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SYNTHESIS REACTIONS AND THERMODYNAMICS OF COMPOUND FORMATION DURING MoMn LAYER SINTERING

LIDIJA I. BELIČ and ALENKA Š. KOSMOS

Institute for Electronics and Vacuum Technique, Teslova 30, 61000 Ljubljana, Slovenia

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Chemical reactions and thermodynamics of high temperature alumina metallization have been investigated. During the firing of MoMn paste, reactions start with oxidation of manganese. The formed Mn_3O_4 reacts with alumina and SiO_2 at a temperature lower than 1200 °C. The formation of the metallizing layer is a consequence of lowering of the free energy of the system. It is caused by redox and dissolution reactions, the formation of the glass phase and crystallization process from the liquid phase. With available thermodynamical data and according to the atmospheric conditions, some reactions were predicted and confirmed by X-ray diffraction.

1. *Introduction*

Many techniques have been used to join ceramics to metals. The most widely known process is the 'moly-manganese' process. The process developed by Nolte and Spurck [1,2] has been accepted by industry as a standard method to metallize ceramic surface.

In this process, a thin layer of metallizing paint is fired onto the surface of debased alumina so that the alumina can be brazed to a massive metall part.

During sintering, the viscous melt is formed at the alumina/metallizing interface. The obtained liquid phase migrates into the porous metallizing layer, enabling a cohesion between partially sintered molybdenum grains.

The liquid phase also creates a bond between the debased alumina and the metallizing layer [3].

2. Experimental

In the experiments, a high-temperature metallizing paste was applied - (Mo:Mn:FeSi = 80:16:4 wt. %). FeSi was used as Si source. These powdered ingredients were combined with a suitable binder to form a paste which was painted on a debased alumina (96 % Al_2O_3). The coating was sintered to the ceramics. The sintering of the metallizing paste occurred at a temperature of 1250–1500 °C in $N_2/H_2/H_2O$ atmosphere with a dew point at 25 °C. The atmosphere was composed of 75 vol. % N_2 and 25 vol. % H_2.

The crystalline components in the liquid phase of the metallizing layer were determined by using X-ray diffraction analysis (with a Philips PW 1349/40 diffractometer). To determine the temperature of the liquid phase formation, differential thermal analysis (DTA) and dilatometric analysis were used.

3. Results and discussion

The temperature of the liquid phase formation is essential for sintering of the metallizing paste. The firing process of the metallizing paste starts with Mn oxidation at the temperature higher than 250 °C; first MnO is formed, then Mn_2O_3. At a temperature higher than 930 °C, Mn_2O_3 decomposed into Mn_3O_4 plus oxygen [4]. Mn_3O_4 reacts with Al_2O_3 and SiO_2. The temperature of the liquid phase formation was compared to the isotherms in the ternary phase diagram MnO-Al_2O_3-SiO_2 [5] and with the corresponding data of the MnO-SiO_2 system [6].

The temperature of the appearance of the Mn-O containing liquid phase was 1185 °C (DTA) and 1191 °C (dilatometric analysis). The measured temperatures are higher than the lowest temperature in the mentioned ternary diagram or in the two component system MnO-SiO_2, where the liquid is formed at 1251 °C. The temperature of the appearance of the liquid phase was also measured on the used ceramic substrate. This temperature (measured by dilatometric analysis) was 1480 °C. It is approx. 200 °C higher than the temperature of the manganese containing glass phase.

The chemical processes in the metallization layer sintering on Al_2O_3 ceramics in wet reduction atmosphere were described as redox and dissolution reactions, the formation of liquid phase and crystallization process from the liquid phase [7].

Thermodynamic constants and free energy data are taken from the literature [8-10].

$\Delta G_{T,P}$ is calculated for different conditions from the Eq. (1) where T is the sintering temperature in protective atmosphere consisting of N_2/H_2 and H_2O vapour.

$$\Delta G_{T,P} = \Delta G^0 + RT \ln(p(\mathrm{H_2})/p(\mathrm{H_2O})) \tag{1}$$

where
$\Delta G_{T,P}$ is free energy of reaction at a given temperature and pressure;
ΔG^0 is standard free energy of reaction;
$p(\mathrm{H_2})$ is pressure of H_2;
$p(\mathrm{H_2O})$ is vapour pressure of H_2O;
T is absolute temperature; and
R is universal gas constant.

In the following text, the reaction equations for oxides, aluminates and silicates are presented. They are proposed as the most probable and simple reactions changing the composition of the metallizing paste.

