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Thermal expansion of beta-alumina-type phases and variation of lattice parameters with potassium content

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When polycrystalline potassium beta-alumina or potassium gallate were bonded to potassium ferrite by a hot pressing technique cracks appeared at the interface. This did not happen when they were bonded to equimolar potassium beta-alumina–potassium ferrite or potassium gallate–potassium ferrite solid solutions respectively. The suspected thermal expansion mismatch was confirmed by thermal expansion measurements which yielded values for potassium ferrite that were twice those for potassium beta-alumina or potassium gallate. Solid solutions gave intermediate expansion coefficients. When the potassium concentration in potassium ferrite was altered by coulometric titration the *a* hexagonal lattice parameter increased slightly with increase of potassium concentration while the *c* lattice parameter decreased. The implication of these factors on the preparation of stable solid solution electrode–solid electrolyte interfaces is discussed.

1. Introduction

Compounds with the beta-alumina structure may be represented by the general formula $M(I)_{1+x}M(III)_{11}O_{17}$ where M(I) is a univalent metal, M(III) is Al, Ga, or Fe and x lies between 0 and 1. This formula is approximate in that when $x > 0$, M(III) vacancies or O interstitials are present, maintaining overall charge neutrality. All are good two-dimensional M(I) ion conductors at temperatures above about 200° C and in addition the iron-containing compounds (ferrites) are also electronic conductors. The latter are thus of considerable interest as electrode materials to use in conjunction with the aluminium or gallium phases as electrolytes in solid state electrochemical cells [1–4]. Because these electrodes and electrolytes are isostructural and have a wide range of mutual solubility [4–6] it would seem likely that they could be bonded together in polycrystalline form to yield a "good" electrochemical interface – that is one with a high ionic exchange current. Hever [1] showed that for symmetrical sandwich cells with sodium or potassium beta-alumina electrolyte and mixed ferrite–beta-alumina electrodes, the current–time behaviour when voltage steps were imposed across the cell could be explained adequately considering only bulk chemical diffusion in the electrodes and a constant ohmic electrolyte resistance, without any "interface effects". This suggests that unhindered self-diffusion of ions can take place across the electrode–electrolyte boundary in either direction. Normal Faradaic electrode processes need not be present since the ions are not "discharged" but their charge merely compensated for by addition of electrons to the iron sub-lattice [3, 7]. Alkali ion self-diffusion coefficients of the order of 10^{-6} cm^2 sec^{-1} at 300° C are typical of these phases [8, 9], from which self-diffusion controlled exchange currents of the order of 10^4 A cm^{-2} (in the easy conduction direction) may be anticipated.

Attempts to fabricate these interfaces by hot-pressing together potassium beta-alumina [KA] and potassium ferrite [KF] at 1150 to 1250° C invariably led to cracking at the interface and the assembly often fell apart completely. Substituting potassium gallate [KG] for KA was no more

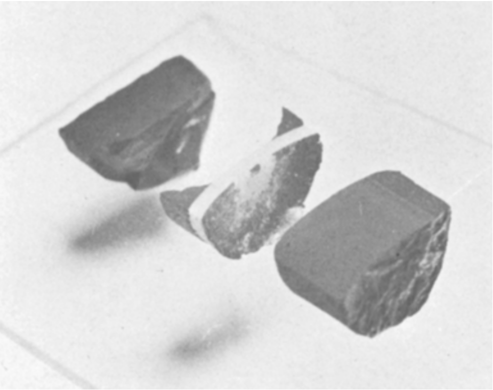

Figure 1 Sectioned sandwich of KF/KG/KF made from cold pressed compacts subsequently hot pressed together in oxygen at 1150° C, 4.5×10^7 Nm^{-2} pressure for 5 h.

successful as can be seen from Fig. 1. The shape of the fracture faces strongly suggests contraction of the KF phase with respect to KG due to a difference in thermal expansion coefficients. Furthermore, when equimolar solid solutions of KF and KA or KF and KG were bonded to KA or KG respectively, cracks did not appear. This led to a study of the thermal expansion behaviour of the three pure phases and of selected solid solutions between them.

Another factor expected to influence the stability of such interfaces is the variation in lattice parameters of the electrode material as the potassium content changes during charge and discharge of the cell. This has also been investigated.

