High Temperature Stability of Potassium Beta"-Alumina

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Electric Power Section

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Objectives:

Evaluate the stability of potassium beta" alumina under potassium AMTEC operating conditions.

Evaluate the stability regime in which potassium beta" alumina can be fabricated.

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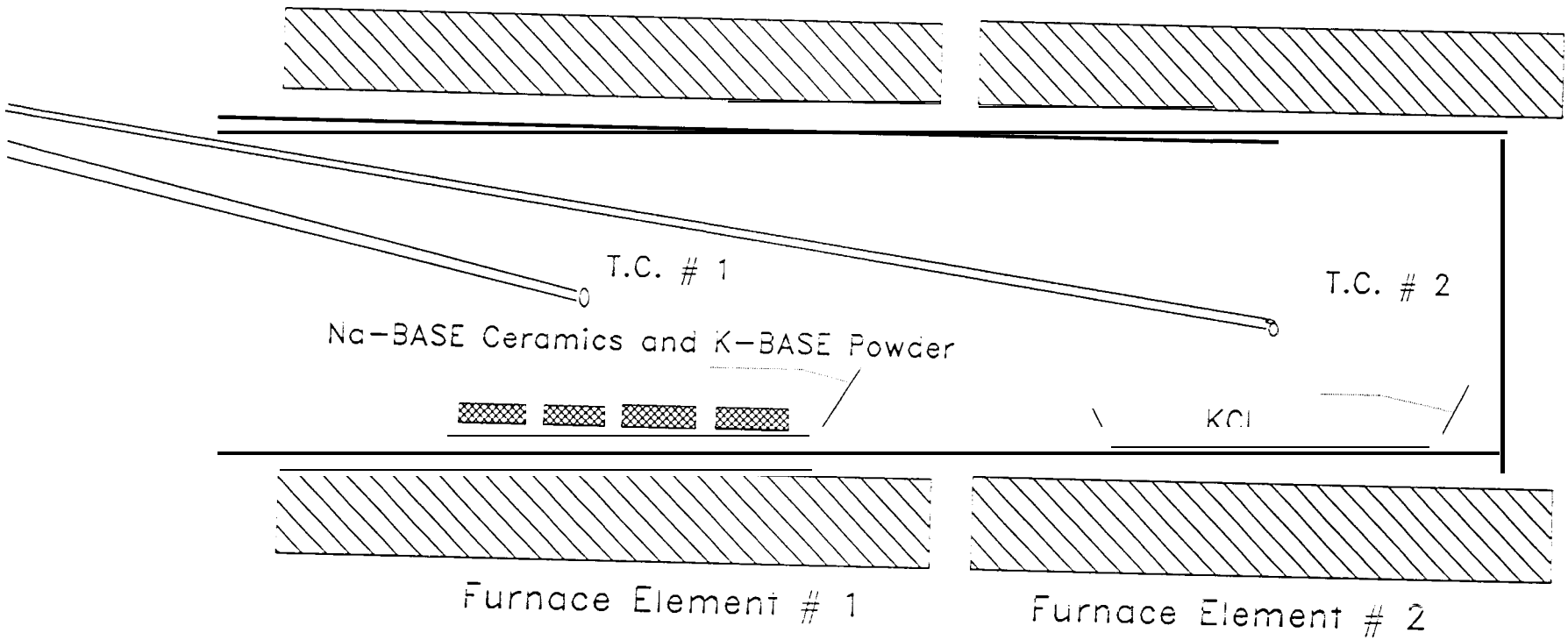

Figure V-3-1. Arrangemen o Furnace , Sample and KCl Boats, and Thermocouples for Exchange of Na-BASE to K-BASE.

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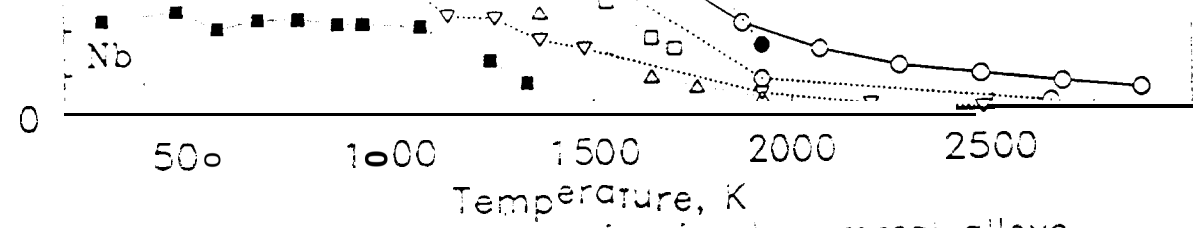


Fig. 2. Typical tensile strengths of refractory metal alloys.

