JOURNAL OF MATERIALS SCIENCE 27 (1992) 3293–3296

Behaviour of molybdenum diboride in resistive thick film

L. T. AKULOVA, M. V. VLASOVA, I. V. VOROPAEVA, O. T. HORPYAKOV
The Institute for Problems of Materials Science of the Ukrainian Academy of Sciences, Kiev, USSR

A study of the resistive composition composed of Mo_2B_5 and glass containing oxides of Si, Pb, Ba, Ca, Sr, Zr, Mo and Al is made. Oxidation of surface boride particles was found to take place prior to glass melting. In the melt, oxidation products diffuse into a glassy binder and Mo oxides are reduced with boride to metallic Mo. Film electrophysical characteristics (ρ, temperature resistance coefficient) are determined by quantitative and three dimensional distribution of the conductive phases Mo_2B_5, MoB, MoO_2, defective MoO_3 and metallic Mo.

1. Introduction

In thick film technology Mo-containing glasses are used to develop resistors, the resistance of which may be changed from ohms to Mohm. This is achieved *via* the introduction of different quantities of MoO_3 during glass synthesis and while preparing resistive paste—by reducing agents of B- and Mo_2B_5-type [1, 2]. Film resistivity is ensured by formation of the glass phase dendrite structure, involving conductive molybdenum oxides and metal Mo [2]. It should be noted that borides of transition elements (Cr, Ti, W, etc.) have been used recently as functional components in resistive fusible glass-based compositions, containing no precious metals [3]. It was found [4, 5] that during paste firing, processes occur initiating formation of diffusion profiles in glass. Thick film conductivity is due to their overlapping.

It is assumed that there is a common feature in conductive phases formation, in both functional Mo-containing glass and passive glassy binder, which is an integral part of Mo_2B_5-based resistive composition.

2. Experimental procedure

A study is made of phase formation in a composition, which is a mixture of Mo_2B_5 and glass No. 279. The glass contains (mass %): SiO_2 (30.7), PbO (26.3), BaO (24.2), CaO (5.8), SrO (3.1), ZrO_2 (2.9), MgO (1.3) and Al_2O_3 (0.6). The temperature of glass softening is in the region of 1123 K. It is widely used to prepare resistive compositions.

Components of Mo_2B_5–glass No. 279 mixture were preliminary dispersed. The glass particle size, d_{glass} = 0–5 μm. Boride particle sizes varied from 0–5 to 10–40 μm. Mo_2B_5 : glass ratio varied from 1 : 99 to 80 : 20 mass %. Heat treatment (HT) was carried out in air by thick film resistors firing [6]. The treatment temperature, T_{tr} varied from 673 to 1173 K. Exposure time at a given temperature was 30 min.

For comparison, a composition of Mo_2B_5 and Mo-containing glass (50 : 50 mass %) was synthesized under analogous conditions. MoO_3 was found to equal 30 mass %.

Structural phase transformations during HT were evaluated according to the quantitative X-ray analysis and electron paramagnetic resonance (EPR) studies. X-ray studies were carried out in CuK_α irradiation using DRON-0.5 unit. Paramagnetic spectra were measured at room temperature using SE/x2547 radiospectrometer. Resistivity (ρ), temperature coefficient resistance (TCR) in the range of 293–423 K and moisture resistance (W) after boiling in distilled water for 10 min were determined using a hCR-E7-8 measuring device.

3. Experimental results

The results of the X-ray studies on Mo_2B_5–30% Mo-containing glass composition are given in Table I. As is seen from the table, under HT MoO_3 precipitates from the glass with subsequent interaction with reducing agent (Mo_2B_5) [2] initiating formation of Mo_4O_{11}, MoO_2, metallic Mo, B_2O_3, β-MoB and products of the newly formed phases interact with the glass components. The presence of conductive oxide phases, metallic Mo and molybdenum borides, (the quantitative content of which is determined by the composition formula and HT regime) defines resistivity of thick film resistors. Glass No. 279 was found to be amorphous to X-rays.

