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MONTHLY REPORT
TO SPACE NUCLEAR SYSTEMS DIVISION
FOR JANUARY 1975

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

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FOR JANUARY 1975

by

H. T. Fullam

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February 1975

On January 19, 1975, research and development programs of the U.S. Atomic Energy Commission (AEC) became part of the newly formed Energy Research and Development Administration (ERDA). In this report, since it refers to work done in 1974, most references are to AEC programs.

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STRONTIUM HEAT SOURCE DEVELOPMENT PROGRAM

At Hanford, strontium will be separated from the high-level waste, then converted to the fluoride, and double encapsulated in small, high-integrity containers for subsequent long-term storage. The fluoride conversion, encapsulation and storage will take place in the Waste Encapsulation and Storage Facilities (WESF). This encapsulated strontium fluoride represents an economical source of ^{90}Sr if the WESF capsule can be licensed for heat source applications under anticipated use conditions. The objectives of this program are to obtain the data needed to license $^{90}\text{SrF}_2$ heat sources and specifically the WESF $^{90}\text{SrF}_2$ capsules. The information needed for licensing can be divided into three general areas:

- 1. Long-term SrF_2 compatibility data.*
- 2. Chemical and physical property data on $^{90}\text{SrF}_2$.*
- 3. Capsule property data such as external corrosion resistance, crush strength, etc.*

The current program is designed to provide the required information.

SHORT-TERM COMPATIBILITY TESTS

Analysis of the short-term compatibility test couples containing high purity $^{90}\text{SrF}_2$ or WESF grade $^{90}\text{SrF}_2$ is approximately 70% complete. Results obtained to date with the high purity $^{90}\text{SrF}_2$ are summarized in Table 1, and results obtained with WESF grade $^{90}\text{SrF}_2$ are given in Table 2. A detailed discussion of the data will be given in the February report when all the results are available. Based on the results available at the present time, it appears that, in general, chemical attack observed in the radioactive couples is slightly greater than that found in equivalent non-radioactive couples. However, changes in microstructure occurred to much greater depths in the radioactive couples compared to the equivalent non-radioactive couples containing high purity SrF_2 (results of the tests with nonradioactive SrF_2 are given in BNWL-1845-6).

TABLE 1. Metal Attack Observed in Couples Containing High Purity $^{90}\text{SrF}_2$

Material Tested	Test Temperature, °C	Depth of Metal Affected, mils			
		Chemical Attack		Change in Microstructure	
		1500 hr	4400 hr	1500 hr	4400 hr
Hastelloy C-276	800	4	2	6	6
"	1000	-	2	-	15
"	1100	-	2	-	6
Hastelloy X	800	1	-	5	-
"	1000	-	4	-	15
"	1100	5	4	20	22
Hastelloy N	800	4	-	10	-
"	1000	6	-	16	-
"	1100	2	-	5	-
Haynes 25	800	< 1	-	3	-
"	1000	-	-	3	-
"	1100	1	-	4	-
Haynes 188	800	4	5	10	13
"	1000	-	3	-	5
"	1100	-	2	-	5
Inconel 600	800	1	-	4	-
"	1000	-	-	-	-
"	1100	2	-	4	-
Inconel 625	800	-	3	-	5
"	1000	-	-	-	-
"	1100	-	2	-	15
TZM	800	-	1	-	0
"	1000	-	< 1	-	0
"	1100	-	1	-	0
Tungsten	800	0	-	0	-
"	1000	< 1	-	0	-
"	1100	< 1	-	0	-

TABLE 2. Metal Attack Observed in Couples Containing
WESF Grade $^{90}\text{SrF}_2$

