N89-13651 59-27 181377 9P.

CERAMIC OXIDE REACTIONS WITH V_2O_5 AND SO_3

R. L. Jones and C. E. Williams
Naval Research Laboratory
Washington, DC 20375-5000

Ceramic oxides are not inert in combustion environments, but can react with, inter alia, SO_3 and Na_2SO_4 to yield low melting mixed sulfate eutectics (mp 700-800°C), and with vanadium compounds to produce vanadates, e.g., YVO_4, or other species.

Assuming ceramic degradation to become severe only when molten phases are generated in the surface salt (as found for metallic hot corrosion), the reactivity of ceramic oxides can be quantified by determining the SO_3 partial pressure necessary for molten mixed sulfate formation with Na_2SO_4. The critical SO_3 pressures measured for Y_2O_3, CeO_2, and ZrO_2, for example, were of the order of < 10 Pa, 100 Pa, and 1000 Pa, respectively. Therefore, use of oxides such as CeO_2 rather than Y_2O_3 for stabilization of ZrO_2 may increase the resistance of ZrO_2-based ceramics to SO_3-Na_2SO_4 attack, as limited experience seems to confirm.

Vanadium pentoxide is an acidic oxide that reacts with Na_2O, SO_3, and the different ceramic oxides in a series of Lux-Flood type of acid-base displacement reactions. To elucidate the various possible vanadium compound-ceramic oxide interactions, a study was made of the reactions of a matrix involving, on the one axis, ceramic oxides of increasing acidity ($Y_2O_3 < CeO_2 < ZrO_2 < GeO_2 < Ta_2O_5$ (most acidic)), and on the other axis, vanadium compounds of increasing acidity ($Na_3VO_4 < NaVO_3 < V_2O_5$ (most acidic)). Resistance to vanadium compound reaction increased, up to ZrO_2, as the oxide acidity increased with, e.g., Y_2O_3 reacting with $NaVO_3$ and V_2O_5, although not Na_3VO_4, while CeO_2 reacted only with V_2O_5, and neither $NaVO_3$ or Na_3VO_4. Oxides more acidic than ZrO_2 displaced V_2O_5 (i.e., acted as a stronger acid than V_2O_5), giving such reactions as: $2\ Ta_2O_5 + 2\ NaVO_3 = Na_2Ta_4O_{11} + V_2O_5$. Sulfur trioxide interacts via the reaction, $2\ NaVO_3 + SO_3 = Na_2SO_4 + V_2O_5$, and can, for example, cause vanadation of CeO_2, which does not react with pure $NaVO_3$, by producing V_2O_5 in the melt.

Examination of Y_2O_3- and CeO_2-stabilized ZrO_2 sintered ceramics which were degraded in 700°C $NaVO_3$ has shown good agreement with the reactions predicted above, except that the CeO_2-ZrO_2 ceramic appears to be inexplicably degraded by $NaVO_3$.

POTENTIAL CERAMIC COATING BENEFITS TO NAVY

IMPROVED THERMAL EFFICIENCY

CORROSION RESISTANCE

USE OF LOW QUALITY FUEL

WITHSTAND 700°C OPERATION

Figure 1.

CERAMIC REACTION WITH FUEL CONTAMINANTS

$\underline{SO_3}$	$Y_2O_3 + SO_3 \leftrightharpoons Y_2O_2(SO_4)$
	$Y_2O_3 + SO_3 + Na_2SO_4 \leftrightharpoons Y_2(SO_4)_3\text{-}Na_2SO_4$
$\underline{V_2O_5}$	$Y_2O_3 + V_2O_5 \leftrightharpoons 2\ YVO_4$
$\underline{V_2O_5 + SO_3}$	$2\ NaVO_3 \leftrightharpoons Na_2O + V_2O_5$
	$2\ NaVO_3 + SO_3 \leftrightharpoons V_2O_5 + Na_2SO_4$
	$CeO_2 + V_2O_5 \leftrightharpoons 2\ CeVO_4$

Figure 2.

