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Reactive Brazing Study of a Silicon Nitride to Metal Joining

G. Chaumat, B. Drevet and L. Vernier

CEA/CEREM, 17 avenue des Martyrs, F38054 Grenoble Cedex 9, France.

Abstract

This paper is a summary of a study focused on high temperature Si_3N_4 brazing in the frame of the EUREKA project: Advanced Gas Turbine for Automobiles, so-called AGATA. This project is devoted to the development of ceramic components needed for performing high-temperature automotive turbomachines. Three filler alloys have been considered in our approach; a discussion is driven from thermodynamical considerations and experimental results. The PdCu + Nb active alloy appears to be a promising solution for a brazing temperature of 1210°C. From preliminary Si_3N_4/metal brazed samples, shear strengths in the (50–150 MPa) range have been achieved. Published by Elsevier Science Limited.

1 Introduction

The European EUREKA project EU209 or AGATA—Advanced Gas Turbine for Automobiles—is a programme focused on the development of three critical ceramic components. In particular, one of the objectives is to develop and test a Si_3N_4 radial turbine wheel and its joining to a metallic shaft as a full-scale feasibility study from an industrial perspective. The Si_3N_4 ceramics are excellent for high-temperature strength, thermal shock, fatigue, erosion/corrosion resistance.

Indeed, the joining of metal to ceramic still raises problems owing to the large difference in the physico-chemical properties between the components.[1–3] The present research is undertaken to study the interfacial reaction between silicon nitride and different active filler metals from the following systems:

- the matrix system of the brazes is the refractory binary alloy Pd50-Cu50 at%,
- the active elements are successively chosen from : Ti, Nb, W;
- the nature of metallic partners is similar to the active elements.

Consequently, refractory alloys have two roles: active elements and structural metallic partner for the joint.

2 Experimental

The aim of the experimental programme is to compare, through the use of a common PdCu matrix, the reactivity of different active elements on a Si_3N_4 substrate. The principle of our brazing trials consisted of melting of the matrix which dissolves a part of the active element at the interface refractory metals/braze, followed by an interfacial reactivity with the ceramic to promote the bonding (Fig. 1). The silicon nitride is manufactured by a thermoplastic injection moulding process. The metallic parts are 15×15×1 mm in size with a purity of 99·95%. The PdCu is formed in an alumina crucible at 1250°C under pure argon atmosphere to limit evaporation of palladium under vacuum and oxidation of copper. After laminating, the final thickness of filler metal is 250μm. Respectively, brazing joints (Si_3N_4/Ti, Si_3N_4/Nb and Si_3N_4/W) were carried out with the same brazing temperature: 1210°C under argon atmosphere.

3 Experimental Results

The main feature is that the behaviour of the three brazes is totally different:

- For the PdCu + Ti system, the reactivity is quite uncontrolled, and practically all the titanium is dissolved by PdCu. Important quantities of intermetallic compounds were precipitated in the systems: Cu-Ti, Pd-Ti, Ti-N, and Ti-Si. No bonding exists after brazing

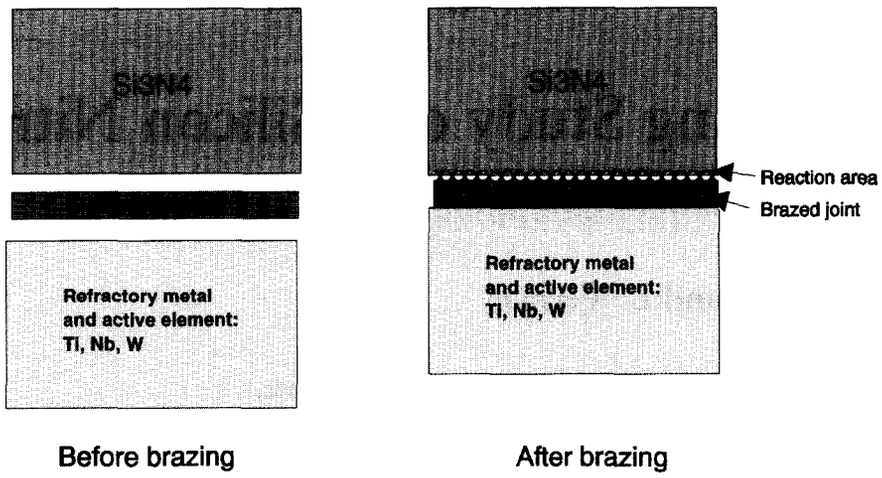

Fig. 1. Principle of the Si_3N_4 brazing approach.

and the ceramic is deeply attacked by the solder which dissolves an important amount of silicon (see Fig. 2). The reaction layer is 80μm thick.

