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PIONEER YEARS OF ELECTRON PROBE MICROANALYSIS IN SLOVENIA

PIONIRSKO OBDOBJE ELEKTRONSKE MIKROANALIZE V SLOVENIJI

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Two periods are found in the pioneer years of electrons probe microanalysis (EPMA) in Slovenia:

- a longer period up to 1969 when an electron probe microanalyser was put in operation in the Institute of Metallurgy in Ljubljana, and
- a shorter period after this date until the spreading of EPMA backed by sufficent research achievents demonstrating it wide field of use and the sufficient mastering of methodology.

The use of EPMA up to 1969 was of marginal extent but not of marginal scientific merit and centred to topics of selective oxydation of alloys of iron with arsenic, copper, tin and antimony. The interest for EPMA and the conviction that it will greatly improve the quality of the actual research as well as open new topics helped significantly were great. Prof. D. Kolar and his collaborators were among the best prepared and also among the must successfull. With the cooperation of some younger scientists he accomplished several projects which found significant interest in the international research community and were realised thanks to the fast governing of EPMA methodology. Let us quote only some achievements published up to some years after the putting in operation of EPMA in 1969:

- binary phase equilibria diagrams were established for niobium, titanium and circonium carbides with iron, nickel, chromium and cobalt;
- binary phase equilibria diagrams were established for uranium sulphide and sulphides of calcium, barium and strontium;
- several projects were accomplished with the aim to understand better the microstructure of ferrite ceramics, its sintering process and the effect of microstructure and sintering on magnetic and electrical properties.

In binary phase equilibria diagrams solid solubilities and eutectic compositions were determined. Also because of the contribution of prof. D. Kolar the pioneer period od EPMA in Slovenia was short and successful and helped to strengthen it as one of the base scientific facility for research of solid materials on microstructure level.

Key words: electron probe microanalysis, selective oxydation, binary phase diagrams Fe - NbC, TiC, ZrC, activated sintering of Ba titanate, binary phase diagrams US and CaS, SrS and BaS

Pionirsko obdobje elektronske mikroanalize (EMA) delimo na dva dela:

- daljše obdobje do postavitve elektronskega mikroanalizatorja na tedanjem Metalurškem inštitutu v Ljubljani leta 1969 in
- krajše obdobje po zagonu naprave in začetku njene široke uporabnosti kot dokaz zadostnega obvladovanja metodologije dela.

Uporaba elektronske mikroanalize je bila do začetka leta 1969 v Sloveniji po obsegu marginalna, vendar ne marginalna po vsebini. Raziskave so od leta 1962 posegale na področje selektivne oksidacije predvsem zlitin železa z elementi z majhno afiniteto do kisika, na pr. arzen, antimon, kositer in baker. Zanimanje za EMA in pričakovanje, da bo omogočila kvaliteten skok v raziskovalnih projektih je bilo veliko, okolje pa pripravljeno na intenzivno uporabo nove metodike. Prof. D. Kolar je bil s sodelavci pri tem gotovo nadpovprečno uspešen. Bil je snovalec in izvajalec vrste raziskav, ki so prinesle temeljne novosti na nekaj področjih raziskovanja. Omenjene bodo le tri, ker so bili izsledki objavljeni najkasneje nekaj let po postavitvi naprave tudi zaradi zelo hitrega osvajanja metodologije dela, še posebej kvantitativne analize:

- določeni so bili binarni ravnotežni fazni sistemi niobijevega, titanovega in cirkonijevega karbida s prehodnimi kovinami železo, krom, nikelj in kobalt;
- določeni so bili binarni ravnotežni fazni diagrami uranovega sulfida s kalcijevim, stroncijevim in barijevim sulfidom;
- izvršena je bila vrsta raziskav s ciljem, da se bolje razpozna mikrostruktura feritne keramike, proces njenega sintranja in vpliv sestavin in procesa sintranja na magnetne in električne lastnosti.