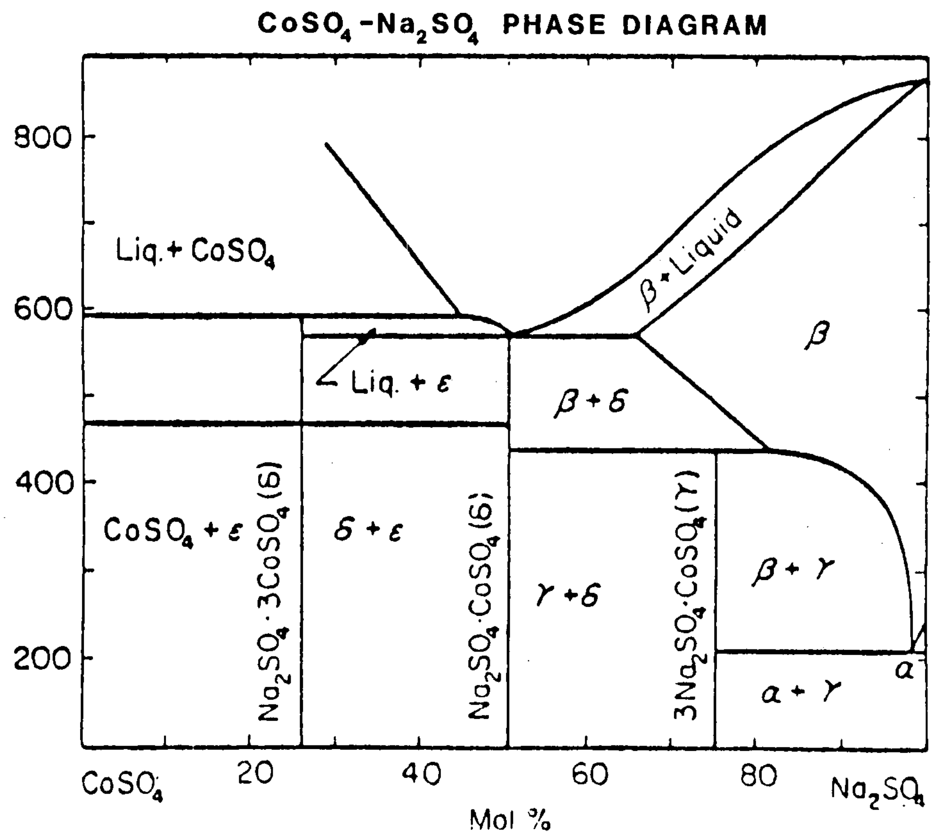

Figure 3.

