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Cosintering of alumina with cobalt or chromium doped tungsten at 1400° C

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The influence of two additions, cobalt and chromium on the behaviour of tungsten powder cofired at 1400° C with an alumina-based ceramic is discussed. The effect of these additions on metal densification and interface morphology depends on the firing atmosphere (H_2 or H_2/H_2O mixtures). They may have a decisive influence on metal to ceramic bond strength and metal layer resistivity resulting from interactions with the atmosphere and the ceramic substrate.

1. Introduction

Alumina-based ceramics, metallized and cofired with tungsten are now commonly used for electronic packaging. Ceramic green sheets are obtained by tape casting, then the metallization is applied by screen printing. The metallized sheets are laminated together before being cofired in a reducing atmosphere. In an earlier study Bettinelli *et al.* [1] pointed out the possibility of lowering the usual firing temperature (typically 1550° C to 1600° C [2–5]) to the 1400° C range. This was obtained by using a fine grained alumina and adding carefully chosen sintering aids to both ceramic [6] and metal. In this first attempt the metallic additives were binary alloys with melting points below the firing temperature. As the results showed that the presence of a metallic liquid phase is not necessary to promote tungsten sintering, further experiments were performed using less complex additives, i.e. pure chromium and cobalt. This report presents the results obtained with these additives.

2. Experimental procedure

2.1. Starting materials

The mineral part of the ceramic greens comprised alumina, $CaSiO_3$ and MoO_3. The characteristics of the powders used and their proportions are given in Table I.

The metallic ink was made by mixing 74 wt % tungsten powder (purity 99.92%, average grain size 0.4 μm, 24.5 wt % terpineol as solvent and 1.5 wt % ethyl-cellulose as binder. Cobalt or chromium were added to tungsten powder in the proportion of 2 wt %.

TABLE I

	Purity (%)	Average grain size (μm)	Proportions (wt %)
Alumina	99.9	0.7	96.75
$CaSiO_3$	99	3	2.25
MoO_3	99	3	1

2.2. Sample preparation

Samples were designed in order to allow both a simple model of manufactured products and a physicochemical characterization. They were green ceramic sheets on which a simple line pattern of ink was applied by screen printing (Fig. 1). They were heated from ambient to 1430° C in three hours and held for three hours at this temperature. The firing atmosphere was hydrogen or hydrogen–water mixtures obtained by passing the gas through a water bubbler, the amount of water being controlled by varying the water temperature. These mixtures are of common use in industrial processes, as they favour the elimination of the carbonaceous residues resulting from the cracking of the organic products.

2.3. Characterization

In order to characterize the interface morphology and the metal densification, scanning electron microscopy (SEM) was carried out, both on the metal layers and on fracture surfaces normal to the interface. These surfaces were then carefully polished using classical metallographic techniques and the repartition of the elements was studied with an X-ray microprobe.

Although no quantitative evaluation of the ceramic to metal bond strength was made, qualitative tests allowed the influence of various parameters on it to be estimated finally. The resistance of the metal lines was measured using a four-point technique and the resistivity was calculated after measuring the dimensions of the lines. However, these values are to be considered with some caution due to the accuracy of the thickness measurements (typically between 5 and 20 μm) made on the scanning electron microscope.

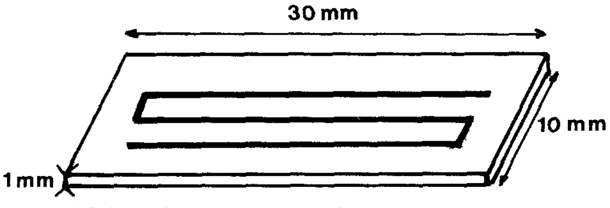

Figure 1 Schematic representation of samples.

