioned and mechanically thinned to about 50 μm . Then, 3 mm in diameter samples were punched out of the thinned samples followed by dimple grinding and Ar-ion beam milling using a Gatan PIPS (Precision Ion Polishing System) apparatus. The effectiveness of the spontaneous infiltration process was determined indirectly by the bending strength of the composites. In this study we used the three point method (LLOYD Instruments LTD machine). Bars (four samples for each composite) with the length of 20 mm, 2 mm width and 1.5 mm height were tested at a strain rate of 0.2 mm/min according to ASTM 1161-94. The velocities of

longitudinal and transverse acoustic waves were determined by the "Pulse-Echo" method using a 5 MHz probe and according to ASTM E494-10. The elastic modulus of the composite was calculated using the ultrasonic sound velocities and Archimedes density measurements.

3. Results and discussions

3.1. Wetting and infiltrated composites microstructure

The final contact angle was obtained during heating before reaching 1423K. In the TaC/Al system, contact angle of $10^\circ \pm 1^\circ$ was measured during the 30 minutes dwell, while $10.5^\circ \pm 1^\circ$ and $11^\circ \pm 1^\circ$ was measured in the TaC/Cu and TaC/Au systems respectively. No new phases or signs of dissolution were found at TaC/Au, Al or Cu interfaces (figure 1). Liquid Al and Au fully infiltrate the TaC preforms (figure 2), TaC particles are homogeneously distributed in metallic matrix.

Cu didn't infiltrate in the preform and TaC/Cu MMC was not obtained. This result matches the results of Shanker et al. [8] which reported difficulties in production of TaC/Cu MMCs'. According to Shanker et al., successful infiltration was achieved over a narrow TaC range (43-50%) at temperatures higher than 1300°C in vacuum.

TEM characterization of the TaC/Al and TaC/Au MMCs' showed no interface interaction or new phases formed at the TaC/Al and TaC/Au interfaces (figure 3).

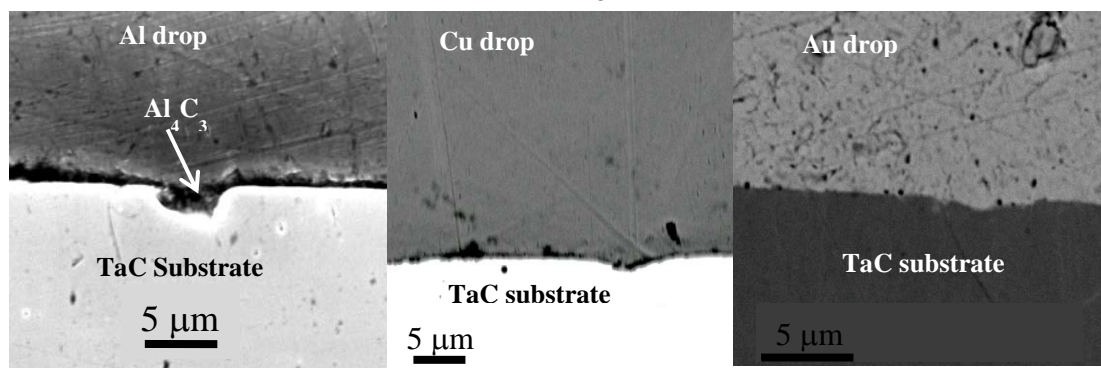


Figure 1. TaC/(Al, Cu, Au) interfaces showing no traces of interaction and dissolution and precipitation of Ta in the solidified melt. In a few discrete points Al_4C_3 particles were found. These phases are related to excess graphite remains after the SPS process.

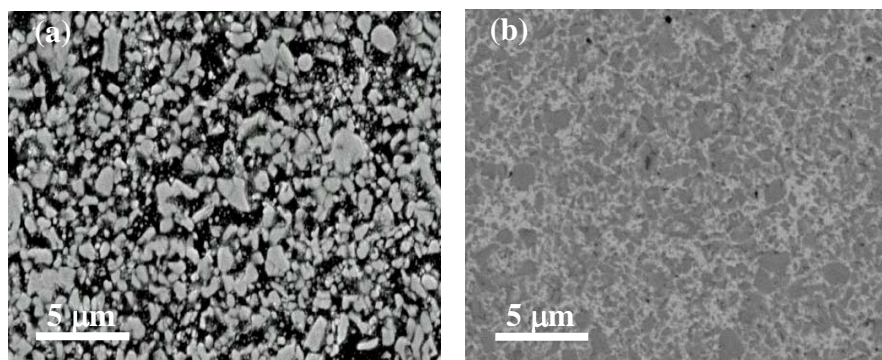


Figure 2. MMCs' bases of TaC-60% porosity, (a) infiltrated in Al (b) infiltrated in Au.

