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CORROSION STUDIES OF TERNARY ZIRCONIUM ALLOYS IN
HIGH-TEMPERATURE WATER AND STEAM

by

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ABSTRACT

The alloying of zirconium to improve corrosion resistance has an empirical basis, and satisfactory explanations for the alloying effects are not available. A theory of compensating valencies in the corrosion oxide is proposed, in which cations of lower and higher valence than zirconium (+4) are present in ratios such that electrostatic neutrality is ensured. An example is an alloy containing equimolar amounts of scandium (+3) and niobium (+5).

A number of zirconium alloys were prepared in which scandium or yttrium were paired with elements capable of a +5 or +6 valence. The ternary alloys containing scandium were superior to the alloys containing yttrium. The alloys containing scandium plus molybdenum, tantalum, or tungsten had relatively long lifetimes in steam at 540°C and 600 psi as compared with other alloy combinations, including Zircaloy-2. A quenched alloy containing 0.025 w/o Sc and 0.053 a/o Mo (that is, 0.05 mol % of each additive) corroded approximately according to a cubic law up to 758 hr, at which point the rate suddenly increased in a manner suggesting hydrogen damage.

Examination of the oxide film from alloys containing scandium and molybdenum showed only monoclinic ZrO_2 . It is believed that stabilization of this form of ZrO_2 instead of the cubic or tetragonal forms is a factor in promoting corrosion resistance. In this way the protective character of the film can be improved independently of the addition of cathodes.

I. INTRODUCTION

The development of zirconium alloys for use in water at high temperature has concentrated on alloys containing various combinations of tin, iron, nickel, and chromium. Extensive screening of zirconium binary alloys has shown that most other elements are deleterious to the corrosion resistance of zirconium.⁽¹⁾

In terms of understanding these effects, the role of iron and nickel is best understood on the basis of the theory of hydrogen damage to the protective oxide film.⁽²⁾ Tin does not fit this picture because this metal has a relatively high hydrogen overvoltage. However, tin is able to counteract the effect of nitrogen in promoting corrosion. Phosphorus can also do this to a lesser extent.⁽³⁾ Thomas has suggested that tin ions associate with nitrogen ions in the ZrO_2 lattice to reduce the mobility of oxygen anions.⁽⁴⁾

A valuable contribution to understanding the role of substitutional ions in a corrosion scale has been made by Hauffe, who formulated rules for selecting additives based on the two cases of predominant ionic or electronic conductivity.⁽⁵⁾ The equilibria which form the basis of the Hauffe rules require that suppression of ionic conductivity will promote electronic conductivity and vice versa. This method is characterized by the name "valency control." The Hauffe rules have not been useful in the case of zirconium, and the reasons for this are not understood. One possibility is that conduction in ZrO_2 is "mixed," and, therefore, both types of conduction must be suppressed.

Very little is known about the effect of two or more elements on the ZrO_2 corrosion scale except for the apparent compensating effect of nitrogen and tin mentioned above. That interactions can take place within the oxide is clear from the observation of Johnson⁽⁶⁾ that ZrO_2 formed a cubic modification in the presence of 3 w/o Y_2O_3 or 3 w/o Nb_2O_5 . In a ternary composition containing 2 w/o Y_2O_3 and 2 w/o Nb_2O_5 the cubic structure did not appear.

The changes to be expected in the ZrO_2 lattice upon the substitution of higher or lower valent foreign cations will depend upon the type of defects which ZrO_2 can form most readily. Available evidence favors an anion-defect structure; therefore adjustments in lattice equilibria will involve changes in the number of oxygen vacancies.

When cations with charge less than four are substituted for zirconium ions, the number of oxygen ion vacancies will increase to maintain electrical neutrality. The foreign cations will have a net negative charge relative to the lattice, while the oxygen vacancies will have a net positive charge.

When cations with charges greater than four are substituted for zirconium ions, the number of oxygen ion vacancies will decrease to a minimum. After this point, the further introduction of higher valent cations requires the presence of electrons in the lattice. Consequently, the ZrO_2 will become a better n-conductor.

If the aliovalent additives are present in such a proportion that their average charge is +4, then compensating changes in the defect

equilibria will not be required. However, the presence of such compensated additives may have other effects which can influence the corrosion process. Changes may take place in the oxide structure, diffusion rates, and electrical conductivity. The diffusion rate of oxygen anions may be influenced by the charges on the lower and higher valent foreign cations.

Depending on the ionization potentials of the foreign cations, the conductivity of the oxide is likely to be increased. The lower valent cations Sc^{3+} and Y^{3+} are not likely to participate in electron exchange because of their noble gas structure, but exchange may occur with nonnoble gas ions such as Fe^{3+} . Combinations of this type, e.g., Fe^{3+} and Ta^{5+} , are worthy of consideration but did not come within the scope of this study.

In summary, the procedure of adding two or more elements to zirconium with the object of influencing the corrosion rate has a number of potential advantages. These include:

- 1) The activation energy of diffusion may be higher if the ZrO_2 lattice contains dissolved cations of differing valence, size, and electronic configurations.
- 2) It may be possible to stabilize a favorable ZrO_2 structure with minimum change in the number of point defects. Stabilization of the monoclinic form is believed to promote maximum resistance to corrosion. The reasons for this are discussed later.
- 3) The ZrO_2 lattice may be strengthened by the incorporation of ions having different types of bonding characteristics. Two (or more) additives may act synergistically to minimize stresses and enhance solubility in the ZrO_2 .

II. EXPERIMENTAL

Based on these considerations, an investigation was begun on the effect of the simultaneous addition of lower and higher valence elements on the corrosion resistance of zirconium. These elements were chosen to avoid the formation of cathodes which might promote corrosion resistance by a different mechanism. Therefore, elements such as iron, nickel, copper, palladium, platinum, etc., were excluded with one exception.

The choice of alloying additives was governed by valence, and melting point or boiling point. The most suitable lower valent additives appeared to be Al, Sc, Y, and Yb* (in order of atomic number), whereas the high valent additives were V, Cr, Mn, As, Nb, Mo, Sb, Ta, W, Pd, and Bi. These elements are capable of forming +5 or +6 cations. In several cases, nickel, tin, and thorium were added. Ionic size and oxide structures were not considered in making this selection.

The lower and higher valent elements were added in atomic ratios of 1 to 1, 1 to 2, or 1 to 3. Larger amounts of the higher valent element were used on the basis that the higher valence might not be fully realized in solution in the ZrO_2 lattice. The total alloying content did not exceed 1 weight per cent.

The alloys were prepared by arc-melting buttons from sections of reactor-grade zirconium crystal bar which was corrosion resistant after 1 week in water at 350°C . Initially, a $\frac{1}{8}$ -in. diameter hole was drilled into each piece of crystal bar and the additives were placed inside. A plug of zirconium rod was then inserted and anchored by hammering the edge of the hole. During the course of the investigation these precautions were found to be unnecessary, and subsequently additives were simply placed under the zirconium. The metals used were in the form of powder or turnings or were cut from sheet. A comparison of specimen weights before and after melting showed that weight changes were very small. The appearance of the water-cooled copper mold was also an indication of possible loss of material from the melt. None of the alloys discussed below gave the appearance of losing the additives during melting.

