WETTING OF TiN BY LIQUID COPPER

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ABSTRACT

In the framework of an extensive study aimed at evaluating the wettability and the surface characteristics of different metal-ceramic systems, the behaviour of TiN in contact with liquid copper was tested.
TiN_x specimens were made by annealing Ti metal sheets (3mm thick) in a cold-wall autoclave at about 9 bar N_2 and at 1900 K for times as long as 200 hours. Through this process all the titanium is converted into compact titanium nitride which allows meaningful wettability experiments, with an accuracy difficult to reach with sintered bodies. The stoichiometry has been determined by X-ray diffraction, XPS and RAMAN spectroscopy.
The wetting experiments have been performed by the sessile drop technique in a ad-hoc furnace under pure fluxing He-5%H_2 mixtures.
In each run, both contact angles and liquid surface tension were measured by using a specially developed procedure (ASTRA©) allowing these data to be recorded in real time.
Results are presented on the wetting characteristics and of the interfacial reactions as a function of time.

INTRODUCTION

Titanium nitride is a highly appreciated ceramic material for its mechanical, electrical properties and the golden metallic lustre [1]. Its high temperature performances suggest its use in contact or joined to metals: as a consequence, its wettability characteristics by liquid metals are of great technological impact.
Wetting is driven by the balance of surface and interfacial energies, but the final chemical and mechanical properties of the joint are determined also by the type and the extent of interfacial reactions.
Few studies exist devoted to the wettability of TiN by liquid metals. As far as we know, few data can be extracted from the work of Samsonov [2] and Naidich [3]; however, quite recently, two contributions have appeared [4,5], in which contact angles and interfacial reactions have been reported for (Cu or Ag)/TiN_x and Cu-Ti/TiN_x as a function of the nitride stoichiometry. These two studies do not come to a common understanding of the phenomena and of the experimental results, mainly due to the difficulty to characterise the solid surface properties and the real experimental conditions. In particular, as shown in Fig. 1, the contact angles found in all the cited works, vary very much, especially for the stoichiometric compound. However, it seems quite accepted that highly hypo-stoichiometric TiN is wetted by liquid copper.

EXPERIMENTAL PART

The wetting experiments have been performed by the sessile drop technique [6] in a special furnace made up of two concentric alumina tubes. Between the two tubes an inert gas was slowly fluxed in order to rule out any oxygen intake due to possible porosity in the alumina when working under high vacuum conditions at high temperatures.
Experiments were carried out, at T=1440 K for 30 min, under pure fluxing He-5%H_2 mixtures. The oxygen partial pressure, measured by a solid state gauge operating at the furnace exit, was set around an average value of 10^{-9} Pa.
In each run, both contact angles and liquid surface tension were measured by using a specially developed procedure (ASTRA©) [7] allowing these data to be recorded in real time. A carefully aligned optical set-up has been used, with a CCD camera equipped with a 300 mm focal length high quality objective. Contact angles are measured with a ±1 ° accuracy for each measure and a repeatability of ±3 ° between the runs. Surface tension values have a reproducibility of 0.5%.

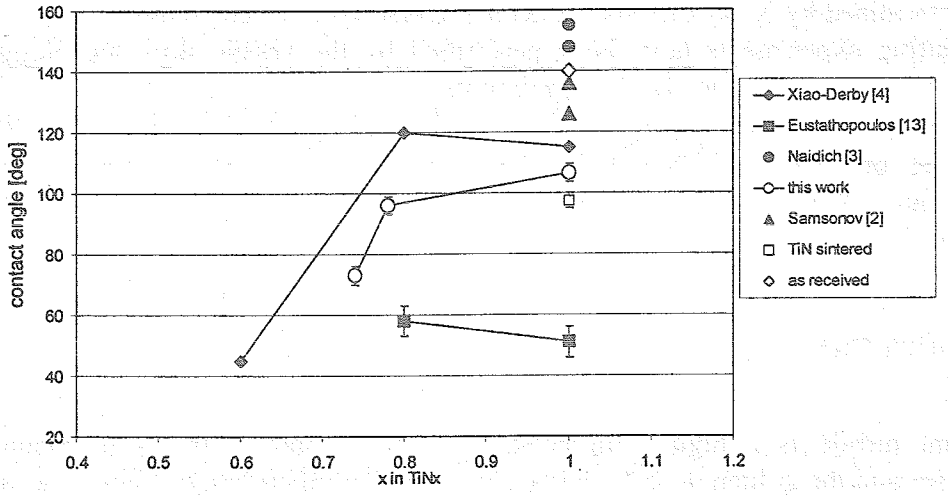


Fig.1 Equilibrium contact angles of liquid Cu at 1440 K on TiN of different stoichiometry.