V binarnih faznih sistemih je bila določena topnost v trdnih fazah ter temperature in sestava evtektikov. Tudi zaradi velikega prispevka prof. D. Kolarja in sodelavcev je bilo pionirsko obdobje EMA kratko in uspešno ter je metodo utrdilo kot eno od temeljnih pri raziskovanju vseh vrst trdne snovi na nivoju mikrostrukture.

Ključne besede: elektronska mikroanaliza, selektivna oksidacija železa, binarni fazni diagrami železa NbC, TiC in ZrC, aktivirano sintranje Ba titanata, fazni diagrami US in CaS, SrS in BaS

1 INTRODUCTION

This paper was prepared in the frame of the celebration of the 65th jubilee of prof. dr. Drago Kolar, eminent scientists at the Institute J. Stefan and teacher of ceramic materials at the University of Ljubljana. I had the opportunity to meet prof. Kolar in major extent after april 1969, when the second electron probe microanalyser (EPMA) in the former Jugoslavia was put in operation in the former Institute of Metallurgy in Ljubljana. The EPMA was purchased by combining funding from the Institute of vacuum technique and electronics, Institute of automation, Institute for research of materials and structures, Institute of metallurgy, Metallurgy dpt of the University of Ljubljana, Slovenian Steelworks, and the Slovenian governement. The project was coordinated by the Institute of metallurgy and the EPMA installed in his premises.

2 EPMA IN THE WORK A SLOVENIAN RESEARCHERS UP TO 1969

From disponible data it seems that EPMA was first used in the work of a slovenian scientist in 1962 in the investigation of the selective surface oxydation of the alloy Fe - 0.075% As[1,2]. Arsenic free energy of oxydation is smaller than that of iron. Consequently, by surface oxydation only iron reacts with oxygen, while arsenic is segregated in the metal layer in contact with the oxyde. By EPMA the distribution of arsenic in the segregated layer obtained by electrolytic dissolution of μm layers of metal and microradiochemical analysis was verified. The distribution was different after surface oxydation above and below AC3 because of the limited solubility of arsenic in γ phase (**figure 1**). The results obtained by both methods did agree very good. In the same reference EPMA was used also to determine the composition of the eutectic FeO - $3FeOP_2O_5$ obtained at surface oxydation of an Fe - 0.092% P alloy.

In the following case EPMA was used also in the investigation of the selective oxydation of iron. In iron alloys with copper, arsenic, tin, and antimony by EPMA point, line and scanning analyses the sequence of formation of solid and liquid phases in binary, ternary and quaternary equilibria was established as consequence of selective oxydation, f.i.:

$$\gamma \rightarrow \gamma_1 + \alpha_1 \rightarrow \gamma_1 + \alpha_1 + lp_1$$

$$\gamma \rightarrow \gamma_1 + lp_2 \rightarrow \gamma_1 + \alpha_1 + lp_2 \rightarrow \gamma_1 + \alpha_1 + lp_1 + lp_2$$

with α, γ as solid and lp_1, lp_2 as liquid phases.

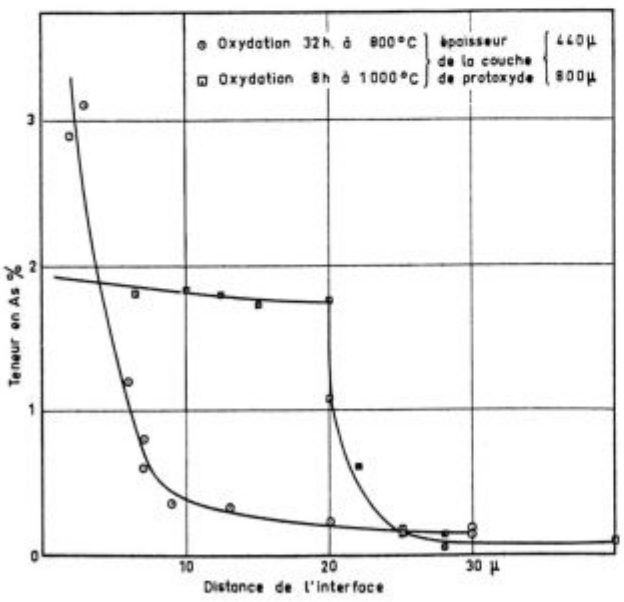

Figure 1: Distribution of arsenic in the segregated layer of an Fe-0.075% As alloy after surface oxydation at 800 and 1000°C determined by electron probe microanalysis (EMA). Ref. 1 and 2

