JOURNAL OF MATERIALS SCIENCE **40** (2005) 2541 – 2546

The effect of Ni, ZrB_2 and MoS_2 additives on certain physico-chemical and mechanical properties of special glasses in the $ZnO\text{-}PbO\text{-}B_2O_3\text{-}SiO_2$ system

B. STANIEWICZ-BRUDNIK*, K. MAJEWSKA-ALBIN
The Institute of Metal Cutting, Cracow, Wroclawska 37a Str
E-mail: bbrudnik@ios.krakow.pl

B. TRYBALSKA
The Technical University of Science and Technology, Cracow, Mickiewicza 30 Ave

The influence of additives of metal compounds (ZrB_2, MoS_2) and nickel to the abrasive masses based on devitrified glasses of $ZnO\text{-}PbO\text{-}B_2O_3\text{-}SiO_2$ system was studied by investigating both the wettability of submicrocrystalline sintered corundum, and the size, structure and chemistry of the interfaces. XRD analysis, scanning electron microscopy with X-ray microanalysis, wettability tests and microhardness measurements were performed. The experimental results were compared with the probability of reaction between the abrasive grain (cBN, submicrocrystalline sintered corundum) and: (1) the additives of metal compounds, (2) devitrified glass binders identified by using a VCS algorithm designed for thermodynamic calculations. It was confirmed that 18–20 compounds (6–9 in condensed phase) out of 230 exhibited chemical stability.

1. Introduction

For economic reasons many investigations have been recently carried out to develop modified abrasive tools with cubic boron nitride (cBN) abrasive grains and vitrified binders, which could be used in conventional grinding machines at the standard, high speed and high-efficiency grinding conditions [1–4].

One of the possible investigation directions is the so called "mixed grinding wheels" connecting a cBN mono or microcrystalline grain with submicrocrystalline sintered corundum (cubitron). The addition of cubitron grains working as assisting grains with many active grains edges helps to decrease the grinding energy and work piece surface roughness [1, 5–7]. The incorporation of Ni, ZrB_2, and MoS_2 to the abrasive masses, which react chemically with the devitrified glass components, causes an increase of the bonding cohesive strength and chemical stability, which are necessary during grinding with the use of metalworking fluids; they also effect the softening temperature and the viscosity of the binder vitrified phase [8, 9].

2. Experimental procedure

Object and scope of the investigation.

The objects of investigations were sintered specimens of two devitrified glasses of the $ZnOPbO\text{-}B_2O_3\text{-}SiO_2$ system (further called the Pb21K and Pb24K specimens), with Ni ZrB_2 and MoS_2 additions at 1, 3 and 6 vol.% of the total abrasive mass volume.

The research program was based on the following steps:

– theoretical calculation of all the stable products of the reactions between the abrasive grain (cBN, cubitron) and bond components using the VCS (Villars, Cruise, Smith) algorithm,
– verification by XRD of the calculated results,
– investigation of the wettability of the cubitron substrates by the devitrified glasses with additives of metals and metal compounds.
– scanning electron microscopy with X-Ray microanalysis of freshly cross-sectioned samples (devitrified glasses with metal compounds additives—cubitron substrate),
– microhardness measurements of abrasive masses with devitrified glasses and metal compound addition (Ni, ZrB_2 and MoS_2).

2.1. Phase equilibria calculations using the VCS algorithm

The chemical stability of the interfacial phases between the abrasive grains (cubic boron nitride,

*Author to whom all correspondence should be addressed.

submicrocrystalline sintered corundum) and the binder components was determined using a thermodynamic potential calculation by the VCS algorithm method, which takes into consideration the stability of all possible reaction products [8–10]. The calculation of equilibria has been carried out for the Pb21K specimens (800, 820, 830, 860°C) and the Pb24K specimens (760, 800, 820, 830°C) at 1013 hPa atmospheric pressure.

The mole component ratios were taken considering the real contents in the abrasive masses. The calculations have been performed using the method of thermodynamic potential minimisation of the whole-mixture, keeping the mass balance and non-negative mole numbers of the individual chemical elements. These calculations did not require the determination of numbers and types of the reactions since the system has reached equilibrium; they have only demanded the determination of the kinds of compounds that could exist with a certain probability. It was assumed that the binder components in these temperature ranges could appear in the multi-component gaseous phase and in the pure condensed phase (liquid and solid). It is not known whether the liquid substances formed pure phases (not mixed liquid phases) or whether they formed a liquid phase of unlimited miscibility, so the calculations have been performed using both assumptions.