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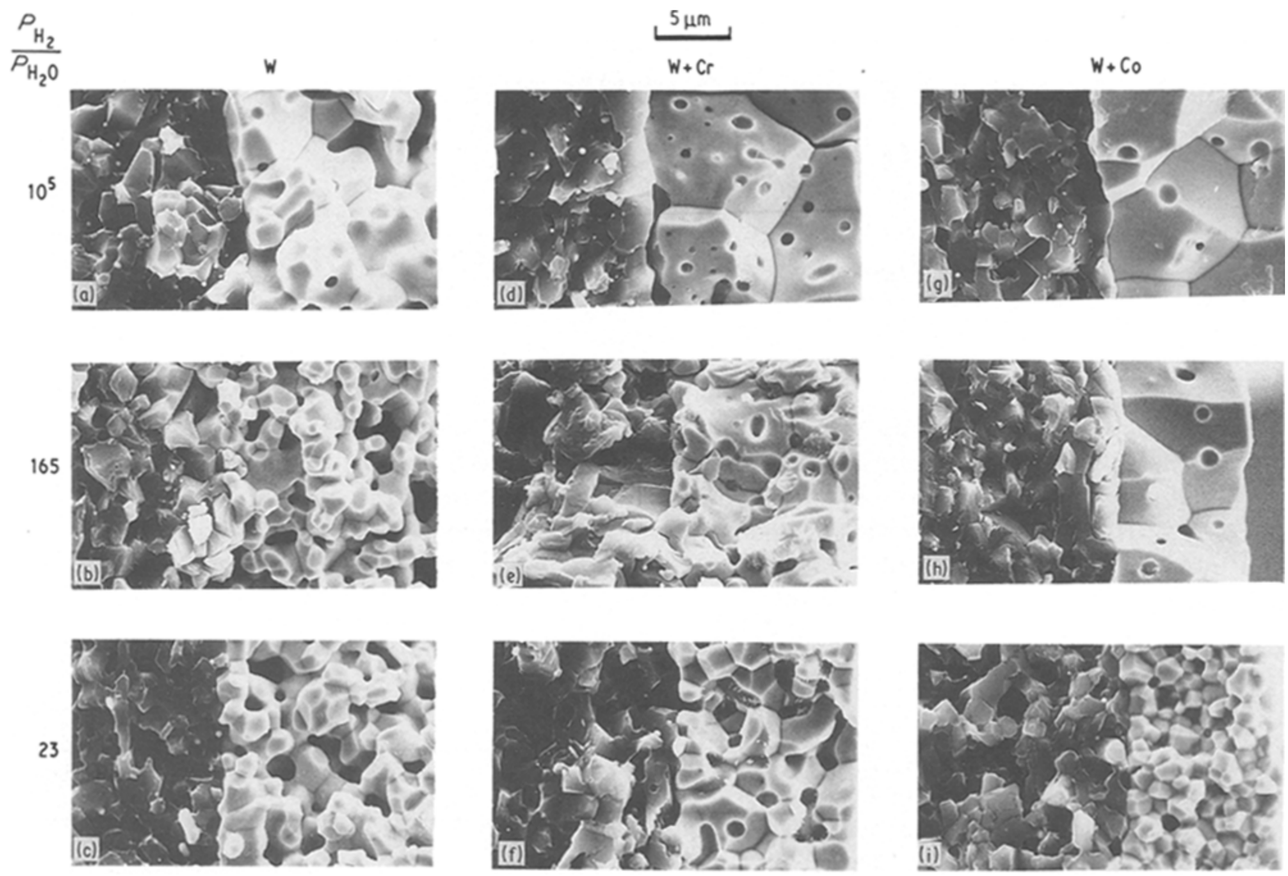

Figure 2 SEM micrographs of the interface. Influence of the metallic addition and the firing atmosphere. Ceramic at the left.

3. Results

3.1. SEM observations

Observations were carried out on samples fired under three different atmospheres: pure hydrogen and two hydrogen–water mixtures in which the pressure ratios P_{H_2}/P_{H_2O} were 165 and 23 (dew points respectively 0° C and 30° C). SEM micrographs are presented in Fig. 2. They suggest the following.

(1) Water has an intrinsic influence on tungsten sintering in reducing both densification and grain growth (Figs 2a, b and c).

(2) Chromium has a strong effect on sintering and grain growth if the water content is not too high (Figs 2d, e and f).

(3) Cobalt enhances densification even for high water content, but the water amount has a pronounced influence on the metal grain size (Figs 2g, h and i).

3.2. X-ray microprobe analysis

X-ray intensities were recorded along an axis normal to the interface for tungsten (WLα) chromium and cobalt (Cr $K\alpha$, Co$K\alpha$) and also for calcium (Ca$K\alpha$) in