For the composition Mo_2B_5–glass No. 279 it was found that under HT, β-MoB, MoO_3, MoO_2, highly defective B_2O_3 and metallic Mo are formed as well as Mo_2B_5 (Fig. 1). Depending on boride dispersivity, components ratio and T_{tr}, the quantitative ratio of the phases varies (Figs 2 and 3). Thus, with a composition 20 mass % Mo_2B_5: 80 mass % glass No. 279, in the region of firing operating temperatures (1173 K) there remains small quantities of Mo_2B_5 and with the increase in boride dispersity of β-MoB as well. With the

0022–2461

TABLE I Data of X-ray analysis in heat treated molybdenum-containing glass and 50 mass % Mo_2B_5 + 50 mass % molybdenum-containing glass

T_{tr} (K)	30% Mo-containing glass	Composition Mo_2B_5 + 30% Mo-containing glass
473	Halo	Mo_2B_5
773	Halo	Much Mo_2B_5; traces of Mo, B_2O_3, β-MoB
973	–	Much Mo_2B_5; β-MoB, MoO_3, MoO_2, Mo_2O_3; traces of B_2O_3, Mo_4O_{11}
1073	MoO_2, Mo_4O_{11}; traces of α-$ZnMoO_4$, Cd and Zn borates; halo	Much Mo_2B_5; β-MoB; MoO_2, MoO_3; traces of Zn borates, B_2O_3, Mo, Mo_4O_{11}
1123	Halo	Much Mo, β-MoB; Mo_2B_5; traces of MoO_2, B_2O_3, Zn borates
1173	Halo	Much Mo, β-MoB; Zn borates, B_2O_3; traces of MoO_2, MoO_3, Mo_4O_{11}, Cd borates

Note: The phases are indicated in the order of their content decrease.