The standard free energy data in kcal/mol are indicated as well. (1 kcal = 4.186 kJ)

Redox reactions:

1) $3\ \mathrm{Mn}_{(s)} + 2\mathrm{O}_{2(g)} \rightarrow \mathrm{Mn_3O}_{4(s)}$ $\Delta G^0 = –331.4 – 36.8\times10^{-3}\ T$ [9]
2) $\mathrm{Si}_{(s)} + \mathrm{O}_{2(g)} \rightarrow \mathrm{SiO}_{2(s)}$ $\Delta G^0 = –217.1 – 10.372\ \times10^{-3}\ T$ [10]
3) $\mathrm{Mo}_{(s)} + \mathrm{O}_{2(g)} \rightarrow \mathrm{MoO}_{2(s)}$ $\Delta G^0 = –217.1 – 10.372\ \times10^{-3}\ T$ [10]

Aluminate and silicates syntesis reactions are:

4) $\mathrm{MnO}_{(s)} + \mathrm{Al_2O}_{3(s)} \rightarrow \mathrm{MnAl_2O}_{4(s)}$ $\Delta G^0 = –503.0 – 25.2\times10^{-3}\ T$ [9]
5) $\mathrm{MnO}_{(s)} + \mathrm{SiO}_{2(s)} \rightarrow \mathrm{MnSiO}_{3(s)}$ $\Delta G^0 = –303.3 – 21.3\times10^{-3}\ T$ [8]
6) $2\ \mathrm{MnO}_{(s)} + \mathrm{SiO}_{2(s)} \rightarrow \mathrm{Mn_2SiO}_{4(s)}$ $\Delta G^0 = –412.8 – 39.0\ \times10^{-3}\ T$ [10]

All the data for the given reactions are available. Unfortunately, there are no reliable data for more complicated three component compounds that are found in the ternary phase diagram ($MnO–Al_2O_3–SiO_2$).

Values of the standard free energies ΔG^0 and free energies $\Delta G_{T,P}$, calculated for the reactions in the protective atmosphere at different temperatures are given in Table 1. The differences between the values of ΔG^0 for the cited reactions (shown on the right side of reactions in the text), and the values presented in Table 1, are the results of the dependence of the values of heat capacity at constant pressure, c_p, on temperature that were used in the calculations of the ΔG^0 values shown in Table 1.

All calculations were made assuming the same parameters: $P = 730$ mbar, $p(\mathrm{H_2}) = 178$ mbar and $p(\mathrm{H_2O}) = 17$ mbar.

From Table 1, it is obvious that the free energy becomes more negative with increasing temperature. The results obtained by X-ray diffraction measurements made on the sintered metallizing layer completely confirm the thermodynamic calculations.

Components which were found by etching the metallizing layer in H_2O_2 to dissolve molybdenum oxide and molybdenum are: tephroite Mn_2SiO_4, galaxite $MnAl_2O_4$, braunite Mn_7SiO_{12} and hausmanite Mn_3O_4.

TABLE 1.
Standard values of free energies ΔG^0 and $\Delta G_{T,P}$ (kcal/mol) calculated for the reactions no. 1 - 6 for the temperatures 1300, 1500 and 1700 K.

No.	1300 K ΔG^0	1300 K $\Delta G_{T,P}$	1500 K ΔG^0	1500 K $\Delta G_{T,P}$	1700 K ΔG^0	1700 K $\Delta G_{T,P}$	Comp.
1	-145.321	-409.353	-453.729	-446.842	-457.976	-459.170	Mn_3O_4
2	-243.687	-237.71	-250.442	-243.555	-257.671	-249.857	SiO_2
3	-170.716	-164.749	-178.520	-171.630	-186.900	-179.094	MoO_2
4	-568.907	-562.939	-585.798	-578.902	- 603.904	-596.098	$MnAl_2O_4$
5	-354.368	-348.400	-366.990	-360.103	-382.124	-374.318	$MnSiO_3$
6	-498.137	- 492.169	-518.459	-511.572	-541.375	-533.569	Mn_2SiO_4

Galaxite ($MnAl_2O_4$) is a consequence of the spesarite ($3MnO.Al_2O_3.3SiO_2$) decomposition [12]. The temperature at which metallizing paste was fired (1350 °C) was not high enough for direct galaxite synthesis from Al_2O_3 and Mn_3O_4. The hausmanite (Mn_3O_4) present is a consequence of a too small quantity of SiO_2 and Al_2O_3 with which manganese oxide reacts.

The detection of these phases shows that there are no kinetic obstacles for the formation of supposed phases.

4. *Conclusions*

The process at the high-temperature metallizing starts with the oxidation of the manganese at a temperature higher than 250 °C. The temperature of the manganese-containing liquid phase determined by DTA is 1185 °C, while it is 1991 °C from dilatometric analysis. The results obtained are in accordance with the ternary MnO-SiO_2-Al_2O_3 phase diagram. Thermodynamic data for some redox and compound formation reactions are presented. X-ray diffraction measurements confirm the existence of the compounds predicted in the thermodynamic calculations.

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REAKCIJE SINTEZE I TERMODINAMIKA STVARANJA SPOJA TIJEKOM SINTERIRANJA SLOJA MoMn

Istraživane su kemijske reakcije i termodinamika visokotemperaturne metalizacije korunda. Tijekom paljenja smjese MoMn, reakcije počnu oksidacijom mangana. Nastali Mn_3O_4 reagira s korundom i SiO_2 na temperaturi ispod 1200 °C. Nastajanje metalnog sloja je posljedica smanjenja slobodne energije sustava. Smanjenje je posljedica redoks reakcije, odvajanja faza, nastajanja staklene faze i kristalizacije iz tekuće faze. Neke su reakcije predvidene i potvrdene rendgenskom difrakcijom.