The additives were reagent grade or were claimed to have purities of 99% or better. In the course of the investigation, the "scandium" and "yttrium" powders initially used were found to be sesquioxides instead of metals. This raised a doubt as to whether these oxides were reduced and alloyed with zirconium or whether they remained as undissolved second phase.

* Ytterbium metal in the form of a button casting was kindly provided by Dr. H. A. Wilhelm of Ames Laboratory, Ames, Iowa.

According to the free energies of formation of ZrO_2 and Y_2O_3 , the latter oxide will be reduced by zirconium at its melting point of 1850°C . Several yttrium-zirconium alloys prepared with Y_2O_3 were analyzed chemically and examined metallographically. The yttrium was present in the nominal amounts and the metallographic structure was consistent with an alloy. Therefore, the use of oxide did not vitiate the results. Data on the free energy of formation of Sc_2O_3 could not be found, but reduction and alloying seem likely in this case also.

Comparable corrosion results were obtained from later zirconium alloys using metallic scandium and yttrium. Therefore, the use of oxide for these additives did not detract from the conclusions of the screening procedure.

Each alloy was arc-melted three times. The buttons were turned over prior to the second and third meltings. They were then tested as cast or after treating in various ways. Details of subsequent treatment are presented with the data for simplicity.

Corrosion testing was carried out in degassed, distilled water at 350°C or in steam at 540°C and 600 psi. In some cases, water testing was followed by steam exposure without cleaning the specimens when the corrosion rate in water was low.

III. RESULTS

Observations of corrosion resistance are presented in a series of tables. For the initial purposes of this survey the alloys were judged only on the basis of appearance. A quantitative comparison did not appear justified at the beginning of a survey of this type, and consequently specific weight gains were not determined. All alloys were kept in test as long as their appearance indicated moderately good corrosion resistance. A specimen was removed from test when the surface was covered with white oxide, or when the oxide was obviously thickening or beginning to break away from the surface. In several cases the tests were discontinued although the appearance justified continuance of the corrosion exposure. These times are indicated by an asterisk. Removal of a specimen because of failing corrosion resistance is indicated by an x.

The first specimens (Tables I, II, III) were cut into halves after arc melting. One-half was left in the as-cast condition and the other half was heated in a stainless steel vacuum tube furnace to 1000°C for one hour. The specimens were then quenched into Wood's metal (approximately 100°C) while still under vacuum.

Table I shows four combinations based on aluminum. All had high corrosion rates indicating that V, Nb, Ta, or W are not able to compensate for the deleterious effect of aluminum. No additional alloys with aluminum were made.

Table I

RESULTS OF CORROSION TESTING ZIRCONIUM ALLOYS CONTAINING ALUMINUM AND OTHER ELEMENTS
(Total Content of Alloying Constituents 1 w/o)

Composition In Atomic Per Cent	Treatment	Appearance after Test			
		Hours in Water at 350° C			
		1	17	185	684
1.2% Al } 1.2% V }	as cast quenched	white, flaking ^x	white, flaking ^x		
0.76% Al 0.76% Nb	as cast quenched		white, flaking ^x white, flaking ^x		
0.43% Al 0.43% Ta	as cast quenched			white, some flaking ^x white, some flaking ^x	
0.43% Al 0.43% W	as cast quenched		turning white ^x turning white ^x		
Zr control	as cast				iridescent black [*]

* Discontinued although appearance justified continuance.

^x Indicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped.

A. Alloys Made with Sc_2O_3 and Y_2O_3

A number of combinations of scandium and yttrium with other additives were prepared next. The results are presented in Table II. It will be noted that the mol ratios of the lower and higher valent elements do not correspond exactly to the indicated proportions. This is so because the percentages were recalculated to correct for the use of oxide.

Table II
RESULTS OF CORROSION TESTING ZIRCONIUM ALLOYS CONTAINING SCANDIUM, YTTRIUM, AND OTHER ELEMENTS
(Total Content of Alloying Constituents 1 w/o)

Mol ratio of alloying components	Composition atomic per cent	Metallurgical history	Appearance after Test					
			Hours in Water at 350° C					
			17	185	276	442	780	971
11 Sc V	0.65" Sc	AC	white flaking ^x					
	0.95" V	Q	white flaking ^x					
11 Y V	0.52" Y	AC	white flaking ^x					
	0.67" V	Q	white flaking ^x					
11 Sc Nb	0.57" Sc	AC	white ^x					
	0.87" Nb	Q	white ^x					
11 Sc Nb	0.43" Sc	AC	turning white ^x					
	0.66" Nb	Q	white flaking ^x					
11 V Nb	0.39" V	AC	white flaking ^x					
	0.50" Nb	Q					grey flaking ^x	
11 Sc Sn	0.36" Sc	AC						black localized white ^x
	0.56" Sn	Q		grey flaking ^x				
11 Y Sn	0.35" Y	AC	severe attack ^x					
	0.44" Sn	Q			severe attack ^x			
11 Sc Ta	0.27" Sc	AC	mottled white ^x and black ^x					
	0.41" Ta	Q						
11 Ti	0.27" Y	AC						still of interest ^a
	0.34" Ta	Q		severe attack ^x				
11 Sc Ti	0.26" Sc	AC		turning white ^x				
	0.4" Ti	Q		turning white ^x				
11 Ti W	0.26" Y	AC		grey flaking ^x				
	0.33" W	Q		turning white ^x				
13 Sc Th	0.085" Sc	AC						still of interest
	0.3" Th	Q			severe attack ^x			
13 Y Th	0.083" Y	AC		severe attack ^x				
	0.33" Th	Q						
Control	Zr	AC						still of interest
Control	Zr	Q				white ^x		
		Ar						still of interest
Control	Zr	Q						still of interest
		Ar						still of interest

^x indicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped

Revised: although appearance justified continuance

The following conclusions were drawn from the data of Table II. First, some gaseous pickup probably occurred during annealing (in the stainless steel tube furnace) because the quenched controls were less corrosion resistant. However, some of the alloys were more resistant in the quenched condition, and it was concluded that contamination could be more than offset by favorable alloying and heat treatment. In general, the appearances of the corrosion films on the quenched specimens were more uniform.

It was apparent that scandium and yttrium were usually deleterious to corrosion resistance. Although not shown in the table, zirconium alloys containing 2 a/o Sc and 2 a/o Y had poor corrosion resistance in 350°C water, developing a white, flaking layer after 16 hr. The effect of scandium was not compensated by the addition of nickel, which can form cathodes to prevent hydrogen damage. Niobium had a favorable influence when yttrium was present but not when scandium was present. The opposite effect was noted with tin, which was able to compensate for scandium but not for yttrium. Another contrast was noted with thorium, which was considered to be a deleterious additive. Scandium and thorium seemed to compensate, but yttrium and thorium did not. This alloy was prepared in a 1 to 3 ratio by miscalculation, and this ratio was maintained in later work. Tantalum seemed to be able to compensate for yttrium to a slight extent.

