Effect of Particle Size and Particle Size Distribution on Physical Characteristics, Morphology and Crystal Structure of Explosively Compacted High-Tc Superconductors

I. Kotsis, M. Enisz, D. Oravetz, A. Szalay*
University of Veszprém, Hungary
*Metalltech Ltd. Budapest, Hungary

ABSTRACT

A superconductor, of composition $Y(Ba,K,Na)_2Cu_3O_x/F_y$ and a composite, of composition $Y(Ba,K,Na)_2Cu_3O_x/F_y + Ag$, with changing K, Na and F content, but a constant silver content (Ag = 10 mass per cent) was prepared using a single heat treatment. The resulting material was ground in a corundum lined mill, separated to particle size fractions of 0-40 μm, 0-63 μm and 63-900 μm and explosively compacted, using an explosive pressure of 10^4 MPa and a subsequent heat treatment. Best results were obtained with the 63-900 μm fraction of composition $Y(Ba_{1.95}K_{0.01})Cu_3O_xF_{0.05}/Ag$: porosity < 0.01 cm^3/g and current density 2800 A/cm^2 at 77 K.

INTRODUCTION

The raw material, synthesized for explosive compaction was a superconducting solid solution, of composition $YBa_2Cu_3O_{7-\Delta}$, with Ba-ions partly replaced by alkali ions, and oxygen ions by fluoride ions. In some of the experiments a superconductor/silver composite was used.

According to I-Wei Chen [1] superconducting properties are less affected by oxygen content and sintering parameters if alkalis are substituted for barium.

Nedkov and Dragieva [2] studied superconductors, of general composition $Y_{1-0.2x}Ba_{2-0.2x}M_xCu_3O_{7-\Delta}$, where M = Li, K, Na, and found that with increasing sintering temperature the shape of the magnetic susceptibility vs. temperature plot is changed as contrasted to pure $YBa_2Cu_3O_7$. The most striking change was shown in case of K-doped sample. As the density of samples was also changed, in the order of nondoped > K > Na > Li, their obvious explanation was that doping ions occupy a part of lattice vacancies. The comparative XPS investigation of the K-containing and nondoped samples showed an increased number of trivalent copper ions, to be explained with the transformation of

$$Cu^{2+} + Ba^{2+} = K^+ + Cu^{3+}$$ [3]

Nedkov and co-workers [4] tried another possibility too: to replace even copper by alkalis (K^+, Na^+, Li^+) in superconducting ceramics. The change in the valency state of copper can be described by the formula

$$Y^{3+}Ba_2^{2+}M_x^+Cu_{3.5-2x}^{2+}Cu_x^{3+}O_{7-\Delta}^{2-}$$
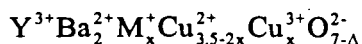
Superconducting crystals increase in size as a consequence of alkali substitution for Ba^{2+} ions (2.5 mol.%), even in case of identical heat treatment (Enisz, Kotsis, [5]). This tendency increases in the order of Na < K.

YBa$_2$Cu$_3$O$_7$F and YBa$_2$Cu$_3$O$_6$F$_2$ should be mentioned among fluoride-containing superconductors [6, 7, 8]. These have been prepared by solid state reactions, from BaF$_2$, CuF$_2$ and YF$_3$ showing a slight improvement of Tc and other superconducting properties. If, however, the YBa$_2$Cu$_3$O$_{7-\Delta}$ phase is thermally treated at 300 °C in NF$_3$ gas, then only the Meissner effect is improved considerably.

The joint partial replacement of Ba^{2+} ions by Na^+ and K^+, and of oxygen ions by fluoride ions (Kotsis and Enisz [9]) result in an increase of Tc (by 6-10 K), of bulk density and of critical current density.

YBa$_2$Cu$_3$O$_{7-\Delta}$/Ag composites were designed primarily for HIP technology (Hendrix, Borofka [10, 11]), showing that the incorporation of silver brings improvements in workability; besides that the composite is denser, has a higher critical current density and even its soldering properties are improved. Silver is present primarily as a metal in this composite. A superconductor, of composition YBaAg$_3$O$_x$ (Tc = 50 K) is also known. A partial replacement of copper by silver in YBaCu$_3$O$_{7-\Delta}$ superconductors results in the formation of a multiphase material, simultaneously with a decreased Tc.