Slika 1: Porazdelitev arzena v segregirani plasti zlitine Fe-0.075% As po oksidaciji pri 800 in 1000°C določena z elektronsko mikroanalizo (EMA). Po virih 1 in 2

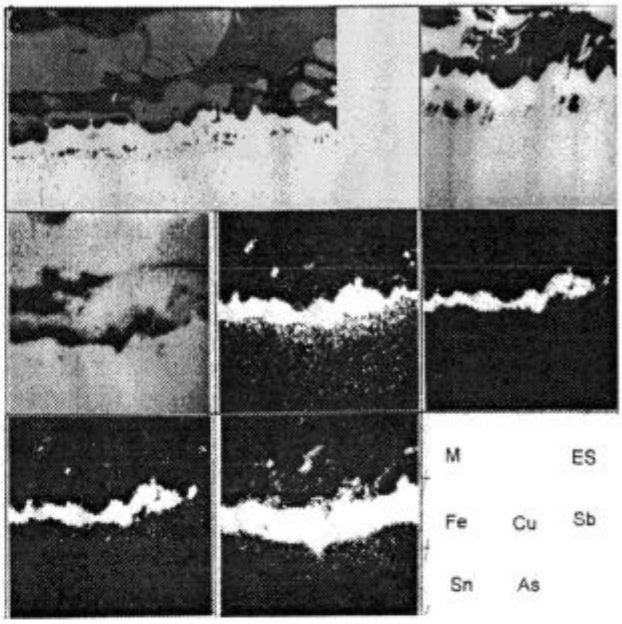

Figure 2: Optical, back scattered electrons and X rays scanning pictures of different elements in the segregated layer after air surface oxydation of an iron alloy at 1200°C. Ref.3 and 4

Slika 2: Optični, elektronski in specifični X posnetki za različne elemente v segregirani plasti na železovi zlitini po oksidaciji na zraku pri 1200°C. Ref. 3 in 4

For EPMA methodology it is of special importance the fact that the distribution of segregated elements was demonstrated also by scanning elemental pictures (**figure 2**). No use of EPMA was found in printed works of Slovenian scientists up to the start of the facility put in operation in 1969.

3 SOME DATA ON THE OPERATION OF EPMA FROM 1969 TO 1974

EPMA was ready for qualitative and semiquantitative work in april 1969. In **table 1** statistics on the work up to

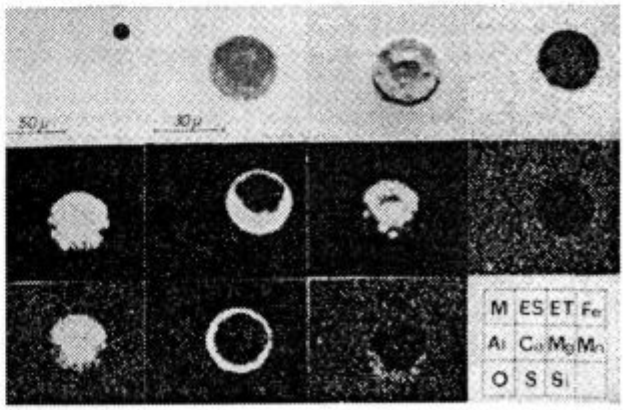

Figure 3: Optical, back scattered electrons and X rays scanning pictures of different elements. Spherical nonmetallic inclusion in steel. Ref. 9

Slika 3: Optični, elektronski in specifični X posnetki za različne elemente. Kroglasti nekovinski vključek v jeklu. Po viru 9

1974 are shown. Allready in the first year the work performed for users outside of the Institute of metallurgy reached a level which did not change significantly up to 1974. This level shows that EPMA was really needed and also satisfactorily exploited. Methods for qualitative and quantitative investigations for basic, applied, and development research as well as routine analysis for different institutions and industrial companies from geology, mineralogy, metallurgy, ceramic, building materials, electronics, and even forensic cases were developed fastly. The reader can have an idea on the level of quality and accuracy from the scanning picture in **figure 3** as well as the composition of carbides and nonmetallic inclusions in **table 2**.