The number of combinations based on scandium and yttrium was expanded further to take in a greater number of elements which could have valences of +5 or greater. Corrosion data for these scandium alloys in the as cast condition are presented in Tables III and IIIA. The scandium-molybdenum alloys were also tested in the annealed condition as shown in the table. Each specimen was tested for a maximum of 80 hr in 350°C water. Nine specimens were rejected at the end of this time. The remainder were transferred to steam at 540°C and 600 psi without cleaning. Most of the specimens were eliminated after 229 hr in steam, with the exception of ScMo, ScTa, and ScW.

The results of corrosion testing as-cast alloys containing yttrium with Cr, Mn, As, Nb, Mo, Sb, Ta, W, Pb, Bi and Th are shown in Table IV. The yttrium-molybdenum alloys were also tested in the annealed condition, as shown in the table. Certain similarities with the scandium combinations are obvious. The manganese combinations were very poor, whereas YTa showed some promise.

After conclusion of the above tests, those specimens which had not corroded too badly were cleaned by vapor-blasting and etching, and were then degassed at 1100°C for 1 hr in a vacuum induction furnace. They were then sealed in evacuated quartz capsules, heated to 1000°C for 15 min, and water quenched. Only a selection of specimens was given this treatment because the most corrosion-resistant compositions were still in test; the least corrosion-resistant compositions were not considered worthy of further attention. The data are given in Table V, Table VI, and Table VIA. The data of Tables V and VI did not change the corrosion picture of the as-cast alloys. The alloys which had superior corrosion resistance in both the as-cast and quenched conditions were the ternaries containing ScMo, ScTa, and ScW. The combinations of yttrium with Mo, Ta and W were inferior although better than most of the other combinations.

Table III

RESULTS OF CORROSION TESTING OF SCANDIUM ALLOYS IN THE AS-CAST CONDITION

Nominal Composition, Atomic Per Cent	Appearance after Test										
	Hours in Water at 350° C		Additional Hours in Steam (540° C and 600 psi)								
	16	80	67	229	326	446	694	928	1136	1344	1794
0.30 Sc 0.44 Cr	chalky white ^X										
0.20 Sc 0.62 Cr	grey and white patches ^X										
0.14 Sc 0.66 Cr	dark grey with interference colors	grey and white patches ^X									
0.29 Sc 0.45 Mn	grey and white	white flaking ^X									
0.19 Sc 0.58 Mn	grey and white	white flaking ^X									
0.14 Sc 0.66 Mn	grey and white	white flaking ^X									
0.25 Sc 0.39 As	black, over-lying white	all white ^X									
0.14 Sc 0.44 As	dark brown, white specks	all white ^X									
0.11 Sc 0.51 As	dark brown, white specks	dark brown and grey	light grey plus oxide mounds	chalky coat ^X							
0.21 Sc 0.32 Nb	grey and white patches ^X										
0.13 Sc 0.40 Nb	interference colors	black, small white patches	grey, light grey mounds ^X								
0.09 Sc 0.42 Nb	interference colors	dark grey, white specks	grey, light grey mounds ^X								
0.22 Sc 0.33 Mo	interference colors, white specks	dark, white specks	dark and light grey	light grey with oxide mounds ^X							
0.13 Sc 0.40 Mo	interference colors, white specks	dark, white specks	dark and light grey	light grey [*]							
0.09 Sc 0.42 Mo	interference colors, white specks	dark, white specks	dark and light grey	medium grey, 1 bad spot							
(Vacuum annealed 1 hr at 1100° C and furnace cooled)											
0.22 Sc 0.33 Mo	not tested	not tested	grey	not examined	grey, white on edges	translucent grey	unchanged plus several bad spots	unchanged	unchanged	unchanged	slow growth of bad spots
0.13 Sc 0.40 Mo	not tested	not tested	grey with white specks	not examined	grey with white specks	translucent grey	unchanged plus several bad spots	unchanged	unchanged	unchanged	
0.09 Sc 0.42 Mo	not tested	not tested	grey with white specks	not examined	grey with white specks	translucent dark grey	unchanged	unchanged	unchanged plus several bad spots	unchanged	
0.18 Sc 0.27 Sb	interference colors	dark grey	dark and light grey	light grey ^X							
0.10 Sc 0.32 Sb	interference colors	dark, some light grey	dark grey, oxide mounds	accelerating attack ^X							
0.075 Sc 0.35 Sb	interference colors	dark, some light grey	dark grey, oxide mounds	accelerating attack ^X							
0.13 Sc 0.20 Ta	interference colors	dark grey, white specks	grey, white patches and mounds ^X								
0.075 Sc 0.23 Ta	interference colors	interference colors and specks	grey, white patches ^X								
0.05 Sc 0.23 Ta	interference colors	dark grey	dark grey, white specks	light grey, edge cracking	unchanged	light grey and brown, edge cracking	unchanged	light grey, edge cracking	similar plus white patches	thick grey layer, edge attack	thick grey layer, edge attack
											See Table IIIA
0.13 Sc 0.20 W	grey, interference colors	dark grey with white specks	grey, white specks	light grey, white patch	unchanged	similar plus edge cracking	unchanged	unchanged	unchanged	unchanged	thick grey layer edge attack
0.07 Sc 0.22 W	interference colors	dark grey	grey, white specks	light grey, edge cracking	unchanged	unchanged	unchanged	unchanged	unchanged	unchanged	thick grey layer edge attack
0.05 Sc 0.23 W	interference colors	dark grey with white specks	grey, white specks	light grey, white patch	unchanged	similar plus edge cracking	unchanged	unchanged	unchanged	unchanged	thick grey layer edge attack
											See Table IIIA
0.12 Sc 0.18 Pb	interference colors	dark and light grey	dark grey, oxide mounds	accelerating attack ^X							
0.065 Sc 0.20 Pb	interference colors, some grey oxide	dark and light grey	white, with oxide mounds	oxide layering and flaking ^X							
0.05 Sc 0.21 Pb	interference colors, some grey oxide	dark brown, grey	white, with oxide mounds	almost disintegrated ^X							
0.12 Sc 0.18 Bi	interference colors, some grey oxide	interference colors, some grey	dark and light grey	dark and ^X light grey							
0.065 Sc 0.20 Bi	interference colors, some grey oxide	interference colors, some grey	light grey with oxide mounds	accelerating attack ^X							
0.04 Sc 0.20 Bi	interference colors, some grey oxide	dark and light grey	oxide mounds	oxide layering and flaking ^X							
0.04 Sc 0.18 Th	interference colors	brown-black with grey patches	dark and light grey	grey with white patches ^X							
100 Zr	interference colors	black	white flaking (after 18 hrs) ^X								

^{*} Removed, although appearance justified continuance.

^X Indicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped.