According to the first assumption, the multi-component gaseous phase and pure liquid and solid phases were present in the equilibrium state. According to the second assumption the multi- component gaseous phase, multi-component liquid phase and pure solid phase were present in the equilibrium state. Calculations proved that among 230 possible reaction products, about 18–20 products were stable, and among them 6–9 were in the solid state, depending on the additives amount (Tables I and II).

It has been noticed that the additives of Ni, ZrB_2 and MoS_2 (1, 3, 6 vol.%), using the first assumption caused an increase of the BN content. This can be explained by the fact that several compounds react with one another. Additionally, the amount of carbon mono-oxide (CO) increases with the temperature. The oxygen of the B_2O_3 phase is probably captured by the carbon mono-oxide and the excess boron of B_2O_3 reacts with the atomic nitrogen, forming BN. Therefore the number of BN moles, which participate in the reaction increases.

TABLE I Calculated equilibrium compositions of Pb21K with 1 vol.% Ni condensed phases formed at different temperatures

	t,°C			
Phase	800	820	830	860
	Amount formed (mole) at different temperatures			
αAl_2O_3	3.086549	3.086549	3.086549	3.086549
ZnO	1.205769	1.205769	1.205769	1.205769
$MgAl_2O_4$	0.113119	0.113119	0.113119	0.113119
Zn_2SiO_4	0.307931	0.307931	0.307931	0.307931
BN	3.614116	3.624524	3.628613	3.637285
V_2O_3	0.061188	0.061188	0.061188	0.061188
Ni	0.473514	0.473514	0.473514	0.473514

TABLE II Calculated equilibrium compositions of Pb21K with 1 vol.% Ni-multi component liquid phases formed at different temperatures

	t,°C			
Phase	800	820	830	860
	Amount formed (mole)			
αAl_2O_3	3.098507	3.112622	3.124080	3.191064
$MgAl_2O_4$	0.097128	0.081891	0.069754	0.000000
Zn_2SiO_4	0.291940	0.276703	0.264566	0.194812
BN	2.790201	2.779679	2.767310	2.682328
V_2O_3	0.061188	0.061188	0.061188	0.061188
Ni	0.473514	0.473514	0.473514	0.473514

Using the second assumption (multi-component liquid phase) the BN content decreases with increasing temperature, most probably due to the BN decomposition. The excess boron combines with oxygen and causes an increase of the B_2O_3 and atomic nitrogen amounts.

According to the calculations, the ZrB_2 additives to the abrasive masses should be transferred (1, 3 vol.%) as ZrO_2. For the first assumption the ZrO_2 is stable in the whole temperatures range, while for the second assumption, the amount the ZrO_2 decreased due to an increased amount of Zr and O in the liquid phase.

At 6 vol.% of ZrB_2 the additives occurred in the form of ZrO_2, $ZrSiO_4$ and ZrB_2. Using the first assumption the zirconium boride was stable in the whole temperature range. The ZrO_2 content increased because of the content of $ZrSiO_4$ decreased. In case of nickel additives a lack of reaction of nickel with the bond component was seen, as well as a stability of its contents in the whole examined range of temperatures.

The addition of MoS_2 additive of 1 vol.% caused an occurrence of ZnS zinc sulfide and MoS molybdenum sulfide of the unchanged content in all the given temperatures. The increase of the MoS_2 content (3 vol.% and 6 vol.%) caused Mo_2C to appear, which increases its content at the expense of MoC.

2.2. X-ray diffraction investigations

The theoretical calculations of the thermodynamic stability were verified by X-ray diffraction analysis. Investigations were performed using the PW1710 diffractometer, with a cobalt tube in the angle range 2Θ $Co_{k\alpha} = 10 \div 85°$. Regarding the solid state compounds it can be stated that:

- about 80% of the theoretically calculated compounds were identified by X-ray diffraction (Table III)
- the V_2O_3, ZnO, PbB_6O_{10}, $Li_2B_6O_{10}$ compounds were not found
- the $ZnAl_2O_4$ and $Al_4B_2O_9$ compounds were identified additionally in all the diffraction patterns, although the theoretical thermodynamic calculations excluded them.