Table 1: Clients for EPMA work

Year	Academic institutions	Companies	Payed working hours	Articles[1]
1969	10	14	1276	
1970	12	17	1330	6
1971	12	10	1335	8
1972	12	11	1330	5
1973	10	11	1301	2
1974	11	17	1241	10

In the year 1969 to 1974 54 different institutions and companies committed once or several times EPMA work, 29 ind. companies committed the investigation from 1 to 18 different specimens yearly.
[1] - Authors from the EPMA laboratory

Table 2: Composition of nonmetallic inclusions and carbides
F. Vodopivec und B. Ralić: Radex Rundschau (1975) 1, 289-294

Inclusion[1]	MnO	FeO	SiO_2 v ut.%	Al_2O_3	CaO	Vsota
1	28.0	8.3	-	63	-	99.3
2	16.4	2.3	37.8	7.5	36.0	100
3	55.5	6.3	31.1	5.9	-	99.8
4	50.3	6.3	32.4	9.7	-	98.6
5	21.4	4.6	30.4	2.4	41	99.8
Carbide[2]	W	V	Fe	Cr	Mo	C
M_6C[2]	56.0	3.1	28.6	4.75	2.25	1.93
$(W_{1.6}Fe_{3.3}V_{0.36}Cr_{0.56}C_1)$						
MC	14.2	57.2	3.3	7.65	1.6	16.95
$(V_{0.91}W_{0.06}Fe_{0.05}Cr_{0.11}Mo_{0.01}C_1)$						

[1] Correction calculation after Bence-Albee[7]
[2] Correction calculation after Philibert[6] and Reed[8]

In combination with optical microscopy it was possible to find reliable answers also for significant technological problems, f.i. inhomogenity and kinetics of homogenisation of steels as well as copper and aluminium alloys, composition of nonmetallic phases in steels and alloys. The allready mentioned **figure 3** shows a non metallic inclusion enriched at the surface by calcium and sulphur[9]. This was one of the first proofs for the reaction between calcium bounds to aluminate or alumosilicate inclusions with sulphur in the liquid steel. The homogenising times for aluminium and copper alloys were diminished on the base of investigations of segregation kinetics to less than half of the so far prescribed length[10]. It was established also that after homogenisation a virtually ideally homogeneus distribution was obtained in some cases, while in case of mutual interactivity also after long time homogenisation the average segregation was approaching a level significantly far from homogeneity.

4 EPMA IN THE RESEARCH OF D. KOLAR

D. Kolar and his research collaborators were frequent clients of the EPMA laboratory during the first year with different topics from ceramic magnets, hard metals and phase equilibria diagrams. Several papers based signifi-