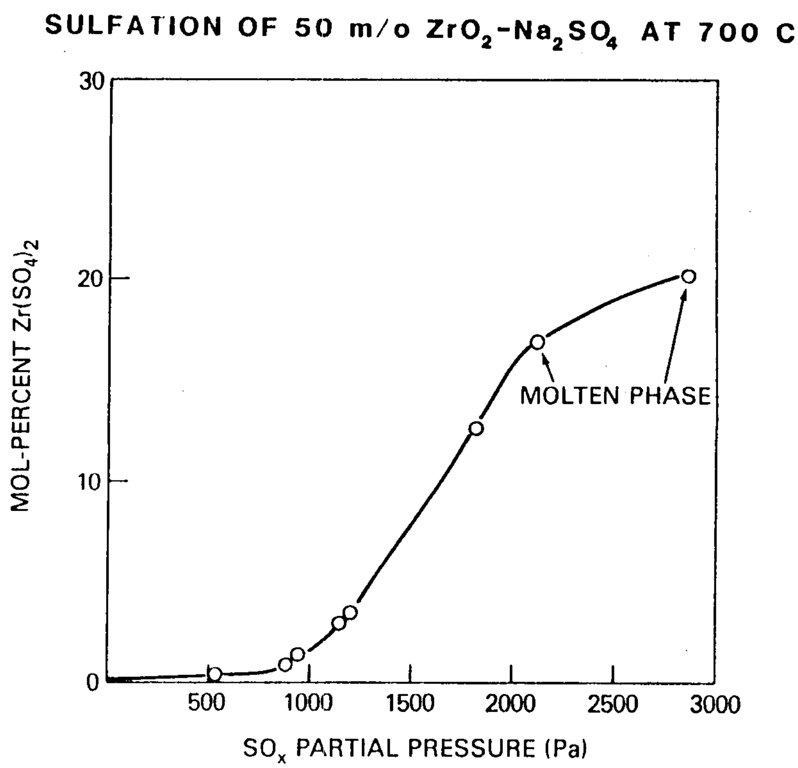

Figure 4.

SO_3 PARTIAL PRESSURE FOR MOLTEN MIXED SULFATE FORMATION AT 700°C

Y_2O_3	<10 Pa
CeO_2	100 Pa
ZrO_2	1000 Pa

Figure 5.

SODIUM VANADATE COMPOUNDS

—DECREASING ACIDITY→

$Na_2O + 6\ V_2O_5 \rightleftharpoons Na_2V_{12}O_{31}$	vanadium bronze I
$Na_2O + 3\ V_2O_5 \rightleftharpoons 2\ NaV_3O_8$	vanadium bronze II
$Na_2O + V_2O_5 \rightleftharpoons 2\ NaVO_3$	sodium metavanadate
$2\ Na_2O + V_2O_5 \rightleftharpoons Na_4V_2O_7$	sodium pyrovanadate
$3\ Na_2O + V_2O_5 \rightleftharpoons 2\ Na_3VO_4$	sodium orthovanadate

Figure 6.

c-2

VANADIUM-CERAMIC OXIDE REACTIONS

	Na_3VO_4	$NaVO_3$	V_2O_5
Y_2O_3	NR	YVO_4	YVO_4
CeO_2	NR	NR	$CeVO_4$
ZrO_2	NR	NR	ZrV_2O_7 (BUT SLOWLY)
GeO_2	$Na_4Ge_9O_{20}$	$Na_4Ge_9O_{20}$(*)	NR
Ta_2O_5	$NaTaO_3$	$Na_2Ta_4O_{11}$	α-$TaVO_5$

NR = NO REACTION

(*) AS PPT FROM H_2O SOL'N

Figure 7.

INFLUENCE OF Na_2SO_4 AND SO_3 IN VANADIUM-CERAMIC REACTIONS

$$2\ NaVO_3 + SO_3 \rightleftharpoons V_2O_5 + Na_2SO_4$$

INCREASING SO_3 PROMOTES VANADATE FORMATION

$$CeO_2 + NaVO_3 + SO_3 \rightarrow CeVO_4$$

$$ZrO_2 + NaVO_3 + SO_3 \rightarrow NR$$

(AT LEAST UP TO 110 Pa OF SO_3 AT 700°C)

Figure 8.