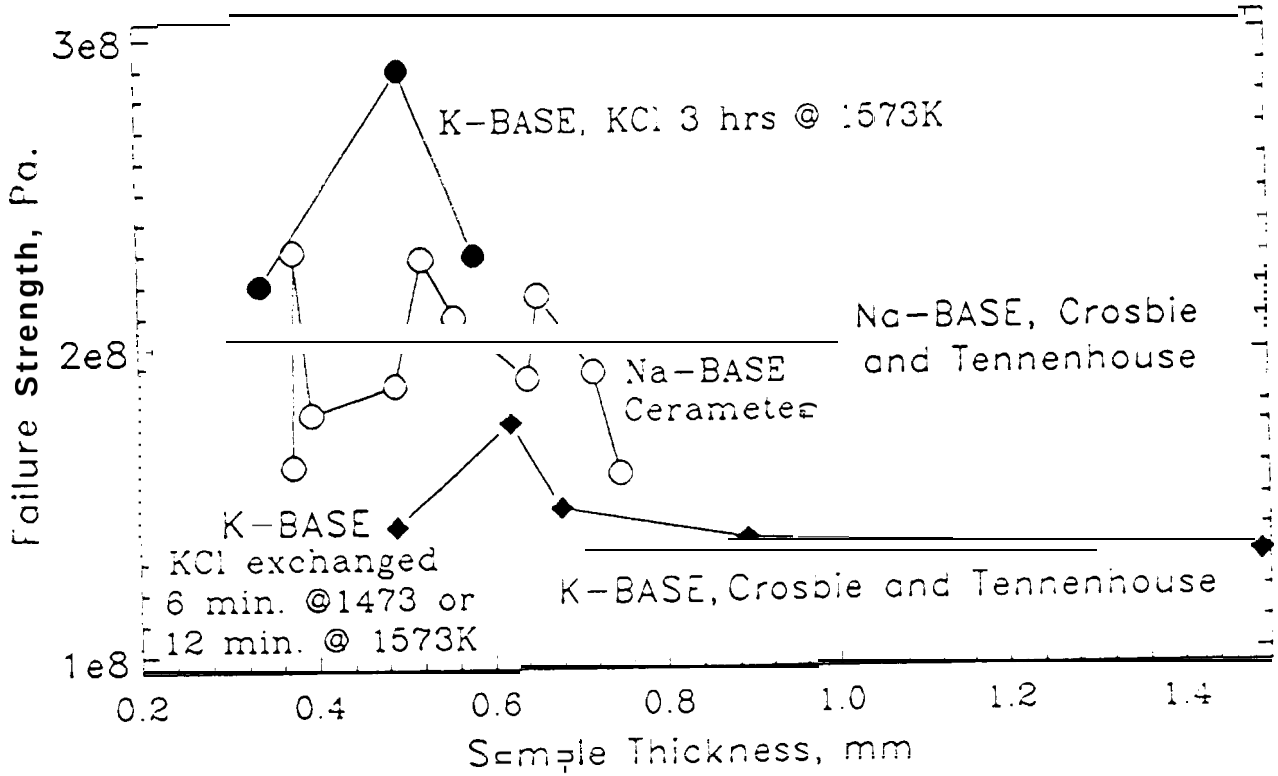


Fig 3 Increase in Failure Strength of K-BASE by Annealing

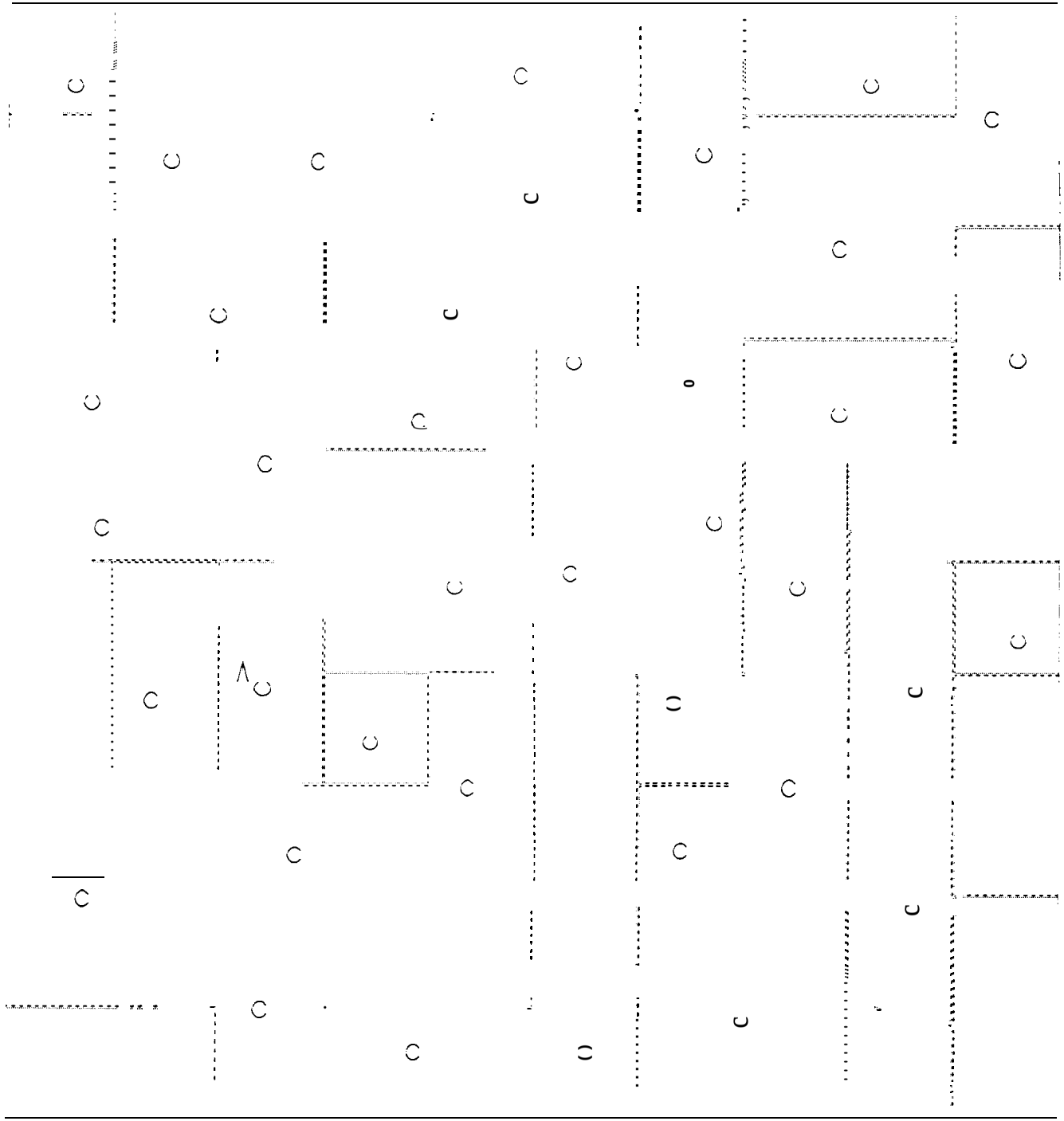
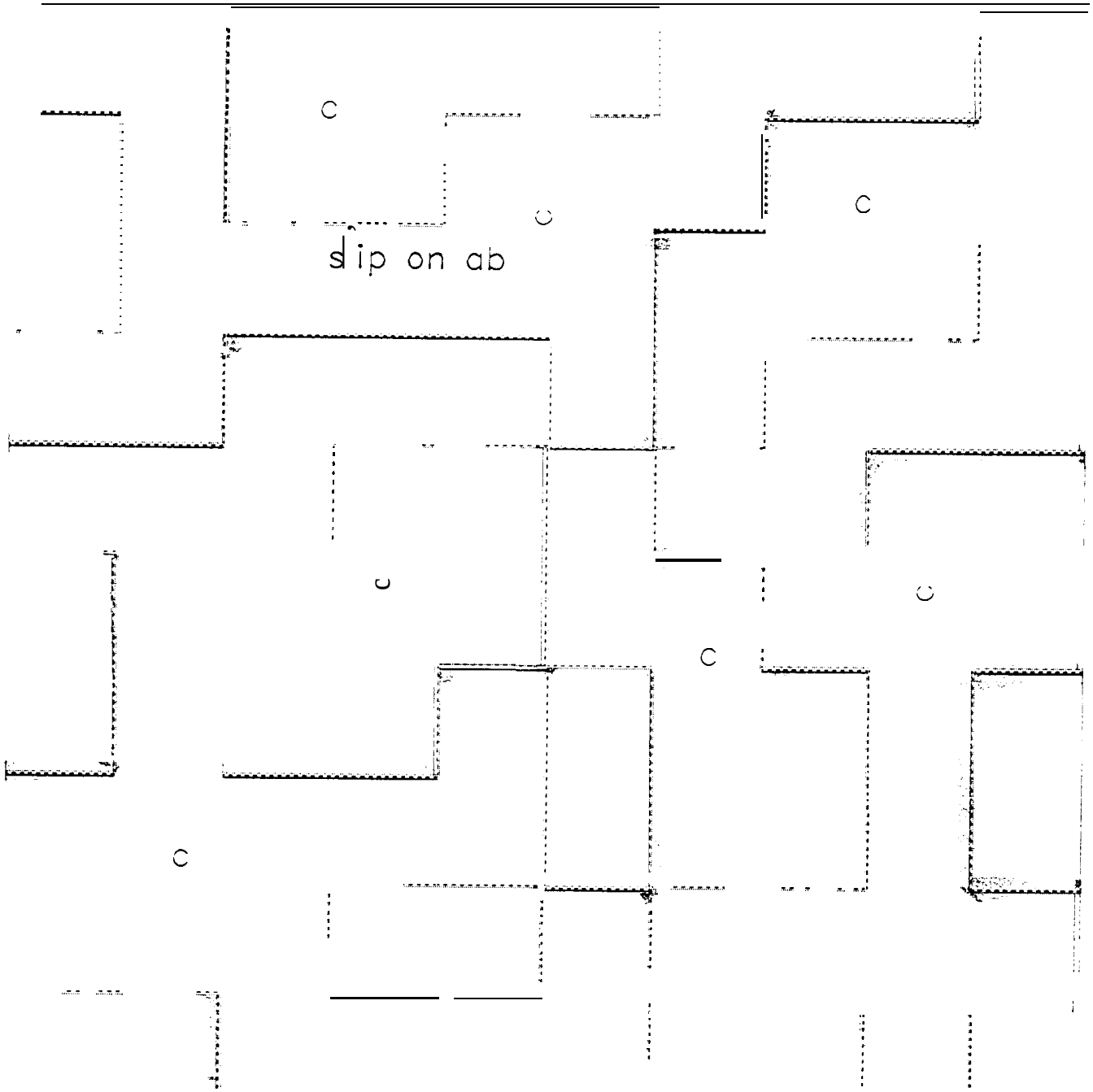


Figure VI-1-2. Orientations of non-isolated crystallites indicated by c orientation



filen arne = MOSAIC4

Figure VI–1–4. So id ines show expectea pattern of microcracks after c/a increases.