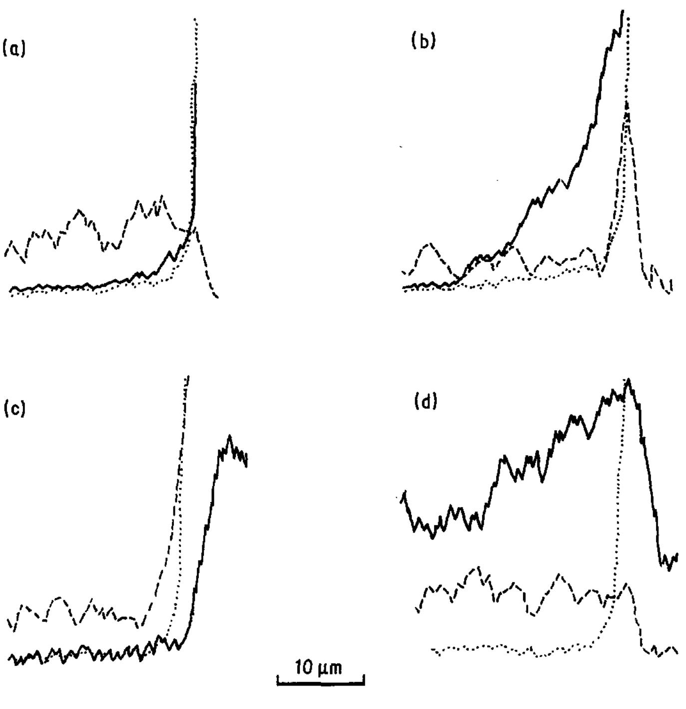

Figure 3 Electron microprobe profile (arbitrary units) near the interface ···· WK$_\alpha$, – – – CaK$_\alpha$, —— metallic addition (cobalt or chromium). Ceramic at the left.

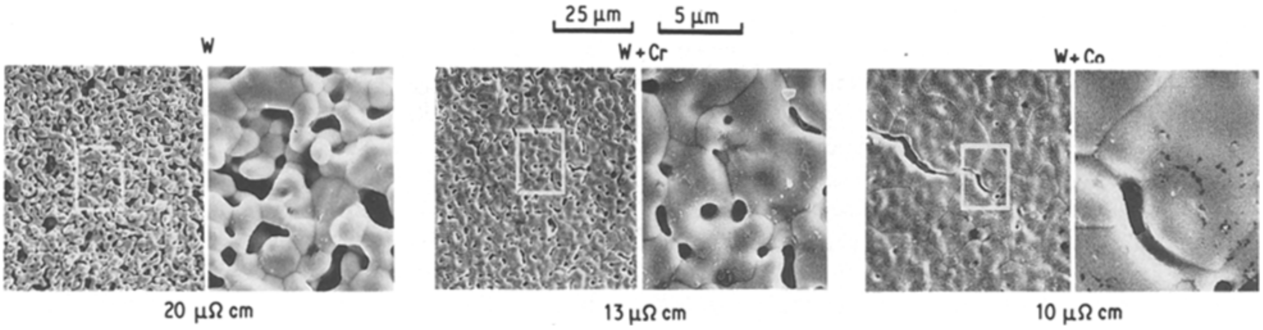

Figure 4 SEM micrographs of the metal layer (top view). Influence of the addition on the morphology and resistivity.

order to obtain information about the liquid or viscous phase present in the ceramic during the sintering. The results are summarized in Fig. 3. From these diagrams the following conclusions may be drawn.

(1) Diffusion from tungsten toward the ceramic never takes place.

(2) Chromium and cobalt do not diffuse appreciably into the ceramic in the absence of water. Chromium diffuses over a longer range than cobalt under wet hydrogen.

(3) The behaviour of calcium and consequently of the liquid phase of the ceramic is more complicated. In the case of the chromium doped ink, migration in the metal layer occurs under dry hydrogen, but not in the presence of water. Whereas in the case of cobalt no migration is observed under dry hydrogen and an accumulation at the interface appears in the presence of water.

3.3. Mechanical and electrical properties

Qualitative tests showed that the metal to ceramic bond is stronger with pure and chromium doped tungsten than with cobalt doped tungsten. On the other hand coarse grained layers are always more brittle than fine grained ones. With regard to the electrical resistivity, examples are given in Fig. 4 for samples cofired under wet hydrogen (dew point 0° C). They show an important decrease of the resistivity related to the gain in metal densification. By comparison, the resistivity of pure massive tungsten is 5.6 μΩ cm.

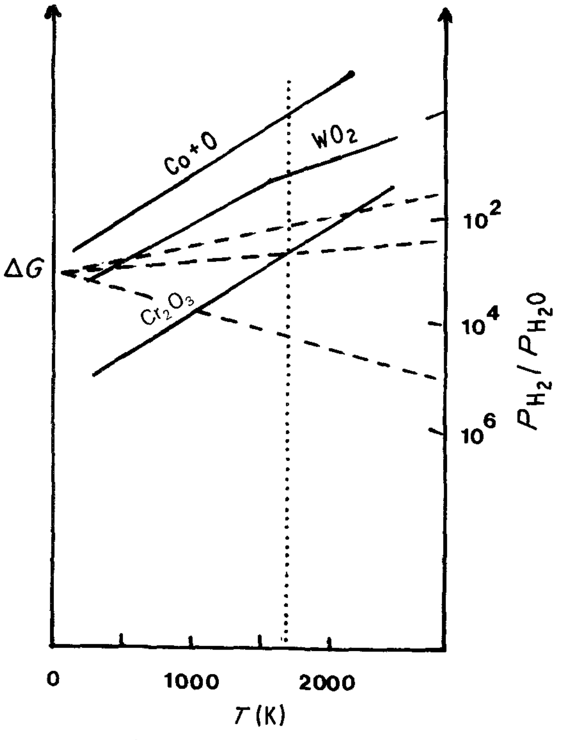

Figure 5 Free enthalpy plotted against temperature. After Kieffer *et al.* [7].