EXPERIMENTAL

Aim:
Preparation of a composite substance, of composition Y(Ba,K,Na)$_2$Cu$_3$O$_x$F$_y$ + Ag which can be well shaped with explosive compacting, and its density, critical current density and solderability enables practical application.

Materials:
The following raw materials were used: Y$_2$O$_3$ (purity 99.99%, surface area 18.1 sq. m/g (Merck); Ba(OH)$_2$.8H$_2$O; CuO (surface area 18.4 sq. m/g, prepared by a 500 °C/1h heat treatment of basic copper carbonate,

$CuCO_3.Cu(OH)_2.nH_2O$; $KF.2H_2O$; NaF; and $AgNO_3$. All chemicals were of r.g.purity.

Weighed batches of dry raw materials were shaped into pressed pellets (dia 25 mm, high 3 mm), and fired in an electric kiln in oxygen (15 dm^3/h flow velocity). Heating and cooling rate was 300 $°C/h$. The pressure used was 25 MPa.

Equipment:

The pore volume of heat treated samples was measured by a Carlo Erba type mercury porosimeter.

The phase composition of the heat treated samples was determined by X-ray diffraction analysis. These measurements were carried out by means of a Philips-1825 type instrument. The lattice parameters were calculated by a regression analysis of data corrected for systematic error.

Magnetic susceptibility was measured in Brucker's device according to Faraday's principle.

Critical current density was investigated with the system consisting of a Solartron-Schlumberger 7071 type voltmeter and a DC Power Supply current generator.

The microstructure of the heat treated samples was examined by a JEOL JSM 50A type scanning electron microscope.

RESULTS

Results are summarized in Table 1. The second column shows calculated compositions of the batches, the third the actual chemical composition of fired samples.

Table 1. Composition of batches and fired samples
(Fired samples contain 10% (m/m) Ag)

Designation	Calculated composition of batch	Composition of fired sample
KF	$Y(Ba_{1.95}K_{0.05})Cu_3O_xF_{0.05}$	$Y(Ba_{1.95}K_{0.02})Cu_3O_xF_{0.05}$
KF/Ag	$Y(Ba_{1.95}K_{0.05})Cu_3O_xF_{0.05}/$ Ag	$Y(Ba_{1.95}K_{0.01})Cu_3O_xF_{0.05}/$ Ag
NaF	$Y(Ba_{1.9}Na_{0.1})Cu_3O_xF_{0.1}$	$Y(Ba_{1.9}Na_{0.1})Cu_3O_xF_{0.1}$
NaF/Ag	$Y(Ba_{1.9}Na_{0.1})Cu_3O_xF_{0.1}/$ Ag	$Y(Ba_{1.9}Na_{0.07})Cu_3O_xF_{0.1}/$ Ag
NaKF	$Y(Ba_{1.9}Na_{0.05}K_{0.05})Cu_3O_x$ $F_{0.1}$	$Y(Ba_{1.90}Na_{0.05}K_{0.02})Cu_3O_x$ $F_{0.1}$
NaKF/Ag	$Y(Ba_{1.9}Na_{0.05}K_{0.05})Cu_3O_x$ $F_{0.1}/Ag$	$Y(Ba_{1.90}Na_{0.03}K_{0.01})Cu_3O_x$ $F_{0.1}/Ag$

Investigation results clearly show that no fluoride losses occur during heat treatment; alkali ions, however, behave in a different way. In silver-free samples, the Na quantity remains unchanged after firing, while the K quantity is reduced by two-thirds; in silver-containing samples, both Na and K are reduced during firing.

Those pellets were selected for further investigation which show favorable $\kappa = f(T)$ characteristics (Fig. 2). As well seen in the figure, a minimum change of the plot, in the presence of silver, is shown by samples containing K-ions.

Fig. 3 shows that the presence of silver, according to XRD patterns, changes the ratios of other crystalline phases. Approx. 5 % (m/m) CuO, $BaCuO_2$ and Y_2BaCuO_5 can be seen, besides approx. 85 % (m/m) orthorhombic superconducting phase and approx. 10 % (m/m) silver phase.