TiN_x specimens were made by annealing Ti metal sheets, 3 mm thick, in a cold-wall autoclave at about 1 MPa N_2 and at 1900±10 K for times as long as 200 hours. Through this process all the titanium disk was converted into a compact and continuous titanium nitride layer whose superficial composition was always found to be stoichiometric (bright golden colour). A compositional gradient exists inside the specimens, depending on the preparation conditions, so that hypo-stoichiometric surfaces can be prepared by careful grinding and polishing of each specimen. The actual surface composition has been determined by X-ray diffraction, through the calculation of the lattice constant of each specimen. Lengauer [8] has observed that a linear relationship exists between the lattice parameter "a" of TiN and its stoichiometry: a_{TiN}=0.4242 nm and $a_{TiN0.5}$=0.4215 nm (Fig. 2). On the basis of our results, the specimens composition spans from x=1 to x= 0.70, as shown in Fig. 2. These data can be taken as significative of a bulk composition, taking into account that the X-ray penetration into TiN can be estimated of the order of 10 μm. It is worth noting that in the Ti-N phase

diagram [9] there are no stable TiN_x compounds for $0.5 \leq x \leq 0.70$ at 1440 K. The TiN_x compounds show a gold-yellow colour degrading to grey when going from x=1 to x=0.7.
XPS analyses have shown that the surface composition is quite a complex one, with the contemporaneous presence of Ti, N and O. The presence of oxygen at the surface, linked as a titanium compound, has been shown also by some Laser-RAMAN spectroscopy tests.
The TiN specimens have been polished on diamond paste, degreased and then outgassed for one hour at 1450 K under a dynamic vacuum (10^{-4} Pa) in the presence of a tantalum sheet wrapped around them to getter any residual oxygen and to fix the nitrogen pressure. This procedure has been checked not to modify the specimen stoichiometry. The average surface roughness was found to be in the order of 50 ±2 nm, which is in the good range for contact angle measurements [10].
Copper specimens (Cu 5N8 Materials Research) have been used in the form of truncated cones (0.3 g) in order to obtain advancing angles; they were put on the ceramic discs just after the above mentioned outgassing treatment in the charging section of the furnace under fluxing reducing gas.

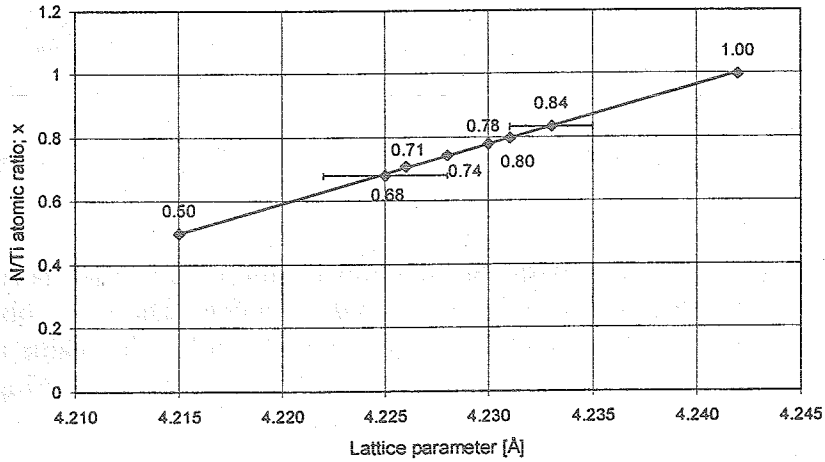


Fig.2 Variation of lattice parameters with N concentration in TiN_x

RESULTS

Contact angles.
The measured contact angles are reported in Fig.1, together with the values of previous works. It can be seen that the general qualitative trend reported in ref. [4] can be confirmed, but with some important differences. On the contrary we were not able to confirm the results reported in [5] both as absolute values and as a trend. Our results show that Cu on "as-received" ceramics exhibits high contact angles (θ = 140 °) and that on stoichiometric TiN the contact angle is some 10° less than that reported in [4]. Two runs made on sintered TiN, whose characteristics are reported in [11] show an even lower contact angle value. With decreasing nitrogen content, the contact angle decreases in a significative way reaching 73 ° for $x \approx 0.7$. The value of $\theta = 45$ ° of ref. [3] could not be reproduced, also because we could not obtain an x value lower than x = 0.7. After all experiments, the copper drop was shining, the ceramic plate showing clear intergranular thermal attack, some interference colours but no other major modifications.