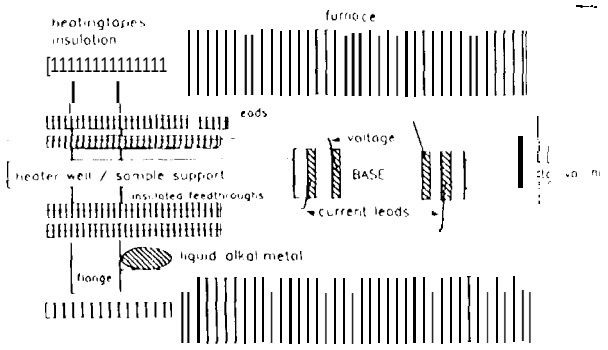


Fig. 1. Schematic diagram, not to scale, of the alkali metal vapor exposure test chamber.

at 1425 K in vacuum or at 1625 K in a KBASE powder bed in air at 1 atm. The two KBASE exchange processes produced somewhat dissimilar ceramics. These are identified as KBASE1425 and KBASE1625 here.

Four thin-film metal electrodes, shaped as either rings or rectangular patches with areas from 4 to --5 cm^2, were deposited on NaBASE and KBASE tube sections. Rh_3W electrodes were deposited cm NaBASE using a photolytic chemical vapor deposition process. Sputter-deposited Mo films were used as electrodes on KBASE. Electrodes were contacted with Mo or Ni meshes tied on with Mo leads and were separated by regions of uncoated BASE. Details of the W/Rh photolytic deposition process, the KBASE exchange process, and AMTEC electrode studies are presented elsewhere.[6,8,25,34]

Sodium and potassium were obtained as reagent grade metals under argon, and were purified by heating the liquid metal with pieces of NaBASE and KBASE, respectively, and filtering the liquid metal through sequential 7 and 2 μm stainless steel filters. This technique removes particulates and lowers the contamination level of the alkali metal by Ca, by removing CaO particles Ca^{2+} substitutes for the alkali ions in the ceramics and reduces their conductivity. The vapor pressure of the alkali metal was calculated using established expressions for the saturated vapor pressure above the liquid at the cold end and correcting for atomic velocity change due to the temperature difference between the pool region and the electrolyte region.[3,38]

The test apparatus (Fig. 1) was a stainless steel tube with feed throughs for leads, thermocouples, pumpout, argon backfill, and introduction of a controlled quantity of alkali metal. Samples were mounted on a central support tube with α-alumina standoffs over a Mo foil wrap. Electrical leads and shielded type K thermocouples were insulated with α-alumina tubing inside the test apparatus. Finally, refractory metal foils (Zr, Mo, Ta) were inserted inside the stainless steel tube for gettering and protection of the samples from high vapor pressure components of the steel, such as manganese. The entire assembly was welded shut. The small gaps between the outer steel feed throughs and α-alumina insulation were hermetically sealed with a slow setting epoxy (Epoxi-Patch®). The apparatus was set up with a pool of alkali metal at one end of the tube assembly (Fig. 1). The alkali metal pool temperature was controlled with heating tapes to 600 K independently of the furnace controlling the temperature of the ceramic samples. The pool temperature was measured with a thermocouple in contact with the pool. The temperature of the rest of the assembly was controlled by externally heating it in a tube furnace. Electrolyte temperatures, characterized by several additional internal thermocouples, could be raised up to 1400 K with minor gradients (<10 K) across the samples.

Conductivities of the BASE samples were measured in a four-probe configuration by ac and dc techniques. Conductivity was measured using two equipment setups. In the first one, a Solartron 1286 frequency analyzer and a 1255 electrochemical interface with an HP digital voltmeter were controlled by an IBM XT computer to carry out impedance measurements with current measured between an outside pair of electrodes and voltage controlled and measured at the inside pair of electrodes, eliminating contributions to the impedance spectrum from interfacial reactions. Typical frequency ranges used spanned 0.1 Hz to 64 kHz, but lower frequencies were used in some lower temperature measurements to evaluate the low frequency limiting behavior, and at temperatures above 1200 K, the lowest frequency measured was increased to 1.0 or 2.0 Hz to minimize the time spent above the nominal stand temperature. Impedance spectra corrected for the sample geometry are shown in Fig. 2. This configuration also was