DEGRADATION OF Y_2O_3-ZrO_2 BY $NaVO_3$ AT 700°C

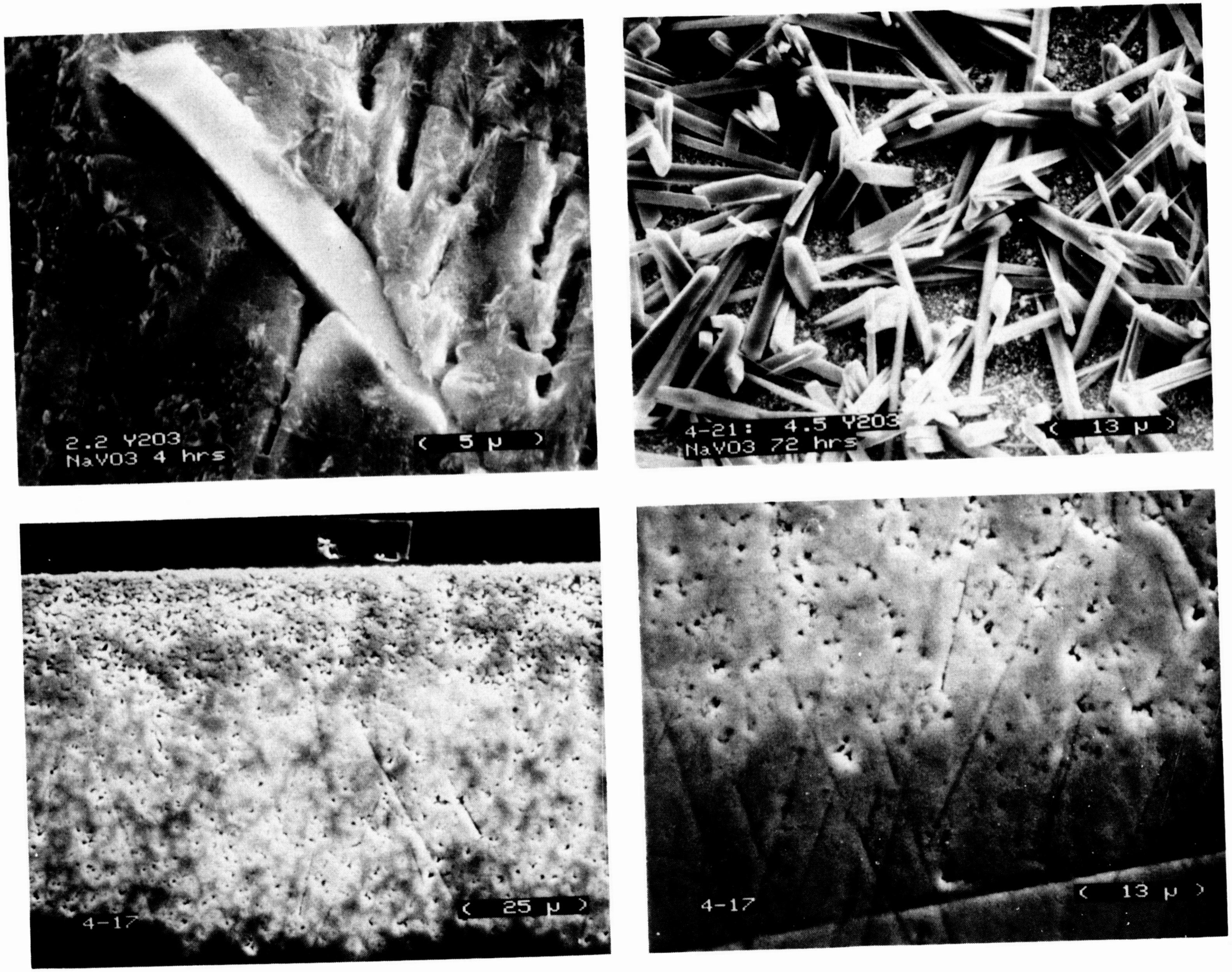

Figure 9.