4. Discussion

The first question to be answered is the one of the stability of the metals toward the firing atmosphere. This can be theoretically predicted for pure metals by considering the free enthalpy against temperature diagrams. It can be seen (Fig. 5) that tungsten and even more so cobalt do not become oxidized in the presence of any of the three atmospheres considered, but that chromium surely does in the presence of the more water rich mixture and perhaps under the less rich one.

In order to control the validity of these predictions when applied to a case different from the ideal one by the fact that the dopants may dissolve in the ceramic or in tungsten, powders mixtures were submitted to the same treatment and analysed by X-ray diffraction. The results are summarized in Table II.

From these results it can be seen that, as predicted, tungsten and cobalt become oxidized under none of the considered atmospheres, and the intermetallic compound W_7Co_6 is formed. Cobalt oxide is reduced even in the presence of the constituents of the ceramic and the aluminate was not detected.

The case of chromium is more complicated as the products obtained depend both on the atmosphere and on the presence of tungsten. It is noteworthy that the reduction of chromium oxide is much easier in the presence of tungsten. This may be attributed to a kinetic effect due to the dissolution of chromium in tungsten. Raising the water partial pressure makes the metal more and more oxidized, and the amount solved

TABLE II

Composition before firing	Firing atmosphere	Phases analysis (X-rays)
Co + W	indifferent	$W + W_7Co_6$
$CoO + CaSiO_3$ $+ Al_2O_3$	$H_2 + H_2O$ (dew point 30° C)	$Al_2O_3 + Co$
Cr_2O_3	H_2	$Cr_2O_3 + \varepsilon Cr$
$Cr_2O_3 + W$ or Cr + W	H_2	WCr* + CrW* $+ Cr_2O_3$
$Cr_2O_3 + W$ or Cr + W	$H_2 + H_2O$ (dew point 0° C)	WCr* $+ Cr_2O_3$
$Cr_2O_3 + W$ or Cr + W	$H_2 + H_2O$ (dew point 30° C)	$W + Cr_2O_3$

*WCr is solid solution of chromium in tungsten.
*CrW is solid solution of tungsten in chromium.

in tungsten smaller. The fact that the same results are obtained whatever the initial form of chromium may be suggests that the equilibrium between chromium oxide and metallic chromium is reached. However, it is to be noted that the presence of the ceramic may have a decisive effect on this equilibrium due to a possible dissolution of the oxide in the ceramic. This occurs effectively with chromium which is highly soluble in alumina and to some extent with cobalt. In this case the oxide probably dissolves more in the amorphous phase of the ceramic since X-ray investigation detected neither cobalt oxide nor aluminate.

With regard to the behaviour of the viscous phase of the ceramic, it depends both on the firing atmosphere and on the nature of the metallic addition. In samples cofired under dry hydrogen, it migrates in the metallic layer if the tungsten is doped with chromium, and does not if doped with cobalt. This may result from the influence of the metallic addition on the sintering temperature of the metal. If the densification occurs at such a temperature that the silicated phase is too viscous to flow between the metal grains, it can not migrate (the case of cobalt). In the opposite case it will if the densification occurs at a higher temperature (chromium). The presence of this phase in the pores of the metal layer (Fig. 2d) confirms this assumption.

The differences observed in samples fired under wet hydrogen may be attributed to the dissolution of the two oxides (CoO and Cr_2O_3). The first one would lower the melting point and the viscosity of the liquid phase, inducing its accumulation at the interface, while the second one would have an opposite effect, impedeing the migration in the metal layer, despite its high porosity.

5. Conclusion

It can be concluded from these results that a metallic addition may be of interest in promoting tungsten sintering if it remains, at least partially in the metallic state and if it forms with tungsten a solid solution or an intermetallic compound with a melting point significantly lower than that of tungsten. If this addition becomes oxidized it can interact with the ceramic and possibly alter its properties. From a more practical point of view, and in the perspective of an application to microelectronic packaging, it is clear that high electric conductivity and high ceramic to metal bond strength are, to some extent, antagonistic requirements: achieving the first one requires highly densified metal layers, when open porosity has a beneficial effect on the bonding due to the penetration of the ceramic's vitreous phase in the pores. It could then be of interest to use different ink compositions depending on the property to be emphasized. For example a cobalt addition may be useful for increasing the conductivity of the internal patterns of a multilayer module, whilst pure or chromium doped tungsten would be preferable for external layers on which components must be reported. At least chromium doped tungsten could be a good compromise if fired under the appropriate atmosphere.

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