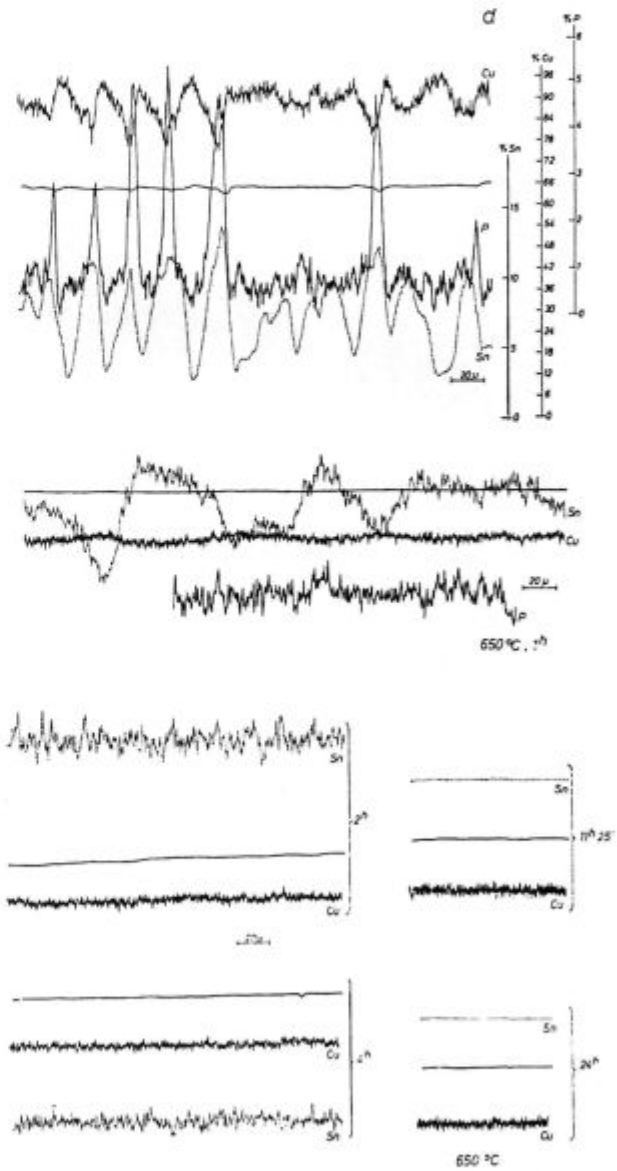

Figure 4: Distribution of alloying elements in an Cu 8% Sn 0,38% P alloy as cast and after homogenisation. Ref. 10
Slika 4: Porazdelitev legirnih elementov v zlitini Cu 8% Sn 0.38% P po litju in po homogenizaciji. Po viru 10

cantly on EPMA work were printed in international journals. The authors is avare of the possibility that some of the phase diagrams were later modified on the base of results of improved EPMA. Also if it happened, it could not change the type of phase diagrams which have therefore a permanent value.

The ambition of the author of the present survey is not to present all the work of D. Kolar in the quoted years, but to show that D. Kolar was prepared for EPMA and prepared to exploit optimally the new research facility in Slovenia due to the putting in operation of EPMA and was able in this way to improve considerably the scientific value of his investigations.

Figure 4 is taken from ref. 11, where Drofenik and Kolar reported on the effect of Bi_2O_3 addition on sintering process and properties of strontium ferrite. The attention of the reader is called on the quality of electron and scanning pictures in **figure 4**, where details near the size of μm are discernible. The morphology of bismuth oxyde containing phase shows that it fills as liquid spaces between polyhedric grains of ferrite with higher melting point. EPMA showed in this phase 50% Bi_2O_3, 31% Fe_2O_3 and 19% of SrO. It was concluded that the addition of bismuth oxyde lowered the sintering temperature and increased the volume density and energy product $(BH)_m$.

In the same year Komac, Golič, Kolar, and Brčič[12] established the crystal structure, phase composition and transformation temperatures in binary phase equilibria systems US-CaS, US-SrS and US-BaS. EPMA was used for the determination of solid solubilities and eutectic compositions shown in **table 3**, while **figure 5** presents the phase diagrams US-CaS and US-BaS. Jurca, Kolar and Trontelj investigated the effect of nickel on activated sintering of tungsten and established that nickel is not found in solid solution in tungsten in a detectable content and that also at grain boundaries nickel is not found in appreriable quantity[13,14]. 1.2 to 2.8% was found for the solid solubility of tungsten in silver, which is lower than the value found in published phase diagrams.