DEGRADATION OF CeO_2-ZrO_2 BY $NaVO_3$ AT 700°C

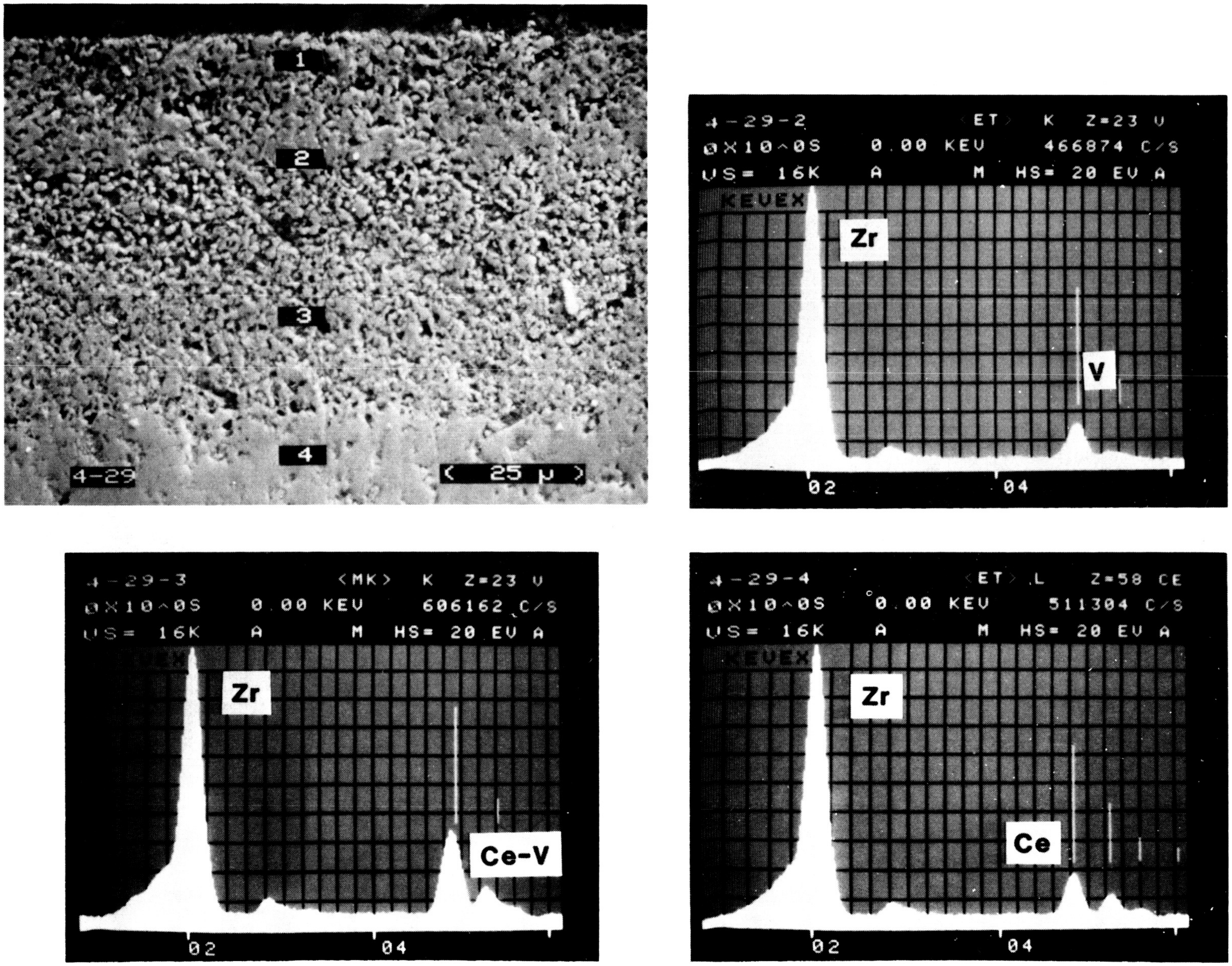

Figure 10.