Table IIIA

Nominal Composition, Atomic Per Cent	Appearance after Test			
	Hours in Steam (540°C, 600 psi)			
	2410	3130	3886	4390
0.05 Sc 0.23 Ta	thick grey layer, cracks on surface, edge attack	unchanged	unchanged	thick grey layer, flaking ^x
0.13 Sc 0.20 W	thick grey layer, edge attack	unchanged	disintegrating ^x	
0.07 Sc 0.22 W	thick grey layer, edge attack	unchanged	unchanged	thick grey layer, flaking ^x
0.05 Sc 0.23 W	thick grey layer, edge attack	unchanged	unchanged	thick grey layer flaking ^x

^xIndicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped.

Table IV

RESULTS OF CORROSION TESTING OF YTTRIUM ALLOYS IN THE AS-CAST CONDITION

Nominal Composition, Atomic Per Cent	Appearance after Test						
	Hours in Water at 350° C		Additional Hours in Steam (540° C and 600 psi)				
	16	18	67	229	467	694	928
0.25 Y 0.32 Cr	dark grey	dark brown with white oxide ^x					
0.19 Y 0.48 Cr	dark grey, white patches	white patches ^x					
0.14 Y 0.56 Cr	dark grey, small patches	dark grey, small patches	accelerating attack ^x				
0.25 Y 0.32 Mn	all white ^x						
0.17 Y 0.45 Mn	all white ^x						
0.14 Y 0.54 Mn	all white ^x						
0.22 Y 0.28 As	interference colors	brown and grey ^x					
0.16 Y 0.40 As	interference colors, some grey	brown and grey	light grey, flaking ^x				
0.11 Y 0.44 As	interference colors, some white	grey, white patches ^x					
0.20 Y 0.25 Nb	interference colors	interference colors, white patches	white, flaking ^x				
0.13 Y 0.33 Nb	dark grey	grey with white specks	grey, white patches	light grey, white patches	grey, white oxide mounds ^x		
0.095 Y 0.38 Nb	dark grey	grey with white specks	white, flaking ^x				
0.20 Y 0.25 Mo	interference colors, white specks	dark brown with white specks	grey, flaking ^x				
0.13 Y 0.33 Mo	interference colors, white specks	dark brown with white specks	accelerating attack ^x				
0.095 Y 0.38 Mo	brown-black with interference colors	iridescent with white specks	grey with white specks	light grey with oxide mounds ^x			
(Vacuum annealed 1 hr. at 1100° C and furnace cooled)							
0.20 Y 0.25 Mo	not tested	not tested	grey, small white patches	grey, flaking ^x			
0.13 Y 0.33 Mo	not tested	not tested	grey, white patches	not examined	light grey, flaking ^x		
0.095 Y 0.38 Mo	not tested	not tested	grey, white specks	grey	translucent dark grey	same plus accelerating attack	thick, light grey coating, accelerating attack ^x
0.17 Y 0.22 Sb	interference colors	grey with white specks	accelerating attack ^x				
0.11 Y 0.27 Sb	interference colors	brown-grey with some white	light grey and white ^x				
0.08 Y 0.30 Sb	interference colors	brown-grey with some white	accelerating attack ^x				
0.13 Y 0.16 Ta	interference colors	grey with interference colors	grey and dark brown	grey, white patches ^x			
0.08 Y 0.20 Ta	interference colors	brown-black	dark grey with white specks	glossy black with specks	grey, white patches (1214 hrs.)	thick grey layer, white patches (1970 hrs.)	thick, light grey layer, ^x edges flaking (2474 hrs)
0.055 Y 0.22 Ta	interference colors	brown-black	brown-black with white flakes ^x				
0.13 Y 0.16 W	interference colors with white specks	dark grey, with white patches	light grey, flaking ^x				
0.08 Y 0.20 W	interference colors with white specks	black with white patches ^x					
0.055 Y 0.22 W	interference colors with white specks	black-brown with white specks	brown-grey with white specks	light grey with some bad spots ^x			
0.13 Y 0.16 Pb	interference colors, small white patches	light grey with white patches ^x					
0.07 Y 0.18 Pb	interference colors, small white patches	light grey with white patches ^x					
0.05 Y 0.19 Pb	interference colors, small white patches	light grey with white patches ^x					
0.13 Y 0.16 Bi	interference colors with grey patches	dark to light grey ^x					
0.07 Y 0.18 Bi	interference colors with grey patches	dark to light grey ^x					
0.05 Y 0.19 Bi	interference colors with grey patches	dark to light grey ^x					
0.11 Y 0.14 Th	black	light grey with large white patches ^x					
0.06 Y 0.17 Th	black	grey with several white patches	grey oxide mounds ^x				
0.05 Y 0.18 Th	black	grey with several white patches	grey oxide mounds ^x				
100 Zr	interference colors	black	white, flaking ^x				

* Removed, although appearance justified continuance.
^x Indicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped.

Table V

RESULTS OF CORROSION TESTING AFTER VACUUM ANNEALING
AT 1000°C FOR 15 MIN (SEALED IN QUARTZ) AND WATER QUENCHING

Nominal Composition Atomic Per Cent	Appearance after Test				
	Hours in Water at 350°C				
	16	80	115	209	280
0 30 Sc 0 44 Cr	chalky white ^x				
0 20 Sc 0 62 Cr	grey and white patches ^x				
0 14 Sc 0 66 Cr	dark grey with interference colors	light grey and white ^x			
0 14 Sc 0 44 As	not inspected	not inspected	dark grey	grey with white specks	grey with white specks ^a
0 21 Sc 0 32 Nb	grey with white patches ^x				
0 13 Sc 0 40 Nb	grey	grey with white patches ^x			
0 09 Sc 0 42 Nb	interference colors	dark grey white specks	dark grey white specks	dark grey white specks	unchanged
0 13 Sc 0 20 Ta	interference colors	interference colors	dark grey white specks	grey white specks	unchanged
0 075 Sc 0 23 Ta	interference colors	iridescent dark grey	dark grey white specks	grey white specks	unchanged
0 05 Sc 0 23 Ta	interference colors	dark grey	dark grey white specks	grey white specks	unchanged
0 13 Sc 0 20 W	interference colors	dark grey white specks	dark grey white specks	grey white specks and patches	unchanged
0 07 Sc 0 22 W	interference colors	dark grey white specks	dark grey white specks	grey white specks	unchanged
0 05 Sc 0 23 W	interference colors	grey	dark grey white specks	grey white specks	light grey and brown specks
0 25 Y 0 32 Cr	not inspected	not inspected	greyish white ^x		
0 19 Y 0 48 Cr	not inspected	not inspected	greyish white ^x		
0 22 Y 0 28 As	not inspected	not inspected	grey	light grey with specks	light grey white patches and specks
0 11 Y 0 44 As	not inspected	not inspected	grey	light grey with specks	light grey with specks
0 08 Y 0 20 W	not inspected	not inspected	light grey white patches ^x		
0 13 Y 0 16 Pb	not inspected	not inspected	white ^x		
0 07 Y 0 18 Pb	not inspected	not inspected	white ^x		
0 05 Y 0 19 Pb	not inspected	not inspected	white ^x		
0 13 Y 0 16 Bi	not inspected	not inspected	light grey with white patches ^x		
0 07 Y 0 18 Bi	not inspected	not inspected	light grey with white patches ^x		
0 05 Y 0 19 Bi	not inspected	not inspected	light grey with white patches ^x		
0 11 Y 0 14 Th	not inspected	not inspected	white ^x		
100 Zr	interference colors	iridescent black	iridescent black	dark grey	dark grey