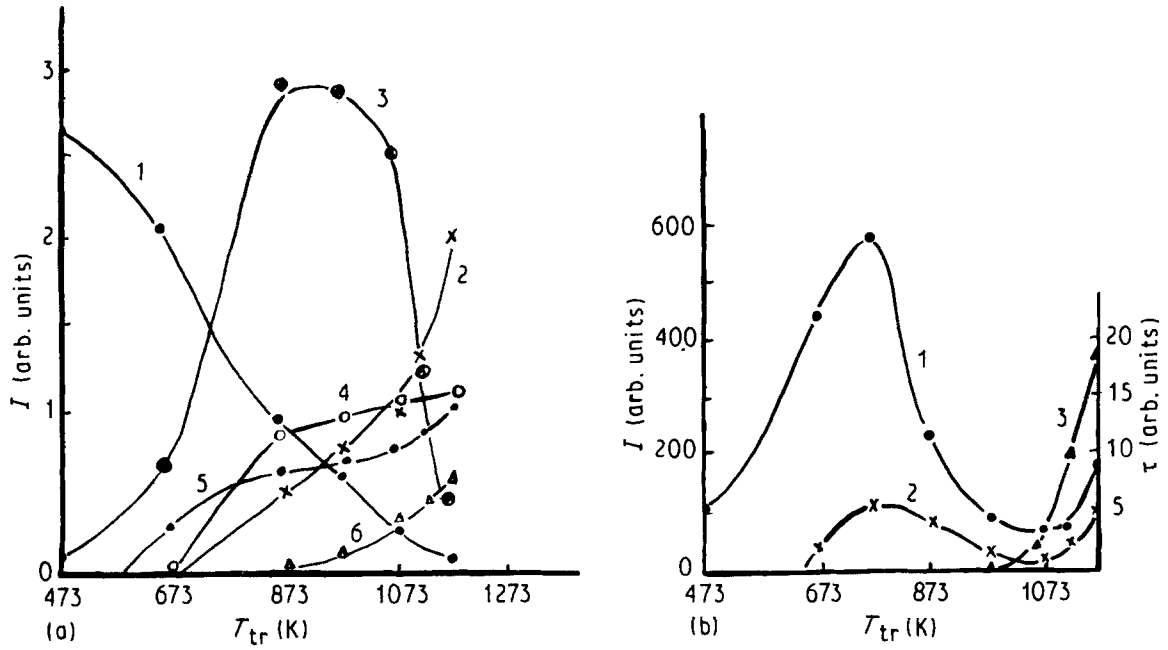

Figure 1 Intensity of X-ray diffraction lines for different phases and EPR signals amplitude versus T_{tr} for a composition of 20 mass % Mo_2B_5 + 80 mass % glass No. 279. T_{tr} = 30 min., d_{glass} = 0–5 μm, $d_{Mo_2O_5}$ = 5–10 μm: (a) (1) Mo_2B_5, (2) β-MoB, (3) MoO_3, (4) MoO_2, (5) B_2O_3, (6) Mo; (b) (1) Mo^{3+} in MoO_3, (2) Mo^{5+} in MoO_3, (3) Mn^{2+} in glass phase.

increase in Mo_2B_5 content bell-like concentration dependencies are formed with the maximum in the region of 50 mass % for phases MoO_3, B_2O_3, Mo; 20 mass % for MoO_2 and 80 mass % for β-MoB. In fact, such dependencies indicate diffusion of refractory compound components into molten glass. Similar results were observed in [4, 5].

According to EPR data, for compositions with an increase in T_{tr} up to 773 K, an increase in signals amplitude from Mo^{5+} and Mo^{3+} ions in MoO_3 is observed [7–13] (Fig. 1b). For the former $g_{||} = 1.923 \pm 0.001$, $g_{\perp} = 1.888 \pm 0.002$. For the latter $g = 2.0020 \pm 0.0005$, $\Delta B \sim 10 \times 10^{-4}$ T. The spectra refer to the isotope with zero nuclear spin, the content of which is 75%. Twenty five per cent of natural Mo content corresponds to Mo^{95} and Mo^{97} isotopes with nuclear spin equal to 5/2. In EPR spectra of Mo^{5+} and Mo^{3+} ions in MoO_3 samples prepared at T_{tr} = 1173 K, hyperfine weak structure lines are present. However, there is no exact agreement with the hyperfine structure constants in MoO_3. By analogy with amorphous films [7] they are somewhat changed depending on MoO_3 concentration and additional impurities. A decrease in EPR signals amplitude of Mo^{5+} and Mo^{3+} ions at $T_{tr} \sim 873$–1073 K, agrees with the decrease in MoO_3 phase content in samples. In the region of $T_{tr} \geqslant 1173$ K some increase in signals indicates an insignificant rise in the given phase contribution. However, X-ray data do not indicate it, evidently due to the weak effect.

An increase in molybdenum boride dispersity results in EPR spectra amplitude changes which agree with quantitative changes of MoO_3 and MoO_2 phases (Fig. 2).

Concentration changes of EPR signals amplitude of Mo^{5+} and Mo^{3+} ions (Fig. 3) correlate as well with oxides in thick films. It should be noted that the presence of Mo^{5+} in MoO_3 indicates reduction has taken place ($Mo^{6+} \rightarrow Mo^{5+}$) and an increase in MoO_2 phase indicates that the next stage of reduction has taken place ($Mo^{5+} \rightarrow Mo^{4+}$).