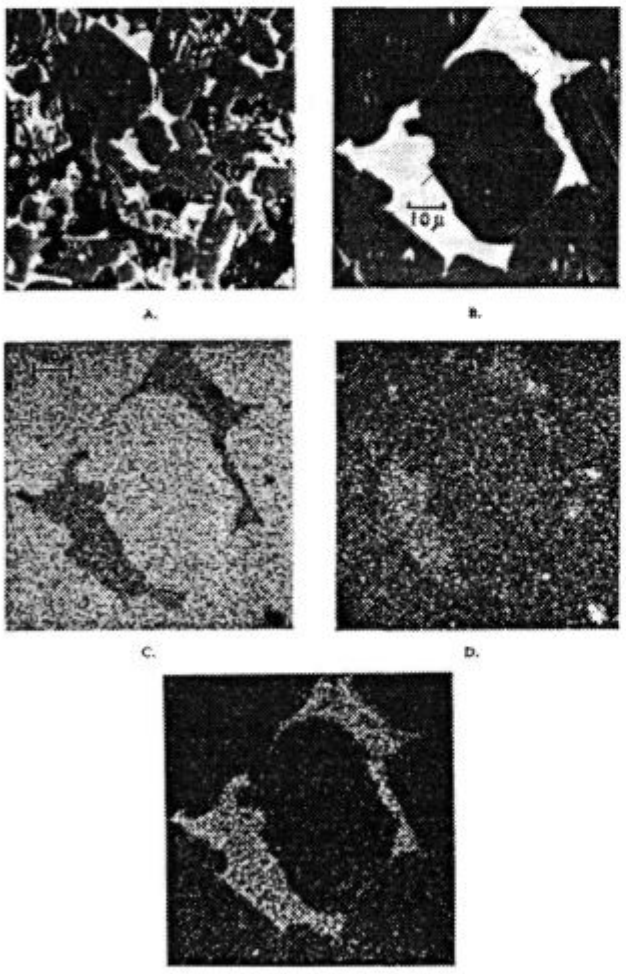

Figure 5: Back scattered electron and X rays scanning picture for different elements. Sintered strontium titanate with addition of Bi_2O_3. Ref. 11

Slika 5: Elektronski in specifični X posnetki za različne elemente. Sintran stroncijev titanat z dodatkom Bi_2O_3. Po viru 11