Material Tested	Test Temperature, °C	Depth of Metal Affected, mils			
		Chemical Attack		Change in Microstructure	
		1500 hr	4400 hr	1500 hr	4400 hr
Hastelloy C-276	800	2	2	3	3
"	1000	2	3	5	8
"	1100	3	3	5	6
Hastelloy X	800	1	3	4	4
"	1000	1	1	6	4
"	1100	3	3	6	10
Hastelloy N	800	4	6	7	6
"	1000	7	-	20	-
"	1100	6	-	8	-
Haynes 25	800	1	-	2	-
"	1000	1	-	2	-
"	1100	1	-	2	-
Haynes 188	800	1	2	2	4
"	1000	3	4	7	10
"	1100	1	2	8	5
Inconel 600	800	1	3	4	11
"	1000	-	-	-	-
"	1100	-	-	-	-
Inconel 625	800	1	-	4	-
"	1000	2	-	20	-
"	1100	4	-	18	-
TZM	800	< 1	< 1	0	0
"	1000	< 1	-	1	-
"	1100	< 1	-	0	-
Tungsten	800	0	-	0	-
"	1000	< 1	-	0	-
"	1100	1	-	0	-

THERMODYNAMIC CALCULATIONS

In the short-term compatibility studies, nine different containment materials were tested with four different grades of strontium fluoride. The nine containment materials tested and their typical compositions are listed in Table 3. An attempt has been made to predict, based on thermodynamic considerations, possible reactions which might occur between WESF produced $^{90}\text{SrF}_2$ and the nine containment materials. The potential for a given reaction occurring was estimated by calculating the Gibbs free energy of reaction (ΔG_R°) between the temperatures of 25 and 1200°C. Results obtained with the WESF $^{90}\text{SrF}_2$ -tungsten system were presented in an earlier report (BNWL-1845-4). The results of the thermodynamic analysis of the other eight WESF $^{90}\text{SrF}_2$ -alloy systems are summarized in the following sections.

TABLE 3. Composition of Containment Materials Evaluated

Element	Typical Composition, Weight %								
	Hastelloy C-276	Hastelloy X	Hastelloy N	Haynes 25	Haynes 188	Inconel 600	Inconel 625	TZM	Tungsten
Al			0.16				0.21		
B		0.001	0.01						
C	0.02	0.09	0.07	0.09	0.08	0.06	0.04		
Cb							3.6		
Co	2.4	1.9	0.16	Ba1	Ba1				
Cr	16.0	21.4	6.2	19.7	21.8	15.7	22.0		
Cu			0.30			0.30			
Fe	6.4	19.0	4.7	2.2	1.6	7.5	3.4		
La					0.05				
Mn	0.53	0.62	0.59	1.4	1.1	0.37	0.05		
Mo	15.3	8.9	16.8				8.9	Ba1	
Ni	Ba1	Ba1	Ba1	10.3	22.3	Ba1	Ba1		
P	0.025	0.015	0.01	0.019	0.01		0.01		
S	0.006	0.006	0.01	0.007	0.006	0.007	0.007		
Si	0.04	0.47	0.72	0.10	0.31	0.24	0.24		
Ti			0.24				0.28	0.46	
V	0.20								
W	3.2	0.44	0.42	14.6	14.1				99.9
Zr								0.09	

Each of the eight fluoride-alloy systems is extremely complex because of the many components present. The WESF $^{90}\text{SrF}_2$ contains a number of impurities in addition to decay products, while each alloy (except TZM) contains at least eight components. The impurities present in the WESF $^{90}\text{SrF}_2$ and their expected concentration ranges are given in Table 4. The cation impurities are present primarily as fluoride. Since the fluoride also contains small amounts of oxygen, some metal oxides may also be present. However, analyses show that the bulk of the oxygen in the fluoride is present as water or nitrate; therefore, the concentrations of metal oxides should be very low. An added complicating factor is the presence of a limited molten fluoride phase at the higher temperatures ($>800^\circ\text{C}$). The composition of the fluoride phase as a function of temperature has not been determined. The amount of molten phase present, even at 1100°C , appears to be less than 1% of the total fluoride present.

