



CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

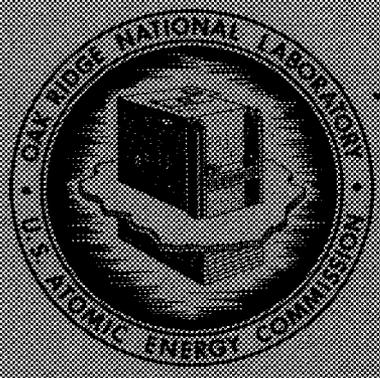
cy. 1

ORNL-4625
UC-33 - Propulsion Systems and
Energy Conversion

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this
document, lend in name with document
and the library will arrange a loan.

COMPATIBILITY OF STRONTIUM COMPOUNDS
WITH SUPERALLOYS AT 900 AND 1100°C

J. R. DiStefano
R. E. McHenry



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-4625

Contract No. W-7405-eng-26

METALS AND CERAMICS DIVISION

ISOTOPES DIVISION

COMPATIBILITY OF STRONTIUM COMPOUNDS WITH
SUPERALLOYS AT 900 AND 1100°C

J. R. DiStefano and R. E. McHenry

NOVEMBER 1971

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

LOCKHEED MARTIN ENERGY RESEARCH LIBRARIES



3 4456 0515796 9

CONTENTS

	<u>Page</u>
Abstract	1
Introduction	1
Theory	2
Strontium-Oxygen System	2
Sr-Ti-O ₂ System	8
Test Materials and Procedures	15
Results	18
Weight Changes in Compounds and Alloys	18
Compositional Changes in Alloys and Compounds	20
Metallography	20
900°C Test - Alloys	20
1100°C Test - Alloys	26
Jacketed SrO - Alloys	29
1100°C Test - Compounds	29
Mechanical Properties - Alloys	34
Discussion	37
Subsequent Short-Term Tests	38
Summary	43
Acknowledgments	44
References	44

COMPATIBILITY OF STRONTIUM COMPOUNDS WITH
SUPERALLOYS AT 900 AND 1100°C

J. R. DiStefano and R. E. McHenry*

ABSTRACT

The compatibility of SrTiO_3 , Sr_2TiO_4 , and SrO with Haynes alloy No. 25, Hastelloy C, and type 316 stainless steel was evaluated in tests for up to 10,000 hr at 900 and 1100°C. Both SrTiO_3 and Sr_2TiO_4 were compatible with all three superalloys at either temperature. Some reaction resulting in a slight reduction of SrTiO_3 was found, but it did not have a significant effect on the superalloys. A reaction between SrO and Haynes alloy No. 25 and Hastelloy C occurred at 900°C. The reaction was more extensive at 1100°C and also included type 316 stainless steel; however, it appeared to reach steady state after 5000 hr. In commercially produced Hastelloy C or C-276 the reaction with SrO appears to be related to the presence of one or more intermetallic phases. In laboratory heats containing very low silicon but relatively high carbon or in alloys containing very high silicon these phases do not form and no attack was observed.

In addition to the reactions reported a theoretical discussion of several types of reactions that could occur in these systems is presented. The effect of an in-growth of zirconium due to decay of ^{90}Sr is also discussed.

A reduction in the room-temperature mechanical properties of Haynes alloy No. 25, Hastelloy C, and type 316 stainless steel was noted after heat treating at 900 or 1100°C. A further reduction in ductility was found in some of the samples exposed to SrO .

INTRODUCTION

The compatibility of three radioisotope power fuel compounds of strontium (SrO , SrTiO_3 , and Sr_2TiO_4) with three potential container materials (Haynes alloy No. 25, Hastelloy C, and type 316 stainless steel) has been studied.

*Isotopes Division.

The energy produced by the radioactive decay of ^{90}Sr has been extensively employed as a source of heat in thermoelectric conversion devices designed to provide electric power in remote applications. Of the 30 current working applications found in the literature,¹ 22 are powered with ^{90}Sr . Twenty-three of the thirty applications are terrestrial and marine (twenty-two ^{90}Sr and one ^{60}Co), and seven are aerospace applications (^{238}Pu).

Although ^{90}Sr power sources with up to six years of service at 540°C have been destructively examined,² adequate quantitative data on the reliability of the fuel containment were not available to predict performances for longer term uses, especially at the higher operating temperatures of later generation conversion devices. It was the purpose of this work to provide that information.

The study described in this report was carried out with nonradioactive compounds of strontium. A similar but more limited study with ^{90}Sr compounds is in progress to establish the validity of the conclusions drawn from this study. Preliminary data from the work with ^{90}Sr compounds indicate that the conclusions in this report are valid.

The three potential container materials chosen are all commercially available and represent Co-, Ni-, and Fe-base alloys. The temperatures studied, 900 and 1100°C , were chosen to bracket the operating temperature of advanced thermoelectric conversion devices and to determine the effect of temperature on reactions that occurred. In addition, we felt that the temperature comparison would also provide a basis for extrapolation to longer times at lower temperatures. The tests were conducted for times up to $10,000$ hr.

THEORY

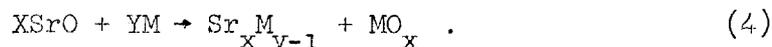
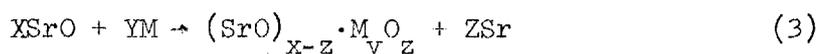
Strontium-Oxygen System

The strontium-oxygen system has been studied by several workers,³⁻⁵ and only two compounds (SrO and SrO_2) are known. Strontium dioxide is readily decomposed at high temperature and/or low oxygen pressure. The decomposition pressure³ of SrO_2 is 1 atm at 365°C and 50 atm at 500°C .

Copeland and Swalin⁵ found no phase other than SrO in the temperature range 800 to 1400°C. Since the conditions for fabrication of the SrO (see p. 17) and the compatibility test conditions both involved heating to well above 800°C, no further consideration of the compound SrO₂ is necessary.

Strontium oxide crystallizes as a rock salt (cubic) structure with a lattice parameter of $5.1600 \pm 0.0005 \text{ \AA}$ (ref. 5). It is among the most stable oxides known, being slightly less stable (at temperatures below 1200°C) than MgO, CaO, the rare-earth sesquioxides, ThO₂ and Ac₂O₃. At temperatures of 1200 to 2200°C, BaO, BeO, Al₂O₃, Sc₂O₃, ZrO₂, and HfO₂ are slightly more stable than SrO.

The stability of SrO in contact with metals can be estimated from free energy data if the assumption is made that all condensed phases have unit activity (that is, there is negligible solubility of any phase in any other phase). Several reactions of SrO with the constituents of Hastelloy C, Haynes alloy No. 25, and type 316 stainless steel can be hypothesized, and calculations can be made to determine if the reactions are energetically favorable. The reactions are:



The free energies of formation of the most stable oxides of all the constituents in the systems SrO-Hastelloy C, SrO-Haynes alloy No. 25, and SrO-type 316 stainless steel are plotted in Fig. 1. Figure 1 shows that SrO has a much higher negative free energy of formation and that reactions of the type in Eq. (1) are unfavorable thermodynamically. Although no specific information has been found in the literature on strontium solubility in the metals of interest, Hansen⁶ reports that barium is insoluble in nickel and that calcium is insoluble in iron. Therefore, it is unlikely that the solubility of strontium in the alloys of interest is sufficient to reduce the activities significantly below unity.

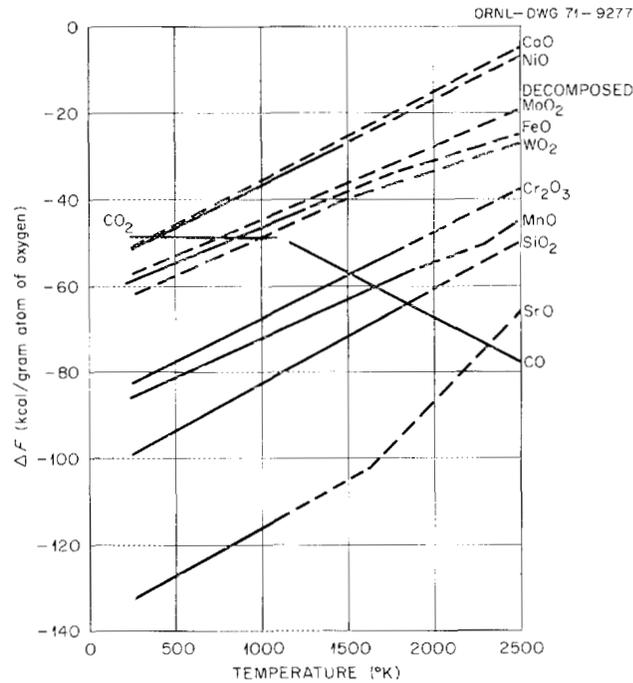
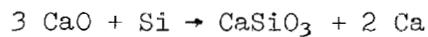


Fig. 1. Free Energy of Formation of Oxide.

Mixed oxides of strontium oxide and other metal oxides of the type shown in Eq. (2) have not been reported. They are possible only if strontium can exist in an oxidation state of less than +2. Since such an oxidation state reportedly⁵ does not exist, it is concluded that the reaction shown in Eq. (2) will not occur.

Most stable mixed oxides of two or more cations occur as one of three basic structural types. These are the spinel, ilmenite, and perovskite structures. In addition to the three structures mentioned above, several structures of mixed oxides of SiO_2 are known. It is likely that all the oxidized constituents of the three alloys of interest (except nickel and cobalt, which have only the +2 oxidation state except under unusual conditions) would form one or more mixed oxides with SrO . One of the few mixed oxides of alkaline earth oxides for which free energy data are available is CaSiO_3 . The following reaction can be postulated:



(5)

$$432 \text{ kcal} \rightarrow 358 \text{ kcal}, \Delta F^\circ = 74 \text{ kcal}.$$

The free energies of strontium compounds in the preceding reaction should be very close to those of calcium compounds. Reaction (5) for SrO is expected to be among the more energetically favorable reactions of the type shown in Eq. (3) because of the high free energy formation of SiO₂. Since Eq. (5) is unfavorable due to a large positive free energy, reactions as shown in Eq. (3) are concluded to be unlikely. In general, the higher free energies of formation of mixed oxides compared with the sum of the free energies of formation of the individual components result from slightly more favorable arrangement of atoms in the lattice and are not believed to be energetic enough to favor Eq. (3). For example, CaCO₃, CaCrO₄, and CaSiO₃ have free energies of formation of -32, -41, and -21 kcal/mole above the sum of the free energies of formation of the individual oxide components of the mixed oxides.

The following reactions [of the type shown in Eq. (4)] are the most likely because of high free energies of formation of SiO₂ and Cr₂O₃:

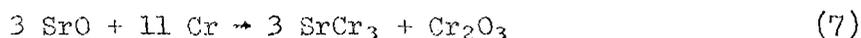
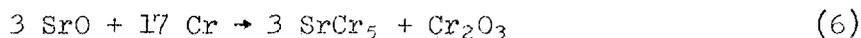


Table 1 lists the minimum free energies of formation for the intermetallic compounds in Eqs. (6) through (8) required to favor the reactions to take place at 1000°C. Table 1 also shows the free energies of formation of the intermetallic compounds estimated from electron binding and Engel's correlation.^{7,8} All the estimated free energies shown in column 2 are larger negative values than those required for the reaction to be energetically favorable; therefore, the reaction could occur.

No description of intermetallic compounds of strontium and chromium has been found in the literature. Westbrook⁹ lists only one compound of the alkaline earths and chromium, Be₂Cr. The compound, SrSi₂, has been reported by Janzon et al.¹⁰ Neshpar et al.¹¹ prepared BaSi₂ using a reaction similar to Eq. (8):

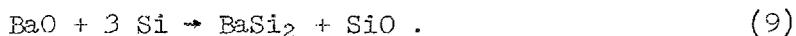


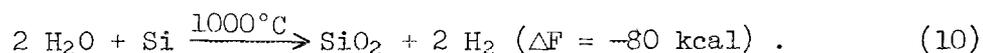
Table 1. ΔF° for Strontium Intermetallic Compounds

Equation Number	Inter-metallic Compound	Intermetallic Compound, kcal/mole	
		Estimated ΔF°	Minimum Required ΔF°
(6)	SrCr ₅	-70 to 105	~ -50
(7)	SrCr ₃	-100 to 150	~ -50
(8)	SrSi ₂	-60 to 90	~ -30

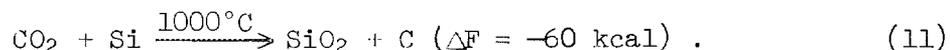
The reaction was reported to be initiated at 1300°C under conditions where SiO is removed from the reaction zone by volatilization. Since from the limited information available it cannot be shown that Eqs. (6) through (8) are energetically unfavorable, they must be considered as energetically possible if not probable.

The foregoing discussion has considered only the net free energy of reactions. Even if a reaction is energetically favorable, it may not occur at a detectable rate because of kinetic factors.

In addition to the constituents which are nominally included in the compatibility couples, impurities must be considered from the standpoint of producing reactions. The impurities which appear to be of the most consequence are oxidizing materials such as CO₂, H₂O, and O₂. At temperatures above 900°C the reaction of H₂O with W, Fe, Cr, Mn, and Si is energetically favorable. The following reaction is typical:



In the temperature range 900 to 1100°C, the reaction of CO₂ with Cr, Mo, and Si is energetically favorable. The following reaction is typical:



Oxygen would readily oxidize all the constituents of the alloys of interest, with Si, Mn, and Cr being most favorable.

A 100-g pellet of SrO made by the identical method (see p. 17) used to prepare the SrO pellets for the compatibility couple was analyzed for

CO₂ content. The SrO was dissolved in acid, and the gas evolved was scrubbed with a Ba(OH)₂ solution. No CO₂ was detected. From this test, it was concluded that CO₂ concentration was negligible (less than 5 ppm by weight), and reactions of the type given in Eq. (11) are not expected.

The preparation of the SrO pellets (by hot pressing at 1250°C in vacuum) is such that the H₂O concentration is thought to be less than a few parts per million. However, no analytical method sufficiently sensitive to detect H₂O in the SrO was found. Since it is a likely impurity and an accurate assay of H₂O was unattainable, reactions of the type shown in Eq. (10) must be considered a possibility.