ORIGINAL PAGE IS
OF POOR QUALITY

ATTACK OF CeO_2-ZrO_2 BY $NaVO_3$ UNDER 40 Pa OF SO_3 AT 700°C

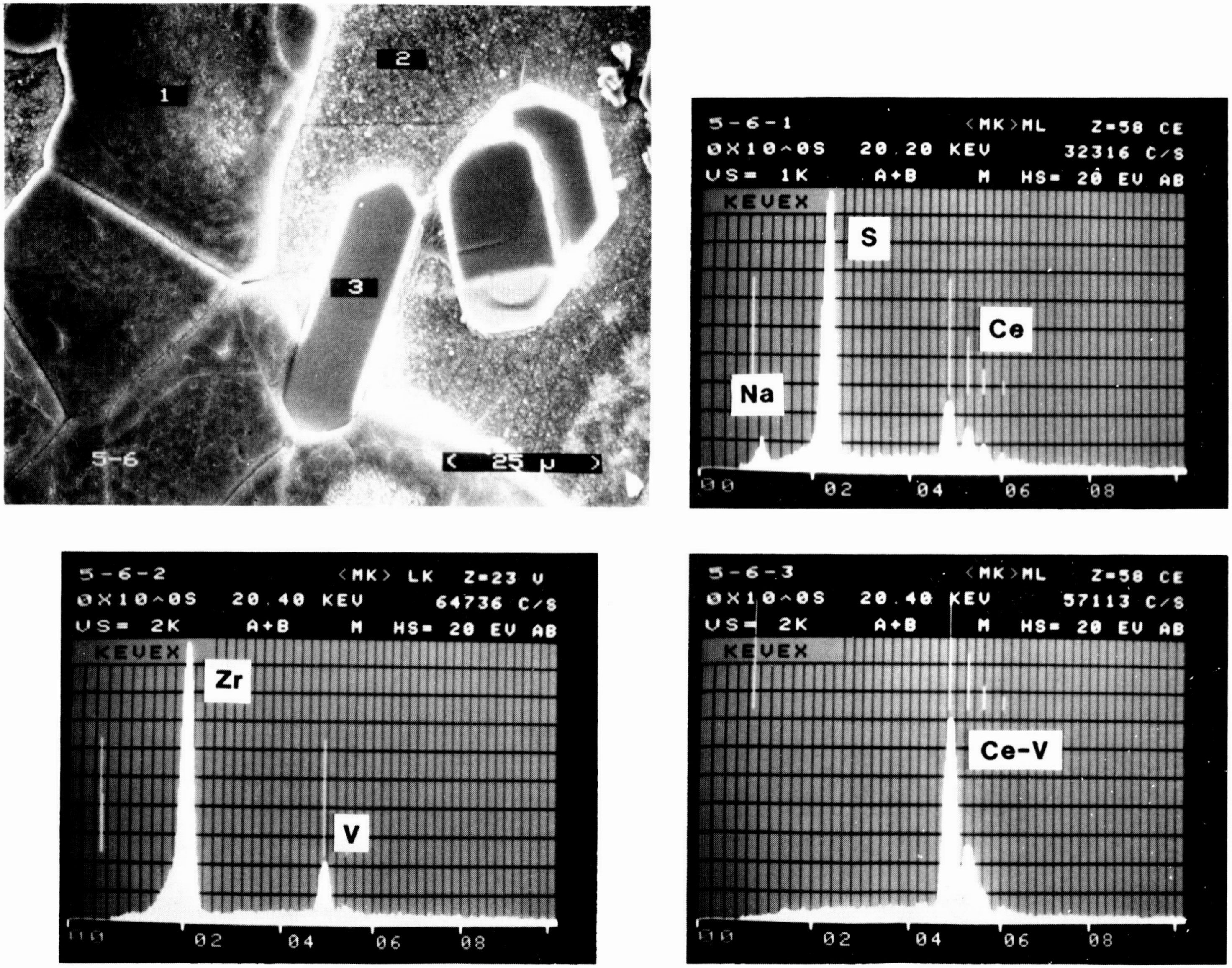

Figure 11.

CONCLUSIONS

CERAMIC CORROSION ELUCIDATED

GUIDELINES LAID FOR DEVELOPMENT OF CORROSION-RESISTANT CERAMICS

EFFECTS OF CERAMIC PROCESSING STILL TO BE IDENTIFIED

Figure 12.