Continued in 540°C 600 psi steam Cf Table VI

^x Indicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped

Table VI

RESULTS OF COPROSTION TESTING AFTER VACUUM ANNEALING AT 1000°C FOR 15 MIN AND ATEP QUENCHING

These specimens had an initial oxide film produced by 280 hr in 350°C; after see Table VII

Nominal Composition Atomic Per Cent	Appearance after Additional Hours in Steam (540°C and 600 psi)											
	18	34	52	118	211	252	489	575	737	1179	1387	2023
0.14 Sc 0.44 As	not inspected	not inspected	not inspected	grey flaking ^x								
0.09 Sc 0.42 Nb	dark grey white specks	dark grey small oxide mounds	heavy oxide on most of surface	oxide layering and flaking ^x								
0.13 Sc 0.20 Ta	dark grey white specks	dark grey white patches	unchanged	grey with white flaking spots	light grey small oxide mounds	unchanged	unchanged	unchanged	similar plus edge cracking	similar plus small white mounds	unchanged	unchanged
0.075 Sc 0.23 Ta	dark grey white specks	unchanged	unchanged	grey with white areas	light grey small oxide mounds	unchanged	unchanged	unchanged	unchanged	similar plus small white mounds	unchanged	unchanged
0.05 Sc 0.23 Ta	dark grey white specks	unchanged	unchanged	dark grey	unchanged	unchanged	grey	grey edge cracking	unchanged	unchanged	unchanged	unchanged
												See Table VIA
0.13 Sc 0.20 V	dark grey white specks	dark grey white patches	unchanged	grey with white areas	light grey	light grey oxide mounds	unchanged	unchanged	unchanged	unchanged	similar plus edge cracking [†]	unchanged
0.07 Sc 0.22 W	dark grey white specks	unchanged	unchanged	grey with white areas	light grey	light grey edge cracking	unchanged	unchanged	unchanged	unchanged	similar plus edge cracking [†]	unchanged
0.05 Sc 0.23	light grey white specks	bronish grey	unchanged	light bronish grey	unchanged	light bronish grey edge cracking	unchanged	unchanged	unchanged	unchanged	similar plus flaking [†]	unchanged
												See Table VIA
0.22 / 0.28 As	not inspected	not inspected	not inspected	grey flaking ^x								
0.11 V 0.44 As	not inspected	not inspected	not inspected	disintegrated ^x								
100 Zr	white flaking ^x											

^x Indicates either that the appearance of the specimens arranged reaction at the time shown or that test was stopped.[†] As the oxide layers slowly thickened they developed a fine network of cracks.

Table VIA

Nominal Composition Atomic Per Cent	Appearance after Test			
	Hours in Steam 540° and 600 ps			
	2453	3172	3929	4433
0.13 Sc 0.20 Ta	grey oxide mounds and edge attack	unchanged	thick light grey layer flaking on edges	thick grey layer flaking ^x
0.075 Sc 0.23 Ta	grey oxide mounds and edge attack	unchanged	thick light grey layer flaking on edges	thick grey layer accelerating attack ^x
0.05 Sc 0.23 Ta	thick grey layer edge attack	unchanged	thick light grey layer flaking on edges	thick grey layer flaking ^x
0.13 Sc 0.20 V	thick grey film several white patches edge attack	unchanged	disintegrated ^x	
0.07 Sc 0.22 V	thick grey film several white patches edge attack	unchanged	thick light grey layer flaking ^x	
0.05 Sc 0.23 V	grey layer now healing and developing cracks	unchanged	thick light grey layer flaking	thick grey layer flaking ^x

^x Indicates either that the appearance of the specimens arranged reaction at the time shown or that test was stopped.

A number of other tests were carried out on alloys containing the combinations YNb, YTa, and YbNb. These alloys were arc melted, cut in halves, and etched. They were then annealed in evacuated quartz capsules at 900°C for 16 hr. One-half button was then water quenched, and the other half was furnace cooled. The corrosion data are presented in Table VII. The atomic per cents of Nb and Ta are different because the alloys were made up originally on a weight per cent basis. The Nb combinations were far superior to the Ta combinations. Corrosion resistance diminished with increasing Nb and Ta content, and heat treatment had only a slight effect. The YNb specimens were weighed periodically, and a linear weight gain with time was indicated. Specific weight gains were not determined.

Table VII

RESULTS OF CORROSION TESTING OF AS-CAST Y, Nb AND Y Ta ZIRCONIUM ALLOYS

Composition, Atomic Per Cent	Heat Treatment	Appearance after Test							
		Hours in Steam (540°C, 600 psi)							
		64	135	294	503	616	704	1030	1190
0.51 Y 0.98 Nb	furnace cooled	dark grey	unchanged	some edge cracking	light grey, some edge cracking	unchanged	unchanged	grey and white, many cracks in the oxide and flaking edges	unchanged ^x
	quenched	iridescent grey	unchanged	some edge cracking	dark grey, some edge cracking	unchanged	unchanged		
0.51 Y 1.96 Nb	F. C.	dark grey	unchanged	some edge cracking	light grey, some edge cracking	unchanged	unchanged		
	Q.	iridescent dark grey	unchanged plus incipient attack	light grey, some edge cracking	light grey, some edge cracking	unchanged	unchanged		
0.51 Y 4.9 Nb	F. C.	very thin white coating	unchanged plus incipient attack	unchanged	white, some edge cracking	white, microscopic cracks	unchanged	uniform white, flaking	white flaking ^x
	Q.	dark grey	dark grey plus incipient attack	unchanged	light grey, some edge cracking	unchanged	unchanged		
0.51 Y 0.5 Ta	F. C.	white, flaking ^x	cream color, accelerating attack ^x						
	Q.	black and white patches							
0.51 Y 1.0 Ta	F. C.	white, flaking ^x							
	Q.	white, flaking ^x							
0.51 Y 2.6 Ta	F. C.	white, flaking ^x							
	Q.	white, flaking ^x							
Zr	F. C.	white, flaking ^x							
	Q.	white, flaking ^x							

^xIndicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped.

Ytterbium-niobium combinations were investigated next because of the close crystallochemical similarity of the Y^{3+} and Yb^{3+} ions. Alloys were prepared in the same way as the YNb series, and the data are presented in

Table VIII. The Yb and Nb were always in a 1:1 atomic ratio. The corrosion results were comparable to those of the YNb series, confirming the similarity to be expected from such closely related additives. At the end of 687 hr, the best specimen appeared to be 0.053 a/o Yb, 0.053 a/o Nb as quenched. This alloy was the poorest in the furnace-cooled condition. All four alloys corroded linearly as judged by periodic weighing.