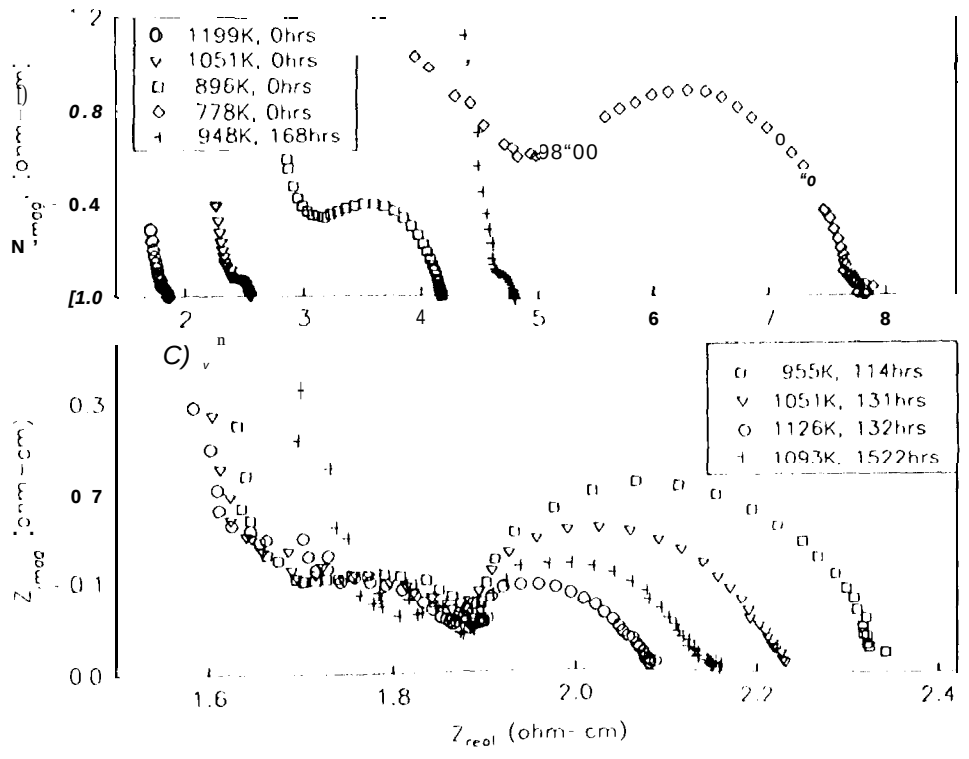


Fig. 2. Impedance data for tap: KBASE 1625 and bottom: NaBASE. Frequencies of measurements range from 0.1 Hz to 64 kHz.

The conductivity of KBASE.— Higher potassium pool temperatures resulted in systematically lower measured electrolyte conductivities, but there was little temperature dependence between 0.1 and 3.0 Pa. The conductivities of KBASE1425 and KBASE1625 electrolytes were measured with respect to temperature at nearly constant ambient potassium pressure on initial heat-up, after 73, 158, 229, 388, and 495 h. No 229 or 388 h data point for the 1425 K electrolyte was included because a lead had shorted to ground during the measurements. The temperature dependence at each time was fit to the Eq. 1.[42] The slopes of the plots changed significantly at temperatures below those shown in Fig. 4. The conductivity at 1000 K was calculated from the fit to the data and plotted against time (Fig. 6). The conductivity of both samples decreased over the first 100 h and then slowly rose with time. The activation energy for conductivity after the initial 100 h was determined to be 0.26-0.28 eV for both samples, as Fig. 4 shows. The high temperature activation energy for KBASE1425 increased with time for the three samples measured, while the activation energy for the KBASE1625 decreased slightly. The conductivity at $T > 900$ K was always higher for the 1625 K material than for the 1425 K material. The KBASE1425 activation energy decreases during the same time period that the overall conductivity drops and shows little change from 120 to 495 h.

The majority phase in both 1425 and 1625 K ceramics remains β-alumina, indicated both by the high conductivity and the XRD pattern. XRD of KBASE1625 ceramic surfaces before and after the test showed that there was an increase in the minority β-alumina phase from 1-2 to 3-4%. Due to absorption effects, XRD measurements using Cu-K_α radiation are most sensitive to material within 10-100 μm of the surface, ruling out a thick layer of the β-phase at the surface. EDS showed a surface composition consistent with an Al/K ratio of about 5.0 indicating that the surface is predominately K-β″-alumina. The limited formation of the β-phase almost certainly occurred transiently and coincidentally with the initial conductivity drop, and in limited regions of the ceramic, since its continuous formation in the bulk ceramic would have resulted in a continuous drop in conductivity of the KBASE. Because formation of the β-phase as a thin surface phase has little effect on the four-probe conductivity measurement, we believe that the β-phase is formed at the grain boundaries, possibly via K_2O loss from $KAlO_2$ initially present at the grain boundaries, and concomitant void formation. It is fairly well established that commercial NaBASE has $NaAlO_2$ at the grain boundaries, and the aluminate phase is refractory enough to persist through the ion exchange process.[43,46] The slow increase in conductivity may be due to voids collapsing at the grain boundaries.

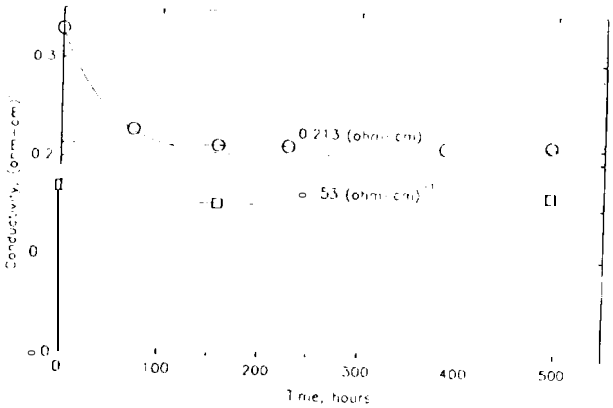


Fig. 6. Time dependence of the conductivity of KBASE at 1000 K, each point calculated from derived fits to conductivity vs. temperature data, at 0.1 to 2.0 Pa K_g. The solid lines show the minimum in conductivity of each curve for reference. The dashed line shows a fit of the data to Eq. 3.

The activation energy is similar to that of single-crystal potassium β-alumina (0.28 eV), although the KBASE conductivity is several times higher than that of single-crystal K-β-alumina and possibly 20 to 50 times higher than the conductivity of K-β-alumina ceramic extrapolated to similar temperatures.[11,14,16,23]

The decrease in conductivity at the beginning of the tests was fit to an exponential decreasing function, Eq. 3

$$\sigma(t) = \sigma(0) + At + B \exp[-t/\tau] \quad [3]$$

The time constant, τ, for NaBASE (holding A to zero) is 44(2) h, using only the galvanostatically controlled dc measurements from the first 100 h of test. The conductivity values obtained from impedance measurements for NaBASE were not used for the calculation of the initial conductivity decrease because there were few impedance measurements made in the first 100 h and because there is substantially less scatter in the galvanostatic data. The ac measurements of the conductivity of NaBASE after 100 h stand at 1150 K showed higher scatter, and (holding B to zero) no significant trend ($A = 0$) for the entire collection of $\sigma(t)$ data, although $\sigma(0) = 0.544(11)$ was higher than expected from the fit to the early galvanostatic measurements.