TABLE III The X-Ray phase analysis of abrasives masses containing Pb24K with 1; 3 and 6 vol.% MoS_2 additives

	Pb24K	Pb24K with 1 vol.% MoS_2	Pb24K with 3 vol.% MoS_2	Pb24K with 6 vol.% MoS_2
Phases	BN α-Al_2O_3- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4 $A1_4B_2O_9$	BN α-Al_2O_3- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4 $ZnAl_2S_4$(32-1458) $Zn_{1.7}Al_{20}S_{32}$	BN α-$A1_2O_3$- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4 $Al_4B_2O_9$ $ZnAl_2S_4$(32-1459) MoS_2	BN α-$A1_2O_3$- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4 Zn_2SiO_4 $Al_4B_2O_9$ $ZnAl_2S_4$(32-1459) $ZnAl_2S_4$(40-1075) MoS_2

TABLE IV The X-Ray phase analysis of abrasives masses containing Pb21K devitrified glass with 1, 3 and 6 vol.% MoS_2 additives

	Pb21K	Pb21K with 1 vol.% MoS_2	Pb21K with 3 vol.% MoS_2	Pb21K with 6 vol.% MoS_2
Phases	BN α-Al_2O_3- corundum $MgAl_2O_4$-1 $MgAl_2O_4$-2 $ZnAl_2O_4$ $A1_4B_2O_9$	BN α-Al_2O_3- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4 $A1_4B_2O_9$ MoC ZnS	BN α-$A1_2O_3$- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4 $Al_4B_2O_9$ MoC ZnS Al_2S_3 $ZnAl_2S_4$	BN α-$A1_2O_3$- corundum $MgAl_2O_4$ $ZnAl_2O_4$ Zn_2SiO_4(37-1485) $ZnAl_2S_4$(32-1458) $ZnAl_2S_4$(40-1074) $ZnAl_2S_4$(40-1075) MoS_2

It was confirmed that metallic nickel did not react with any of the binder components, and it was present in a pure form in both devitrified glasses. After molybdenum disulfide (MoS_2–1 vol.%) was introduced into the Pb21K devitrified glass, the presence of molybdenum carbide (MoC) and zinc sulfide (ZnS) was observed. In the case of the 3 vol.% MoS_2 additives, the presence of $ZnAl_2S_4$ was noticed. For the 6 vol.% MoS_2 additives the presence of MoS_2 and $ZnAl_2S_4$ was observed in three different structures (Table IV).

- For the Pb24K devitrified glass the addition of 1 vol.% MoS_2 caused the non-stoichiometric zinc-aluminosulfide ($Zn_{1,7}Al_{20}S_{32}$) and $ZnAl_2S_4$ phases to be present but the V_2O_3, ZnO, C (graphite), PbB_6O_{10}, $Li_2B_6O_{10}$, ZnS, MoC and Mo_2C phases were not confirmed.
- In the presence of 6 vol.% MoS_2 additives, MoS_2, $ZnAl_2S_4$ were observed, while the formation of Al_2SiO_5, V_2O_3, ZnS, MoC and Mo_2C was not confirmed.

In the presence of 1 vol.% ZrB_2 additives the formation of ZrO_2 was noted to occur but V_2O_5 was not found. At 3 vol.% of ZrB_2 the occurrence of $ZrSiO_4$ and ZrO_2 was identified.

3. Wettability tests

Wetting of abrasive grains by the binder during the thermal treatment is necessary for obtaining the required tool strength and this is a basic criterion in a performance assessment of the binder. It is assumed that the contact angle Θ should be lower than 30°, to guarantee relevant adhesion of the binder (devitrified glass) to the grain surfaces, intensifying binding forces of the bridges [8, 9]. The temperature corresponding to the condition $\Theta \leq 30°$ was named as t_Θ.

The contact angle measurements were carried out using the Leitz-Watzlar high temperature microscope by the sessile drop method in the temperature range 25 to 950°C [11, 12].

For each specimen the temperature t_Θ, was determined. The results are presented in Table V.