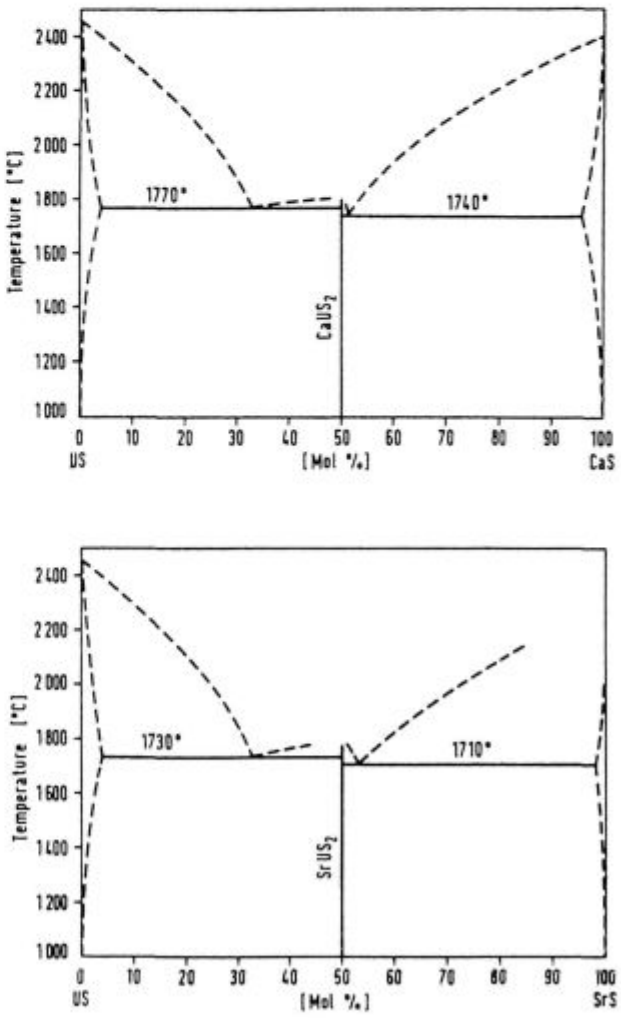

Figure 6: Phase diagrams US-CaS and US-BaS. Ref. 12

Slika 6: Fazna sistema US-CaS in US-BaS. Po viru 12

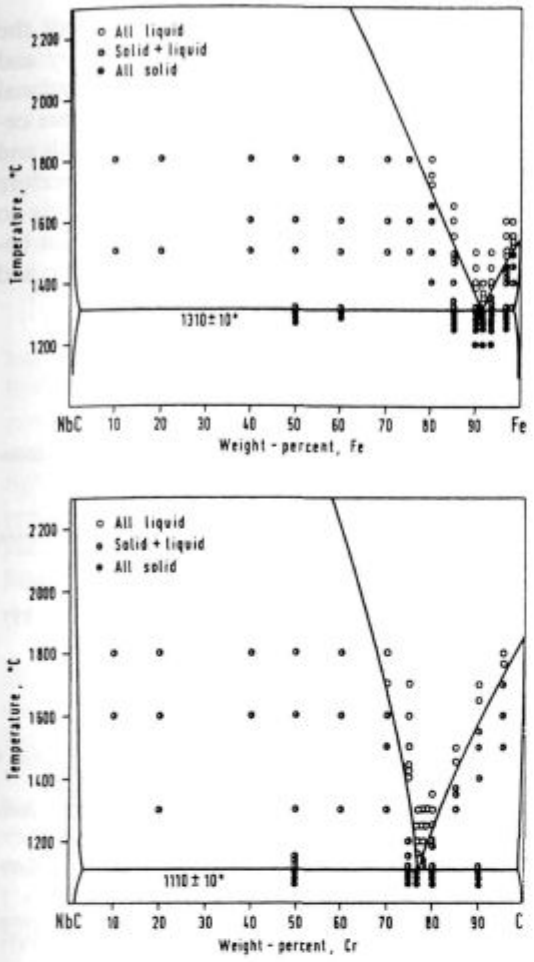

Figure 7: Phase diagrams NbC-Fe and NbC-Cr. Ref. 15
Slika 7: Fazna diagrama NbC-Fe in NbC-Cr. Po viru 15

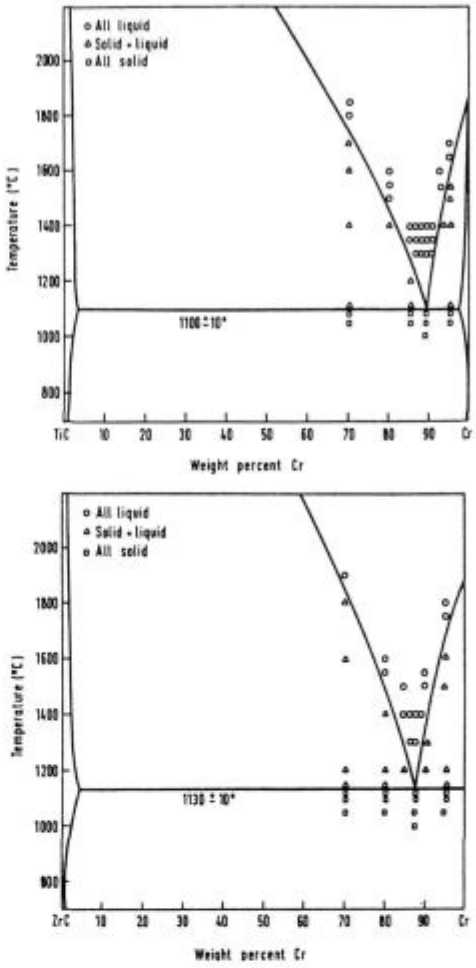

Figure 8: Phase diagrams TiC-Cr and ZrC-Cr. Ref. 16
Slika 8: Fazna diagrama TiC-Cr in ZrC-Cr. Po viru 16

Table 3: Phase composition in binary phase equilibria systems US-CaS, US-BaS in US-SrS
M. Komac, L. Golič, D. Kolar and B. S. Brčič: *J. Less-Common Metals*, 24 (1971) 121-128

System Phase	US-CaS	US-SrS	US-BaS
Solid solution US[1],%	3.5	3.5	3.0
Solid solution MS[1],%	4.0	n.d.	n.d.
Intermediate phase,%	50	50	50
	$CaUS_2$	$SrUS_2$	$BaUS_2$
Eutectic 1,%	33.0	33.0	38.0
Eutectic 2,%	50.5	53.0	n.d.