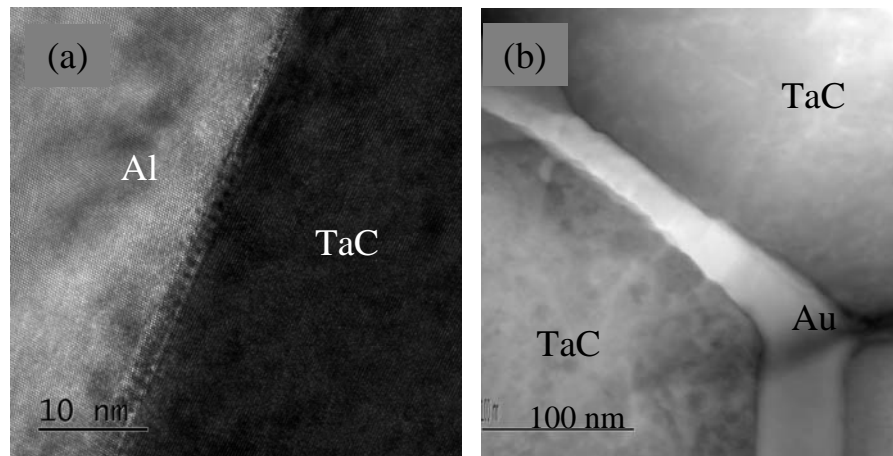


Figure 3. TEM images of representative TaC particles in contact with the infiltrating metal (a) Al (b) Au.

3.2. Mechanical properties Interpretation

The properties of the composites strongly depend on the metal to ceramic ratio. Moreover, the bending strength of the TaC-Au composites is higher than that for the TaC-Al composites (table 1). The image of the fractured surface of the TaC-60vol.%Au composite clearly demonstrates that the fracture mode is ductile and the cracks propagate rather through the ceramic phase than through the metal/ceramic interfaces (figure 4). Characteristic bending stress curves in the TaC/Al system are presented in figure 5 and support the ductile behavior of the high metal content composites. Despite the fact that no interface interaction is observed in the two studied systems, according to the results presented in table 1, TaC/Au interfaces are stronger than TaC/Al ones. This feature may be correlated with the work of adhesion, W_a , between liquid metal and solid substrate. The work of adhesion depends on contact angle θ and liquid vapor surface energy of the metal γ_{LV} (comprehensive review of the subject [17]),

$$W_a = \gamma_{LV} (1 + \cos\theta) \quad (1)$$

According to Keene [18], the surface energies of liquid Au and Al at 1423K are 1.14 J/m² and 0.8 J/m², respectively and the calculated values of the work of adhesion are 2.25 J/m² and 1.6 J/m², respectively. Furthermore, thermal stresses might develop at the interface during cooling. Due to the mismatch between the thermal expansion coefficient (CTE) of the metal and TaC and the fact that the CTE of TaC is lower than the CTE of Al and Au, the ceramic at the interface is under compression stresses and the metal is under tensile stresses.

The thermal stress at the TaC/metal interface could be expressed by the following equations [19]:

$$\sigma_{TaC} = (-E'_{metal} \cdot E'_{TaC}) / (E'_{metal} + E'_{TaC}) \cdot \Delta T \cdot (\alpha_{metal} - \alpha_{TaC}) = \sigma_{metal} \quad (2)$$

And $E' = E / (1 - \nu)$, where E is the Young's modulus, α = CTE and ν is the Poisson's ratio.

The data and the calculated interface stresses are summarized in table 1. The calculated values obtained show that while the compression stresses which undergoes the ceramic is beneath the yield of TaC, the tensile stresses of both metals exceeds their yield stress. Yet the stresses at the TaC/Al interface are twice higher than the ones at the TaC/Au interface, which should have a contribution to the decreasing bonding strength of the Al/TaC MMC.