4. Discussion

The basic process to occur during the HT of

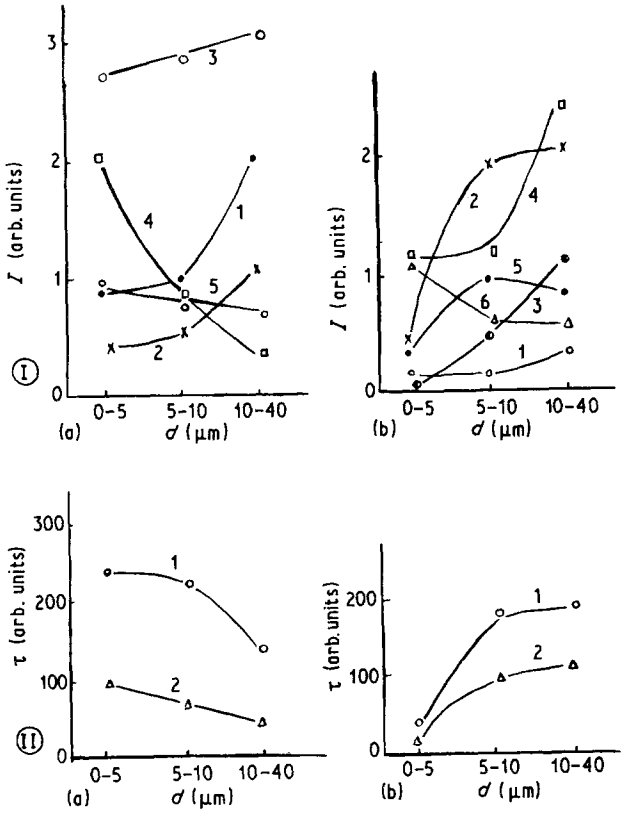

Figure 2 Intensity of X-ray diffraction lines for different phases (I) and EPR signals amplitudes (II) versus Mo_2B_5 particles dispersity in a composition of 20 mass % Mo_2B_5 + 80 mass % glass No. 279 (a) T_{tr} = 873, (b) T_{tr} = 1173 K. For (I) key as Fig. 1a, for (II) key as Fig. 1b.

Mo_2B_5–molybdenum-containing glass is the reduction of MoO_3 and its other oxides which evolve from the glass, and are formed due to boride oxidation prior to glass melting. The presence of oxides series (see Table I) and metallic Mo, indicates simultaneous and continuous reducing reactions occurring for all molybdenum oxide forms. A sharp decrease in Mo_2B_5 content and MoB appearance indicates that during the $Mo_2B_5 \rightarrow MoB$ transformation a significant quantity of boron evolves from the boride. Excess of boron and/or B_2O_3, like Mo_yB_x themselves, promote Mo oxide reduction and borate formation.

In Mo_2B_5–glass No. 279 composition processes occur similar to the above. In the low temperature region, boride particles are already oxidized. With the increase in T_{tr} the process is intensified. According to Voitovich [14] and the phases registered, the following reactions are possible:

1. $4/9\ Mo_2B_5 + O_2 \rightleftarrows 8/9\ MoB + 2/3\ B_2O_3$
2. $4/15\ Mo_2B_5 + O_2 \rightleftarrows 8/15\ Mo + 2/3\ B_2O_3$
3. $4/27\ Mo_2B_5 + O_2 \rightleftarrows 8/27\ MoO_3 + 10/27\ B_2O_3$
4. $2/9\ Mo_2B_5 + O_2 \rightleftarrows 2/9\ MoO_3 + 2/9\ MoB + 4/9\ B_2O_3$
5. $1/3\ Mo_2B_5 + O_2 \rightleftarrows 2/3\ MoO_3 + 5/2\ B$
6. $4/9\ MoB + O_2 \rightleftarrows 4/9\ MoO_3 + 2/9\ B_2O_3$
7. $4/3\ MoB + O_2 \rightleftarrows 3/4\ Mo + 2/3\ B_2O_3$
8. $2/3\ MoB + O_2 \rightleftarrows 2/3\ MoO_3 + 2/3\ B.$

The feasibility of these reactions is different. As a result, Mo_2B_5 particles are found to be covered with a

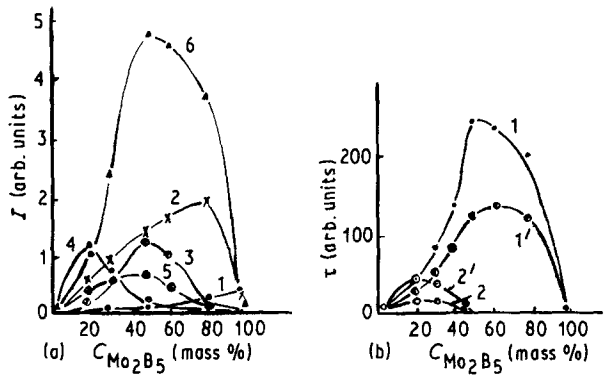

Figure 3 Intensity of X-ray diffraction lines for different phases (a) and EPR signals amplitudes (b) versus Mo_2B_5 content in a composition. T_{tr} = 1173 K, $d_{glass} = d_{Mo_2B_5}$ = 0–5 μm. For (a) key as Fig. 1a, t_{tr} = 30 min, for (b) (1.1′) Mo^{3+} in MoO_3; (2, 2′) Mo^{5+} in MoO_3, (1, 2) t_{tr} = 30 min. (1′, 2′) t_{tr} = 60 min.