Table VIII

RESULTS OF CORROSION TESTING OF ZIRCONIUM ALLOYS CONTAINING Yb AND Nb

Composition, Atomic Per Cent	Heat Treatment	Appearance after Test			
		Hours in Steam (540°C and 600 psi)			
		113	201	527	687
0.026 Yb 0.026 Nb	F. C.	glossy black	grey, small bad spots	light grey, tiny flakes	similar ^x
	Q.	glossy black	grey, small bad spots	tan, tiny flakes	similar ^x
0.053 Yb 0.053 Nb	F. C.	accelerating attack ^x			
	Q.	glossy black	brown and grey, small bad spots	tan and dark grey	tan and grey, small bad spots ^x
0.14 Yb 0.14 Nb	F. C.	glossy black	grey, small bad spots	light grey	light grey, bad spots ^x
	Q.	glossy black	brown and grey	tan and dark grey	tan and grey, bad spots ^x
0.26 Yb 0.26 Nb	F. C.	glossy black	grey, small bad spots	light grey	light grey, small flakes ^x
	Q.	glossy black	brown and grey	light grey	light grey, small flakes ^x
Zr	F. C.	disintegrating ^x			
	Q.	disintegrating ^x			

^xIndicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped.

B. Alloys Made with Scandium and Yttrium Metal

Following the above surveys a quantitative comparison was made of selected compositions in a lower range of concentrations. Each component was present in the concentration 0.05 atom per cent. The combinations were YNb, YTa, YbNb, YbTa, ScTh, and ScMo. In contrast with all the previous alloys, in which Sc and Y had been added as Sc₂O₃ and Y₂O₃, these alloys were prepared using arc-melted Sc and Y.

Each alloy was prepared as an arc-melted button. Sample discs were analyzed spectroscopically,* and the data are given in Table IX. The agreement between nominal and analyzed composition appeared reasonable with the exception of ytterbium.

Table IX

SPECTROSCOPIC ANALYSIS OF TERNARY ALLOYS CONTAINING
0.05 ATOMIC PER CENT A, 0.05 ATOMIC PER CENT B

Content of A, Weight Per Cent		Content of B, Weight Per Cent		Analyzed Content of Fe, Weight Per Cent
Nominal	Analyzed	Nominal	Analyzed	
0.049 Y	0.04 Y	0.051 Nb	0.05 Nb	0.03
0.049 Y	0.04 Y	0.099 Ta	0.10 Ta	0.03
0.095 Yb	<0.01 Yb	0.051 Nb	0.07 Nb	0.04
0.095 Yb	<0.01 Yb	0.099 Ta	0.10 Ta	0.02
0.025 Sc	0.03 Sc	0.13 Th	0.3 Th	0.04
0.025 Sc	0.03 Sc	0.053 Mo	0.06 Mo	0.06
Zr	-	-	-	0.07

Each button was cold-pressed at 90,000 lb and was stress-relieved by heating in vacuum for one-half hour at 700°C. After furnace cooling, the buttons were cold-rolled to $\frac{1}{16}$ -in. thickness and die-punched to produce $\frac{1}{2}$ -in.-diameter discs. Each disc was then stamped, polished, and etched. The discs were divided into three groups. The first group was left as rolled; the second was vacuum annealed at 900°C for 16 hr in a quartz capsule and water quenched; the third group was annealed in the same way and furnace cooled. After quenching, the second group required recleaning and etching to remove a thin layer of oxide.

Each composition was first tested in 350°C water in the cold-rolled condition. The specimens were examined after 16, 86, and 422 hr. All specimens had interference colors after 16 hr and metallic dark grey films after 86 hr. After a total of 422 hr all but two alloys and the control had a white, flaking coat. The YTa alloy was black, while the zirconium control and scandium molybdenum alloy were iridescent black.

Another set of specimens representing all three treatments was then exposed to steam at 540°C and 600 psi. The results are shown in Table X. As expected, all the specimens which failed in water test were eliminated rapidly in steam. The zirconium control corroded rapidly, whereas the ScMo alloy did not.

* The analyses were made by B. H. Meng of the Chemistry Division.

Table X
RESULTS OF CORROSION TESTING OF SELECTED ZIRCONIUM ALLOYS IN STEAM (540°C 600 psi)
All components are 0.05 atomic per cent (ΔW in mg/dm²)

Treatment*	Composition Weight Per Cent	Hours in Test												
		4	21	39	55	73	139	232	273	373	510	596	758	992
C D E	0.049 Y 0.051 Nb	640 ^X # X # X												
C D E	0.049 Y 0.099 Ta	215 ^X # X # X												
C D E	0.095 Yb 0.051 Nb	732 ^X 615 ^X # X												
C D E	0.095 Yb 0.099 Ta	# X # X # X												
C D E	0.025 Sc 0.13 Th	145 126 ^X 230 ^X	202 ^X											
C D	0.025 Sc 0.053 Mo	85 32	934 ^X 60	73	85	95	120	148	151	174	196	205	230	severe edge attack ^X
E		35	60	76	88	98	117	170	199	259	347	394	495	severe edge attack ^X
C D E	Zr	508 [?] 495 ^X 811 ^X												

* C - as cast and cold rolled D - annealed at 900°C for 16 hr and water quenched E - annealed at 900°C for 16 hr and furnace cooled

^X Indicates either that the appearance of the specimens warranted rejection at the time shown or that testing was stopped

[?] Not weighable because of flaking

After 758 hr, the two remaining ScMo specimens began to suffer accelerated attack on the edges. The appearance of the specimens upon removal is shown in Figure 1, where the specimens from left to right are the cold rolled, quenched, and furnace cooled, respectively. The cold-rolled specimen corroded very rapidly, the annealed and furnace-cooled specimen much less rapidly, and the annealed and quenched specimen had the lowest rate. The weight gains for these specimens are shown in Figure 2. When the data for the quenched specimen were plotted on log-log coordinates, a straight line was obtained as shown in Figure 3. The slope was 0.37, closer to the cube law (slope of 0.33) than to the parabolic law (slope of 0.50). Such curves are typical of zirconium oxidation in oxygen.⁽⁷⁾

C. Microstructure of a ScMo Alloy

The rapid attack on the specimens of Figure 1 obviously began at the edge of the $\frac{1}{16}$ -in.-thick disc and moved toward the center. By metallographic polishing parallel to the flat surfaces, it was possible to observe differences in microstructure (hydride precipitation) adjacent to the rapidly corroding area and at the center of the disc. By comparison, any hydride contributed by corrosion of the flat surfaces was negligible. After obtaining micrographs, the specimens were removed from the Lucite mounts and small portions corresponding to the micrographs were cut out by means of shears.

Figure 1

Specimens of 0.025 w/o Sc, 0.053 w/o Mo zirconium alloy after exposure to steam at 540°C and 600 psi. From left to right: cold rolled (21 hr in steam), annealed and quenched (992 hr in steam), annealed and furnace cooled (992 hr in steam).