The solution of oxygen in SrO has been reported at temperatures above 600°C (refs. 4, 5). Copeland et al.⁵ measured the solubility of oxygen at 1-atm oxygen partial pressure for temperatures of 1100 to 1300°C using thermal gravimetric analysis (TGA). The solubility at 1100 and 1300°C was 8.3×10^{-4} and 1.95×10^{-3} mole fraction oxygen, respectively. They concluded that the oxygen is held interstitially as oxygen ions. Kozlenko et al.⁴ used a volumetric method to measure the solubility of oxygen in SrO at partial pressures of oxygen up to 5 torr at temperatures of 950 and 1150°C. They derive equations for the solubility at 950°C,

$$N_{O_2} = 6.15 \times 10^{-5} p^{0.381} \quad (12)$$

and at 1150°C,

$$N_{O_2} = 4.65 \times 10^{-5} p^{0.377} \quad (13)$$

where

P = oxygen partial pressure, torr, and

N_{O₂} = mole fraction of oxygen in solution.

No data have been found on the solubility of oxygen in SrO at low temperatures. It should be noted that the results of the experiments by Copeland and Kozlenko show opposite temperature effects.

Fabrication of SrO pellets included heating the pellets to 1250°C in vacuum. From Eq. (13), assuming equilibrium is established during hot pressing, the mole fraction of oxygen should not exceed 2.3×10^{-5}

(assuming P for $O_2 = 0.5$ torr) or 2.5×10^{-6} moles of oxygen (0.16 mg) per couple. Since both refs. 2 and 3 report that oxygen diffuses rapidly in SrO and since the SrO pellets were handled in argon (100 ppm O_2) after they were hot pressed, dissolved oxygen should be a negligible factor.

Sr-Ti- O_2 System

In this discussion only the compositional regions of the phase diagram,^{12,13} shown in Fig. 2, at or near the compounds $SrTiO_3$ and Sr_2TiO_4 will be considered. Of the bounding binary systems, Sr-O has already been discussed and also need not be considered because no Sr-O phases exist in the compositional region of interest. From Fig. 2 the compounds that may be present in approximately stoichiometric $SrTiO_3$ and Sr_2TiO_4 are: TiO_2 , $SrTiO_3$, Sr_4TiO_{10} , $Sr_3Ti_2O_7$, Sr_2TiO_4 , and Sr_3TiO_5 .

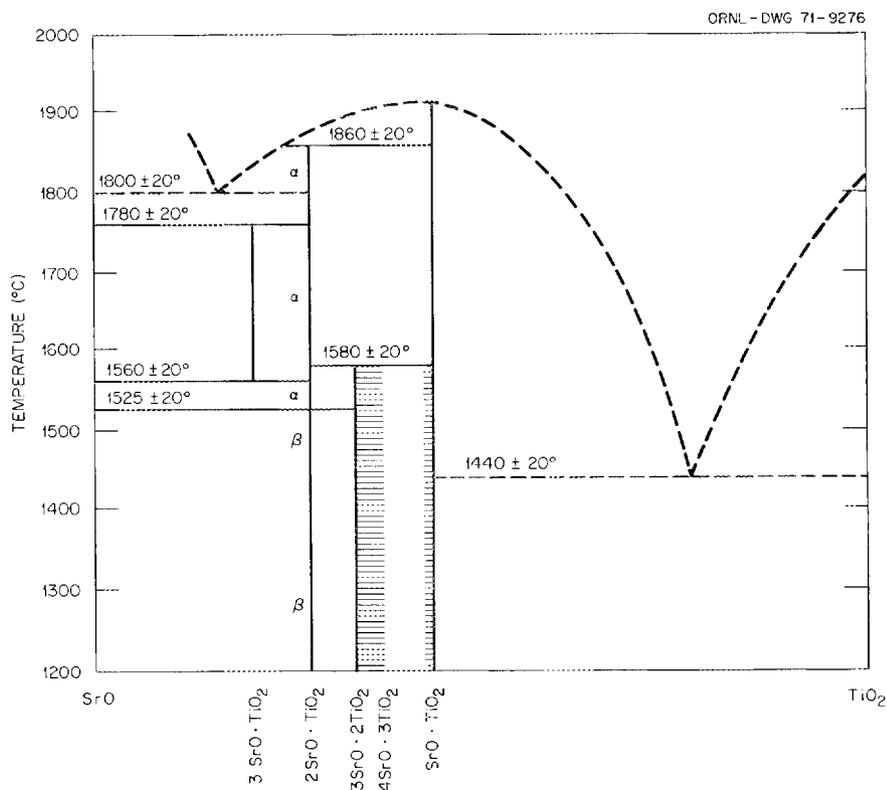


Fig. 2. The SrO-TiO₂ Phase Diagram. [Ref., A. Cocco and F. Massazza, "Microscopic Examination of the System SrO-TiO₂," *Ann. Chim. (Rome)* 53(7), 883-893 (1963)].

The bounding binary system Ti-O must be considered because of the existence of TiO₂ in TiO₂-rich SrTiO₃.

The most significant reactions involve the reduction of TiO₂ or TiO₂-SrO mixed oxides by the metallic constituent of the alloys Hastelloy C, Haynes alloy No. 25, and type 316 stainless steel. Both the SrTiO₃ and Sr₂TiO₄ used in the compatibility tests to be described were prepared by vacuum hot pressing and as a consequence have the nominal composition SrTiO_{3-x} and Sr₂TiO_{4-x}, where x has a small value. From the work of Moser et al.¹⁴ and Kofstad¹⁵ on TiO₂, it is estimated that x does not exceed 0.015. Values of x were measured on typical hot-pressed titanates by determining the weight gain of a sample on oxidation. These data indicate a typical value of 0.015 for x.

Strontium titanate has a perovskite structure with $A = 3.920 \pm 0.002 \text{ \AA}$. Kestigian¹⁶ investigated the extent of reduction possible in SrTiO_{3-x} and found the lower limit to be SrTiO_{2.5}. The structure and lattice parameter did not change. SrTiO₄ has a body-centered tetragonal K₂NiF₄ structure with $A_0 = 3.88 \text{ \AA}$, $C_0 = 12.60 \text{ \AA}$. This can be described¹⁷ as alternating layers of perovskite SrTiO₃ and rock salt SrO along the C direction. No study of Sr₂TiO_{4-x} has been found in the literature. It is presumed to behave analogously with SrTiO_{3-x}.

The mixed oxides of SrO and TiO₂ and the TiO₂ will be in thermodynamic equilibrium in contact with a metal when the partial molar free energy of dissociation of TiO₂ or the mixed oxide (a positive value) is equal in magnitude to the free energy of formation of the metal oxide (a negative value). Kofstad¹⁵ has derived from TGA data the equation:

$$\overline{\Delta F}_{\frac{1}{2}\text{O}_2} = 3RT \ln x + 131,000 - 29.8T \quad (14)$$

for the partial molar free energy (ΔF) of dissociation of TiO_{2-x}. Equation (14) does not fit well when x is less than 0.0001 (near stoichiometry). Partial molar free energy data for the dissociation of SrTiO_{3-x} and Sr₂TiO_{4-x} have not been found in the literature. Due to the increased stability of the mixed oxides above that of TiO₂, the partial molar free energies for the mixed oxides (SrTiO_{3-x} and Sr₂TiO_{4-x}) will

be slightly higher than that of TiO_{2-x} . If calculations are made for the reduction of SrTiO_3 and Sr_2TiO_4 using data from the TiO_{2-x} system, the reduction predicted would be maximum values. Values of x for various values of $\Delta\bar{F}$ are shown in Fig. 3.

Table 2 shows the maximum reduction of TiO_2 , SrTiO_3 , and SrTiO_4 by metals in the alloys of interest. The reactions are:

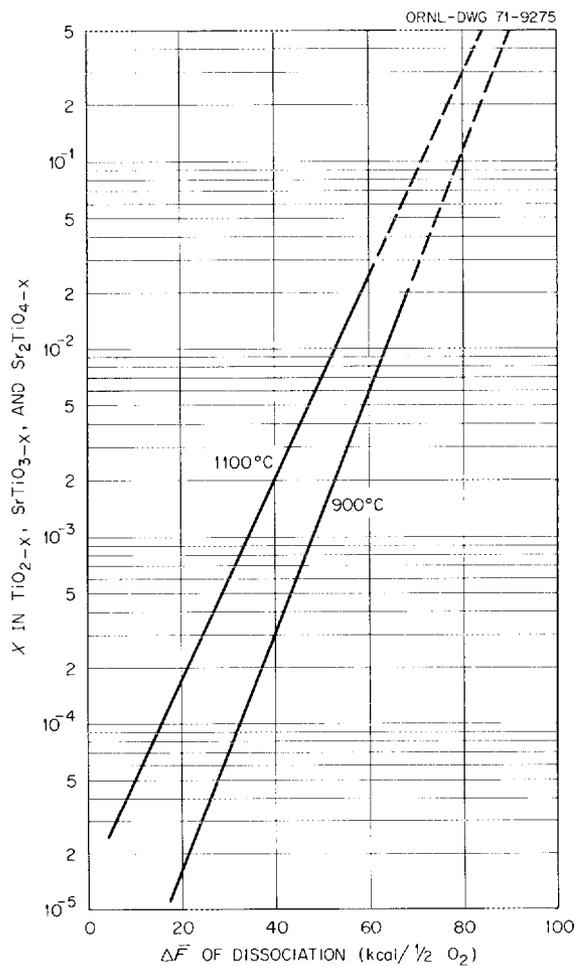
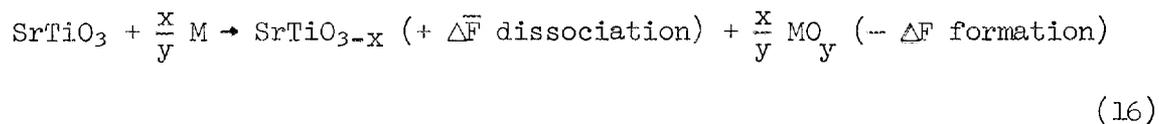
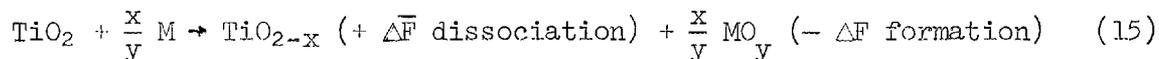


Fig. 3. Values of x in TiO_{2-x} , SrTiO_{3-x} , and SrTiO_{4-x} Versus $\Delta\bar{F}$.

Table 2. Calculated Equilibrium Composition for Titanate-Metal Systems and Weight Loss (Oxygen) from 24 g of Titanate Sample

Metal	Temperature (°C)	Composition (and Weight Loss, mg)			
Si	900	TiO _{1.9}	SrTiO _{2.9}	(176)	Sr ₂ TiO _{3.9} (110)
Mn	900	TiO _{1.98}	SrTiO _{2.98}	(11)	Sr ₂ TiO _{3.98} (6.7)
Si	1100	TiO _{1.85}	SrTiO _{2.85}	(283)	Sr ₂ TiO _{3.85} (180)
Mn	1100	TiO _{1.95}	SrTiO _{2.95}	(69)	Sr ₂ TiO _{3.95} (48)
Cr	1100	TiO _{1.975}	SrTiO _{2.975}	(21)	Sr ₂ TiO _{3.975} (13)
C ^a	1100	TiO _{1.986}	SrTiO _{2.986}	(~0)	Sr ₂ TiO _{3.986} (~0)

^aStarting composition following hot pressing at 1250°C in a graphite element vacuum furnace is SrTiO_{2.985} and Sr₂TiO_{3.985}.



(17)

In the preceding reactions, $\overline{\Delta F}$ of dissociation is positive (the reduced oxide is energetically unfavored) while ΔF of formation of the metal oxide is negative (the oxidation of the metal is energetically favored). The reactions are at equilibrium when $\overline{\Delta F} - \Delta F^\circ = 0$. In the systems of interest only Cr, Mn, and Si will reduce the compound to less than the fabrication value of x.

Each compatibility couple contains 24 g of titanate. If the maximum reduction occurs (the reaction with Si), the SrTiO₃ would release 200 and 300 mg of oxygen at 900 and 1100°C, respectively. The Sr₂TiO₄ would release 134 and 200 mg of oxygen at 900 and 1100°C, respectively.

The kinetics for the release of oxygen from the titanate phases is very rapid. Paladino¹⁸ reports the diffusion coefficient for the oxidation-reduction of SrTiO₃ in the temperature range 850 to 1460°C by the equation:

$$D = 0.33 \exp\left(-\frac{22.5}{RT}\right), \quad (18)$$

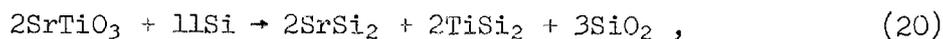
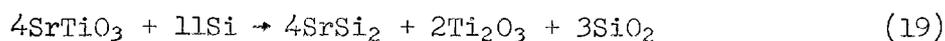
where

D = diffusion coefficient, cm^2/sec , and

T = temperature, $^{\circ}\text{K}$.

At 900°C , $D = 2 \times 10^{-5} \text{ cm}^2/\text{sec}$ and at 1100°C , $D = 1 \times 10^{-4} \text{ cm}^2/\text{sec}$.

Reactions of titanates with Si to form intermetallic compounds [similar to Eqs. (6) through (8)] are among the most likely reactions of this type due to the high free energy of formation of SiO_2 . Two reactions,



will be considered. In Eq. (19) the total free energy of formation of the reactants at 1000°C is -1200 kcal [$4(-300)^* + 0$], while the total free energy of formation of the products, except 4SrSi_2 , is -1008 kcal [$2(-279) + 3(-150)$]. For the reaction shown in Eq. (19) to be energetically favorable, the free energy of formation of SrSi_2 must be more negative than -48 kcal/mole $\left(\frac{1200 - 1008}{4}\right)$. In Eq. (20) the free energy of formation of the reactant is -600 kcal [$2(-300) + 0$] while the free energy of formation of the products, except SrSi_2 and TiSi_2 , is -450 kcal [$3(-150)$]. For the reaction shown in Eq. (20) to be energetically favorable, the free energies of formation of SrSi_2 and TiSi_2 must be more negative than -37.5 kcal/mole $\left[\frac{(-600) + (-450)}{4}\right]$. Since both Sr and Ti form known compounds⁹ with Si which theory predicts^{7,8} to have free energies of formation sufficiently negative to favor the reactions shown in Eqs. (19) and (20), this reaction must be considered as possible.