layer of Mo oxides and B_2O_3. It should be noted that in pure borides, according to EPR data after calcination at 1023–1173 K, a weak signal of Mo^{5+} ions is registered in MoO_3. At high temperatures interaction of boron anhydride and lower boron oxides (BO, B_2O_2) with Mo oxides takes place and a pyroborate protective film is formed on the boride particle surface [14]. However, in the composition studied, this effect was not observed: Mo_2B_5 and MoO_3 content is continuously decreasing and MoB and Mo content is increasing (Fig. 1). The data obtained, show that under HT, first the oxide film is removed from the boride particles surface and then Mo_2B_5 takes part in oxides reduction and finally B_2O_3 (and B) is partially involved in molten glass. The smaller particle size, the more intensive are the reducing processes (Fig. 2) which may be defined briefly as $Mo^{6+} \rightarrow Mo^{4+} \rightarrow Mo^0$.

The form of concentration dependencies (Fig. 3) is also determined by some effects. With sufficient quantity of the glassy binder, the phase content is determined mainly by Mo oxide reduction, MoO_3 sublimation, MoO_2 disproportioning and formation of new compounds, e.g., molybdates and borates, and as a result by thickness of the glass layers between boride particles [4, 5]. With the layers thinning, e.g., increase in Mo_2B_5 content in the composition, diffusion processes are retarded and Mo boride particles are blocked with a pyroborates layer.

Formation of Mo and B oxides in the multicomponent molten glass inevitably results in glass phase change. Really, the temperature of softening of the composite material prepared at T_{tr} = 1173 K is found to be different than for the initial glass (Table II).

To verify the given assumption, we used the glasses containing about 0.05 mass % Mn^{3+}. Under HT, Mn^{2+} ions observed on an EPR spectrum comprised of a sextette with the constant of hyperfine structure, $A \approx 94 \times 10^{-4}$ T and $g_{eff} \sim 2.0$. X-ray patterns showed no new lines. Judging from the hyperfine structure, line form and width, Mn^{2+} ions are in almost cubic field characteristic for oxide glasses [15]. Spectrum intensity increases with the increase in T_{tr} and B_2O_5 content in a film. It indicates boron ion diffusion into molten glass.

TABLE II Contact angle of glassy binder versus temperature and alloying additives

T_{tr} (K)	Glass No. 279	Glass No. 279 + 10 mass % B_2O_3 (deg.)	Glass No. 279 + 10 mass % B_2O_3 + 5 mass % MoO_3 (deg.)	80 mass % glass No. 279 + 20 mass % Mo_2B_2 (deg.)
1053	–	90	–	–
1073	–	60	90	90
1123	90	45	60	70
1173	60	30	45	50
1223	30	15	20	25