100967

 $1\frac{1}{2}X$

Figure 2

Weight gains in mg/dm^2 for three specimens of the alloy 0.025 w/o Sc 0.053 w/o Mo corroded in steam at 540°C, and 600 psi. C = cold-rolled, D = annealed and quenched, E = annealed and furnace cooled.

Figure 3

Log-log plot of the data for Specimen B in Figure 2.

These samples were analyzed for hydrogen by heating to 1200°C in vacuum. Micrographs from the cold-rolled specimen (on the left in Figure 1) are given in Figures 4 and 5. More second-phase is evident in Figure 4 than in Figure 5. The annealed and quenched specimen (in the center of Figure 1) provided the micrographs for Figures 6, 7 and 8. Figure 6 shows more than 50% second phase, which was presumed to be zirconium hydride because it diminished toward the center of the specimen as shown in Figure 8.

The hydrogen contents are given in the captions of the figures and summarized in Table XI. It is seen that the alloy before corrosion testing had slightly more hydrogen than the parent zirconium, but the difference was negligible when compared with the amounts after corrosion testing. The rapidly corroding surface of the quenched specimen had a higher hydrogen concentration than the corroding surface of the cold-rolled specimen. It is possible that a higher diffusion rate in the cold-rolled alloy was responsible for this difference.

D. Examination of Stripped Corrosion Films

The corrosion film was examined from an alloy containing 0.16 w/o Sc and 0.34 w/o Mo (0.32 a/o Sc and 0.32 a/o Mo). The alloy was arc melted, machined to a cylinder, vacuum annealed for 16 hr at 900°C, and water quenched. After cleaning, the specimen was corrosion tested in steam at 540°C and 150 psi for 212 hr. The specimen had a black oxide film and a weight gain of 427 mg/dm².

The oxide was removed in the following way. The specimen was molded in a solution of methyl and ethyl methacrylate and most of the metal was removed by grinding. The remainder of the metal was removed anodically in a saturated ZnCl₂ solution at room temperature, using approximately 15 V. After removing the products of electrolysis, the transparent corrosion film was examined in an electron microscope.

Figure 4

Cold-rolled, 0.025 w/o Sc-0.053 w/o Mo alloy showing the interface between metal (light area on left) and oxide (darker area) after corrosion in steam. Rapid oxide penetration had just begun in this region. 2420 ppm hydrogen in the zirconium.

28300

250X

Figure 5

Interior of specimen shown in Figure 4; 1210 ppm hydrogen.

28301

250X

Figure 6

Annealed and quenched 0.025 w/o Sc-0.053 w/o Mo alloy showing the interface between oxide (darker area on left) and metal (light area) after corrosion in steam. Rapid oxide penetration was well advanced in this area. 3570 ppm hydrogen in the zirconium.

28304

250X

Figure 7

Annealed and quenched 0.025 w/o Sc-0.053 w/o Mo alloy showing the interface between oxide (grey band on left) and metal (light area) after corrosion in steam. Rapid oxide penetration had just begun in this area. 1020 ppm hydrogen in the zirconium.

28302

250X

Figure 8
Interior of specimen shown in Figures 6 and 7.

28303

250X

Table XI

HYDROGEN ANALYSES OF ZIRCONIUM SPECIMENS BEFORE AND
AFTER CORROSION IN STEAM (540°C AND 600 psi)

Specimen Composition	History	Hydrogen Concentration in Specimen (ppm)
Zirconium	Cold rolled but not corrosion tested (control)	36.1 } 36.3 average 36.4 }
0.025 w/o Sc 0.053 w/o Mo alloy	Cold rolled but not corrosion tested (control)	41.1 } 49.7 average 58.2 }
0.025 w/o Sc 0.053 w/o Mo alloy	Sample from the metal shown in Figure 4. Cold rolled and exposed for 38.5 hr in steam.	2,420
0.025 w/o Sc 0.053 w/o Mo alloy	Sample from the metal shown in Figure 5. Cold rolled and exposed for 38.5 hr in steam.	1,210
0.025 w/o Sc 0.053 w/o Mo alloy	Sample from the metal shown in Figure 6. Cold rolled, annealed, and quenched. Exposed for 992 hr in steam.	3,570
0.025 w/o Sc 0.053 w/o Mo alloy	Sample from the metal shown in Figure 7. Cold rolled, annealed, and quenched. Exposed for 992 hr in steam.	1,020

For comparison, dark, iridescent film from corrosion-resistant zirconium crystal bar was examined in the same way. This film resulted from exposure to 315°C water for two weeks. The film from zirconium is shown in Figure 9. The dark mottled areas were probably metal. The diffraction pattern showed monoclinic ZrO_2 , polycrystalline and randomly oriented. Figures 10 and 11 show the film from the ScMo alloy. The clear areas gave a mixed diffraction pattern of Zr and ZrO_2 . The Zr was discretely crystallized without evident preferred orientation, and the ZrO_2 was monoclinic, finely crystallized, and randomly oriented.

Figure 9

Oxide film from zirconium crystal bar exposed to 315°C water for two weeks.

100742

20,000X

Figure 10

Oxide film from an alloy containing 0.15 w/o Sc and 0.34 w/o Mo, corroded in steam (540°C, 150 psi) for 212 hr.

100813

20,000X

Figure 11

Different area from the same specimen as in Figure 9.

100815

20,000X

IV. DISCUSSION

An important aspect of the influence of ternary additions is the solubility of the individual elements in zirconium. The uniformly bad influence of aluminum may be due to the formation of Zr_3Al , which reacts with water and thus can disrupt the ZrO_2 film. Because the scandium and yttrium alloys had large differences in corrosion resistance, it is assumed that sufficient solubility existed to permit interaction with the other additive in the oxide film.

In general, scandium was superior to yttrium as an additive. This superiority could be due to any number of factors, and the most profitable investigative approach is believed to lie in examination of the ScMo alloy in detail. Because the oxide on this alloy has no detectable second phase, it is likely that the additives do not appreciably exceed the solid solution range. Because the oxide was monoclinic, it is possible that a compound such as $ScMoO_4$ may exist which favors a monoclinic structure.

Evidence for such a compound is available for combinations of a similar type as seen in the work of Komkov⁽⁸⁾ who studied rare earth niobates. The lattice parameters for these mixed oxides are in good correspondence with the parameters for monoclinic ZrO_2 . An example is $YbNbO_4$, for which a , b , c , and β are 5.030 kx, 10.798 kx, 5.237 kx, and $85^\circ 30'$, respectively, as compared with 5.21 kx, 5.26 kx, 5.37 kx, and $80^\circ 32'$ for ZrO_2 . The b value for ZrO_2 is doubled when making the comparison. Because Yb^{3+} and Y^{3+} have similar ionic radii (1.00 and 1.06 Å, respectively), a $YNbO_4$ compound may also exist. Consequently, the YNb and $YbNb$ combinations were expected to show good corrosion resistance, but this expectation was only partly fulfilled.