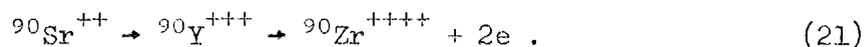
There are no known reactive impurities in the titanate samples used in the compatibility tests. Any that may be present are considered to be of negligible significance.

In the discussion in this section the constituents of the alloys of Hastelloy C, Haynes alloy No. 25, and type 316 stainless steel have been assumed to be present as discrete phases of the elements. If a constituent

*The free energy of formation of SrTiO_3 was approximated by adding 21 kcal/mole to the sum of the free energies of formation of SrO and TiO_2 .

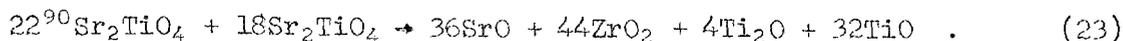
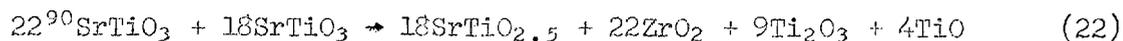
of the alloy is present in solution or as an intermetallic phase, then the reactions concluded to be favorable energetically will be less favorable or unfavorable.

An aspect of the compatibility of radioactive compounds of strontium not evaluated in the work described in this report is the effect of the in-growth of zirconium due to the decay of ^{90}Sr :

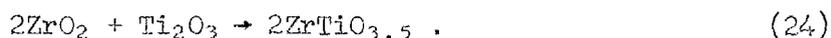


The equilibrium quantity of ^{90}Y due to its short half-life is insignificant and is ignored. After decay of ^{90}Sr the titanate fuel will contain Sr, Zr, Ti, and O (fission product Sr is 55% ^{90}Sr). In a closed system, such as an encapsulated heat source, a deficiency of oxygen will exist due to the valence change occurring as a result of reaction (21). At temperatures below approximately 1700°C, the relative ratios of the free energies of formation to that of TiO_2 for the several possible oxides are: SrO , 1.30; ZrO_2 , 1.20; TiO , 1.12; Ti_2O_3 , 1.08; Ti_3O_5 , 1.05; TiO_2 , 1.00. The absence of any compound of Sr and O between Sr^0 and SrO has been discussed previously (p. 3). Neither does the system Zr-O exhibit compounds between Zr^0 and ZrO_2 (ref. 19) (Fig. 4). Since the reduction of titanium oxides is favored thermodynamically, the decay of ^{90}Sr titanate will result in the reduction of Ti (ref. 20) to varying degrees (Fig. 5) depending on the amount of decay of ^{90}Sr .

The total decay of ^{90}Sr in $^{90}\text{SrTiO}_3$ and $^{90}\text{Sr}_2\text{TiO}_4$ should give products as shown in the following reactions:

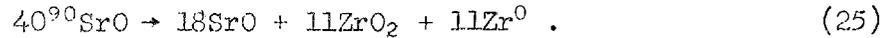


It is probable that the ZrO_2 and Ti_2O_3 shown in Eq. (22) will react:



The compound ZrTiO_4 is known²¹ in the system ZrO_2 - TiO_2 but a description of the system ZrO_2 - Ti_2O_3 has not been found in the literature. Several mixed oxides including SrZrO_3 are possible with the products of Eq. (23).

The decay of ^{90}Sr in SrO will produce zirconium metal as follows:



TEST MATERIALS AND PROCEDURES

The design of the test system used in these studies is shown in Fig. 6. A center specimen of one of the superalloys was sandwiched between two pellets of a strontium compound, and a second superalloy specimen in the form of a cylindrical sleeve was used to measure changes in mechanical properties. Specimens and pellets were enclosed in an outer capsule of the superalloy being tested by welding in an argon atmosphere. Concentrations of the major elements in both the strontium compounds and the superalloys are shown in Tables 3 and 4.

The Isotopes Division of ORNL prepared SrTiO_3 , Sr_2TiO_4 , and SrO by starting with a 1 M HNO_3 solution of $\text{Sr}(\text{NO}_3)_2$ having a strontium concentration of 15 g/liter of solution. The composition of the strontium compounds was adjusted to simulate material normally obtained from reactor

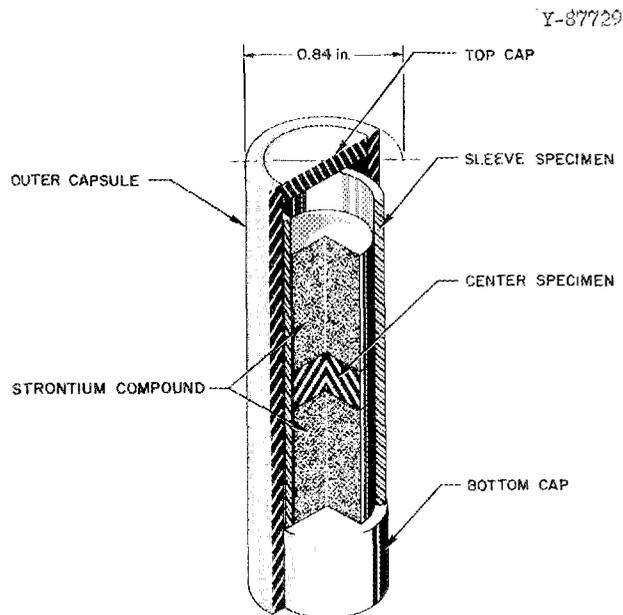


Fig. 6. Compatibility Test Assembly.

Table 3. Composition of Strontium Compounds

Compound	Composition, ^a wt %						
	Ca	Ba	Sr	Mg	Ti	O	C
SrTiO ₃	1.72	1.76	43.5	0.17	26.19	26.47	0.03
Sr ₂ TiO ₄	2.24	2.27	55.8	0.21	16.93	22.61	0.05
SrO	3.07	3.15	77.7	0.30		15.69	0.15
Compound	Constituent		Composition, wt %				
SrO	SrO		91.69				
	CaO		4.29				
	BaO		3.52				
	MgO		0.49				
Sr ₂ TiO ₄	Sr ₂ TiO ₄		90.83				
	Ca ₂ TiO ₄		5.28				
	Ba ₂ TiO ₄		3.19				
	Mg ₂ TiO ₄		0.70				
SrTiO ₃	SrTiO ₃		90.35				
	CaTiO ₃		5.83				
	BaTiO ₃		3.00				
	MgTiO ₃		0.82				

^aCalculated from starting solution composition except for carbon analysis.

Table 4. Composition of Superalloys

Material	Concentration, wt %									
	Ni	Fe	Co	Cr	W	Mn	Mo	Si	C	O
Hastelloy C	55	6		16	3	0.5	16	0.5	0.05	0.001
Haynes alloy No. 25	10	2.5	50	20	15	1.0	0.4	0.5	0.10	0.001
Type 316 stainless steel	13	63		17		2	2.5	0.5	0.04	0.016

fuel reprocessing waste. The SrTiO₃ was prepared by adjusting the starting solution to pH 3 to 5 with NH₄OH. The stoichiometric quantity of TiO₂ was slurried into the solution followed by the addition of an excess of NH₄CO₃ (256 g/liter of solution). Ammonium hydroxide was used to adjust the solution to pH 8 before it was digested at 72°C for 30 min. The solution was filtered and the precipitate (SrCO₃ and TiO₂) was

calcined at 1100°C for 4 hr to convert the mixed oxides to strontium titanate.

An alternative procedure for preparing SrTiO₃ used KOH, KHCO₃, and K₂CO₃ to precipitate the strontium from the starting solution. The starting solution was adjusted to pH 1 with KOH, and the TiO₂ was slurried into the solution, which was then adjusted to pH 3 and heated to 70°C. The solution was adjusted to pH 10 with K₂CO₃ and digested at 82°C for 2 hr, cooled to 45°C, and filtered. The mixed oxides were converted to SrTiO₃ by calcining at 1100°C for 4 hr.

Strontium orthotitanate and SrO were prepared by identical procedures except in the preparation of Sr₂TiO₄ the quantity of TiO₂ added is less than that used for SrTiO₃; and in the preparation of SrO, no TiO₂ is added.

The 0.5-in.-diam by 0.75-in.-long pellets of SrTiO₃, Sr₂TiO₄, and SrO were prepared by vacuum hot pressing in graphite dies. The SrTiO₃ and Sr₂TiO₄ pellets were hot pressed at 4000 psi for 30 min at temperatures of 1250 and 1285°C, respectively. The densities of the SrTiO₃ and Sr₂TiO₄ pellets exceeded 95% of the theoretical value. However, highly calcined, pure SrO cannot readily be hot pressed to high density. Therefore, two procedures, both employing a pressing aid, were used to prepare dense SrO for our compatibility tests. In one procedure the calcined SrO was exposed to moist air to convert a small percentage of the SrO to Sr(OH)₂. The resulting mixture was readily densified by hot pressing at 4000 psi and 800°C. Subsequent to densification, the pellets were heated to 1300°C in vacuum to convert Sr(OH)₂ to SrO. The second procedure for the preparation of dense SrO used colloidal SiO₂ (0.012 μm diam) as a pressing aid. The SrO powder to be hot pressed was first blended with the colloidal silica, and then the blended powders were hot pressed at 4000 psi for 30 min at 1250°C. Both procedures gave SrO densities of greater than 95% of the theoretical value. After the SrO pellets were pressed, they were protected from reacting with moisture in the air by storing them in a dry argon environment until they were used.

The fabrication of large ⁹⁰SrO heat sources in hot cells that do not have provision for maintaining an inert atmosphere has required that the ⁹⁰SrO sources be hot pressed in platinum jackets to protect them from

atmospheric moisture. Therefore, strontium oxide pellets with platinum jackets were hot pressed for tests with Hastelloy C as part of our compatibility program.

All of the superalloy components were machined from bar stock by the Materials and Fabrication Services Division of Thermo Electron Corporation, Woburn, Mass. Each cylindrical sleeve specimen received a special honed and polished finish to give a smooth inner diameter surface, and the center specimens were metallographically polished on both sides.

The capsules were assembled as shown in Fig. 6 and then closed by tungsten-arc welding in an atmosphere chamber containing argon. Each capsule was enclosed in a larger protective capsule that was also closed by welding in the atmosphere chamber. The test capsules were then exposed in a conventional air furnace for the prescribed time and temperature.

After thermal testing the couples were disassembled for examination. Dimensional, weight, chemical, metallographic, and mechanical properties changes were recorded to evaluate the extent of any interactions between the strontium compounds and superalloys. The center disk specimen from each test was sectioned longitudinally. One half was submitted for metallographic examination, and a wedge-shaped sample was cut from the other half for chemical analysis. A full longitudinal section from one of the strontium compound pellets was used for metallographic examination, while a 0.125-in. disk was cut from the other pellet at the end that was in contact with the superalloy and submitted for chemical analysis.

RESULTS

Weight Changes in Compounds and Alloys

No significant dimensional changes in either the strontium compounds or superalloy specimens were found in these compatibility tests. Weight changes are summarized in Tables 5 and 6. We found it difficult to separate the components after the 1100°C tests; in some instances we were unable to obtain useful weight change data. This occurred mainly with

Table 5. Weight Changes in Haynes alloy No. 25, Hastelloy C, and Type 316 Stainless Steel After Exposure to Strontium Compounds

Compound	Weight Change, mg			
	1100°C			900°C
	1000 hr	5000 hr	10,000 hr	10,000 hr
<u>Haynes alloy No. 25</u>				
SrTiO ₃	-24.5	-19.1	-20.2	-8.2
Sr ₂ TiO ₄	-1.0	-3.4	+4.0	+0.2
SrO	+22.1	-21.5	+36.1	-28.8
<u>Hastelloy C</u>				
SrTiO ₃		+21.6 ^a	+60.6 ^a	-3.8
Sr ₂ TiO ₄	+1.4	+21.4	+29.3	+0.5
SrO	+37.1	+41.5	+38.7	+34.1
<u>Type 316 Stainless Steel</u>				
SrTiO ₃	-18.7		-14.3	-18.3
Sr ₂ TiO ₄	0	+3.2	-2.6	-0.2
SrO	+34.3	+26.8	-17.0	+6.3

^aThis specimen showed evidence of mass transfer of metal from the sleeve specimen which lost weight.

Table 6. Weight Changes in SrTiO₃ and Sr₂TiO₄ After Exposure to Superalloys

Compound	Weight Change, mg			
	1100°C			900°C
	1000 hr	5000 hr	10,000 hr	10,000 hr
<u>Haynes alloy No. 25</u>				
SrTiO ₃		+16.3	+15.7	+20.0
Sr ₂ TiO ₄	-19.6	-29.5	-70.9	-11.7
<u>Hastelloy C</u>				
SrTiO ₃		+7.5		+9.7
Sr ₂ TiO ₄	-50.0	-88.0	-200.3	-2.5
<u>Type 316 Stainless Steel</u>				
SrTiO ₃			-34.9	+33.5
Sr ₂ TiO ₄	-80.3		-116.7	-18.8

cylindrical sleeve specimens which tended to bond to the outer capsules; therefore, the data for these specimens were not tabulated. Examination of the data in Table 5 shows a trend of weight losses in alloy specimens exposed to SrTiO_3 and weight gains in those exposed to SrO . Except for Hastelloy C, changes in alloy specimens exposed to Sr_2TiO_4 were quite small.

The SrTiO_3 showed consistent weight gains (as opposed to weight losses by the superalloys), while Sr_2TiO_4 showed even larger weight losses (compared with small gains or losses by the superalloys). Due to the reactivity of SrO with moisture in air, weight changes in SrO were not measured.

Compositional Changes in Alloys and Compounds

Results of the chemical analyses of the test materials after exposure are shown in Tables 7 through 11. No statistically significant changes in the metal constituents of the superalloys were noted at either 900 or 1100°C. However, at 1100°C Haynes alloy No. 25 was decarburized when tested with SrTiO_3 , and, generally, the superalloys gained oxygen in the SrO test. The only significant changes in the strontium compounds were the increases of chromium and manganese by SrTiO_3 , and, to a lesser extent, by SrO . The SrO , which initially contained more carbon than the other strontium compounds, lost carbon in several of the tests.