The analysis of the results has shown that both the Ni and MoS_2additives improve wetting properties. For Pb21K devitrified glass, an increase of the amount of Ni and MoS_2 (1, 3, 6 vol.%) results in a decrease of both t_Θ (877, 880, 903°C) and Θ (17°, 14°, 13°). This effect can be related to the zinc silicate ($ZnSiO_4$ willemite) formation and next, with the appearance of two structures of the same compound. For the Pb24K devitrified glass the nickel additives caused an increase of the t_Θ temperature and a decrease of the contact angle Θ (26°, 15°, 23°). The presence of Zn_2SiO_4 caused probably an

TABLE V Contact angles of Pb21K and Pb24K devitrified glasses with Ni, ZrB_2 and MoS_2 additives, formed on the cubitron substrate at corresponding temperature

Additives	Pb21K	Pb24K
with 1 vol.% Ni	25°/852°C, 17°/877°C	26°/862°C
with 3 vol.% Ni	20°/857°C, <14°/880°C	24°/867°C, 15°/911°C
with 6 vol.% Ni	22°/876°C, 13°/903°C	76°/859°C, 23°/942°C
with 1 vol.% MoS_2	25°/750°C, 20°/762°C	34°/750°C, 25°/764°C
with 3 vol.% MoS_2	25°/761°C, 19°/768°C	25°/768°C, 14°/816°C
with 6 vol.% MoS_2	19°/795°C, 14°/819°C	20°/794°C, 16°/828°C
with 1 vol.% ZrB_2	24°/874°C	25°/779°C
with 3 vol.% ZrB_2	33°/880°C	25°/837°C, 23°/849°C
with 6 vol.% ZrB_2	–	25°/868°C, 20°/875°C
Pb21K (pure)	26°/874°C, 23°/893°C	–
Pb24K (pure)	–	27°/749°C, 20°/801°C

increase in the t_Θ temperature. In the case of the Pb21K devitrified glass—the MoS_2 additives caused a drastic decrease in the t_Θ temperature (of 131, 126 and 74°C) as well as in this angle (20°, 19°, 14°). A reason of this is probably related with the occurrence of chemical reactions between molybdenum disulfide and the binder components or the cubitron grains, leading to the formation of MoC, ZnS and $ZnAl_2S_4$. With reference to the Pb24K devitrified glass the situation was similar; the addition of molybdenum disulfide also resulted in a decrease of both t_Θ and Θ (25°, 14°, 16°). Also in that case the lowest contact angle corresponds to the highest amount of additives.

This can be explained in a similar way as it was in case of the Pb21K devitrified glass, namely by the chemical reaction between the additives, the bond components and the cubitron grains, resulting in the formation of non-stoichiometric $Zn_{1.7}Al_{20}S_{32}$ and $ZnAl_2S_4$compounds in two structural forms. In case of the ZrB_2 (1, 3 and 6 vol.%) the additives caused an abrupt increase in the contact angle and in the t_Θ temperature.

3.1. Scanning electron microscopy examinations of the devitrified glasses with Ni, ZrB_2 and MoS_2 additives

Scanning electron microscopy (SEM) examination and X-ray microanalysis (analysis of point, line and surface distribution of chemical elements) were carried out on the freshly cross-sectioned samples. These investigations showed the presence of interfacial phases between the cubitron substrate and the binder material [8, 9]. In case of the Pb21K devitrified glass the initially small interface enlarged abruptly with the addition of 6 vol.% nickel or molybdenum disulfide, at variance with the Pb24K devitrified glass, for which the low amounts of additives (1 and 3 vol.%), results in an increase of the thickness of the interface, while with a much higher amount of MoS_2 additive (6 vol.%), this layer diminished drastically. It can be assumed that changes of transition layer size are resulting from the different devitrified glass chemical compositions. The enlargement of the interface occurred with the Pb21K devitrified glass doped with 1, 3 and 6 vol.% MoS_2 additives (Fig. 1); this was probably the result of the formation of three structurally different compounds of zinc aluminosulfide ($ZnAl_2S_4$). In the case of the Pb24K devitrified glass (1, 3 vol.% MoS_2 additive), the formation of non-stoichiometric compounds had an influence on the increase of the transition layer size. The decrease in the interface size at 6 vol.% MoS_2 additive could be caused presence of $ZnAl_2S_4$ and MoS_2 stoichiometric compounds which have formed at the interface (Fig. 2).