2. Experimental

Interfaces between electrodes and electrolytes were prepared by assembling flat disks of the two phases, wrapping in platimum foil and hot pressing in alumina powder in an alumina die in an oxygen atmosphere. Pressures in the region (2.5 to 5.0) $\times 10^7$ N m^{-2} were applied for 5 to 6 h whilst the samples were at temperatures between 1150 and 1250° C. Pressure was released during cooling. The disks used were either already hot pressed and machined flat (method A) or just cold pressed powder in the β'' modification (which converted to the beta form during hot pressing), (method B). Further details of preparation of the individual phases are given in [4]. A Cambridge Instruments Stereoscann IIA was used to study the composition variations across the interface. Samples were cut on an annular diamond saw with oil lubricant, ground and polished through a series of laps down to 1 μm diamond paste, and finally carbon coated.

Preliminary thermal expansion measurements were conducted on dense, hot-pressed polycrystalline samples of KA, KF and KG that had been machined into cubes of side 6 mm. A simple dilatometer was used employing a silica support tube and push rod, resistance furnace and a linear transducer. This showed KF to have an unexpectedly high thermal expansion coefficient compared to the other two phases. Since the beta-alumina structure is hexagonal and thus non-isotropic a knowledge of the thermal expansion coefficients in both the *a* and *c* directions is desirable. The main measurements were therefore made using an evacuable high temperature X-ray diffractometer. The powdered sample was spread thinly onto a platinum support which also acted as an internal standard according to the technique described by Henderson and Taylor [10]. Cobalt Kα radiation was used and the diffraction patterns were indexed with the help of data reported by Dyson and Johnson [11]. The 2θ values obtained were corrected by reference to the 1 1 1, 2 0 0, and 2 2 0 reflections of platinum using data by Campbell [12]. Eight to fourteen reflections were used in a least squares computation of the lattice parameters. For each material, the lattice parameters were determined at four temperatures between ambient and 400° C and finally again at room temperature. Except in the case of KA, higher temperatures were not used in order to lessen the risk of potassium evaporation or possible reduction of iron by traces of oil vapour.

To investigate the effect of changes in potassium content on the lattice parameters of KF, a polycrystalline sample was cut into three slices. One piece was used unchanged, whilst the other two were subjected to coulometric titrations at 300° C using the cell:

Pt / K ferrite / Kβ-alumina / K ferrite / Pt
"pump" sample

The ferrite marked "pump" acted as a source or sink of potassium ions, and a constant current was passed for a measured time in order to transfer a known quantity of potassium into or out of the sample of known mass. The whole assembly was maintained in a purified argon atmosphere. The lattice parameters were measured at room temperature using an ordinary X-ray powder diffractometer

TABLE I

Phases	Thermal expansion coefficient × 10^6					
	Diffractometer				Dilatometer	
	α_a	α_c	$\bar{\alpha}_{calc}$	Temp. range (° C)	$\bar{\alpha}$	Temp. range (° C)
KA	7.0	5.6	6.5	25–570	–	
$KA_{0.5}KF_{0.5}$	7.5	7.8	7.6	25–370	8.4	50–600
KG	6.4	7.3	6.7	25–390	7.1	50–600
$KG_{0.5}KF_{0.5}$	8.8	6.6	8.1	25–400	8.1	50–600
$KG_{0.25}KF_{0.75}$	10.0	6.9	9.0	25–360	–	
KF	13.8	–	–	25–400	12.1	50–600
Naβ-alumina	7.7	5.7	7.0	500–600 [14]		
$MgAl_2O_4$	7.81 (calculated from expression in [10] for 50–650° C)					
Fe_3O_4	15.6 [13]					

with CuKα radiation and a graphite monochromater. The samples were ground finely in a dry glove manipulater box, mixed with silicone grease and spread onto a glass slide. Exclusion of water vapour was further prevented by covering with a thin mylar film. Approximately 30% finely ground $MgAl_2O_4$ (spinel) was also mixed with the samples as an internal standard [10]. The potassium content of the unaltered sample was established by flame emission analysis after dissolution of a sample in cold concentrated hydrochloric acid.