Metallography

900°C Test - Alloys

The metallographic appearances of the superalloys after the 900°C tests are shown in Fig. 7. We noted the precipitation of one or more phases in each of the alloys as a result of heating them for 10,000 hr at 900°C. In addition, alloy specimens exposed to SrTiO_3 had slightly roughened surfaces, and there were some subsurface voids in Haynes alloy No. 25 and Hastelloy C. The alloy specimens exposed to Sr_2TiO_4 showed little evidence of damage. Both Haynes alloy No. 25 and Hastelloy C were attacked by SrO as evidenced by the 2- to 4-mil reaction zone. Type 316 stainless steel, however, was unattacked at this temperature.

Table 7. Chemical Analyses of Hastelloy C^a Before and After Exposure to Strontium Compounds at 900 and 1100°C

Time (hr)	Concentration, wt %											
	Cr		Mn		Sr		Ti		C		O	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
	<u>SrTiO₃</u>											
1,000	16.1	16.4	0.5	0.6	< 0.005	< 0.005	< 0.01	< 0.01	0.049	0.005	0.0014	0.0057
5,000	16.1	16.0	0.5	0.5	< 0.005	< 0.005	< 0.01	< 0.01	0.049	0.091	0.0014	0.017
10,000	16.1	15.2	0.5	0.6	< 0.005	0.008	< 0.01	< 0.01	0.050	0.166	0.0015	0.0023
10,000 ^b	16.1	15.7	0.5	0.5	< 0.005	< 0.005	< 0.01	< 0.01	0.050	0.045	0.0015	0.0034
	<u>Sr₂TiO₄</u>											
1,000	16.1	15.4	0.5	0.7	< 0.005	0.07	< 0.01	< 0.01	0.049	0.051	0.0014	0.011
5,000	16.1	15.0	0.5	0.5	< 0.005	< 0.005	< 0.01	< 0.01	0.049	0.037	0.0014	0.036
10,000	16.1	15.0	0.5	0.4	< 0.005	0.008	< 0.01	< 0.01	0.050	0.048	0.0015	0.0029
10,000 ^b	16.1	15.7	0.5	0.5	< 0.005	0.002	< 0.01	< 0.01	0.050	0.036	0.0015	0.0031
	<u>SrO</u>											
1,000	16.1	16.0	0.5	0.5	< 0.005	< 0.005	< 0.01	< 0.01	0.049	0.067	0.0014	0.150
5,000	16.1	15.6	0.5	0.5	< 0.005	< 0.005	< 0.01	< 0.01	0.049	0.080	0.0014	0.019
10,000	16.1	14.8	0.5	0.4	< 0.005	0.005	< 0.01	< 0.01	0.050	0.068	0.0015	0.082
10,000 ^b	16.1	14.5	0.5	0.4	< 0.005	0.250	< 0.01	< 0.01	0.050	0.074	0.0015	0.032

^a0.250-in.-thick sample.

^bTested at 900°C.

Table 8. Chemical Analyses of Haynes Alloy No. 25^a Before and After Exposure to Strontium Compounds at 900 and 1100°C

Time (hr)	Concentration, wt %											
	Cr		Mn		Sr		Ti		C		O	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
	<u>SrTiO₃</u>											
1,000	20.2	20.4	0.8	0.5	< 0.005	< 0.005	< 0.01	0.02	0.096	0.020	0.001	0.006
5,000	20.2	20.0	0.8	1.4	< 0.005	< 0.005	< 0.01	< 0.01	0.096	0.020	0.001	0.005
10,000	20.2	19.8	1.4	1.4	< 0.005	0.025	< 0.01	< 0.01	0.100	0.014	0.001	0.007
10,000 ^b	20.2	20.0	1.4	1.1	< 0.005	< 0.005	< 0.01	< 0.01	0.100	0.089	0.001	0.006
	<u>Sr₂TiO₄</u>											
1,000	20.2	21.0	0.8	0.7	< 0.005	0.07	< 0.01	0.02	0.096	0.107	0.001	0.008
5,000	20.2	20.0	0.8	1.4	< 0.005	< 0.005	< 0.01	< 0.01	0.096	0.026	0.001	0.018
10,000	20.2	19.9	1.4	1.4	< 0.005	0.036	< 0.01	< 0.01	0.100	0.120	0.001	0.013
10,000 ^b	20.2	20.0	1.4	1.4	< 0.005	< 0.005	< 0.01	< 0.01	0.100	0.092	0.001	0.002
	<u>SrO</u>											
1,000	20.2	19.0	0.8	0.4	< 0.005	< 0.005	< 0.01	0.02	0.096	0.121	0.001	0.049
5,000	20.2	20.0	0.8	1.4	< 0.005	< 0.005	< 0.01	< 0.01	0.096	0.024	0.001	0.016
10,000	20.2	20.0	1.4	1.4	< 0.005	0.001	< 0.01	< 0.01	0.100	0.015	0.001	0.041
10,000 ^b	20.2	20.4	1.4	1.4	< 0.005	0.005	< 0.01	< 0.01	0.100	0.104	0.001	0.004

^a0.250-in.-thick sample.

^bTested at 900°C.

Table 9. Chemical Analyses of Type 316 Stainless Steel^a Before and After Exposure to Strontium Compounds at 900 and 1100°C

Time (hr)	Concentration, wt %											
	Cr		Mn		Sr		Ti		C		O	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
	<u>SrTiO₃</u>											
1,000	17.5	17.7	2.1	1.0	< 0.005	0.02	< 0.01	< 0.01	0.043	0.023	0.016	0.019
5,000	17.5	17.0	2.1	1.7	< 0.005	< 0.005	< 0.01	0.02	0.043	0.057	0.016	0.008
10,000 ^b	17.5	17.4	2.1	1.9	< 0.005	< 0.005	< 0.01	0.03	0.043	0.046	0.016	0.006
10,000 ^b	17.5		2.1	1.8	< 0.005	< 0.005	< 0.01	< 0.01	0.043	0.042	0.016	0.002
	<u>Sr₂TiO₄</u>											
1,000	17.5	17.9	2.1	1.0	< 0.005	0.05	< 0.01	< 0.01	0.043	0.050	0.016	0.021
5,000	17.5	17.0	2.1	1.7	< 0.005	< 0.005	< 0.01	0.02	0.043	0.054	0.016	
10,000 ^b	17.5	17.6	2.1	1.9	< 0.005	< 0.005	< 0.01	0.03	0.043	0.056	0.016	0.004
10,000 ^b	17.5		2.1	1.9	< 0.005	< 0.005	< 0.01	< 0.01	0.043	0.044	0.016	0.003
	<u>SrO</u>											
1,000	17.5	17.0	2.1	1.8	< 0.005	0.10	< 0.01	< 0.01	0.043	0.095	0.016	0.097
5,000	17.5	17.1	2.1	1.5	< 0.005	0.10	< 0.01	< 0.01	0.043	0.058	0.016	0.057
10,000 ^b	17.5	17.6	2.1	1.4	< 0.005	< 0.005	< 0.01	0.03	0.043	0.036	0.016	0.003
10,000 ^b	17.5		2.1	1.8	< 0.005	< 0.005	< 0.01	< 0.01	0.043	0.045	0.016	0.003

^a0.250-in.-thick sample.

^bTested at 900°C.

Table 10. Chemical Analyses of Strontium Compounds^a Before and After Exposure to Superalloys at 1100°C

Material	Concentration, wt %													
	1000 hr						5000 hr						10,000 hr	
	Cr		Mn		C		Cr		Mn		C		C	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
	<u>SrTiO₂</u>													
Hastelloy C	0.004	1.3	0.0004	0.4	0.03	0.02	0.002	0.200	0.001	0.150	0.030	0.007	0.030	0.020
Haynes alloy No. 25	0.004	0.4	0.0004	0.1	0.03	0.06	0.002	0.300	0.001	0.300	0.030	0.007	0.030	0.006
Type 316 stainless steel	0.004	4.0	0.0004	> 0.4	0.03	0.06	0.002	0.050	0.001	0.100	0.030	0.009	0.030	0.010
	<u>Sr₂TiO₄</u>													
Hastelloy C	0.004	0.040	0.002	0.010	0.02	0.09	0.002	0.050	0.001	< 0.010	0.041	0.027	0.020	0.022
Haynes alloy No. 25	0.004	0.001	0.002	0.001	0.02	0.05	0.002	0.050	0.001	< 0.010	0.041	0.011	0.020	0.008
Type 316 stainless steel	0.004	0.004	0.002	0.001	0.02	0.03	0.002	0.050	0.001	< 0.010	0.041	0.006	0.020	0.008
	<u>SrO</u>													
Hastelloy C	0.001	0.050			0.150	0.050	0.001		0.001		0.150		0.150	0.020
Haynes alloy No. 25	0.001	0.070			0.150	0.100	0.001	0.050	0.001	0.010	0.150	0.102	0.150	0.031
Type 316 stainless steel	0.001	0.100			0.150	0.020	0.001	0.050	0.001	0.050	0.150	0.260	0.150	0.076

^aAnalyses made on 0.125-in. slice cut from 0.75-in.-thick pellet.

Table 11. Chemical Analyses of Strontium Compounds^a After Exposure to Superalloys for 10,000 hr at 900°C

Material	Concentration, wt %																	
	SrTiO ₃						Sr ₂ TiO ₄						SrO					
	Cr		Mn		C		Cr		Mn		C		Cr		Mn		C	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Hastelloy C	0.002	0.200	0.001	0.200	0.030	0.021	0.002	0.002	0.004	0.002	0.020	0.020	0.001	0.003	0.004	0.005	0.150	0.132
Haynes alloy No. 25	0.002	0.200	0.001	0.100	0.030	0.008	0.002	0.002	0.004	0.002	0.020	0.040	0.001	0.002	0.004	0.002	0.150	0.049
Type 316 stain- less steel	0.002	0.200	0.001	0.200	0.030	0.010	0.002	0.002	0.004	0.002	0.020	0.005	0.001	0.100	0.004	0.020	0.150	0.055

^aAnalyses made on 0.125-in. slice cut from 0.75-in.-thick pellet.

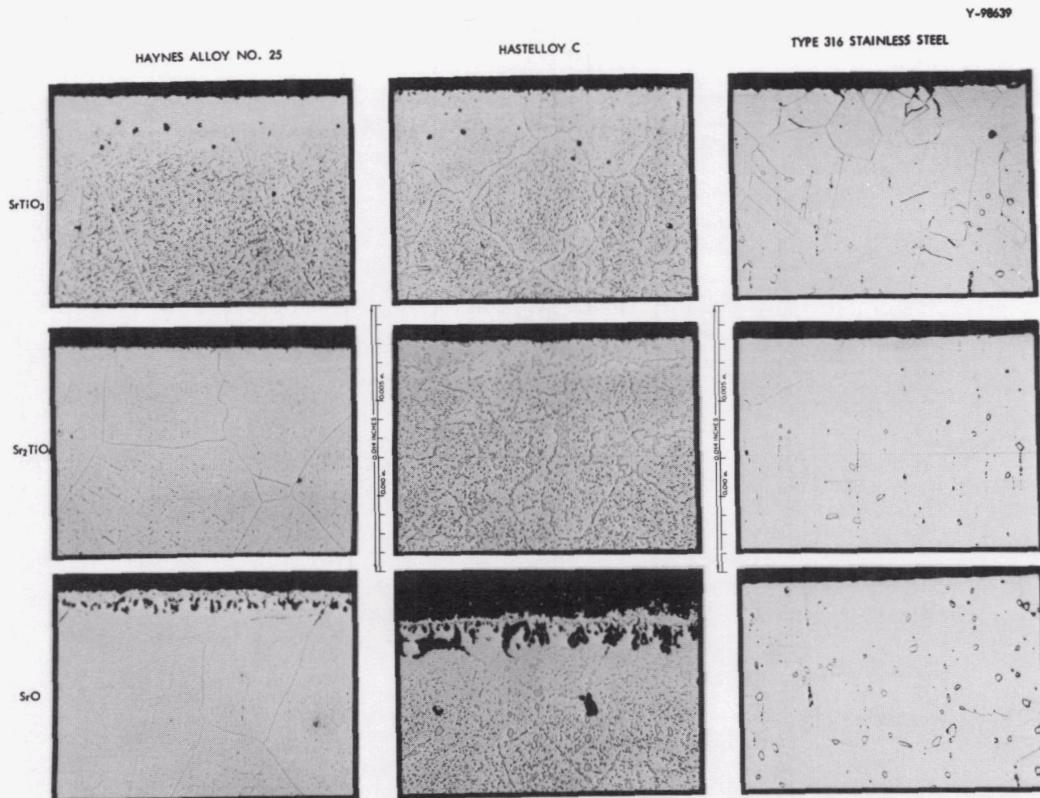


Fig. 7. Cross Sections of Superalloys After Exposure to Strontium Compounds for 10,000 hr at 900°C.

1100°C Test - Alloys

The effect of exposure times up to 10,000 hr at 1100°C on the metal specimens is shown in Figs. 8 through 10. Surface roughening occurred in all of the samples exposed to SrTiO₃, and heavy subsurface voids were found in Haynes alloy No. 25. After 5000- and 10,000-hr exposures to Sr₂TiO₄, there was some grain-boundary attack (1 to 2 mils) in Haynes alloy No. 25 and Hastelloy C, and a number of large subsurface voids in type 316 stainless steel. In general the metal samples showed only slight evidence of attack after exposure to either SrTiO₃ or Sr₂TiO₄ at 1100°C. However, there was greater interaction between SrO and the superalloys than we had seen previously at 900°C. Attack to a depth of 10 mils occurred along grain boundaries in Haynes alloy No. 25 and Hastelloy C and up to 5 mils deep in type 316 stainless steel.