Porosity of fired pellets is shown in Table 2. In this table total porosity (ΣV_p), porosity over 7500 nm (r >7500 nm V_p) and porosity below 7500 nm are shown; in the latter case, pore size distribution is indicated too. Here "r" means pore radius, while "$R\%$" the quantity of the pores $> r$, expressed in % (V/V).

Table 2. Porosity of sintered KF and KF/Ag samples

Designation	ΣV_p (cm³/g)	V_p (cm³/g)			
		$r >$7500 nm	$r <$7500 nm	r (nm)	$R\%$
KF	0.2570	0.1159	0.1411 {	1500	73
				1250	83
				682	93
				183	100
KF/Ag	0.0612	0.0462	0.0150 {	1250	73
				682	83
				183	91
				150	100

As well seen in Table 2., the porosity of the KF sample is decreased to its quarter upon the addition of 10 % Ag. The volume ratio of pores > 7,5 μm radius increases from 45 % to 75 %, while that of <7,5 μm decreases from 55 % to 25 %, with a simultaneous decrease of pore sizes.

Samples in pellet form were ground in a corundum mill and the ground product separated to particle size fractions 0-40 μm, 0-63 μm and 63-900 μm. These fractions were then explosively compacted in the device shown in Fig. 1. By increasing explosive pressure from 10^3 MPa to 10^4 MPa, the surface of crystals became destructed (fraction 0 - 40 μm, sample KF) as seen in the polished surface electron micrograph (Fig. 4.). Table 3. summarizes the porosities of explosively compacted samples (explosive pressure = 10^4 MPa).

Table 3. Porosity of explosively compacted samples

Designation	Particle size range (μm)	Total porosity (cm^3/g) ΣV_p after explosive compaction
KF	0 - 40	0.05
	0 - 63	0.0375
	63 - 900	0.0322
KF/Ag	0 - 40	0.0306
	0 - 63	0.0282
	63 - 900	0.0203

The comparison of porosities clearly shows that highest density can be achieved of the 63 - 900 μm fraction of sample KF/Ag: this is only one third of the same sintered, and only 1/13 part of the silver-free sintered sample.

Fig. 5. clearly shows that the decrease of porosity causes only little changes in the susceptibility vs. temperature plot in case of the KF and KF/Ag samples. In explosively compacted samples critical current density increases with decreasing porosity, to reach a highest value of 800 A/cm^2 at 77 K. The porosity can be reduced to a value of < 0.01 cm^3/g using a subsequent heat treatment (850 °C, 10 h, 15 dm^3 oxygen/h). This increased the critical current density up to 2800 A/cm^2 at 77 K. Figs. 6., 7. show SEM micrographs of the fracture surfaces of sintered KF and KF/Ag samples; the similar micrograph of the explosively compacted, 63 - 900 μm sample is shown in Fig. 8. It is striking that average crystal size in Fig. 8. is smaller than individual crystal size in Fig. 7. All this means that explosive shock separates relatively coarse particles, glued either via a bond phase or a boundary phase to yield a favorable, dense steric arrangement. A disintegration of particles takes place too, albeit to a lesser extent only.

As a result of subsequent heat treatment the particle size increased (Fig. 9.) besides decreasing of porosity causing a higher value of critical current density.

CONCLUSIONS

- The heat treatment of $Y(Ba,K,Na)_2Cu_3O_xF_y$-based superconducting ceramics does not decrease the Na and F content of the batch, while the K content is reduced to 1/3 of the original.
- The heat treatment of a composite containing 90 % (m/m) $Y(Ba,K,Na)_2Cu_3O_xF_y$ and 10 % (m/m) Ag results in the constancy of F, a

decrease of K to 1/5 of its original value and a decrease of Na by 30 - 35 % (m/m).