The width of interface increased with an increase of the ZrB_2 additives (3 vol.%) amounts and stabilised at ZrB_2 additives (6 vol.%) amounts. The appearance of tetragonal $ZrSiO_4$ probably caused an increase, and next—a stabilisation of the transition layer.

In all the cases the following chemical elements were present {(+) presence, (±) trace amounts} in the transition layers:

- Pb21K (additives free)—aluminum, lead traces, silicon, zinc and vanadium
- Pb21K with (1, 3, 6 vol.% Ni)—aluminum, lead, silicon, zinc, vanadium and nickel
- Pb21K with (1, 3, 6 vol.% MoS_2)—aluminum, lead (−, +, +), zinc, silicon, vanadium, molybdenum
- Pb24K (additives free)—aluminum, lead, silicon, vanadium
- Pb24K with (1, 3, 6 vol.% Ni)—aluminum, lead, silicon, zinc, vanadium and nickel
- Pb24K with (1, 3, 6 vol.% MoS_2)—aluminum, lead (−, +, −), zinc (±, +, ±) silicon, vanadium, molybdenum

3.2. Microhardness of sintered abrasive masses with additives

Microhardness measurements have been carried out on the sintered abrasive masses with ZrB_2, MoS_2 and Ni additives (1, 3, 6 vol.%) using the FM7 digital microhardness tester at 490 mN load. The results suggest that the devitrified glasses can be considered as the hard ones (with respect to traditional glass, the Pb21K devitrified glass hardness was 6.16 GPa, the Pb24K devitrified glass hardness was 6.65 GPa).

The ZrB_2 addition initially caused an increase in the sintered body microhardness (7.49 GPa), and subsequently at higher amounts of additives—caused a decrease in the microhardness values (the Pb21 K with 6 vol.% of ZrB_2 − 6.18 GPa, the Pb24K with 6 vol.% of ZrB_2 − 5.88 GPa). This tendency is maintained in all the additives sintered abrasive masses, though the highest microhardness value was reached in the case of the 3% MoS_2 additives (10.43 GPa).

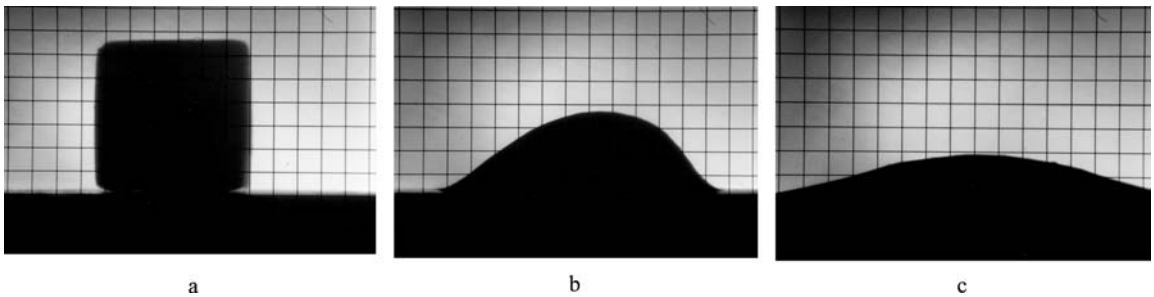

Figure 1 Wettability of the cubitron substrate by the Pb21K devitrified glass with 3% Ni additives: (a)145°C, (b)836°C(Θ < 56°), (c)880°C (Θ < 14°).