3. Results and discussion

3.1. Thermal expansion

Thermal expansion coefficients are shown in Table I. The only literature values for β-type phases known to the authors are those for sodium beta alumina from 500 to 600° C referred to in [14], which are close to those for KA in this work. $\bar{\alpha}$ represents one third of the volume expansion coefficient and is therefore given by $\bar{\alpha} = 2\alpha_a/3 + \alpha_c/3$. The dilatometer gave $\bar{\alpha}$ values directly, since results obtained with the samples parallel to the hot pressing axis were the same within experimental error as results with the sample turned through 90°, indicating an essentially random orientation of crystallites within the polycrystalline samples. Agreement between the two methods of measurement is within the ± 5% experimental accuracy estimated for both techniques. In the case of KF no value is given for the *c*-axis thermal expansion coefficient due to problems discussed in Section 3.3. It can be seen that the *a*-axis values for KA and KF are very similar to those for the spinels $MgAl_2O_4$ and Fe_3O_4 respectively. In retrospect this is not surprising in view of the close resemblance between the $Al_{11}O_{16}$ "spinel block" units of the β-alumina structure and that of a true spinel. (For details of the β-alumina structure the reader is referred to [14]). The *a* parameter of the beta-alumina structure corresponds to one half of the 1 1 0 unit cell distance of the corresponding spinel. In the *c* direction the situation is more complicated. Thermal expansion in this direction can be divided into a contribution due to the spinel blocks and another from the conduction plane regions. The spinel blocks might be expected to expand isotropically, i.e. to the same extent as the *a* parameter, while the conduction plane contribution would be expected to be reasonably constant irrespective of the trivalent metal. The present data, however, are of insufficient accuracy to test this model adequately.

3.2. Variation of lattice parameters of potassium ferrite with potassium content

Fig. 2 shows the lattice parameters of KF as a function of potassium concentration x. The "as prepared" composition was $x = 0.50$. In addition corresponding literature data for sodium beta-alumina are shown for comparison. The *a* parameter as expected is relatively insensitive to alkali concentration in both cases. The *c* parameters on the other hand decrease as x increases, at least for low x values. If it is assumed again that the spinel blocks change isotropically there must be a considerable decrease in the width of the conduction planes (approx 4% on going from $x = 0.17$ to $x = 0.60$ in KF). This is not what might at first be expected on the basis of the results of ion-exchange experiments, which show that substitution of large alkali ions for small generally results in an increase in the c parameter. In that case,

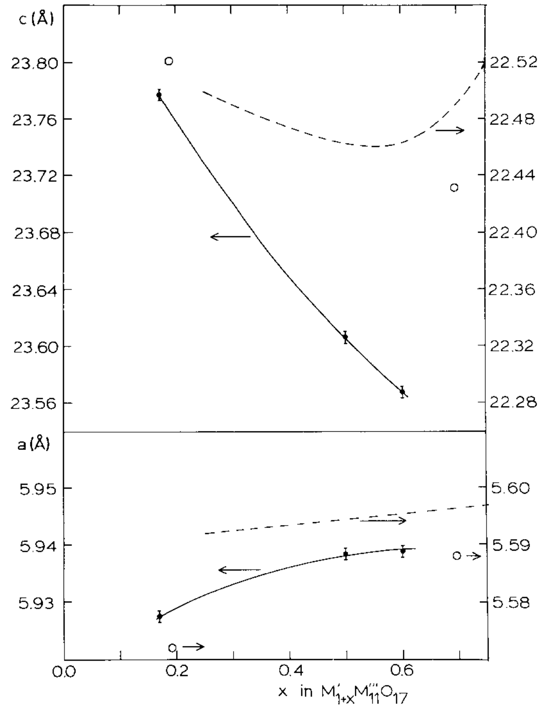

Figure 2 Variation in lattice parameters of KF as a function of potassium concentration x in K_{1+x} $Fe_{11}O_{17}$ (solid line). Data for sodium beta-alumina are shown for comparison; dotted lines: Harata [16], open circles: Liebertz [15].