It is apparent that properties of the metal and oxide outside the scope of this study may be important variables. In particular, the role of cathodes in preventing film damage must be considered. If the ScMo alloy has a more stable film, then modification of this alloy by the addition of nickel, palladium, or similar elements should be considered for further development.

The interesting behavior of scandium with molybdenum, tantalum, and tungsten suggests a more detailed examination of these elements with reference to their role in the ZrO_2 lattice. One of the parameters of interest is the molar volume, which is compared for dioxides in Table XII. These data were obtained from various sources and no attempt was made at critical evaluation.

The available data limited the comparison largely to the rutile structure. The sequence from smaller to larger volumes is probably not very different from what it is in other structures. The volumes for CeO_2 , UO_2 , and ThO_2 are given because of the close chemical similarity of their cations to Zr^{4+} .

Table XII

MOLAR VOLUMES OF MO₂ COMPOUNDS

Structure Type	Compound	Molar Volume, cm ³	Vol % Difference from ZrO ₂
Rutile tetragonal C4	α -MnO ₂	17	-22.7
	ϵ -CrO ₂	17.1	-22.2
	TiO ₂	18.9	-14.1
	VO ₂	19.1	-13.2
	RuO ₂	19.2	-12.7
	MoO ₂	19.7	-10.5
	ϵ -WO ₂	20.0	- 9.1
	NbO ₂	20.4	- 7.3
	δ -TaO ₂	20.4	- 7.3
	SnO ₂	21.6	- 1.8
	HfO ₂	21.8	- 0.9
	ZrO ₂	22.0	0.0
	PbO ₂	25.5	+15.9
	TeO ₂	26.5	+20.2
	SeO ₂	26.6	+20.9
	OsO ₂	28.1	+27.7
CaF ₂	CeO ₂	23.6	+ 7.3
f.c.	UO ₂	24.8	+12.7
Cubic C1	ThO ₂	26.4	+20.0

In the rutile series two groups are of particular interest. These are Mn, Cr, Ti, V, and Mo, W, Nb, Ta. The first group did not produce good corrosion resistance in combination with Sc and Y, whereas the latter group produced some promising combinations. It is suggested that some deleterious structural changes may be produced in the protective ZrO₂ layer when cations of too small a volume are incorporated. Cations of too large a volume may also be harmful, judging by the effect of PbO₂. However, data are insufficient on this point.

The favorable combinations involved MoO_2 , WO_2 , NbO_2 , and TaO_2 with slightly smaller molar volumes than ZrO_2 . Therefore, adjustment to the ZrO_2 lattice will not be difficult and some compensation for compressive stresses in the film may be possible. If these ions are found in the penta- or hexavalent state when dissolved in ZrO_2 , then a further decrease in molar volume of an " MO_2 " unit is to be expected.

If scandium and molybdenum ions are both present in the ZrO_2 lattice, it is probable that the lattice will be expanded in the vicinity of scandium and contracted in the vicinity of molybdenum. This is evident because of the different coulombic attraction by cations of different valence and the fact that Mo^{6+} is much smaller than Sc^{3+} . Presumably a favorable volume change can be produced by a certain ratio of lower to higher valence additive and this may be the case for scandium and molybdenum.

Another factor which will determine the effect of a dissolved cation is the cation field strength relative to Zr^{4+} . This factor is defined as Z/a^2 , where Z is the valence and a is the distance from the cation to the nearest oxygen. Dietzel and Tober⁽⁹⁾ compiled a table of such values in reviewing phase diagrams of ZrO_2 and other oxides. The list is presented in Table XIII, and it is obvious that the oxides which form compounds with ZrO_2 have cation field strengths which differ appreciably from that of zirconium. The oxides between MgO and TiO_2 correspond to field strengths which are within ± 0.3 unit of the two values for ZrO_2 . The two values come from the monoclinic and cubic structures, which have different coordinations.

It is apparent that scandium is closer in cation field strength than yttrium but that both are within the solid solution range. The oxides of molybdenum, tantalum, and tungsten did not appear in the original table.

All the elements which are known to be favorable to the corrosion resistance of zirconium fall within the ± 0.3 range. This criterion is obviously limited, however, because many of these oxides, such as ThO_2 and Al_2O_3 , are harmful. Certain of these harmful oxides are known to promote the cubic form of ZrO_2 , and this property may be a factor in lowering the corrosion resistance of zirconium. Conversion of part of the protective layer to cubic ZrO_2 would result in cracks, thereby rendering most of the oxide barrier ineffectual. Additives such as molybdenum may compensate for a tendency of scandium and yttrium to favor the cubic form of ZrO_2 . In the presence of two different ions, such as Sc^{3+} and Mo^{6+} , the less symmetrical monoclinic structure may be favored as opposed to the cubic structure, which is favored by symmetrical coulombic bonding.

Table XIII

RELATIVE CATION FIELD STRENGTHS AND
COMPOUND FORMATION WITH ZrO_2
(Dietzel and Tober)

Oxide	Z/a^2	Coordination	Compounds	
			Formula	Melting Point
Na_2O	0.17	VIII	Na_2ZrO_3	incongr. ?
Li_2O	0.23	VI	Li_2ZrO_3	?
BaO	0.24	VIII	BaZrO_3	congr.
SrO	0.27	VIII	SrZrO_3	congr.
CaO	0.33	VIII	CaZrO_3	congr.
PbO	0.34	VI	PbZrO_3	?
CdO	0.44	VI	CdZrO_3	?
La_2O_3	0.44	VIII	?	
MgO	0.45	VI	none	
MnO	0.48	VI	"	
Y_2O_3	0.49	VIII	"	
FeO	0.52	VI	"	
CoO	0.53	VI	"	
NiO	0.55	VI	"	
ZnO	0.59	IV	"	
ThO_2	0.64	VIII	"	
Sc_2O_3	0.65	VI	"	
ZrO_2	0.78	VIII 0.95 VI	-	
CeO_2	0.83	VIII	none	
Al_2O_3	0.84	VI	"	
BeO	0.87	IV	"	
Cr_2O_3	0.95	VI	"	
TiO_2	1.25	VI	none	
B_2O_3	1.45	IV	?	
SiO_2	1.57	IV	ZrSiO_4	incongr.
V_2O_5	1.85	IV	ZrV_2O_7	incongr.
P_2O_5	2.08	IV	ZrP_2O_7	incongr.
As_2O_5	2.15	IV	$\text{ZrO}(\text{As}_2\text{O}_3)_2$	incongr.
			$(\text{ZrO})_2\text{As}_2\text{O}_7$	incongr.
			$(\text{ZrO})_3(\text{AsO}_4)_2$	incongr.

On the basis of the above considerations, the structural requisite of a protective ZrO_2 film is believed to be the maintenance of a uniform barrier of monoclinic oxide. Any factor that will cause this barrier to break up will increase the corrosion rate. Some possibilities in this

regard are the formation of cracks due to the metastable formation of tetragonal or cubic ZrO_2 , the hydrolyzing of foreign oxide inclusions, e.g., Al_2O_3 , or the presence of zirconates or other zirconium compounds.

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