The time constant, τ, for KBASE1625 is 49(4) h, using the values of the conductivity at 1000 K calculated from the fits of the conductivity/temperature data to the Eq. 1. Values of $\sigma(0)$, A and B are 0.192(4) $(\Omega\text{-cm})^{-1}$, $4.7(6) \times 10^{-5}$ $(\Omega\text{-cm-h})^{-1}$, and 0.136(5) $(\Omega\text{-cm})^{-1}$, respectively.

Conclusion

The apparent activation energy for ionic conductivity of Li^+-stabilized NaBASE ceramic for the temperature range of 780 to 1160 K is smaller than the activation energy reported for sodium β″-alumina single crystals at 673 to 773 K, but is generally consistent the trend toward lower apparent activation energies at higher temperatures, and with earlier results on NaBASE ceramic at temperatures up to 1273 K.[15,43-45] We find conductivities of similar magnitudes but a significantly lower activation, compared with the results of Cole *et al.*[15] However, our fit to Eq. 1 uses data over a narrow temperature range, <400 K, while the fit of Cole *et al.* covers an 800 K range.[15] Their high temperature activation term contributes the dominant term to the resistance over >700 K of this range of their measurements. The resistivity is the directly observed quantity, and the agreement between our resistivities and those from previous work is excellent. The high temperature resistivity of NaBASE clearly is not due to a single process, as is indicated both by our impedance spectra, showing substantial high and lower frequency arcs, and by previous work.[15] Other factors including time at high temperature, minor changes in the sodium β″-alumina ceramic provided by Ceramatec since 1979, differences in experimental procedure, and variation in purity of alkali metals used in the experiments may have had small effects.

A small decline in conductivity early in the test may be due to loss of some Na_2O, with the conductivity later in the test either stable or improving at a very slow rate. The conductivity of NaBASE is stable after a small initial decline, and there is no reason to expect that conductivity decline limits long-term AMTEC operation. At low AMTEC condenser temperatures, some reduction of the NaBASE conductivity may occur if the sodium working fluid is not free from potassium contamination and the ambient sodium pressure in the cold zone is less than ~0.3 Pa.

The conductivity of Li^+-stabilized KBASE at high temperatures (600-1200 K), after 100 h at 1200 K, has an activation energy close to that observed for the conductivity of single-crystal potassium β alumina from 298 to about 700 K. However, the KBASE conductivity is several times higher than that of single-crystal potassium β-alumina extrapolated to high temperature and much higher than is expected for polycrystalline potassium β-alumina ceramic. The grain boundaries of KBASE may be expected to contain K/Al/O phases without Li^+, and long exposure at test

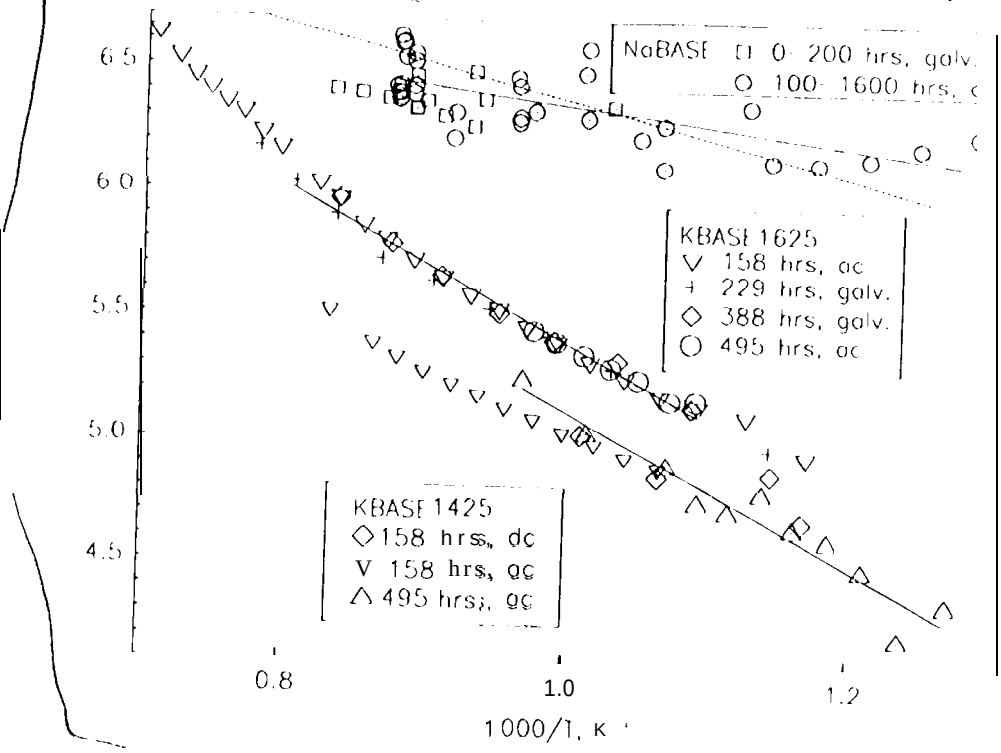


Fig. 4. Temperature dependence of the conductivity of NaBASE, KBASE 1425, and KBASE 1625, after >100 h exposure to alkali metal vapor at high temperature. Initial NaBASE data from t < 100 h; and some data outside the temperature ranges indicated by the solid line fits was not used in determining the fitting parameters, but is shown. Only the 495 h data was used in fitting the KBASE1425 data. The solid lines are fits of the data to Eq. 1, and the dashed line is the fit to the data in Ref. 21,43-45 to Eq. 2.

parameters have been reformulated in Table I to be consistent with Eq. 1.