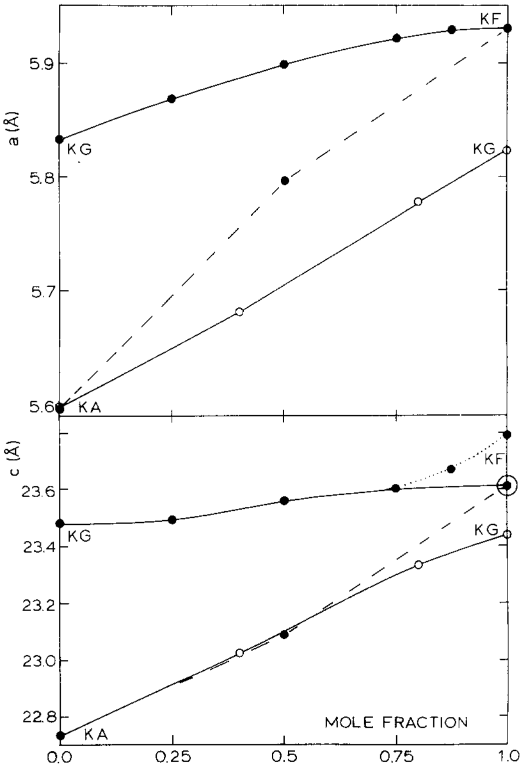

Figure 3 Lattice parameters for the three binary systems KG–KF, KA–KF and KA–KG at 25° C. Closed cirles: this work, open circles: Brinkhoff [18]. Encircled result is for dry KF. Results probably affected by water uptake are joined by dotted line.

however, the total mobile ion concentration remains the same and their simple point-change electrostatic contribution to the lattice would also remain unchanged, leaving only the effect of change in ion size. In the present case this is not so, and the changes in chemical bonding due to the added ions outweighs simple size effects accompanying increase in the conduction plane alkali ion population.

The rate of decrease in c with x is considerably larger in KF than in sodium beta-alumina. This may be explained by the nature of the defects that must be introduced to compensate for the charge carried by the extra alkali ions. In KF this is simply an electron added to an iron atom in the spinel block [3, 7], whereas in sodium beta-alumina two basic possibilities exist, aluminium vacancies or interstitial oxygen ions in the conduction plane [17]. If the last of these operates, the size effect mentioned above would be considerably enhanced.

The width of the conduction plane or "slot width" has been used frequently to account for variations in ionic conductivities between different size ions in different beta-alumina structure compounds [6, 14, 18]. The decrease in slot width with x in KF may well contribute significantly to the observed potassium ion conductivity as a function of x [4].

3.3. Lattice parameters of beta-alumina-type phases

Fig. 3 shows lattice parameters for the three binary systems formed from KA, KG and KF. Values for KA–KG are taken from Brinkhoff [18]. From the steady change of lattice parameters with composition and from the absence of double diffraction peaks at any composition used in the present work it would seem that complete solid solubility occurs in all three systems. However, magnetic susceptibility measurements have indicated a solubility gap between 38 and 57 mol% KF in KA [5] and the possibility of two phases with closely similar lattice parameters coexisting at some compositions cannot be completely ruled out. Lattice parameters of the three pure phases are compared with previously

TABLE II

Phase	Lattice parameters at 25°C						
	This work			Literature values			
	a(Å)	c(Å)	x	a(Å)	c(Å)	x	Ref.
KA	5.597	22.74		5.595	22.710		[11]
				5.596	22.729		[14]
				5.6000	22.738		[18]
KG	5.834	23.48		5.8229	23.439		[18]
				5.835	23.50		[19]
KF	5.928	23.78	0.17	5.932	23.80	0.06	[20]
	5.938	23.61	0.50	5.932	23.74	0.56	[20]
	5.939	23.57	0.60	5.916	23.79		[11]
				5.929	23.80		[7]
				5.93	23.91		[6]

published data in Table II. Agreement is close, considering the grossly non-stoichiometric nature of the compounds, except in the case of the c parameter of KF. The values obtained in Section 3.2 under strictly dry conditions are lower than most literature values as well as those obtained at room temperature during the thermal expansion measurements. The ferrite behaved anomalously during temperature cycling as can be seen from Fig. 4. This is believed to be due to water uptake by the sample at the lower temperatures and subsequent loss on heating. It was not possible to maintain a very high vacuum in the X-ray camera and the finely divided nature of the sample (compared to the dense sample used in the dilatometer) would greatly increase the rate of absorption. Large increases in the c parameter of β'' form sodium gallate have also been observed on exposure of small crystallites to damp air, the process reversing at 200 to 300° C [21]. It is not clear why KF should be more sensitive to water than the other beta-alumina-type compounds.