Table 1. Results of three point bending strength and Young modulus of TaC/Al and TaC/Au MMCs'

Composite	Bending strength, MPa	Young modulus GPa
TaC -60vol.% Al	697 \pm 50	151 \pm 10
TaC -20vol.% Al	632 \pm 45	349 \pm 14
TaC -60vol.% Au	987 \pm 48	198 \pm 12
TaC -20vol.% Au	720 \pm 35	365 \pm 12
TaC	590	537 [20]

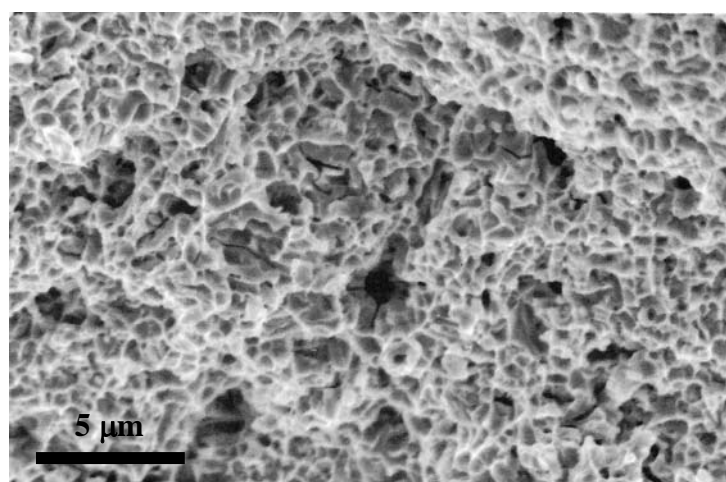


Figure 4. Fractography image of the TaC (60%por)/Au MMC after three point bending experiment showing dimples with are characteristic to ductile fracture.

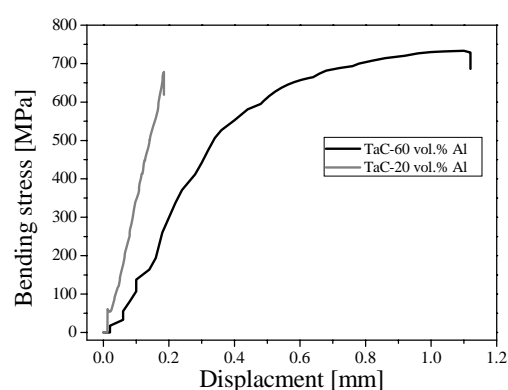


Figure 5. Characteristic three point bending stress diagram for TaC/60vol.% Al and TaC/20vol.% Al composites.

Just for comparison, the bending strength reported by Frage et al. [6] in the TiC/Cu (in the range of 20-50% porosity) is 500 – 960 MPa.

3.3. Thermodynamic considerations

The difference between the three studied systems was considered in the perspective of the thermodynamic properties of the systems. The carbon solubility in the various liquid metals is negligible. Therefore the thermodynamic properties of the various metals-Ta and the composition range of TaC at 1423K were taken into account.

The equilibrium content of Ta within the liquid melt were calculated according to equations (3-5), where

$$\mu_{Solid}^{Ta} = \mu_{Liquid}^{Ta} \quad (3)$$

$$\mu_i^0(Ta(S)) + RT \ln(a_i(Ta(S))) = \mu_i^0(Ta(L)) + RT \ln(a_{Ta}^L) \quad (4)$$

$$RT \ln(a_i(Ta(S)))/(a_i(Ta(L))) = \mu_i^0(Ta(L)) - \mu_i^0(Ta(S)) = [\Delta G]_{Fusion}^{Ta} \quad (5)$$

The activities of Ta (μ_{Liquid}^{Ta}) in the various Al, Cu and Au melts are described by the Redlich-Kister formalism [21] using the interaction parameters, L^0 , L^1 and L^2 (**Error! Reference source not found.**) and the data concerning the Ta activity within its composition range at 1423K. While the binary phase diagrams of Al-Ta and Au-Ta exhibits the existence of various stable intermetallics, Cu and Ta don't have any. This behavior implies that Ta and Cu should have a positive departure from ideality while the former systems should show a negative departure from ideality as could be seen through the interaction parameters.

Table 1. The interaction parameters of Ta-Al, Cu and Au binary liquid solutions at 1423K.