- Concerning PdCu + Nb filler metal, a homogeneous reaction area at the ceramic/braze interface has been obtained. A continuous thin layer composed of Nb_5Si_3 compounds is observed. The joint is mainly constituted of copper and Pd-Nb phases (see Fig. 3). The interfacial reaction thickness is limited to 15 μm unlike the Ti case.
- Finally, with the third alloy PdCu + W, no spreading of the braze and no reaction occurred with the ceramic, even at 1210°C.

4 Thermodynamic Approach

Often, reactivity calculations allow us to predict what actually will happen in such a system if thermodynamic equilibrium at the interface is assumed; however the relative reaction kinetics may also be of importance. The considered approach has aimed to assess the reactivity between Si_3N_4 and the active element dissolved in the liquid CuPd matrix leading to synthesis of nitride and/or silicides of the active element. The Gibbs free energy (ΔG) is calculated with the three systems at the brazing temperature for different compounds: Nb_2N, Nb_5Si_3, TiN, Ti_5Si_3, W_2N, W_5Si_3.

For instance, the reaction with titanium is of the type:

$$< Si_3N_4 > + 9(Ti)_{CuPd} \Longleftrightarrow 4 < TiN > + < Ti_5Si_3 > \quad (1)$$

and Gibbs free energy is given by the following formula by assuming the liquid is a regular solution:

$$\Delta G = 4\Delta G^{\circ}_{f<TiN>} + \Delta G^{\circ}_{f<Ti_5Si_3>} - \Delta G^{\circ}_{f<Si_3N_4>} - 9\Delta \overline{H}^{\infty}_{Ti(CuPd)}(1 - X_{Ti})^2 - 9RTlnX_{Ti}\gamma_{Ti} \quad (2)$$

in which:

X_{Ti}: mole fraction of Ti;

γ_{Ti}: activity coefficient of Ti in the liquid phase;

$\Delta G^{\circ}_{f<Ti_5Si_3>}$, $\Delta G^{\circ}_{f<Si_3N_4>}$: standard Gibbs free energies of formation of Ti_5Si_3 and Si_3N_4;

$\Delta \overline{H}^{\infty}_{Ti(CuPd)}$: partial enthalpy of mixing of Ti at infinite dilution in CuPd.

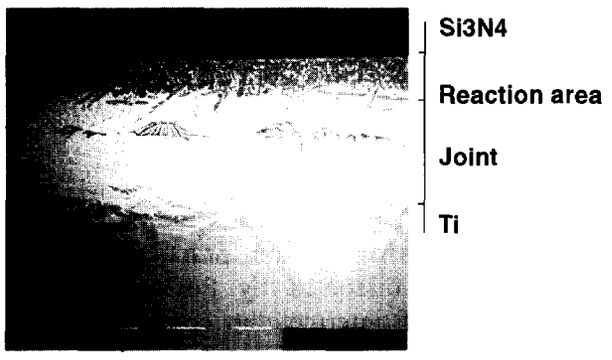

Fig. 2. Metallograph of Si_3N_4/CuPd + Ti interface obtained by SEM.

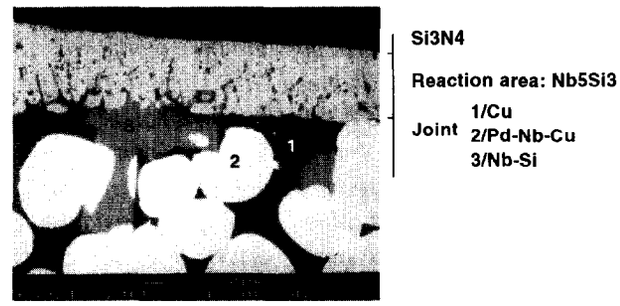

Fig. 3. Metallograph of Si_3N_4/CuPd + Nb interface obtained by SEM.