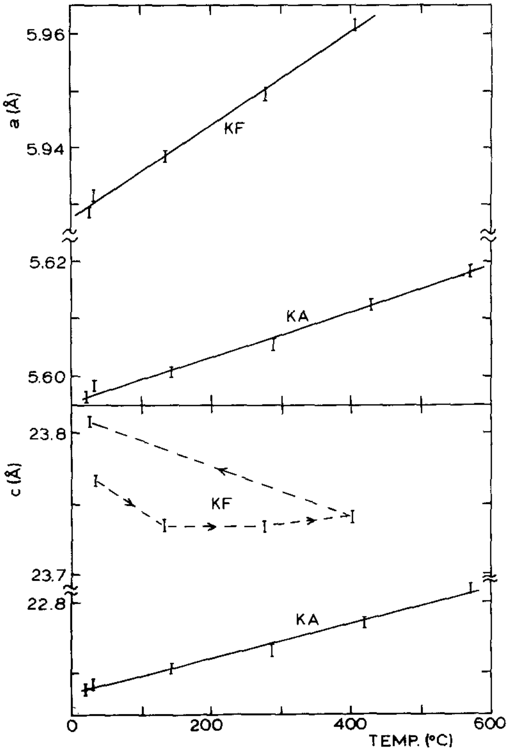

Figure 4 Variation of lattice parameters of KF and KA during temperature cycling.

3.4. Examination of interfaces

Fig. 5 shows the variations in composition across the interface of several compacts made under different conditions. Preparation of the compacts from pre-hot pressed pellets (method A) led to higher densities than when unsintered powders were hot pressed together in one operation, (method B) since the optimium sintering temperature varied in the order KA ⩾ KG > KF and a compromise temperature had to be chosen which led to low density in the higher temperature sintering phase or risked large grain growth in the other phase. Sample (a) was the KG–KF interface made by method B that fell apart after hot pressing and was shown in Fig. 1. The SEM photograph, taken across part of the interface that was still intact shows that the interface is associated with a very poorly sintered region from which cracks emanate. The remaining three samples all have "diluted" ferrite as one phase, and remained free of cracks. (b) and (c), both made by method A, show few pores and a reasonably smooth transition from one phase to the other. The region of interdiffusion of iron and gallium or aluminium is visible from the microprobe scans. From the sharper variations in composition at the low iron content ends compared to the high iron ends it may be inferred that the chemical diffusion coefficient varies in the same way as does the ease of sintering. In (d) a series of five cold pressed discs 0.5 mm thick with compositions ranging from 50 mol% KF–KG to KG were stacked together in sequence and hot pressed together to give a "graded seal". Although no cracks appeared the density was poor. Attempts to make graded seals from KF to KG have however still led to cracking.

4. Conclusions

In any electrochemical cell with solid electrodes and electrolyte a key requirement is to maintain