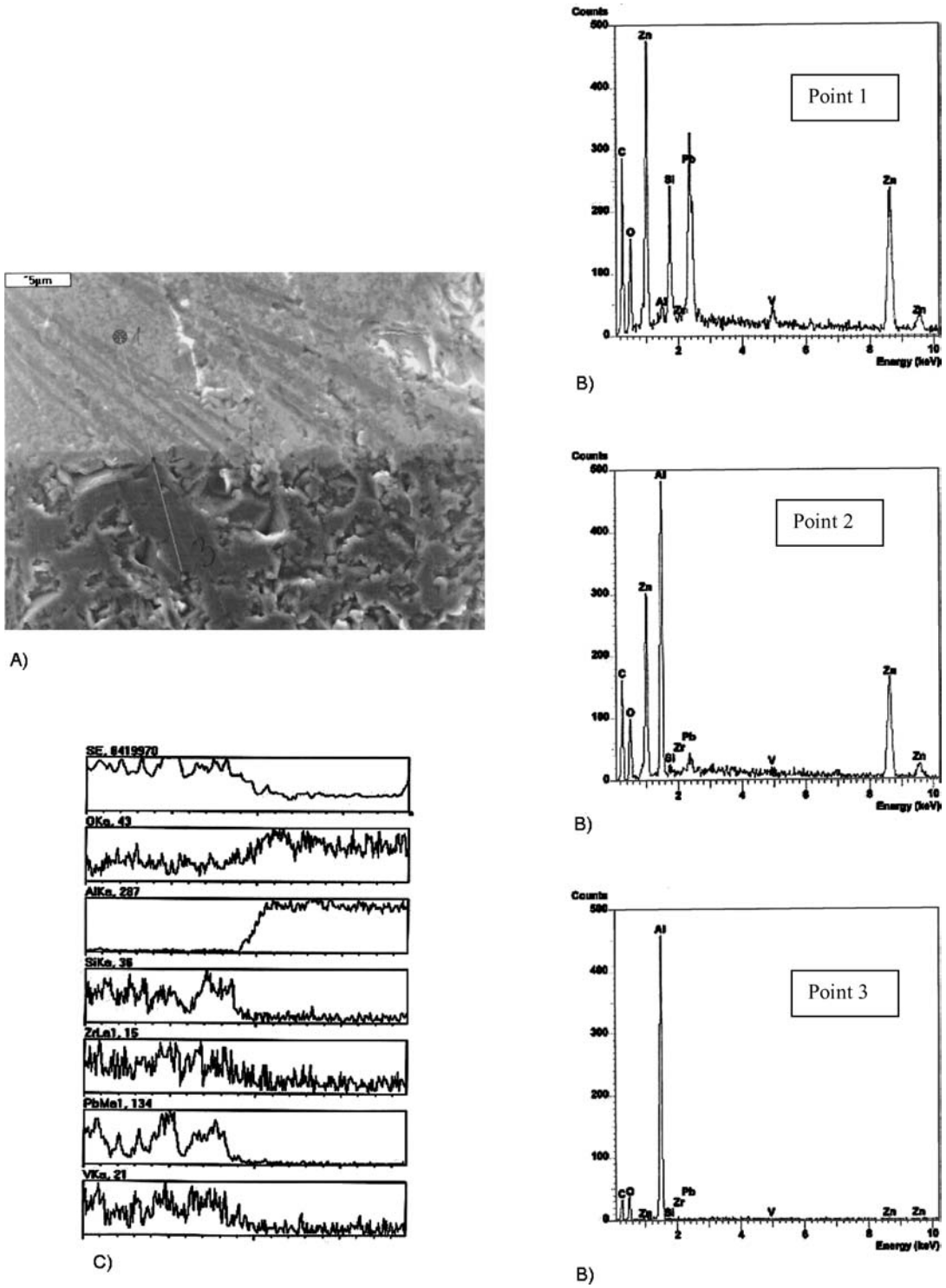

Figure 2 (A) SEM picture of the cross-section of the Pb21K devitrified glass—cubitron substrate sample, magnification 500×; (B) chemical compositions at the devitrified glass—cubitron substrate interface in the three marked points (1, 2, 3); (C) line analysis of the elements along the marked line.

4. Conclusions

- The application of the VCS algorithm for the determination of the chemical stability of reaction products at the abrasive grains-binder interface made it possible to find 20 compounds out of 230, that appeared to be stable at the determined temperatures; 6–9 out of them were in the condensed phase. The presence of 5–8 of them was confirmed by XRD identification.
- X-ray diffraction analysis has shown the presence of the compounds $ZnAl_20_4$ and $Al_4B_20_9$ while the VCS algorithm calculations have not revealed their formation.
- In the case of nickel additives into the abrasive masses, according to the VCS algorithm and XRD analyses, only metallic nickel was found.
- In the case of molybdenum disulfide additives into the abrasive masses containing the Pb24K devitrified glass, according to the VCS algorithm, the zinc sulfide (ZnS) and molybdenum carbide (MoC, Mo_2C) should have formed and according to the XRD measurements results the following

compounds were found: $ZnAl_2S_4$, $Zn_{1.7}Al_{20}S_{32}$ MoS_2; in the abrasive masses with the Pb21K devitrified glass—$ZnAl_2S_4$in three different structures and MoS_2 were identified.