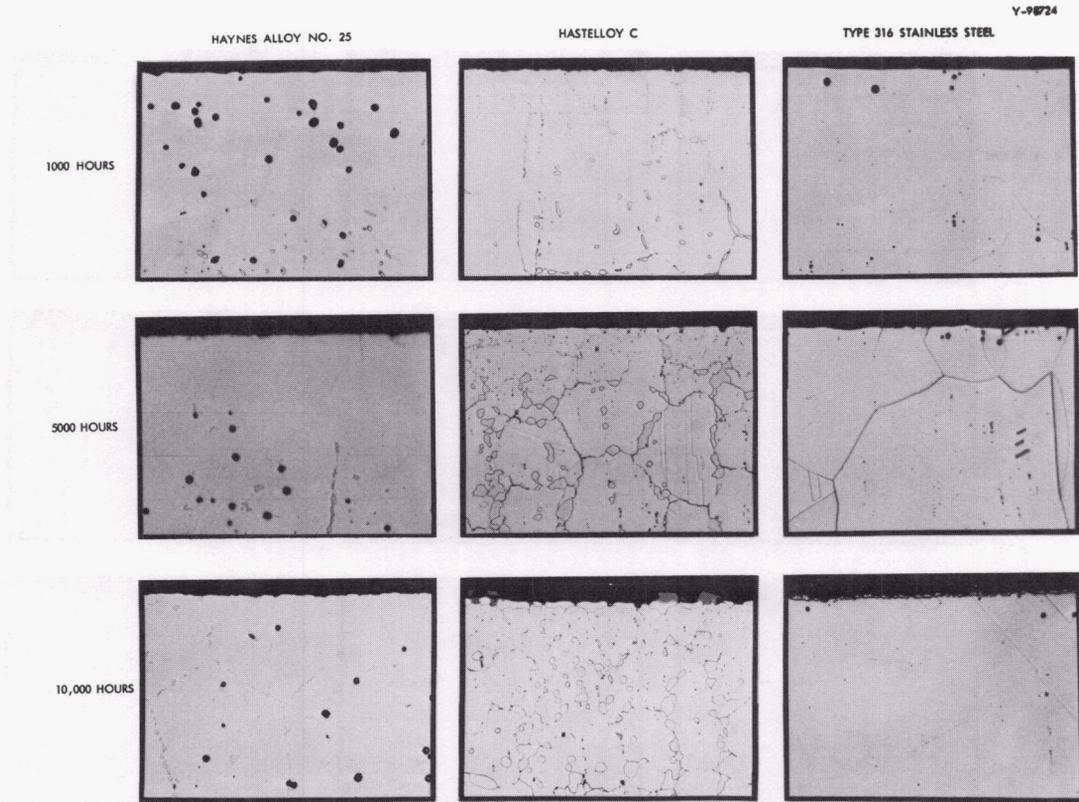


Fig. 8. Cross Sections of Superalloys After Exposure to SrTiO_3 at 1100°C .

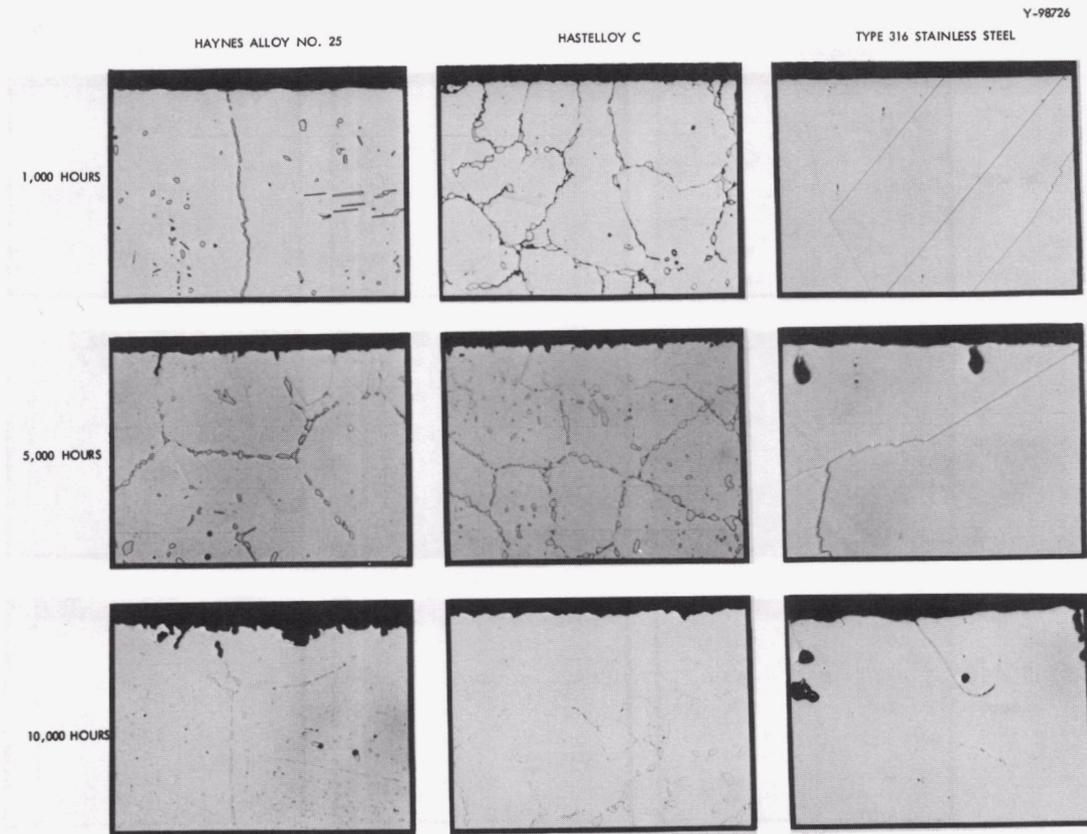


Fig. 9. Cross Sections of Superalloys After Exposure to Sr_2TiO_4 at 1100°C .

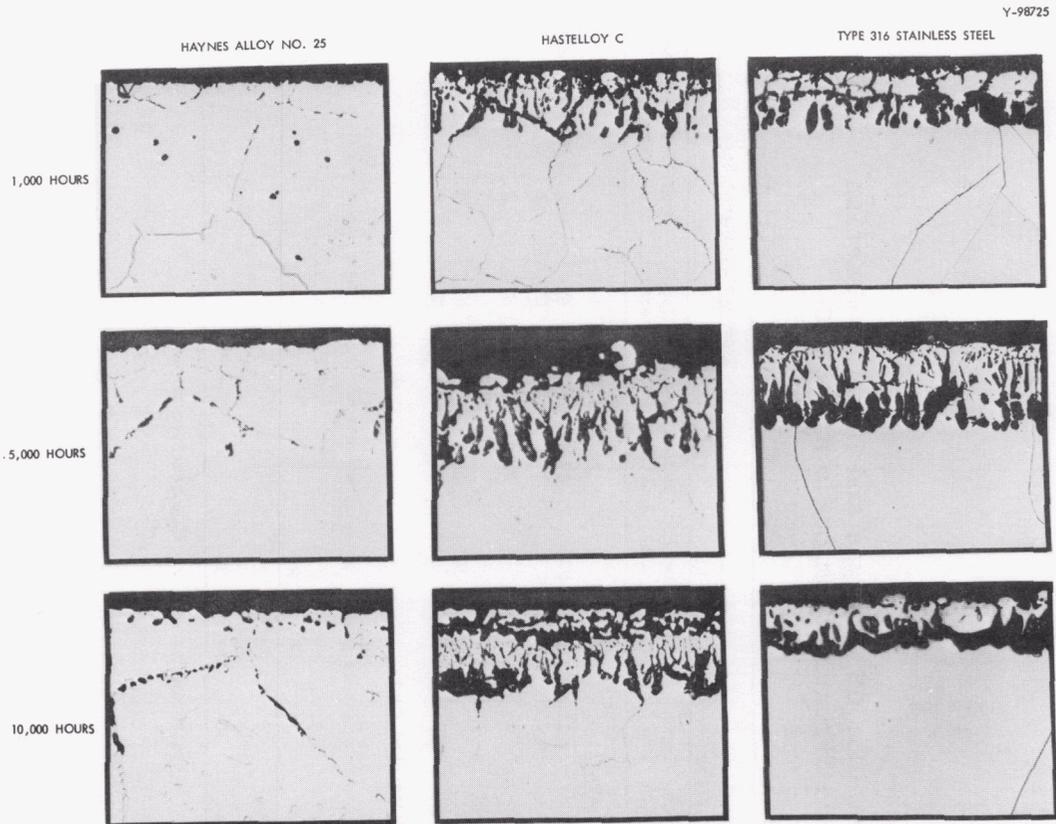


Fig. 10. Cross Sections of Superalloys After Exposure to SrO at 1100°C.

Jacketed SrO - Alloys

The results with the platinum-jacketed strontium compounds tested in Hastelloy C were generally the same as reported above except for interdiffusion of Pt, and Cr, Ni, Mo, and W from Hastelloy C, which left subsurface voids in both materials (Fig. 11). A summary of the metallographic results for the superalloys is given in Tables 12 and 13.

1100°C Test - Compounds

The appearance of SrTiO₃ and Sr₂TiO₄ before and after exposure to the superalloys for 1000 hr at 1100°C is shown in Figs. 12 and 13. We detected a 1- to 2-mil surface layer on the SrTiO₃ that electron-beam microprobe analysis identified as containing Cr, Mn, Ti, and O, but little or no Sr. The bright particles distributed throughout the surface layer, as well as in the SrTiO₃ below, contained a high concentration of

Table 12. Summary of Metallographic Observations of the Type and Depth of Reaction in Superalloys Exposed to Nonradioactive Strontium Compounds at 1100°C

Compound	Haynes alloy No. 25						Hastelloy C						Type 316 Stainless Steel					
	1,000 hr		5,000 hr		10,000 hr		1,000 hr		5,000 hr		10,000 hr		1,000 hr		5,000 hr		10,000 hr	
	Type ^a Reaction	Depth (mil)																
	<u>Bare Fuel</u>																	
SrTiO ₃	SV	10	SV	15	SV	12	SR	< 1	SR	< 1	SR	< 1	SV	2	SR	< 1	SR	< 1
									SV	< 1	GB	< 1			SV	2	SV	2
Sr ₂ TiO ₄	SR	< 1	SR	1	SR	2	SR	< 1	SR	1	SR	1	None		SV	2	SV	4
			GB	1	GB	2												
SrO	GB	5	GB	7	GB	8	GB	4	GB	10	GB	10	GB	3	GB	5	GB	4
	SV	10					TG	4	TG	10	TG	10	TG	3	TG	5	TG	4
	<u>Platinum-Jacketed Fuel</u>																	
SrTiO ₃									RZ	5	RZ	5						
											SV	30						
Sr ₂ TiO ₄									RZ	5	SR	2						
											SV	20						
SrO									GB	8	GB	8						
									TG	8	TG	8						
									SV	10	SV	30						

^aSV - subsurface voids; SR - surface roughening; GB - grain-boundary attack; TG - transgranular attack; RZ - reaction zone.

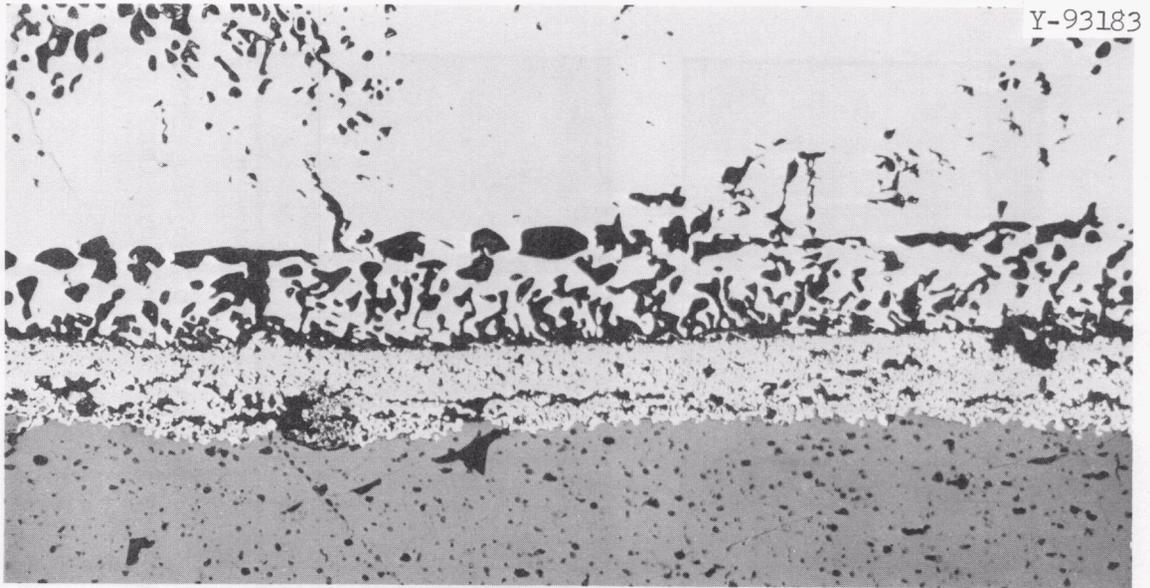


Fig. 11. Interface of Platinum-Jacketed Hastelloy C and SrTiO_3 After Exposure for 10,000 hr at 1100°C (Gray Material at Bottom is SrTiO_3 , Hastelloy C is at the Top and Platinum is Between the Two). 100X.

Table 13. Summary of Metallographic Observations of the Type and Depth of Reaction in Superalloys Exposed to Nonradioactive Strontium Compounds for 10,000 hr at 900°C

Compound	Haynes alloy No. 25		Hastelloy C		Type 316 Stainless Steel	
	Type ^a	Depth (mil)	Type ^a	Depth (mil)	Type ^a	Depth (mil)
			<u>Bare Fuel</u>			
SrTiO_3	SV	5	SV	4	SR	3
					GB	3
Sr_2TiO_4	SR	< 1	SR	< 1	None	
SrO	GB	2	GB	5	None	
	TG	2	TG	5		
			SL	1		
			<u>Platinum-Jacketed Fuel</u>			
SrTiO_3			SV	10		
Sr_2TiO_4			SV	3		
SrO			GB	3		
			TG	3		
			SL	1		
			SV	10		

^aSV, subsurface voids; SR, surface roughening; GB, grain-boundary attack; TG, transgranular attack; SL, surface layer.