- The minimum amount of explosive pressure to reach a satisfactory density is 10^4 MPa, in case of $Y(Ba,K)_2Cu_3O_xF_y$ and $Y(Ba,K)_2Cu_3O_xF_y/Ag$ samples.
- The density of the product can be affected to a high extent by changing the particle size of the starting material.
  - The silver-containing composite gives higher density.
  - Density of final samples shows the order of 0 - 40 μm < 0 - 63 μm < 63 - 900 μm.
- Best result achieved in this series of experiments: critical current density = 2800 A/cm^2 at 77 K, porosity < 0.01 cm^3/g, using a $Y(Ba,K)_2Cu_3O_xF_y$ + Ag (90 + 10 % m/m) composite, 63 - 900 μm fraction, 10^4 MPa explosive pressure and a subsequent heat treatment.

REFERENCES

[1] I-Wei Chen, S. Keating, C.Y. Keating, X. Wu, J. Xu, P.E. Reyes-Morel, T.Y. Tien: Adv. Cer. Mat. 2, 3B (1987) 457-470

[2] I. Dragieva, I. Nedkov: IEEE, Trans. Magn. Mag., 26 (5) (1990)

[3] I. Felner: Thermochimica Acta, 174 (1991) 41-69.

[4] I. Nedkov, I. Iliev, S. Tinchev, M. Taslakov, V. Kojucharov: Supercond. Sci. Technol. 1 (1989) 324-325.

[5] M. Enisz, I. Kotsis, T. Korim, D. Oravetz, É. Kristóf: Relation between the physical properties and microstructure of the high-T_c $YBa_2Cu_3O_x$-based ceramic superconductors containing K$^+$ and Na$^+$ ions. 7th CIMTEC, Satellite Symp. Triest 2-5 July (1990), 135.

[6] J.S. Kim, J.S. Swinnea, A. Manthiram, H. Steinfink: Solid State Commun. 66 (1987) 287.

[7] K. Kobayashi: J. Am. Ceram. Soc. 73 (1) (1990) 146-147.

[8] A.G. Klimenko, V. Ye. Fedorov: Thermochimica Acta 174 (1991) 71-83

[9] I. Kotsis, M. Enisz: Effect of Alkali fluoride additives on the properties of superconductors of the system Y-Ba-Cu-O, 8th SIMCER Int. Symp. on Ceramics, Rimini 9-14 Nov. (1992), Proceedings of the Conference

[10] B.C. Hendrix, T. Abe, J.C. Borofka, P-C Wang, J.K. Tien: J. Am. Ceram. Soc. 76 (4) (1993) 1008-1010.