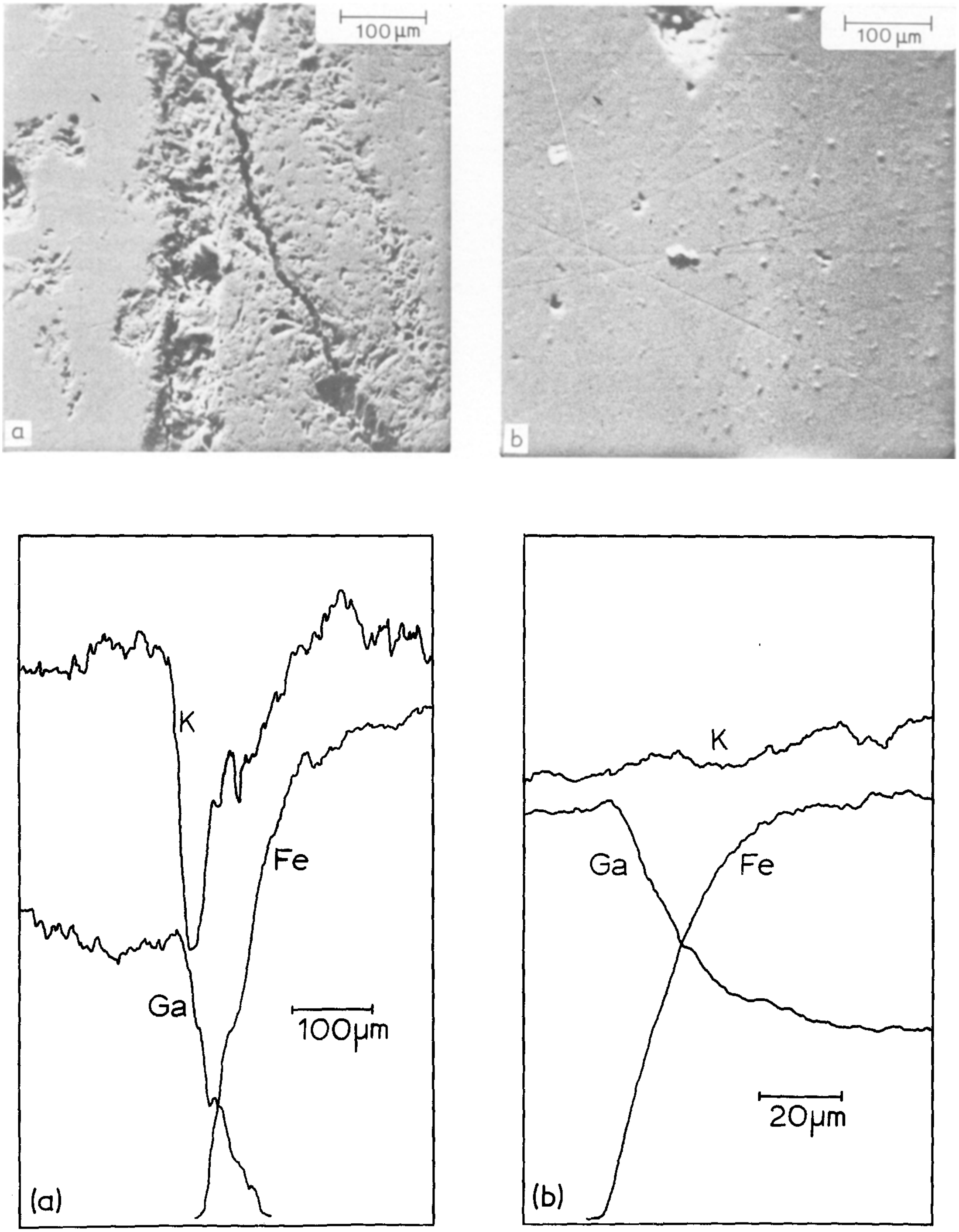

Figure 5 Electron microprobe examination of interfaces. In all photographs the interface runs vertically down the centre of the picture. (a) Part of sample shown in Fig. 1. (b) Assembly: $KF_{0.5}$–$KG_{0.5}$/KG using pre-hot-pressed pellets, hot pressed together in oxygen at 1150° C, × 10^7 N m^{-2} pressure, for 6 h.