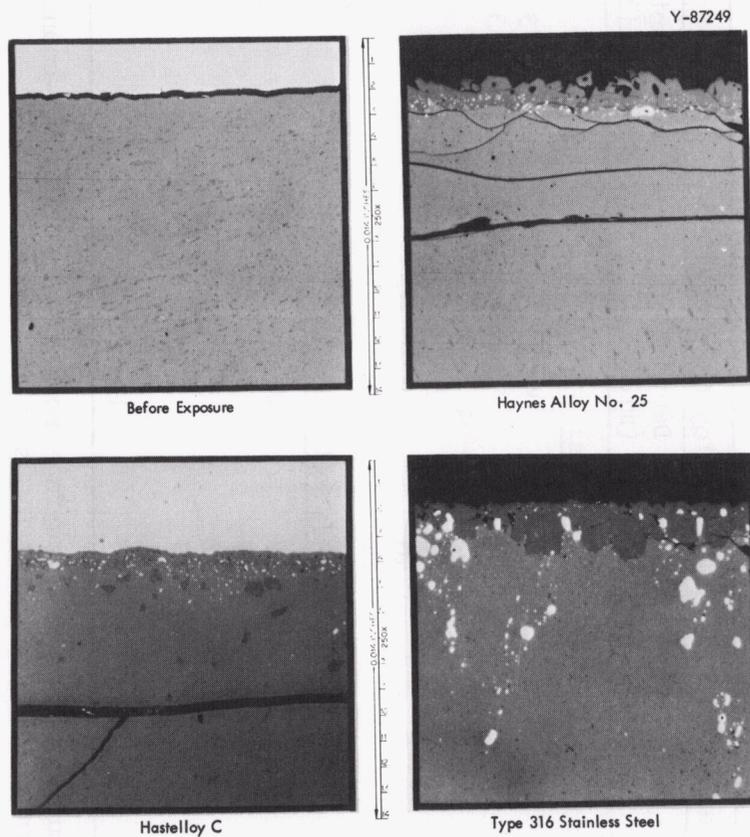


Fig. 12. Cross Sections of SrTiO_3 Before and After Exposure to the Superalloys for 1000 hr at 1100°C .

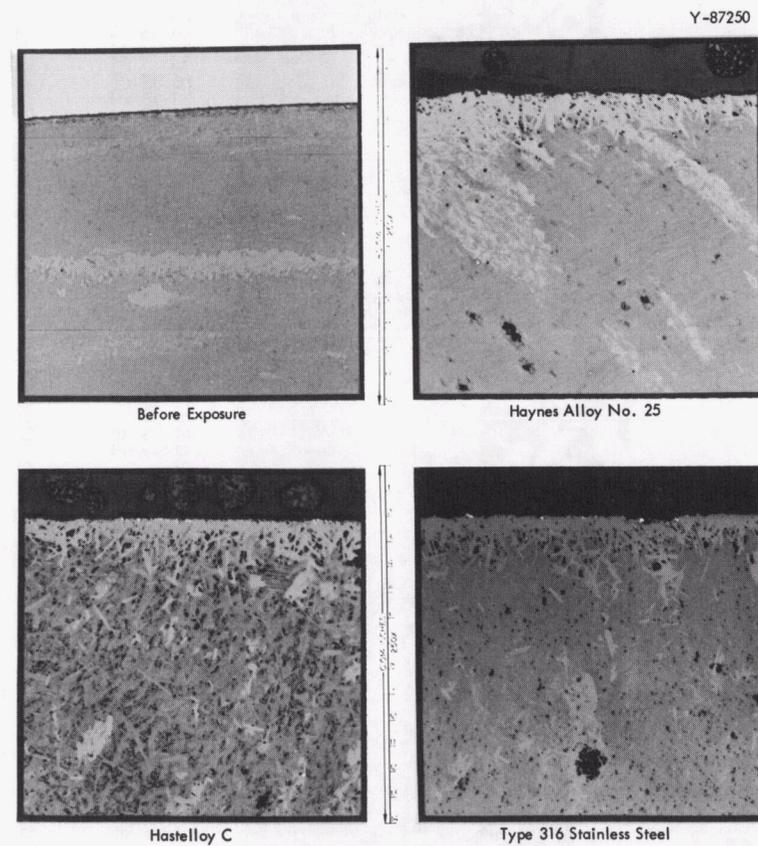


Fig. 13. Cross Sections of Sr_2TiO_4 Before and After Exposure to the Superalloys for 10,000 hr at 1100°C .

chromium with minor amounts of Co, Ni, or Fe, depending on whether it had been in contact with Haynes alloy No. 25, Hastelloy C, or type 316 stainless steel, respectively.

There was a change in the appearance of the surface of the Sr_2TiO_4 ; however, no difference in composition could be detected from a comparison of the concentrations obtained from electron-beam microprobe data of Sr and Ti in the two phases. The bright particles on the surface of some of the samples were high in titanium.

It was difficult to metallographically prepare samples of SrO for examination because SrO tends to react with moisture in the air, which causes it to powder. One sample is shown in Fig. 14. Several samples were submitted for microprobe analysis, but the only consistent result was a high silicon concentration near the surface with some samples showing high Cr and C contents. Metallographic examination at high magnifications indicated the reaction may have been associated with a carbide or intermetallic phase in the superalloy.

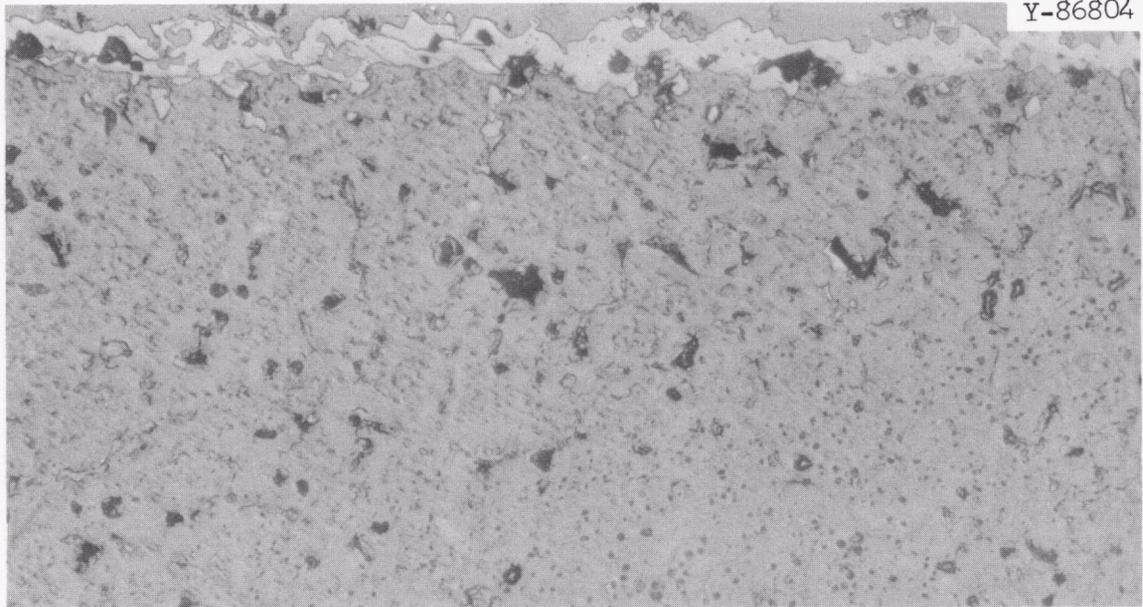


Fig. 14. Cross Section of SrO After Exposure to Haynes alloy No. 25 for 1000 hr at 1100°C. 250x.

Mechanical Properties - Alloys

To evaluate the effect of exposure to the strontium compounds on the mechanical properties of the superalloys, we ran room-temperature tensile tests on the sleeve-insert specimens. To verify the accuracy of tensile test data from specimens of this geometry, we first compared our results with the two other types of geometries shown in Fig. 15 for a single heat of type 316 stainless steel. These results are shown in Table 14; although the results are comparable, they indicated we could expect a smaller yield strength and percent elongation compared with a standard rod specimen. Tensile test results after exposure to the strontium compounds are given in Tables 15 and 16. Heat treating at 1100°C generally lowered the ultimate tensile strength and the yield strength of all three alloys, as well as the ductility of Hastelloy C. Changes in properties after exposure to the strontium compounds were not large if the results are compared with those after heat treating. However, the samples exposed to SrO did show somewhat less strength and ductility, especially Haynes alloy No. 25 and Hastelloy C.

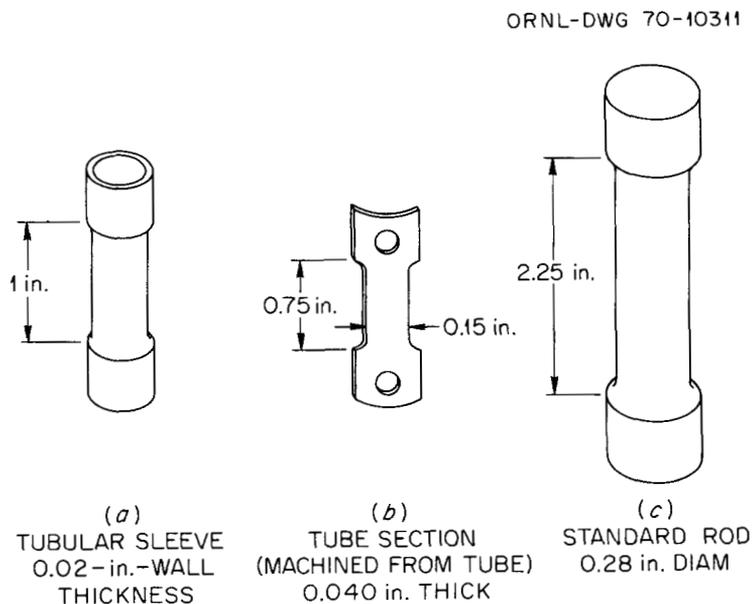


Fig. 15. Tensile Test Specimen Geometries for Type 316 Stainless Steel.

Table 14. Comparison of Room-Temperature Tensile Properties of Type 316 Stainless Steel Specimens with Different Geometries^a

Specimen Geometry	Strength, psi		Elongation (%)
	Ultimate Tensile	Yield	
Rod	83,300	40,000	73
Tube section	82,400	30,500	62
Tube sleeve	81,000	31,000	62

^aData for specimens annealed for 1 hr at 1100°C in argon and air cooled.

Table 15. Effect of Exposure to Strontium Compounds for 10,000 hr at 900°C on Mechanical Properties of Haynes alloy No. 25, Hastelloy C, and Type 316 Stainless Steel

Condition	Room-Temperature Tensile Properties		
	Strength, psi		Elongation in 1 in. (%)
	0.2% Yield	Ultimate Tensile	
<u>Haynes alloy No. 25</u>			
Annealed ^a	89,000	140,000	22
Heat treated ^b	78,000	139,000	10
SrTiO ₃	78,000	109,000	3
Sr ₂ TiO ₄	77,000	104,000	2
SrO	82,000	114,000	2
<u>Hastelloy C</u>			
Annealed ^a	88,000	130,000	30
Heat treated ^b	60,000	105,000	7
SrTiO ₃	68,000	139,000	11
Sr ₂ TiO ₄	63,000	112,000	8
SrO	48,000	71,000	2
<u>Type 316 Stainless Steel</u>			
Annealed ^a	31,000	81,000	62
Heat treated ^b	29,000	89,000	55
SrTiO ₃	26,000	73,000	55
Sr ₂ TiO ₄	32,000	85,000	61
SrO	27,000	78,000	54

^a1 hr at 1100°C - before-test specimen.

^b10,000 hr at 900°C - control specimen.

Table 16. Effect of Exposure to Strontium Compounds for 1,000, 5,000, and 10,000 hr at 1100°C on Mechanical Properties of Haynes alloy No. 25, Hastelloy C, and Type 316 Stainless Steel.

Condition	Room-Temperature Tensile Properties		
	Strength, psi		Elongation in 1 in. (%)
	0.2% Yield	Ultimate Tensile	
<u>Haynes alloy No. 25</u>			
Annealed ^a	89,000	140,000	22
Heat treated ^b	53,000	109,000	24
SrTiO ₃	54,000	111,000	28
Sr ₂ TiO ₄	53,000	98,000	20
SrO	55,000	84,000	11
<u>Hastelloy C</u>			
Annealed ^a	88,000	130,000	30
Heat treated ^b	50,000	93,000	16
SrTiO ₃	57,000	122,000	29
Sr ₂ TiO ₄	52,000	86,000	11
SrO	47,000	75,000	11
<u>Type 316 Stainless Steel</u>			
Annealed ^a	31,000	81,000	62
Heat treated ^b	24,000	68,000	45
SrTiO ₃	25,000	71,000	37
Sr ₂ TiO ₄	24,000	67,000	45
SrO	23,000	54,000	38

^a1 hr at 1100°C - before-test specimen.

^bAverage of 1,000, 5,000, and 10,000 hr at 1100°C - control specimen.

Tensile test results after testing at 900°C showed that there was a substantial loss of ductility in Haynes alloy No. 25 and Hastelloy C after they had been heat treated for 10,000 hr. Examination of the microstructures in Fig. 7 indicates a large amount of precipitation had occurred at 900°C, much more than occurred at 1100°C. At 900°C these precipitates (either metal carbides or intermetallic compounds) were present both along grain boundaries and within the grains. At 1100°C the precipitates were primarily in a chain-like network along the grain boundaries and were larger than at 900°C. Type 316 stainless steel did not show as much precipitate as the other alloys, and we found that its properties were relatively unchanged.

DISCUSSION

In the Theory section of this report, it was anticipated that the strontium compounds and alloys under test would be compatible and only inconsequential reactions would be observed. The data given in the Results section for SrTiO_3 and Sr_2TiO_4 essentially substantiate those conclusions.

In the tests of SrTiO_3 with the superalloys, a 1- to 2-mil reaction zone containing Cr, Mn, Ti, and O was observed in the titanate. No Si was observed and little or no Sr was found in the reaction zone. These data indicate that Eqs. (15), (16), (17), (19), and (20) involving Si did not occur to a detectable extent. A probable explanation for the absence of these reactions is that Si exists in the alloys not as the element with unit activity but as a compound (oxide, silicide, or carbide) with an appreciable free energy of formation.