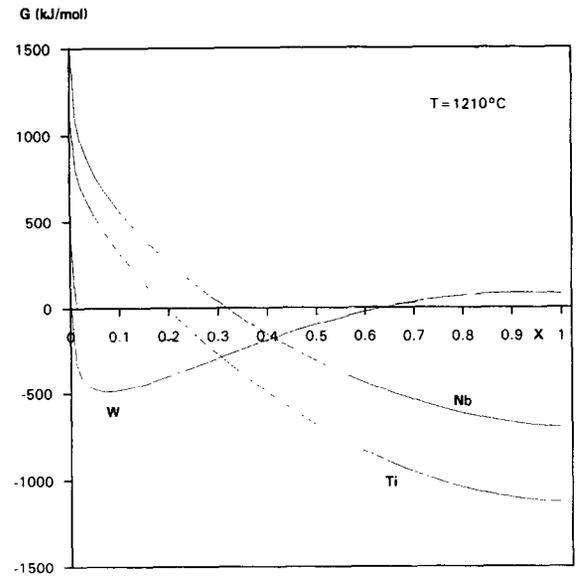

Fig. 4. $\Delta G_i = f$(molar fraction: X_i) curves: (a) i = Ti, (b) i = Nb and (c) i = W.

Table 1. Partial enthalpy of mixing of active element 'i' at infinite solution in CuPd matrix*

i	$\Delta\overline{H}^{\infty}_{i(CuPd)}$ *(kJ/mole)*
Ti	−163·3
Nb	−84·5
W	+88·2

* These values are calculated from Miedema[4] data dealing with enthalpy of binary mixing.

Table 2. Standard Gibbs free energy of 'j' formation

j	$\Delta G^{\circ}_{f<j>}$ *(kJ/mole)*
Si_3N_4	−254·4
Nb_2N	−105·6
Nb_5Si_3	−527·9
TiN	−198·0
Ti_5Si_3	−588·3
W_2N	0 (arbitrary value)
W_5Si_3	−175·5

Similar expressions are obtained with Nb and W reactive elements. The different curves $\Delta G_i = f$ (molar fraction: X_i) have been drawn in Fig. 4 at T = 1450K by considering the necessary data shown in Tables 1 and 2.

The main feature about the curves of Fig. 4 is the consistency between the metallographic investigation and the thermodynamic approach. Indeed, the niobium curve exhibits a controlled reactivity, whereas the Ti one is displaced towards low X_i values, i.e. reactions occur at a lower critical value X_{Ti} than for the Nb case. The minimum in the W curve is incorrect. This feature comes from γ_i calculation. Indeed, there are low W-Cu and W-Pd liquid interactions: the binary diagrams disclose a miscibility gap; consequently, only the ends of the curve close to a homogeneous liquid case can be considered. These parts show positive values, i.e. W reactivity on Si_3N_4 cannot occur.

5 Discussion—Conclusion—Perspectives

- The results show trends, although, important assumptions have been made: the solutions are considered as regular, the mixing enthalpies are calculated and not experimental, and furthermore, it is assumed that the alloy remains liquid at 1250K in over the compositional range (0 < X < 1). This point is true only for low X values.
- Nevertheless, a good fit is observed between experimental and thermodynamic approaches. The conclusions are similar with the following order of reactivity: Ti > Nb > W.

Consequently, it appears that Nb is the best candidate as an active element in a PdCu matrix for future studies on refractory filler alloys suitable for Si_3N_4.

Further to this physico-chemical analysis, there is also a mechanical analysis which must be undertaken, currently driven by considering another problem which has not yet been treated in this paper: residual stresses induced by thermal expansion mismatch.

A first attempt of four Si_3N_4/PdCu + Nb/W brazed samples exhibits promising results with a shear strength ranging between a 50 and 150 MPa range.

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