[1] - Maximal solubility by eutectic temperature

Guha and Kolar[15] investigated the phase equilibria diagrams niobium carbide with transition metals iron, chromium, nickel, and cobalt. Solid solubilities and eutectic compositions are shown in **table 4** and the phase systems NbC-Fe and NbC-Cr in **figure 6**. Eutectic points are deplaced near the metal side and the solid solubilities are in the range 1 to 4.3% Guha and Kolar[16] investigated also the phase diagrams TiC-Cr and ZrC-Cr in **figure 7**. EPMA results in **table 5** indicate small solid solubility and eutectic point deplaced on metal side.

Table 4: Phase composition in binary phase equilibria systems NbC-Fe, NbC-Cr, NbC-Ni, and NbC-Co
J. P. Guha and D. Kolar: *J. Less-Common Metals*, 29 (1972) 33-40

System	Eutectic	Solid solution[1],wght.%	
	wght.% metal	metal in NbC	NbC in metal
NbC-Fe	91.2	1.8	0.98
NbC-Cr	76.0	2.8	0.85
NbC-Ni	89.0	1.8	3.5
NbC-Co	88.0	1.2	4.3

[1] - Maximal solubility by eutectic temperature

Table 5: Phase composition in binary phase equilibria systems TiC-Cr and ZrC-Cr
J. P. Guha in D. Kolar: *J. Less-Common Metals*, 31 (1973) 331-343

System	Eutectic	Solid solution[1],wght.%	
	Metal,wght.%	Metal in carbide	Carbide in metal
TiC-Cr	89.0±0.5	3.5	3.5
ZrC-Cr	88.0±0.5	4.5	0.2

[1] - Maximal solid solubility at eutectic temperature

Finally Guha and Kolar[17] established also the phase diagram $BaTiO_3$-$BaGeO_3$ on **figure 8 and 9**, determined

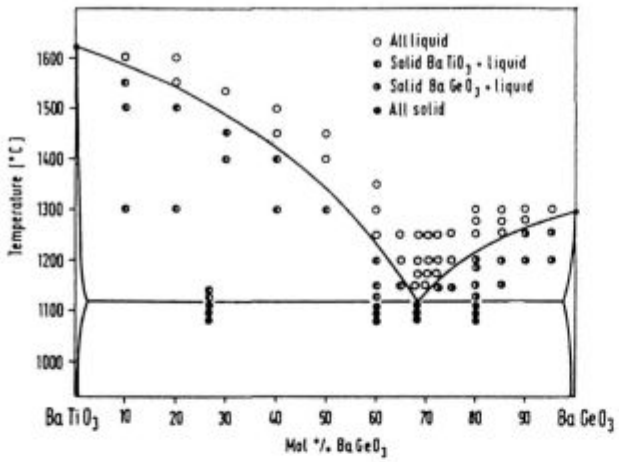

Figure 9: Phase diagram $BaTiO_3$-$BaGeO_3$. Ref. 17
Slika 9: Fazni diagram $BaTiO_3$ - $BaGeO_3$. Po viru 17

the liquidus and solidus temperature, the eutectic composition as well as the solid solubilities 1 of mol % $BaTiO_3$ in $BaGeO_3$ and 2.2 mol % of $BaGeO_3$ in $BaTiO_3$ at eutectic temperature.

5 CONCLUSION

The slovenian research community obtained relatively late the possibility to use EPMA at acceptable time and expense as standard research method for in situ quali and quantitative investigations of solid materials. Statistical data show that the community was well prepared for the use of the new facility. For that reason, the use expanded relatively fast in research academic and industrial laboratories in metallurgy, geology, mineralogy, ceramic, building materials and electronics. On average, in the first years more EPMA work was performed for industrial companies than academic institutions. D. Kolar was between the researchers which did profit the must from EPMA. Based on optical microscopy and EPMA he and his collaborators reported in international journals on significant findings on topics of magnet ceramics and binary phase equilibria systems of metals and carbides as well as sulfide compounds. It is therefore justifield to conclude that D. Kolar helped greatly to strengthen EPMA as rutine investigation method for basic, applied and development research of metallic and non metallic materials.

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