Analysis of the 1- to 2-mil reaction zone between SrTiO_3 and the superalloys did not identify the Cr and Mn compounds found. It is likely that Cr and Mn in solution in the alloys had sufficiently high activities to react as shown in Eqs. (15) and (16) to produce oxides. Even if the reactions were carried out to equilibrium, only a small amount of oxide would be expected (see Table 2, p. 11). If the reaction layer was formed at the SrTiO_3 alloy interface by the diffusion of Cr and Mn from the alloy and the diffusion of oxygen from the SrTiO_3 , Sr would not be expected to be found in the reaction layer. A logical explanation for the presence of Ti in the reaction layer in the absence of Sr is not apparent.

The microprobe analysis of the bright particles seen on or near the surface of the SrTiO_3 showed them to be of a high chromium content. Only minor amounts of other elements were indicated. However, although these particles are metallic-like in appearance, we do not believe they are the pure metal. The absence of other metals in the bright particles precludes the possibility that the phase is an intermetallic. Since chromium is a strong carbide former, a likely possibility is that the bright particles are chromium carbide (such as Cr_{23}C_6) formed by reaction with carbon in the surface of the titanate which was present from the

hot pressing of the samples in graphite dies. The microprobe analysis would not have detected carbon, and the analysis of the titanate samples (Tables 10 and 11, pp. 24 and 25) indicates small amounts of carbon were present initially, and were less after test.

From the data in Table 12, p. 30, which show the depth of attack of bare titanate fuels on the encapsulating metals, it can be seen that no significant difference was observed between the 5,000- and 10,000-hr tests. This tends to support the conclusion that the attack observed is due either to an impurity which is consumed or to a reaction which reaches equilibrium within 5,000 hr and that greatly extended times of exposure would not significantly increase the depth of attack of titanate or the metals tested.

Although SrO is an exceedingly stable compound thermodynamically, the most extensive reactions observed occurred with this candidate fuel. Excepting the reaction of SrTiO₃ with Haynes alloy No. 25, the reaction depth of SrO with the metals was several times that of the titanates. Reactions of the type shown in Eqs. (1) through (5) were not expected, and the data gave no indication that these reactions took place. Reaction with impurities in the SrO such as H₂O [Eq. (10)], CO₂ [Eq. (11)], or dissolved oxygen seems unlikely due to the methods of preparing the SrO. Reactions of the type shown in Eqs. (6) through (8) are most likely responsible for the penetration observed. While the data are not conclusive, the observation of Si and Cr at the interface of the SrO supports this conclusion.

The reaction of SrO with the alloys tested, like those involving the titanate, seemed to cease after 5,000 hr. This can possibly be due to the consumption of the silicon in the vicinity of the interface.

SUBSEQUENT SHORT-TERM TESTS

Following the completion of the test described in this report, further short-term (1000-hr) tests were carried out to attempt to define the mechanism of the interaction between SrO and the superalloys and to evaluate the effect on compatibility of strontium compounds prepared by the K₂CO₃-KOH procedure (see p. 17).

In the Discussion section of this report, we surmised that the interaction seen between SrO and alloys was due to an impurity in the SrO (either dissolved O_2 , H_2O , or CO_2) or the reaction of SrO with Si in the alloys. If this conclusion could be firmly established, then long-term compatibility could be predicted with confidence since alloys without Si could be used for encapsulation and the impurity reaction would be limited as apparently observed.

To investigate the role of water vapor and SiO_2 in the SrO, and Si in the Hastelloy C, a series of tests for 1000 hr at $1100^\circ C$ were made. The results are shown in Fig. 16. The commercial Hastelloy C that was used in all of the earlier tests contained about 0.5% Si. The low Si Hastelloy C was obtained by arc melting a special heat of material.*

*This work was performed by the Melting and Casting Laboratory of the Metals and Ceramics Division of ORNL.

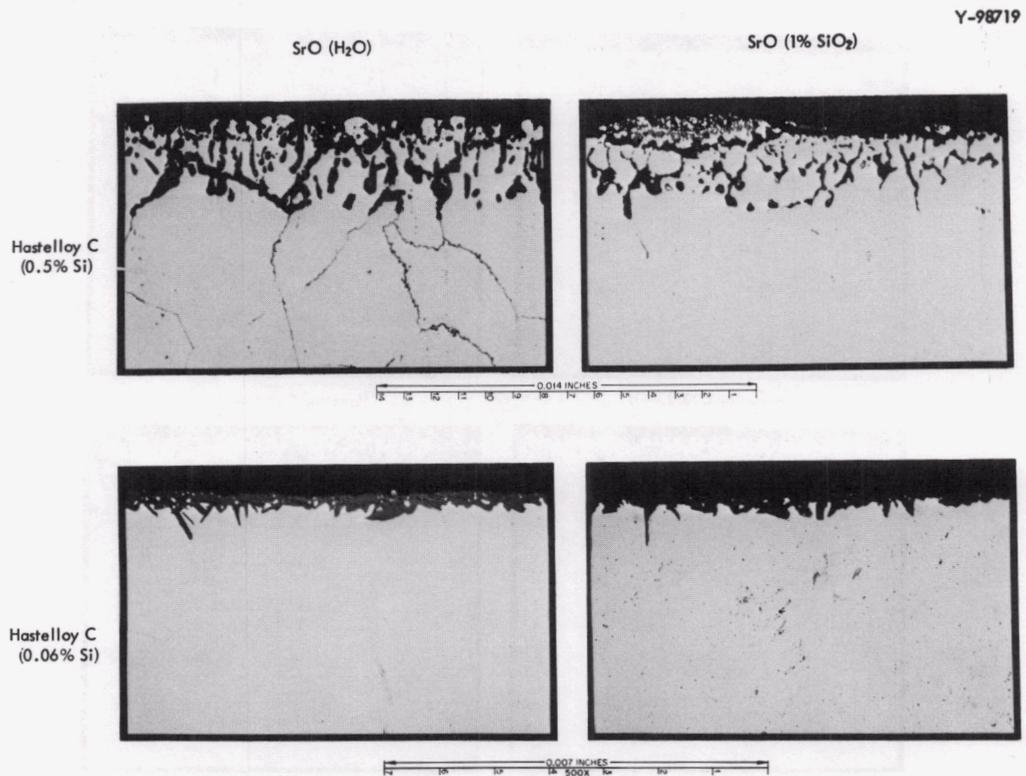


Fig. 16. Effect of Silicon on the Compatibility of Hastelloy C with SrO After 1000 hr at $1100^\circ C$.

Note that although similar results were obtained with the SrO prepared with either water vapor or SiO_2 , the laboratory heat of low Si Hastelloy C did not show the same type or depth of attack as the commercial Hastelloy C. The dark surface layer on the low Si Hastelloy C was found to contain high concentrations of Cr and Sr and some Ni. The bright metallic-looking particles within the surface layer were high in Ni but also contained some Cr and Sr.

Our data were further confounded by results from testing a commercially obtained low Si heat of Hastelloy C designated C-276. This alloy contained 0.04% Si (but < 50 ppm C compared with 500 ppm in the laboratory alloys), and when tested with SrO for 1000 hr at 1100°C it was attacked in the same manner as regular Hastelloy C containing from 0.3 to 0.5% Si. There was, however, a difference in the microstructure of the various types of Hastelloy C as shown in both Figs. 17 and 18.

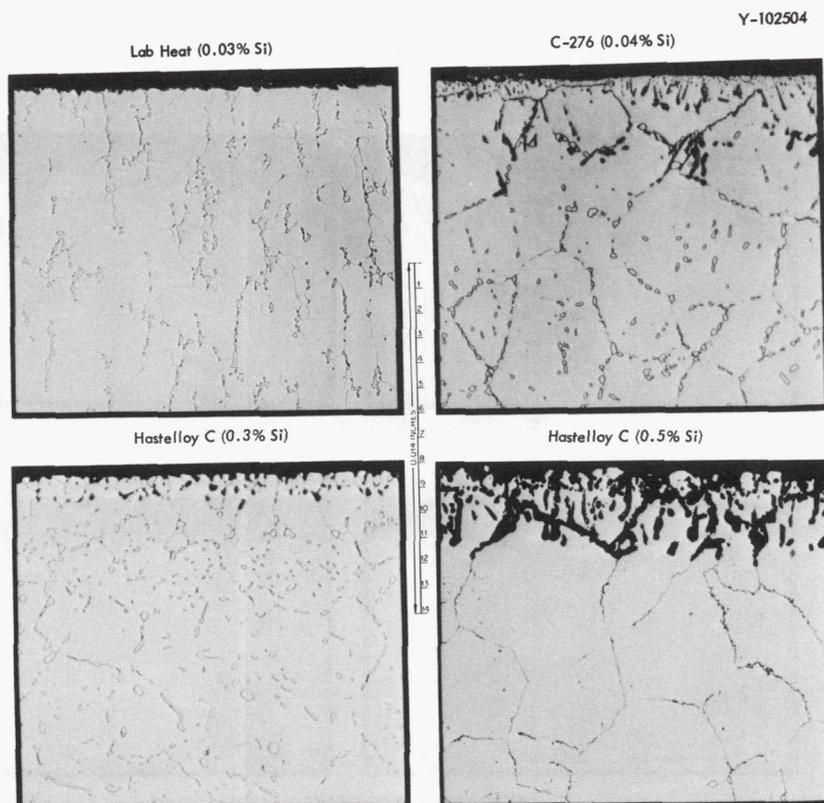


Fig. 17. Hastelloy C Containing Varying Silicon and Exposed to SrO for 1000 hr at 1100°C .

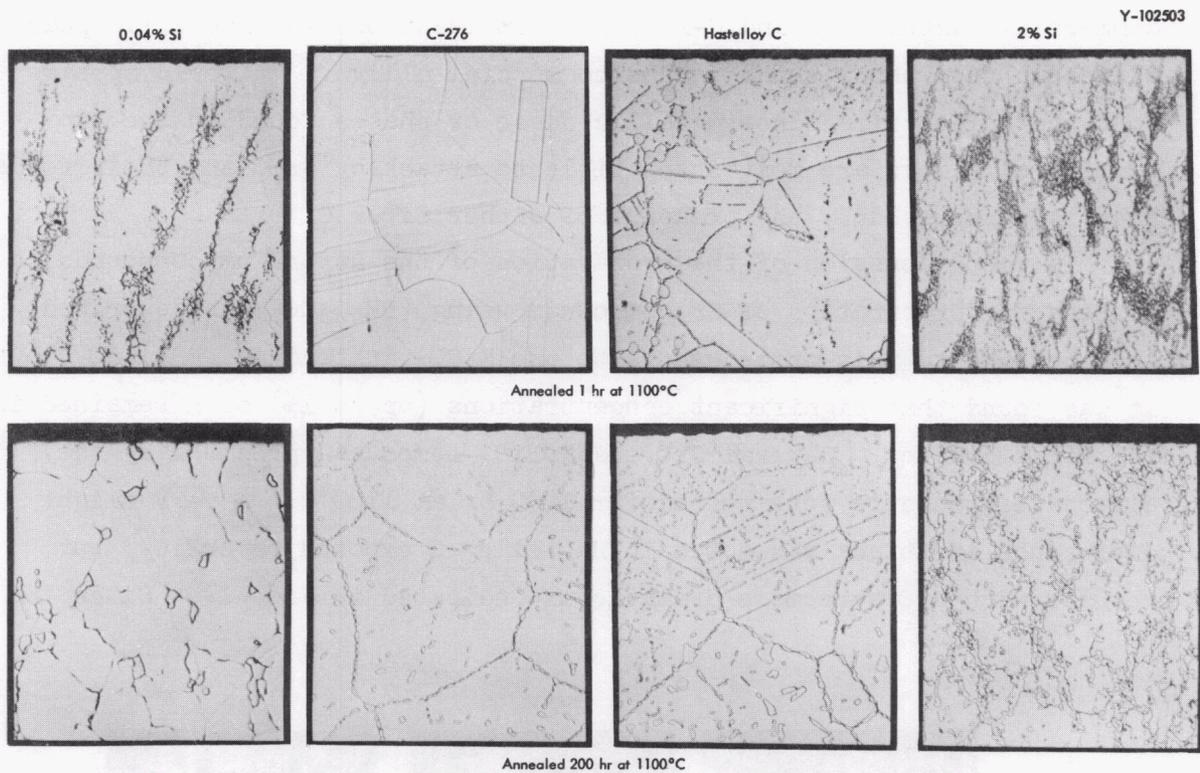


Fig. 18. Microstructure of Some Commercial and Laboratory Heats of Hastelloy C Containing Varying Silicon Concentrations.

Notice the similarity between the two commercial alloys, Hastelloy C and C-276. The alloy containing 2% Si exhibited much greater second phase precipitation which was also considerably different in appearance than that in the commercial alloys. A phase-extraction process was performed on these samples in which the base metal is dissolved away and x-ray or other techniques are used to identify the residue.* The residues from commercial Hastelloy C and C-276 exhibited similar x-ray diffraction patterns with μ (Ni-Mo intermetallic) and one or more other intermetallic phases being the principal constituents. The residue from the low Si (but with ~ 500 ppm C compared with 50 ppm in C-276) laboratory heat showed an M_6C type of carbide as its principal constituent. The high Si laboratory heat showed no M_6C , smaller amounts of μ compared with

*This work was performed by R. E. Gehlbach of the Electron Microscopy Laboratory of the Metals and Ceramics Division of ORNL.

commercial Hastelloy C and C-276, plus at least one intermetallic phase different from those noted in the commercial alloys. It would appear that the unidentified intermetallic phase or phases found in the two commercial alloys are most susceptible to attack by SrO, and their formation is suppressed by the presence of either Si or C.