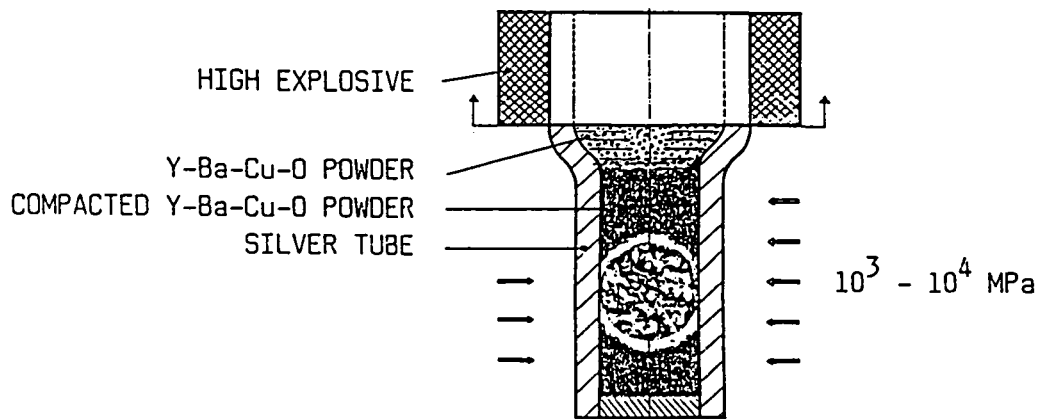[11] J.C. Borofka, B.C. Hendrix, A.J. Attarwala, J.K. Tien: J. Am. Ceram. Soc, 76 (4) (1993) 1011-1016.]
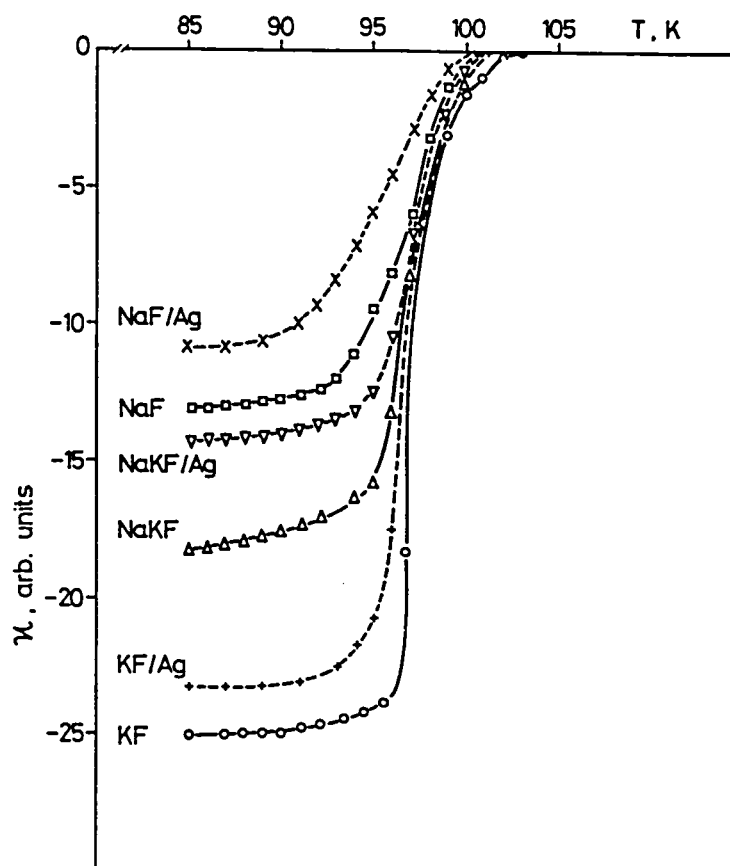
Fig. 1. Scheme of explosive powder compaction

Fig. 2. $\kappa = f(T)$ for superconducting pellets (B = 1 tesla)
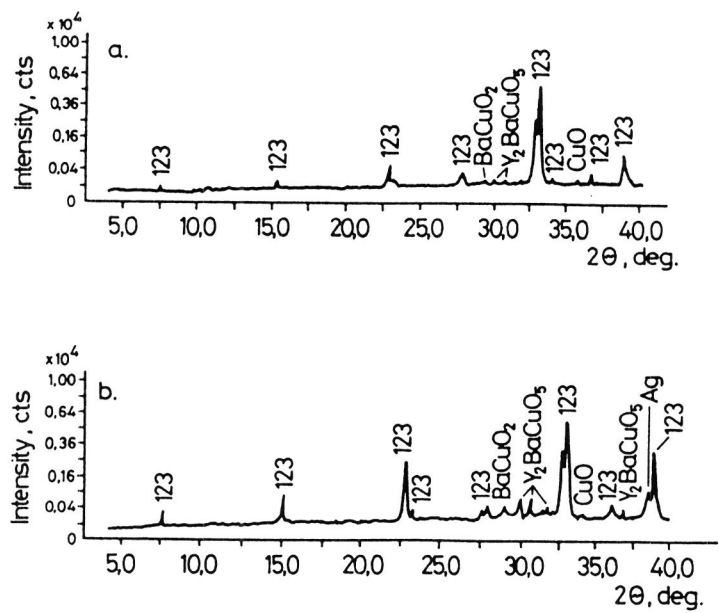
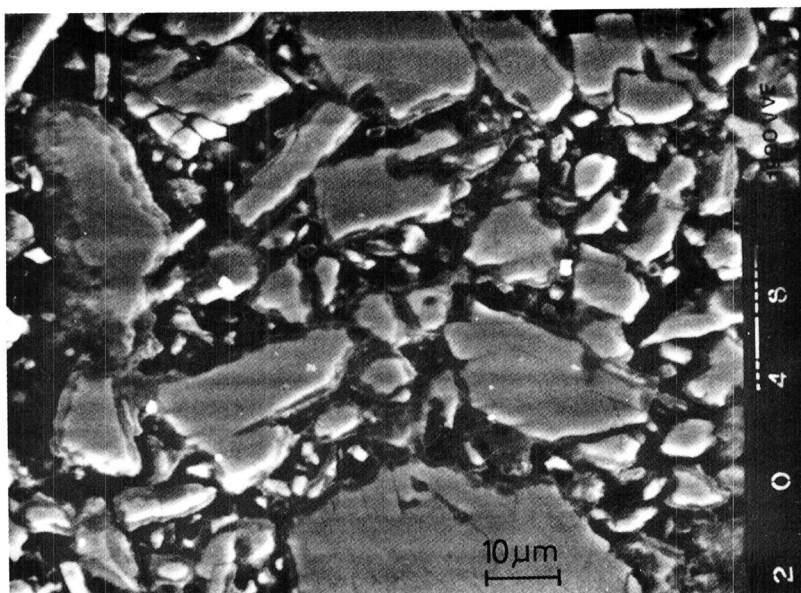Fig. 3. X-ray diffraction patterns of KF (a) and KF/Ag (b) pellets