System	L^0 [J/mol]	L^1 [J/mol]	L^2 [J/mol]
Al-Ta [22]	-41521.2	-4732.84	19928.86
Cu-Ta [23]	99366.18	0	0
Au-Ta [24]	-135370	0	0

The thermodynamic properties of TaC_x were extracted from [25]. At 1423K, Ta composition in

Ta_xC_{1-x} varies between 0.5 < x < 0.55. The calculated content of Ta in various melts as a function of tantalum carbide stoichiometry is shown in figure 6. The calculated results express the high affinity of Au towards Ta and the repulsion between Ta and Cu. These huge differences in thermodynamic properties are not expressed in the sessile drop experiments, which mean that the spreading kinetics is faster than dissolution. Yet, the thermodynamic differences between the studied systems are qualitatively observed in the spontaneous infiltration and bending strength results. Cu was not able to infiltrate at all, at the bending strengths of TaC/Au composites were higher than those of TaC/Al.

When questioning the differences between the TaC/Cu and TiC/Cu systems, first the Ti-Cu liquid system exhibits a negative departure from ideal solution ($\ln(\gamma_0) = 1.02$ at 1423K [26]), second the formation Gibbs energy of TiC is lower than that of TaC. The thermodynamic calculation in the case of titanium carbide within its composition range is based on Frage et al. [6]. Figure 7 expresses the differences between Ta solubility in molten Cu in equilibrium with tantalum carbide compared to Ti solubility in molten Cu in equilibrium with titanium carbide at 1423K.

It could be seen that the solubility of Ti in Cu is about two orders of magnitude higher than Ta in Cu in the stoichiometric state (x=0.5) and about one order of magnitude for lower content of carbon in the carbides.

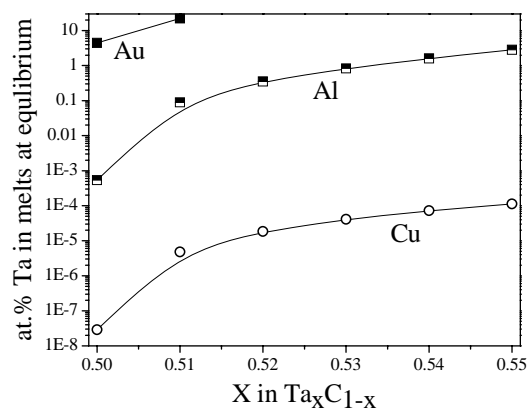


Figure 6. Calculated Ta content in various liquid metals (Au, Al, Cu) as a function of tantalum carbide stoichiometry.

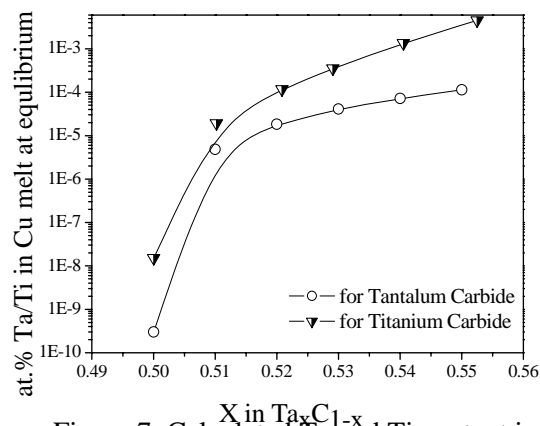


Figure 7. Calculated Ta and Ti content in liquid Cu as a function of tantalum carbide and titanium carbide stoichiometry.

4. Conclusions

The sessile drop experiments in the TaC/(Al, Cu and Au) at 1423 K systems showed almost perfect wetting and predicts that spontaneous infiltration should occur in all cases. The flat interfaces and the lack of reaction products or detected solubility of Ta, led to the conclusion that improved wetting in the TaC/(Al, Cu and Au) occurs due to the "metal-like" nature of TaC. The pressure free infiltration experiments and bending strength exhibited best results in the TaC/Au system while in the case of TaC/Cu no infiltration took place, which is in qualitative correlation with the thermodynamic properties of the studied systems. The fractography images show ductile fracture implying that the bonds at the interface are stronger than the strength of the metals. In contrast, Cu partially wets TiC ($\theta=90^\circ$) [8] but infiltrates it perfectly [7]. Although TiC is more stable thermodynamically than TaC, the interaction parameter of Cu-Ti dilute liquid phase (L^0 or $RT\ln\gamma^0$) at 1423K is ~ -13 kJ/mol (attraction forces) while the interaction parameter in the Cu-Ta dilute liquid phase is ~ 99 kJ/mol (repulsion forces). These differences could lead to different behavior in the spontaneous infiltration process but are unable to explain the wetting results differences. Lastly, the correlation between wetting and spontaneous infiltration in some cases as the ones showed here is not straight forward and more studies and calculations on the atomistic level should be done in order to clarify this matter.

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