In the discussion of the preparation of the strontium compounds, a process for preparation of Sr compounds using $(\text{NH}_4)_2\text{CO}_3$ was described. An alternate to this procedure is to use K_2CO_3 instead of $(\text{NH}_4)_2\text{CO}_3$, but it was found that significant concentrations (up to 1%) of K remained in the final product. Several SrO and SrTiO_3 compounds prepared by the alternate procedure were tested for 1000 hr at 1100°C . A very slight difference in attack was noted in Hastelloy C exposed to SrTiO_3 , but results with SrO were more dramatic as indicated in Fig. 19. Since the

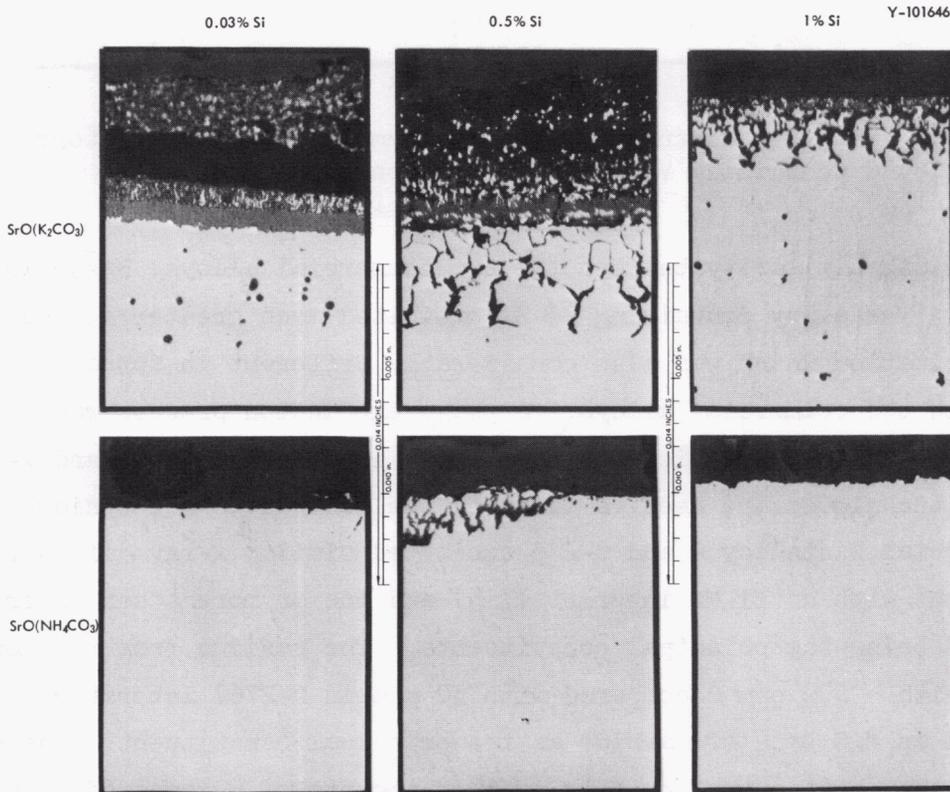


Fig. 19. Effect of Silicon in Hastelloy C on the Compatibility with SrO Produced by Different Procedures.

only difference between the tests was the method of preparation of the SrO, we must conclude that the presence of K in the SrO adversely affects the corrosion resistance of Hastelloy C.

SUMMARY

Two strontium compounds, SrTiO_3 and Sr_2TiO_4 , seem to be very compatible with Haynes alloy No. 25, Hastelloy C, and type 316 stainless steel even after 10,000 hr at 1100°C . The slight interaction observed in SrTiO_3 is believed to be due to reaction of Cr and Mn in the alloy that caused some reduction of the titanate. This reaction appears to reach steady state and cease after 5000 hr. A reaction between SrO and these alloys does occur, but is significantly less at 900°C compared with 1100°C and appears to cease after 5000 hr at 1100°C . In Hastelloy C the reaction is perhaps related to the presence of one or more intermetallic phases. In laboratory heats containing very low Si and relatively high C or in alloys containing very high Si, these phases do not form and no attack was observed. The presence of K in SrO was also found to decrease its compatibility with Hastelloy C.

The use of platinum as a liner between Hastelloy C and the strontium compounds resulted in significant interdiffusion between the two metals at 1100°C . A large number of subsurface voids to depths of 5 to 30 mils were found in both the platinum and Hastelloy C. Since this could seriously impair the properties of a container material, we feel that platinum should either be eliminated or some sacrificial or inert material be used between the platinum and container alloy.

Slightly poorer mechanical properties of the three alloys were found primarily after heat treating at both 900 and 1100°C . Some additional effects, mainly in the form of lower ductility, were noted in samples exposed to SrO.

ACKNOWLEDGMENTS

This program was a joint effort between the Metals and Ceramics and the Isotopes Divisions of ORNL. Considerable assistance in planning the program was provided by T. A. Butler, R. G. Donnelly, K. H. Lin, and W. D. Box. Technical assistance in test fabrication was provided by D. E. Mahaffey and T. D. Owings and metallographic preparation of the specimens was done by C. E. Zachary.

REFERENCES

1. R. A. Robinson, personal communication, Oak Ridge National Laboratory, May 1971.
2. E. Lamb, ORNL Isotopic Power Fuels Quart. Progr. Rept. Dec. 31, 1967, ORNL-4237 (February 1968). CLASSIFIED
3. C. B. Holterman, Anal. Chem. 14(11), 121-206 (1940).
4. T. A. Kozlenko, P. V. Kovtunencko, E. V. Kiseleva, and A. A. Bundel, "Reaction Between Oxygen and Alkaline Earth Metal Oxides. II. Equilibria in the System Strontium Oxide-Oxygen at Low Pressures," Russ. J. Chem. 41(5), 588-590 (May 1967).
5. W. D. Copeland and R. A. Swain, "Studies on the Defect Structure of Strontium Oxide," J. Phys. Chem. Solids 29, 313-325 (1968).
6. Max Hansen and Kurt Anderko, Constitution of Binary Alloys, 2nd ed., McGraw-Hill, New York, 1958.
7. Leo Brewer, "Thermodynamic Stability and Bond Character in Relation to Electronic Structure and Crystal Structure," in Electronic Structure and Alloy Chemistry of the Transition Elements, ed. by Paul A. Beck, Interscience, New York, 1963.
8. L. Brewer, "A Most Striking Confirmation of the Engel Metallic Correlation," Acta Met. 15, 553-556 (March 1967).
9. J. H. Westbrook (ed.), Intermetallic Compounds, p. 200, Wiley, New York, 1967.
10. K. Janzon, H. Schaefer, and A. Weiss, "Crystal Structure of Strontium Disilicide $SrSi_2$," Angew. Chem. 77(6), 258-259 (1964).

11. V. S. Neshpar and V. L. Yupko, "An Investigation of the Preparation Conditions and Some Properties of Barium Disilicide," Zh. Prikl. Khim. 36(5), 1139-1142 (1963).
12. A. Cocco and F. Massazza, "Microscopic Examination of the System SrO-TiO₂," Ann. Chim. (Rome) 53(7), 883-893 (1963).
13. M. Drys and W. Trzebiatawski, "The System Strontium Oxide-Titanium Dioxide," Roczniki Chem. 31, 489-496 (1957).
14. J. B. Moser, R. N. Blumenthal, and D. H. Whitmore, "Thermodynamic Study of Nonstoichiometric Rutile (TiO_{2-x})," J. Am. Ceram. Soc. 48(7), 384 (1965).
15. P. Kofstad, "Thermogravimetric Studies of the Defect Structure of Rutile (TiO₂)," J. Phys. Chem. Solids 23, 1579-1586 (1962).
16. Michael Kestigian, J. G. Dickinson, and Roland Ward, "Ion-Deficient Phases in Titanium and Vanadium Compounds of the Perovskite Type," J. Am. Chem. Soc. 79(21), 5598-5601 (1957).
17. G. J. McCarthy, W. B. White, and R. Roy, "Phase Equilibria in the 1375°C Isotherm of the System Sr-Ti-O," J. Am. Ceram. Soc. 52(9), 463-467 (1969).
18. A. E. Paladino, "Oxidation Kinetics of Single-Crystal SrTiO₃," J. Am. Ceram. Soc. 48(9), 476-478 (1965).
19. R. P. Elliot, Constitution of Binary Alloys, First Supplement, pp. 708-709, McGraw-Hill, New York, 1965.
20. P. G. Wahlbeck and P. W. Gilles, "Reinvestigation of the Phase Diagram for the System Titanium-Oxygen," J. Am. Ceram. Soc. 49(5), 180-183 (1966).
21. E. M. Levin, C. R. Robbins, and H. F. McMurdie, Phase Diagrams for Ceramists, p. 143, American Ceramic Society, Columbus, Ohio, 1964.

ORNL-4625
UC-33 - Propulsion Systems and
Energy Conversion

INTERNAL DISTRIBUTION

- | | | | |
|--------|-------------------------------|--------|-------------------------------|
| 1-3. | Central Research Library | 64. | Lynda Kern |
| 4. | ORNL - Y-12 Technical Library | 65. | E. Lamb |
| | Document Reference Section | 66. | R. E. Leuze |
| 5-24. | Laboratory Records Department | 67. | K. H. Lin |
| 25. | Laboratory Records, ORNL RC | 68. | R. E. McDonald |
| 26. | ORNL Patent Office | 69-78. | R. E. McHenry |
| 27. | G. M. Adamson, Jr. | 79. | A. J. Miller |
| 28. | P. S. Baker | 80. | M. E. Ramsey |
| 29-31. | T. A. Butler | 81. | R. A. Robinson |
| 32. | F. L. Culler | 82. | A. F. Rupp |
| 33. | J. E. Cunningham | 83. | A. C. Schaffhauser |
| 34. | J. H. DeVan | 84. | A. H. Snell |
| 35-54. | J. R. DiStefano | 85. | V. J. Tennery |
| 55. | R. G. Donnelly | 86. | D. B. Trauger |
| 56. | D. E. Ferguson | 87. | A. M. Weinberg |
| 57. | J. H. Frye, Jr. | 88. | C. M. Adams, Jr. (consultant) |
| 58. | W. O. Harms | 89. | Leo Brewer (consultant) |
| 59. | R. F. Hibbs | 90. | Walter Kohn (consultant) |
| 60-62. | M. R. Hill | 91. | Jan Korringa (consultant) |
| 63. | H. Inouye | 92. | Sidney Siegel (consultant) |

EXTERNAL DISTRIBUTION

93. F. W. Albaugh, Director, WADCO Corporation, P. O. Box 999, Richland, WA 99352
94. R. D. Baker, Los Alamos Scientific Laboratory, P. O. Box 1663, Los Alamos, NM 87544
95. F. P. Baranowski, Director, Division of Production, AEC, Washington, DC 20545
96. R. T. Carpenter, Division of Space Nuclear Systems, AEC, Washington, DC 20545
- 97-98. E. G. Case, Director, Division of Reactor Standards, AEC, Washington, DC 20545
99. D. F. Cope, RDT, SSR, Oak Ridge Operations
100. W. B. Creamer, Area Manager, Dayton Area Office, AEC, Miamisburg, OH 45342
101. D. C. Davis, Laboratory and University Division, AEC, ORO
102. G. P. Dix, Division of Space Nuclear Systems, AEC, Washington, DC 20545
103. S. L. Fawcett, WADCO Corporation, P. O. Box 999, Richland, WA 99352
104. E. E. Fowler, Director, Division of Isotopes Development, AEC, Washington, DC 20545

105. G. L. Hagey, Naval Facilities Engineering Command, Nuclear Power Division, Washington, DC 20390
106. R. C. Hamilton, IDA - Room 19, 400 Army-Navy Drive, Arlington, VA 22200
107. John N. Hatsopoulos, Metals Division, Thermo Electron Corporation, 9 Crane Court, Woburn, MA 01801
108. R. E. Hopkins, U.S. Army Mobility Equipment Research and Development Center, Ft. Belvoir, VA 22060
109. M. Klein, Director, Division of Space Nuclear Systems, AEC, Washington, DC 20545
110. F. E. Kruesi, Director, Savannah River Laboratory, Aiken, SC 29801
111. J. A. Lieberman, RDT, AEC, Washington, DC 20545
112. C. L. Matthews, RDT, OSR, AEC, Oak Ridge National Laboratory
113. W. A. McDonald, Isotopes, Inc., Nuclear Systems Division, 110 West Timonium Road, Timonium, MD 21093
- 114-117. Peter A. Morris, Director, Division of Reactor Licensing, AEC, Washington, DC 20545
118. R. L. Neubert, Vice President and Director, Mound Laboratory, Miamisburg, OH 45342
119. G. A. Newby, Division of Space Nuclear Systems, Washington, DC 20545
120. J. A. Powers, Division of Space Nuclear Systems, AEC, Washington, DC 20545
121. A. A. Pitrolo, Manager, MHW-RTG Program, Isotope Power Systems Operation, General Electric Company, P. O. Box 8661, Philadelphia, PA 19101
122. W. Remini, Mail Code Z-S5, NASA Manned Spacecraft Center, Houston, TX 77052
123. H. M. Roth, AEC, Oak Ridge Operations
124. F. C. Schwenk, Division of Space Nuclear Systems, AEC, Washington, DC 20545
125. S. J. Seiken, RDT, AEC, Washington, DC 20545
126. M. Shaw, RDT, AEC, Washington, DC 20545
127. J. M. Simmons, RDT, AEC, Washington, DC 20545
128. E. E. Stansbury, University of Tennessee, Knoxville, TN 37916
129. J. A. Swartout, Union Carbide Corporation, 270 Park Avenue, New York, NY 10017
130. D. G. Williams, WADCO Corporation, P. O. Box 999, Richland, WA 99352
131. Commander, Naval Undersea Research and Development Center, San Diego, CA 92132, Attn: Technical Library, Code 133
- 132-136. Executive Secretary, Advisory Committee on Reactor Safeguards, AEC, Washington, DC 20545
137. Isotopes, Inc., 110 West Timonium Road, Timonium, MD 21093
138. Laboratory and University Division, AEC, Oak Ridge Operations
139. NASA Goddard Space Flight Center, Greenbelt, MD 20771, Attn: Library
140. NASA Langley Research Center, Hampton, VA 23365, Attn: Library
141. NASA Marshall Space Flight Center, Huntsville, AL 35812, Attn: Library
142. Naval Facilities Engineering Command, Nuclear Power Division, Code 042, Washington, DC 20390

143. Navy Space Systems Activity
144. Sanders Nuclear Corporation, AEC, 95 Canal Street,
Nashua, NH 03060
145. Savannah River Operations Office, Aiken, SC 29801
146. Thermo Electron Corporation, 9 Crane Court, Woburn, MA 01801
- 147-327. Given distribution as shown in TID-4500 under Propulsion Systems
and Energy Conversion category (25 copies - NTIS)