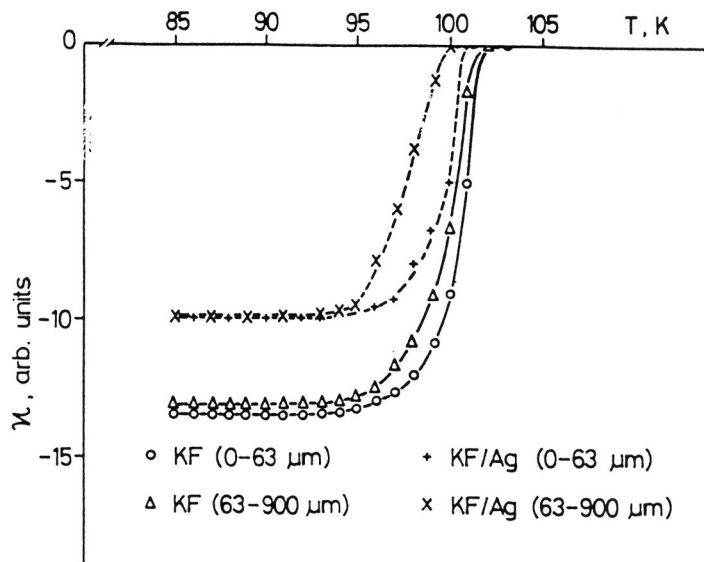Fig. 4. Polisched surface of an explosively compacted sample

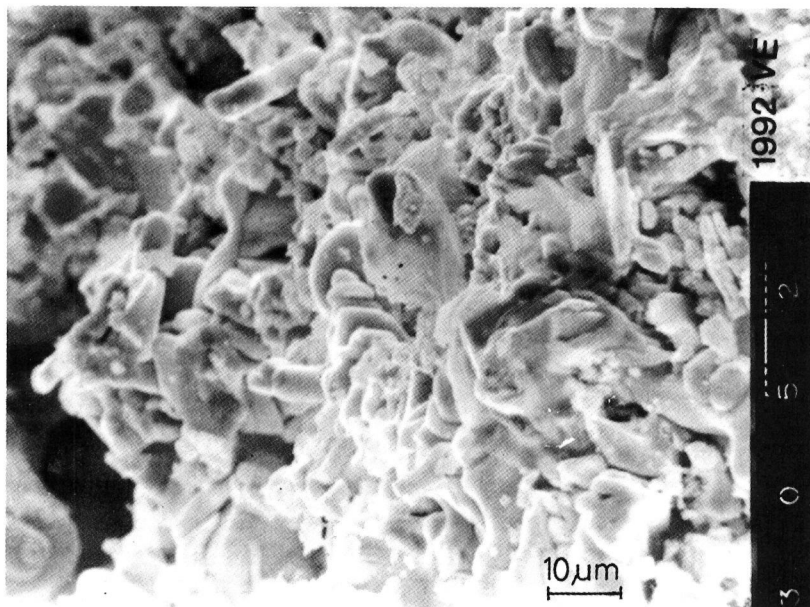Fig. 5. $\kappa = f(T)$ for explosively compacted samples (B = 1 tesla)
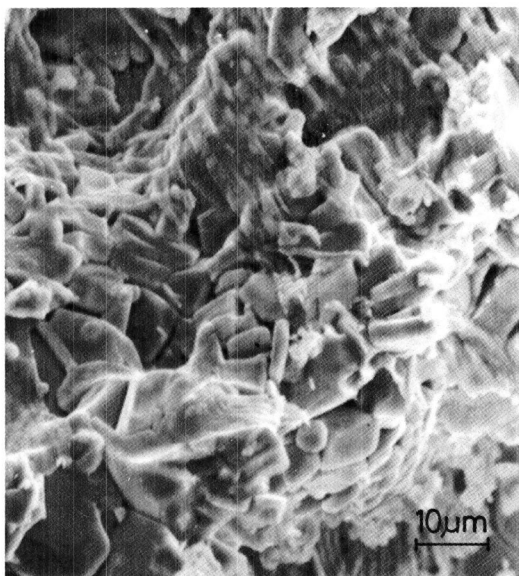