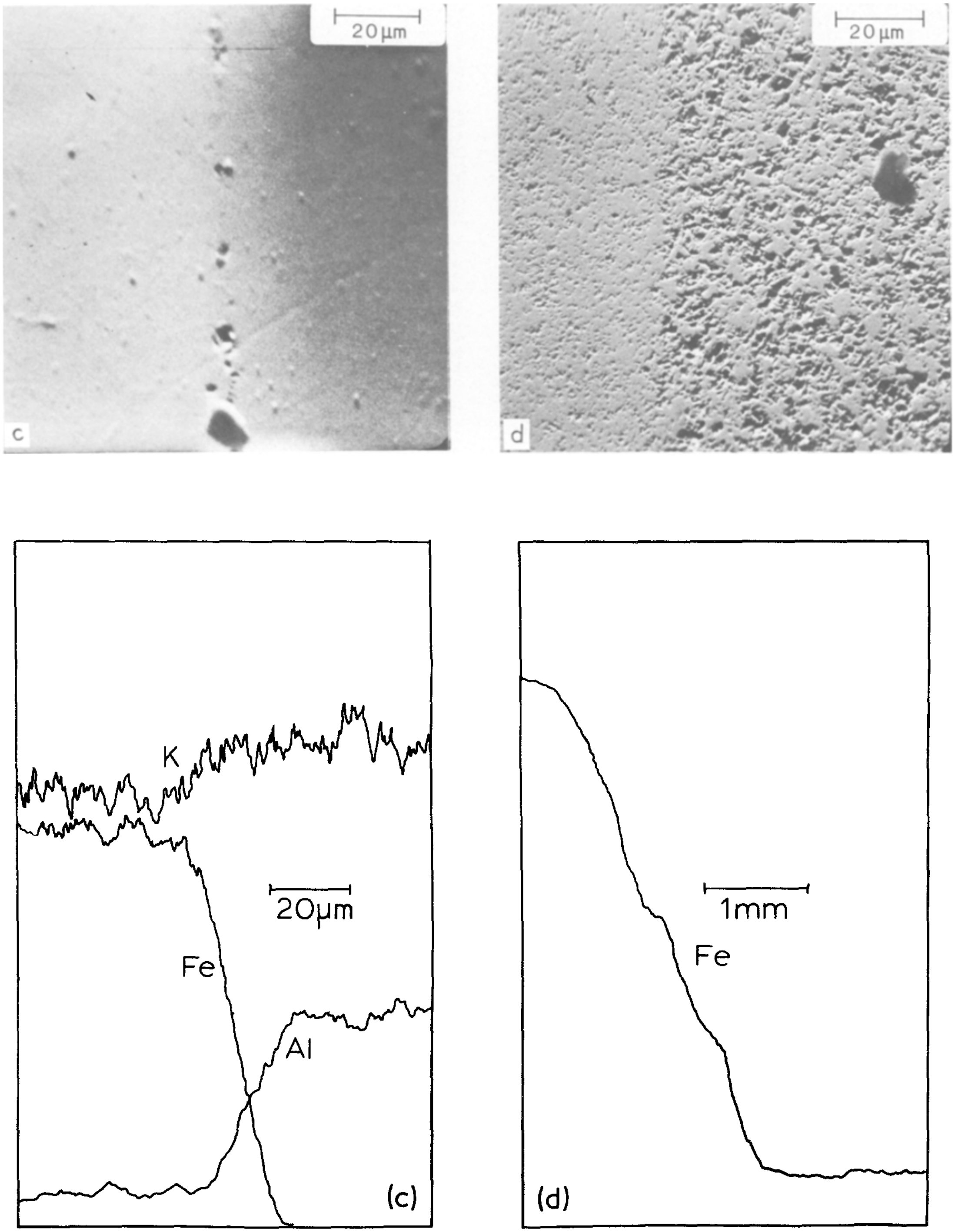

Figure 5 (c) Assembly: $KA/KF_{0.5}-KA_{0.5}$ using pre-hot-pressed pellets,hot pressed at 1250° C, 2.5×10^7 N m^{-2}, for 7 h. (d) "Graded Seal": $KF_{0.5}-KG_{0.5}/KF_{0.37}KG_{0.67}/KF_{0.25}KG_{0.75}/KF_{0.12}KG_{0.88}/KG$ made from cold pressed pellets. Subsequently hot pressed together in oxygen at 1150° C, 5×10^7 N m^{-2} pressure, for 6 h.

intimate contact between the two phases at all times. In a solid solution electrode [22] no new phases are produced during charge/discharge but the lattice parameters of the host structure must in general change. In this respect framework structures such as that of KF are better than layer structures such as titanium disulphide [23]. In addition the compounds KF and KA or KG have the advantage of mutual solubility. Nevertheless the change in volume accompanying charge/discharge between the KF compositions $x = 0.17$ and $x = 0.6$ is 0.51% compared with 0.3% for cooling KF (with $x = 0.6$) from 900° C (at which the material is probably no longer plastic) to 25° C (assuming $\alpha c = 9 \times 10^{-6}$ and that the thermal expansion coefficients are constant up to 900° C). Furthermore on cooling a KF–KG or KF–KA compact the KG or KA will itself contract by about half this value leaving a differential between the two phases of about 0.15%. Yet this last amount still resulted in fracture of the interface. Mechanical strength data are not available for KF so that the critical stresses involved cannot be calculated. However it must be remembered that in KF by itself the *c*-axis will be under considerable internal compression due to its anisotropic thermal expansion which is at least equal to and most probably greater than that of KA or KG. At the temperature of formation KF is only stable between the compositions $x = 0.62$ and $x = 0.83$ [24]. Thus initial compositions must be in this range of stoichiometry and subsequent lowering of x electrochemically will add further to the strain.

Further work on "graded seals" may solve some of the difficulties encountered in forming electrode–electrolyte interfaces in this system, but the study has indicated some of the severe problems which can arise.

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