The Conductivity of NaBASE. The conductivity of NaBASE was unaffected by ambient sodium vapor pressures between 0.3 and 2.0 Pa; data taken over this pressure range have been used to determine the temperature and time dependence of NaBASE conductivity (Fig. 4 and 5). The temperature dependence of NaBASE conductivity from 780 to 1200 K is shown in Fig. 4. The conductivity varies systematically by <5% in the temperature range from 1000 to 1200 K, the range in which most of the data were measured. Therefore, conductivities measured at temperatures from 1028 to 1201 K were used to evaluate the time dependence of NaBASE conductivity. Our data show no apparent change in the activation energy of NaBASE conductivity with time, but measurements with systematic temperature variation within the first 50 h were not performed. The high temperature activation energy of NaBASE, 0.067 eV, was determined from the plot in Fig. 4. It is significantly smaller than the value of 0.115 eV reported in 1979 by Cole *et al.* on Ceramatec NaBASE, although the magnitudes of the high temperature conductivity are similar.[15]

The data taken early in the test, shown in the inset of Fig. 5, were measured galvanostatically and indicate that the there is a small decrease in the magnitude of the conductivity in the first hundred hours at high temperature. Data points from later in the test were generally determined from the low frequency limit of the impedance response, and displayed greater scatter and no systematic time dependence over 1450 h. Previous XRD analysis of NaBASE has indicated that no significant degradation of the sodium β″-alumina occurs following cycling from 300 to 1273 K and back in vacuum.[10,39,40] Several very weak peaks appeared in the NaBASE diffraction pattern following XRD measurements at 1273 K in vacuum for ~5 h, but they were not β-alumina peaks, and could not be reliably assigned.[40,41] The NaBASE appeared free of β-alumina by XRD both before and after cycling to high temperature.[40]

Table I. Preexponential factors and activation energies from fits to Eq. 1 for the high temperature conductivities of NaBASE and KBASE. Standard errors from the fits are given in parenthesis.

Electrolyte	σ_0 [K/(Ω-cm)]	E_{act} (eV)	E_a kJ/(mol-K)
NaBASE			
t = 0 h[15,43-45 a]	1.98×10^3	0.115	11.9
t = 100-1550 h	$1.27(19) \times 10^3$	0.067(12)	6.50(13)
KBASE1425 no. 1, 2			
t = 0 h[17 a]	$2.89(29) \times 10^3$	0.186(8)	18.0(8)
KBASE1425 no. 2			
t = 100 h	$3.60(13) \times 10^3$	0.280(3)	27.0(3)
KBASE1425 no. 3			
t = 0 h	$2.71(77) \times 10^3$	0.246(28)	23.7(2.7)
t = 495 h	$3.9(1.2) \times 10^3$	0.267(24)	25.8(2.3)
KBASE1625			
t = 0 h	$11.0(2.0) \times 10^3$	0.302(16)	29.1(1.6)
t = 158-495 h	$5.06(34) \times 10^3$	0.269(6)	26.0(6)

[a] The published values of σ_0 term for K-BASE conductivity in Ref. 17 was incorrectly given as 2.89×10^4, the correct value is 2.89×10^3. The parameters fitting the resistivity expression for NaBASE in Ref. 15, were corrected by the authors.[43-45]

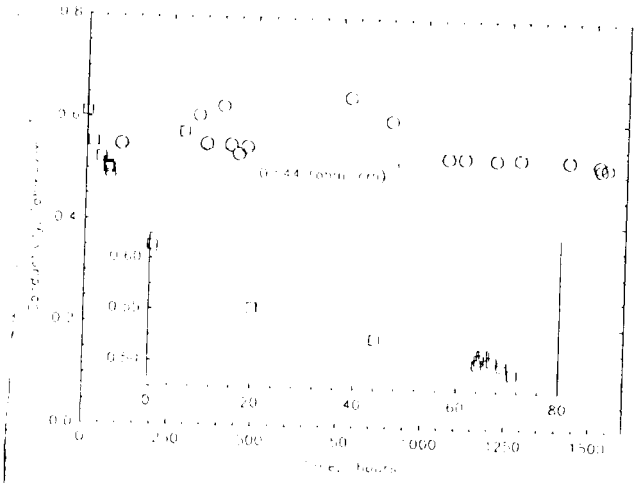


Fig. 5. Time dependence of the conductive of NaBASE, 1028-1201 K, at 0.3 to 2.0 Pa Na_g, with the dashed line showing a fit to data as a linear function of time. The inset shows the initial 100 h on an expanded scale with dashed line showing a fit of this data to an exponential decrease.

with rapid current increase at (he. potassium ionization potential. This effect is important to applications of series connected AMTECs; in general, series connected cells should not exceed 4.0 V for potassium AMTECs or 5.0 V for sodium AMTECs, unless it can be assured that there arc no possible vapor discharge pathway between cells with potential differences greater than the.se values