Spreading kinetics

Contact angles and drop base diameter have been measured as a function of time. The results show (Fig. 3) that a transient regime exists in the first five minutes, when the angle reaches its "equilibrium" value and the diameter does not increase any more in a significant way. However, for the sintered specimens, a certain evolution of both angle and diameter still exists even after 30 min.

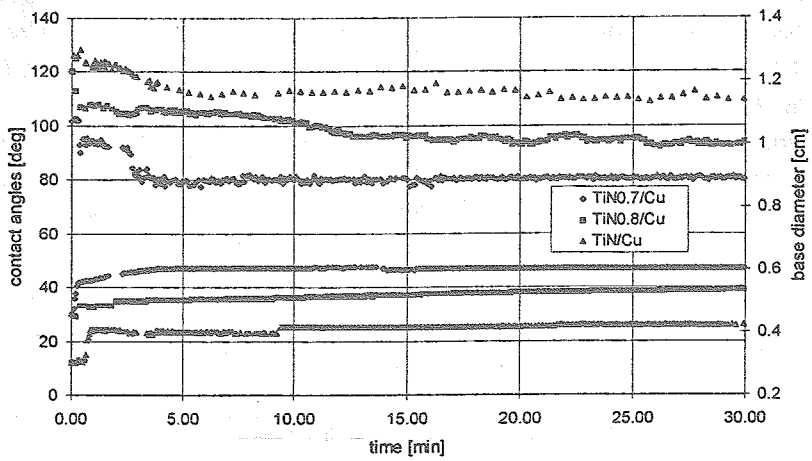


Fig.3 Contact angles and sessile drop base diameters as a function of time at 1440 K

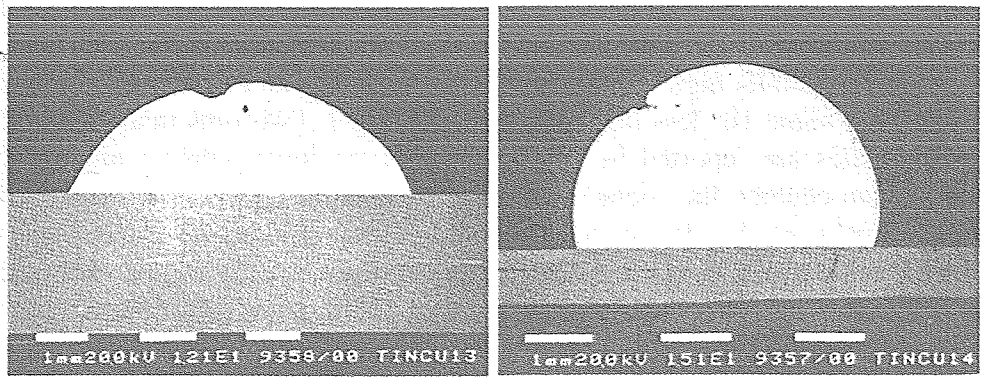
Surface tension

Copper surface tension in contact with the titanium nitride ceramic has been measured in some dedicated runs together with contact angle measurements. The value obtained did not change with time and was set around 1326 ±10 mN/m at 1435 K. This value compares very favourably with that given in the review [12] (1340 mN/m). Moreover, during each contact angle measurement session, the liquid metal surface tension has been monitored, showing no variations.

Interface characterisation

Optical, SEM and EDAX analyses have been made on all specimens, just after each run and on metallografic sections perpendicular to the solid-liquid interface (Fig.4).

Optical and SEM microscopy have shown that, in general, no reactions have taken place at the interface, which is sharp, with no reaction products at the microscopic scale both for wetting and non-wetting specimens. Some Ti and Cu diffusion has occurred, over a region some 5 μm thick.