Fig. 6. Fracture surface of the sintered KF sample

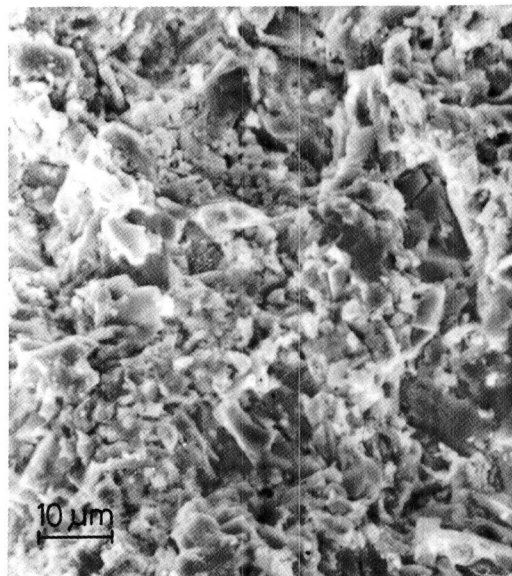Fig. 7. Fracture surface of the sintered KF/Ag sample

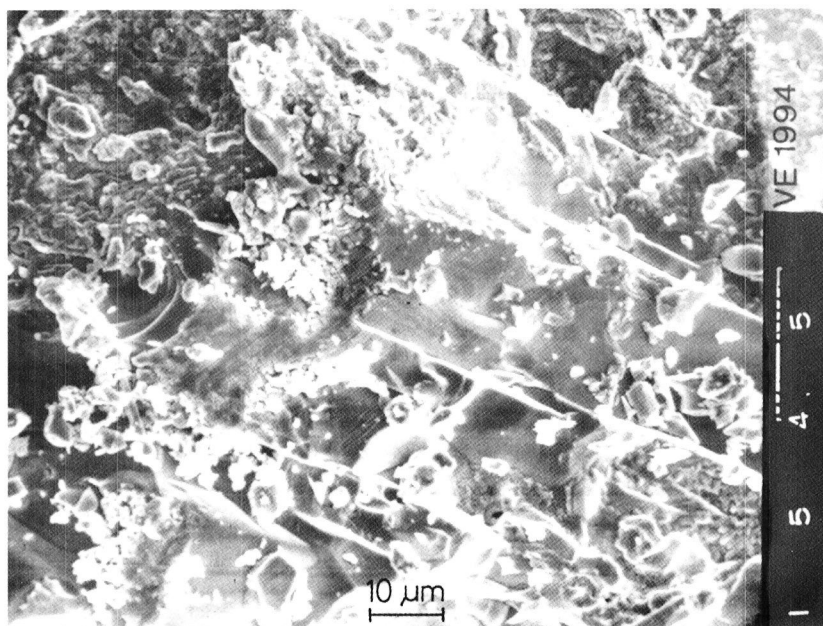Fig. 8. Fracture surface of the explosively compacted, 63-900 μm KF/Ag sample

Fig. 9. Fracture surface of the explosively compacted KF/Ag sample after subsequent heat treatment