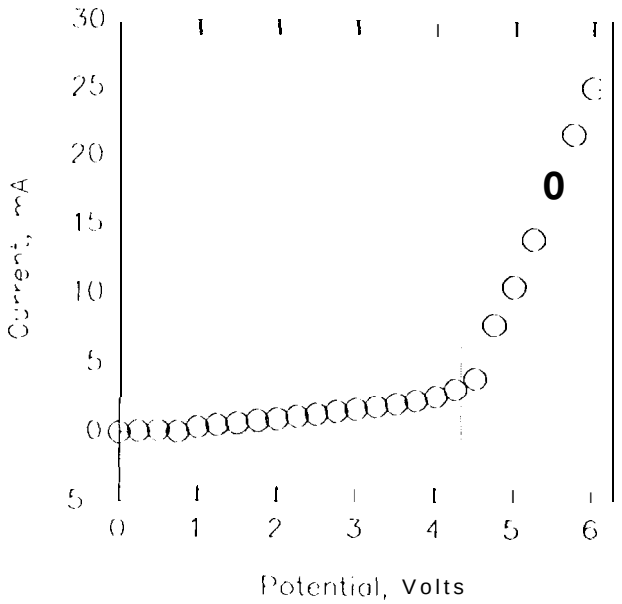


Fig. 5 Current between non-contacted leads in potassium vapor at 992K. Vertical line is at potassium ionization potential = 4.318V

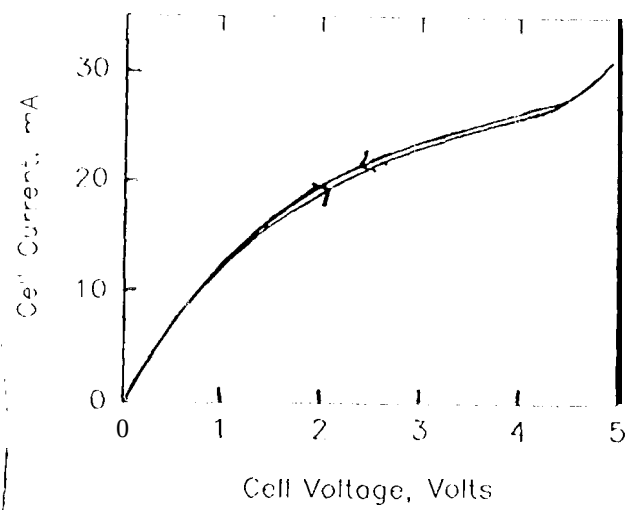


Fig. 6 Current-voltage curves of two AMTEC (>I(ctr-odes to 5.0 volts, Increase at V>4.3 is due to plasr nadischarge.

Potassium AMTEC Test

The K-BASE tube, prepared as described above, was successfully brazed to a niobium tube transition, with TiCuNi filler metal, to a small stainless steel flange. The tube was sputtered with molybdenum thin film electrodes for an potassium AMTEC test.

The c-en was operated at a nominal temperature of 687 K (at the bottom of the heater well), and onc current-voltage curve, shown in Fig. 7, of a 14.4 cm^2 electrode at an estimated temperature of 725-750 K was obtained, with an open circuit voltage of 0.6 volts, short circuit current of 2.5 amps and a total power of 0.3 watts. This performance is modest, but substantially better than the performance of a comparable sodium AMTEC cell at this low temperature. The sodium cell would have a higher open circuit voltage, but current and power densities would be significantly lower at this temperature. However, this was an early-in-life molybdenum electrode, probably containing substantial quantities of K_2MoO_4, which wc would expect to be a fairly good ionic conductor at elevated temperature. 'l"his phase might persist for viable operation lifetimes at lower cell temperatures, as it is higher melting and slightly less volatile than Na_2MoO_4. Based on the results from both AMTEC and vapor cell tests, we would anticipate 1.0 μm thick molybdenum electrodes to be very useful at 900K < T < 1100K in potassium AMTECs and molybdenum electrodes will not sinter to a diameter exceeding 0.5 μm within periods of years at the. lower temperatures.

CONCLUSIONS

Two low temperature routes to nearly phase pure K-BASE (or Na-BASE) have been demonstrated and characterized. While not directly sintered to dense ceramics except for microscopic areas, this material is useful in ion exchange via ceramic firing at controlled K2O activity and in potassium metal purification,

Wc have demonstrated high temperature direct synthesis from aluminates which increases density of K-BASE. This technique could potentially provide high density ceramic with further refinement. Our results generally confirm those of Schäfer and Weppner, although we did not achieve as high a ceramic density.[ig]

Based on improved understanding of the temperature and K_2O stabilit y regime of K-beta" -alumina, the exchange process of Crosbie and Tennenhouse was improved by carrying out the exchange at a higher temperature with better control of K_2O activity. The resulting ceramic shows the appropriate weight gain of about 4, 5% after exchange, shows only a small anomalous volume expansion (<1 %) over the expected volume expansion due to increase. in the lattice

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Conclusions:

Potassium beta” alumina solid electrolyte ceramic shows improve conductivity over 500 hours at potassium AMTEC operating conditions.

Potassium beta” alumina can be prepare by vapor exchange at temperatures 10 about 1600K if K2O act ivity is maintained,

Potassium beta” alumina prepared by vapor exchange at higher temperat ures is stronger, and has a higher ionic conductivity at AMTEC operating temperatures.

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