(a) (b)

Fig.4 Metallographic sections: (a) Cu/TiN $_{0.7}$; (b) Cu/TiN

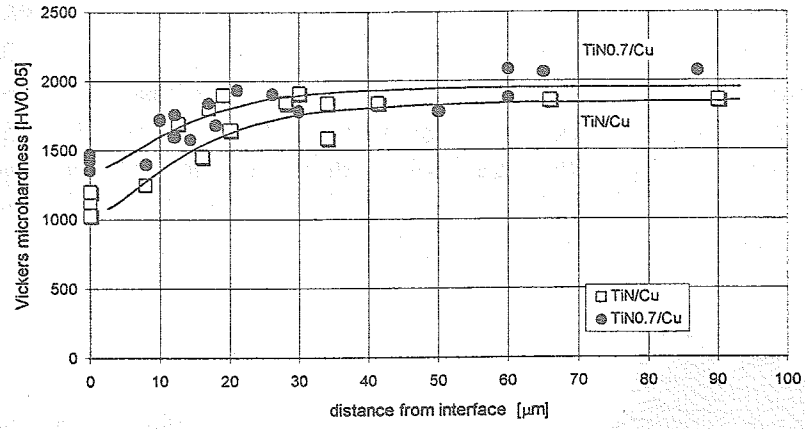


Fig.5 Evolution of microhardness in the ceramic phase vs. the distance from interface.

This diffusion layer can also be consistent with micro-hardness measurements (Fig. 5) made both in the bulk phases and near the interface, which show a continuous variation from bulk copper to the ceramic phase, over a region which is much thicker, i.e. of the order of 15 μm.

DISCUSSION

The wetting experiments have shown that liquid copper exhibits a non-wetting behaviour on stoichiometric titanium nitride whereas wetting increases as the nitrogen content in the nitride decreases (hypo-stoichiometry). This behaviour is in line with the common understanding that wetting of ceramics by liquid metal increases with increasing the metallic character of the ceramic itself [13]. Previous experiments reported by different authors [2,3,4,5] have shown contrasting results: the present study seems to confirm the trend reported in ref. [4] .
It is important to underline the role of the ceramic surface in the whole process. XPS spectra have shown the presence of oxygen in the surface layer, the higher its concentration the lower the wettability by liquid copper. In order to obtain reproducible results it was necessary to work under extremely controlled conditions, namely to pre-treat the solid under a vacuum in the presence of a specific getter (tantalum foil) and controlling the oxygen partial pressure, and then to perform the wetting experiments under He-5%H_2 atmosphere, always in the presence of the getter. The SEM and chemical (EDAX) analyses have shown no reactions at the microscopic scale at the solid-liquid interface. However, a dissolution process has been detected at the triple-line junction, under the liquid edge, by profile analysis of the ceramic plate where the Cu drop had been leached out (see also [14]). The small but evident ridge and valley conformation (Fig.6), has dimensions of the order of 100 nm. This means that the increase in wettability is due to a decrease of the solid-liquid interfacial energy, which in turn is due to the increase of the "metallic" contribution, and that some dissolution of the substrate can take place under the special conditions at the three-phase line. A possible confirmation of this effect can be seen also in the decrease of micro-hardness near the interface (Fig. 5), which is found over a region which should also be affected by interdiffusion processes.

CONCLUSIONS

The wettability of TiN by liquid metals, performed on a specially grown TiN (high compactness, absence of sintering aids etc.) has confirmed that the contact angle of liquid copper on TiN depends strongly on the surface stoichiometry. Under well defined operating conditions (low oxygen pressure and low surface roughness) we obtained:

on the stoichiometric nitride, sintered: $\theta = 98° \pm 2°$
on the stoichiometric nitride, grown from the gas phase: $\theta = 106° \pm 3°$
on the hypo-stoichiometric nitride (x = 0.8) grown from the gas phase : $\theta = 96° \pm 2°$
on the hypo-stoichiometric nitride (x = 0.74) grown from the gas phase: $\theta = 73° \pm 1°$.
Good adhesion is always obtained, the copper phase does not react with the ceramic body, but some diffusion of copper into the nitride takes place, modifying its hardness, probably due to the set up of tensile stresses in the interfacial structure.

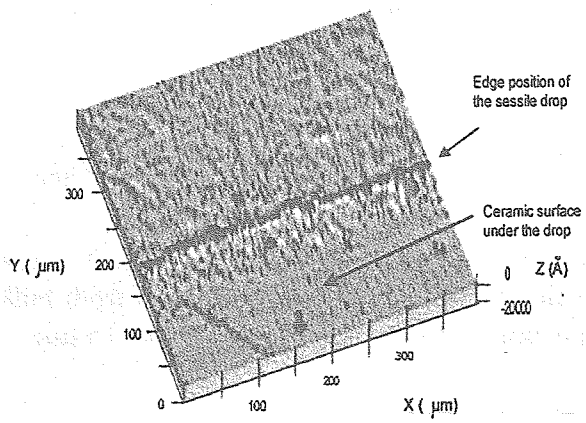


Fig. 6. Interfacial profile, under the liquid drop (chemically etched). The ridge corresponds to the edge position of the sessile drop.

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