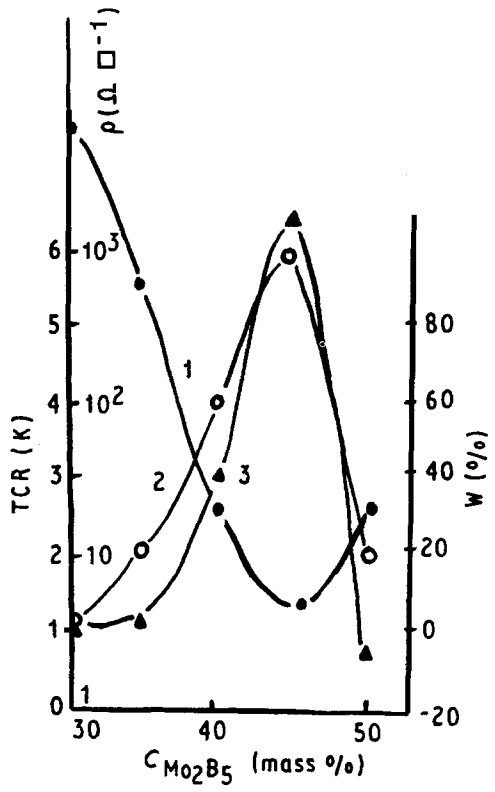

Figure 4 Thick film resistors parameters versus content of glass No. 279 and Mo_2B_5 in compositions. T_{tr} = 1173 K, t_{tr} = 30 min., $d_{glass} = d_{Mo_2B_5}$ = 0–5 μm, (1) ρ, (2) temperature resistance coefficient and (3) W.

Thick films resistive characteristics are determined by quantitative and three dimensional distribution of conductive phases, such as Mo_2B_5, MoB, MoO_2, defective MoO_3, metallic Mo. Due to their high content in thick films, its electric conductivity crucially depends on concentration and technological conditions of the paste firing. Thus, from Figs 4 and 3a it is seen that free molybdenum has the greatest effect. Presence of free B_2O_3 determines film moisture resistance.

5. Conclusion

The studies show that a Mo_2B_5–glass No. 279 mixture under heat treatment forms a composite material composed of the glassy and crystalline phases. Material electrophysical properties, in particular, electrical conductivity and temperature resistance coefficient are defined by quantitative and three dimensional distribution of conductive phases: Mo_2B_5, MoB, MoO_2, defective MoO_3 and metallic Mo. Their content depends, first of all, on the starting components ratio chosen. The basic mechanisms of Mo oxides and metallic Mo formation are oxidation of Mo_2B_5, solution of oxide film in the molten glass, reduction of Mo oxides with borides to metal Mo.

References

1. R. E. ANDRONOVA, O. N. DEMIC, T. M. MOROZOVA *et al. Elektronaya tekhnika. Ser. 3. Mikroelektronika.* **I(117)** (1986) 107.
2. R. E. ANDRONOVA, O. N. DEMIC, T. M. MOROZOVA *et al. ibid.* **2(122)** (1987) 101.
3. B. M. RUD, L. T. AKULOVA and E. Y. TEL'NIKOV, *Sci. Sinter.* (1984) 129.
4. L. T. AKULOVA, M. V. VLASOVA and N. G. KAKAZEI, *Fizika i khimiya stekla.* **12** (1986) 574.
5. M. V. VLASOVA, D. E. DISHEL and N. G. KAKAZEI, *Poroshkovaya metallurgiya.* **11** (1990) 28.
6. D. HAMER and J. BIGGERSE, in "Tekhnologiya tolstoplyenochnych gibridnych integralnych skhem" (Mir, Moscow, 1975) p. 496.
7. G. SPERLICH, *Solid State Commun.* **13** (1973) 1513.
8. R. S. MANN and K. C. KHULBE, *Bull. Chem. Soc. Japn.* **48** (1975) 1021.
9. H. J. WAGNER, P. DRIESSEN and C. F. SCHWERDTFEGER, *Non-Cryst. Solids*, **34** (1979) 335.
10. M. ELAHI, M. H. HEKMAN-SHOAR, C. A. HOGARTH and K. A. K. LOTT, *J. Mater. Sci.* **14** (1979) 1997.
11. M. ANWAR, C. A. HOGARTH and K. A. K. LOTT, *Phys. stat. sol. (a).* **114** (1989) 225.
12. *Idem, ibid.* **113** (1989) 483.
13. *Idem, J. Mater. Sci.* **24** (1989) 1660.
14. R. F. VOITOVICH, in "Tugoplavkiye soyedineniya. Termodynamicheskiye kharakteristiki. Spravochnik" (Naukova Dumka, Kiev, 1971) p. 220.
15. Y. G. KLYAVA, in "EPR-spektroskopiya neuporyadochennih tverdih tel" (Zinatne, Riga, 1988) p. 320.

Received 26 February
and accepted 1 July 1991