- In the case of 1 vol.% zirconium boride into the abrasive masses with Pb21K devitrified glass, only the zirconium oxide was revealed by XRD for 3 and 6 vol% ZrB_2 additive—apart from $Zr0_2$ also $ZrSi0_4$ was observed.
- The wettability of cubitron substrates by both devitrified glasses with nickel additives was higher than in case of the initial materials (the Pb24K, Pb21 K without additives): it means that the contact angle was lower, but the temperature, at which the Θ value was lower, has increased (of 100°C for the Pb24K and 20°C for the Pb21 K glasses). The larger the additives amount was, the higher the wettability angle temperature.
- Molybdenum disulfide additives into devitrified glasses caused an abrupt decrease in the temperature of wetting angle (for the Pb21K—of 130°C and for the Pb24K—of 50°C). The increase in the amount of additive caused a decrease of wetting angle but an increase in the wetting angle temperature.
- The wettability of cubitron substrate by both devitrified glasses (the Pb21K and Pb24K) decreased due to the ZrB_2 additives; an increase in the ZrB_2 amount caused an increase in the wetting angle and in the wetting angle temperature.
- The interface width which was present in the devitrified glasses–cubitron substrate system has increased abruptly at 6 vol.% of Ni, MoS_2 and ZrB_2 additives for the Pb21K glass and has decreased strongly for the Pb24K glass. The differences may result mainly from the chemical composition of the transition layers.
- All the additives caused the increase in the microhardness of sintered abrasive masses comparing to the initial masses. The sintered masses with the molybdenum disulfide additives reached the highest microhardness of all the samples.

Acknowledgements

This work was supported by Polish State Committee for Scientific Research (KBN) under the Grant 7T08D02720.

References

1. J. PLICHTA, "Foundations of Grinding Process Using Grinding Wheels with Microcrystalline Grains of the Regular Boron Nitride with Vitrified Bond" (Koszalin Technical University, Koszalin, Poland, 1996, No. 58).
2. CZ. NIŻANKOWSKI and L. PRZYBYLSKI, in Proc. XXV Scientific School of Grinding Treatment (Technical University of Wrocław, Poland 2002) p. 17.
3. J. COOK, *Canadian Machinary and Metalworking* **2** (1992) 37.
4. E. A. BONDARENKO and A. E. SHILA, *Sverhtvierdye Materialy* **5** (2000) 38.
5. V. G. SAVINSKAJA, A. M. SARAJKIN and A. A. ADAMOWSKI, *Poroskovaja Metalurgija* **8** (1991) 94.
6. H. K. TONSHOFF, B. KARPUSCHEVSKI, P. ANDREA and A. TURICH, *Ann. CIRP* **47** (1998) 723.
7. J. A. BORKOWSKI and A. SZYMANSKI, "Uses of Abrasives and Abrasive Tools" (PWN, Warszawa, 1992).
8. B. PROCYK, B. STANIEWICZ-BRUDNIK and K. MAJEWSKA-ALBIN, *Trans. IWRI* **30** (2001) 149.
9. B. STANIEWICZ-BRUDNIK, B. PROCYK, M. ŚRODA and K. MAJEWSKA-ALBIN, *Optica Applicata* **1** (2003) 167.
10. E. BENKO and A. WYCZESANY, *J. Eur. Cer. Soc.* **14** (1994) 557.
11. E. RABKIN, D. CHATAIN, J. BERNARDINI and D. MONHOUX, *Trans. IWRI* **30** (2001) 1.
12. N. SOBCZAK, M. KSIĄŻEK, W. RADZIWIŁŁ, L. STOBIERSKI and B. MIKUŁOWSKI, *ibid.* **30** (2001) 125.

Received 31 March
and accepted 10 October 2004