TABLE 4. Probable Impurities in WESF $^{90}\text{SrF}_2$

Impurity	Probable Form	Concentration Range (wt%)
Na	NaF	1 - 4
Ca	CaF_2	0.1 - 1.0
Ba	BaF_2	0.1 - 1.0
Mg	MgF_2	0.05 - 0.5
Mn	MnF_2	< 0.1
Fe	FeF_3	< 0.2
Pb	PbF_2	< 0.2
Cu	CuF_2	< 0.01
Al	AlF_3	< 0.5
Cr	CrF_3	< 0.2
Cd	CdF_2	< 0.1
Ni	NiF_2	< 0.1
K	KF	< 0.1
O_2	H_2O	< 0.05
H_2	H_2O	< 0.01
NO_3	$\text{Sr}(\text{NO}_3)_2$	< 0.05
Si	SiO_2	< 0.02
R ^(a)	RF_3	< 2.0

^(a)Rare earth

The chemical composition of $^{90}\text{SrF}_2$ decay products has not been adequately determined.

The existence of ZrF_2 has been reported, but the compound is said to be unstable at high temperatures disproportionating to ZrF_4 and metal.

It is impossible at this time to say what the chemical form of the decay product would be in an operating heat source ($\geq 800^\circ\text{C}$). Any ZrF_2 present should disproportionate, but this has not been demonstrated experimentally. For the thermodynamic analysis it has been assumed that ZrF_4 , ZrF_2 , and Zr metal can be present in WESF $^{90}\text{SrF}_2$.

Because of the large number of constituents present in each of the eight $^{90}\text{SrF}_2$ -alloy systems, a rigorous analysis of a given system would involve literally hundreds or thousands of potential reactions. A rigorous analysis is hampered by a lack of thermochemical data for most of the complex compounds and solid solutions which are potentially possible in the various systems. In analyzing each system, the following simplifying assumptions were made in order to reduce the reactions to be considered to those involving compounds for which thermochemical data are available:

1. The impurities and decay products in the WESF $^{90}\text{SrF}_2$ are present as simple compounds, and not as complex compounds with SrF_2 or each other.
2. The reaction products are not present as complex compounds with the SrF_2 , its decay products and contained impurities, or each other.
3. There is no compound formation between components of a given alloy.

These assumptions preclude the presence of complex fluorides, complex oxides, oxyfluorides, and intermetallic compounds in the reaction systems. They limit the reactions to be considered to those involving the simple fluorides and oxides for which thermochemical data are available. It is possible that the fluorides or oxides could exist as solid solutions.

Unfortunately information on the existence and composition of such phases is unavailable, as is any thermochemical data for assumed compositions. Therefore, in the thermodynamic analysis, the possible existence of fluoride or oxide solid solutions was ignored. It was also assumed in the analysis that each fluoride-alloy system was a closed system, as would be the case with an operating $^{90}\text{SrF}_2$ heat source.

Free energy of formation data for the fluorides and oxides of interest in the eight $^{90}\text{SrF}_2$ -alloy systems under consideration are given in Tables 5 and 6. The data are given in kilocalories (kcal)/g atom of anion and were obtained primarily from Rosenqvist,⁽¹⁾ Glassner,⁽²⁾ Smithells,⁽³⁾ and Kubaschewski and Evans.⁽⁴⁾ The accuracy of the thermochemical data available for the metal fluorides is poor. Only a small fraction of the data was obtained experimentally, and the thermochemical data for most of the fluorides was estimated by various theoretical techniques. To illustrate the accuracy of the fluoride data, the following values have been published recently for the free energy of formation of NaF at 298°C:

ΔG_R° kcal/mole	Reference
-128.5 $\pm$ 3	Smithells ⁽³⁾
-130 $\pm$ 10	Rosenqvist ⁽¹⁾

For most other fluorides the accuracy of the data is as bad or worse as that for NaF. The poor accuracy of the fluoride data makes free energy of reaction calculations of limited value, especially when the value of ΔG_R° is near zero. In the case of metal oxides, the same difficulties apply, although to a lesser degree than with the fluorides. The available thermochemical data on oxides has somewhat better accuracy than the data on the fluorides, and a greater fraction of the data was obtained experimentally.

As stated previously, it was assumed that there was no compound formation between constituents of a given alloy. Instead it was assumed that each alloy was a solid solution, and the partial molar free energy of mixing ($\Delta \bar{G}_M$) was calculated for each alloy constituent using the method

TABLE 5. Free Energy of Formation of Various Fluorides

Compound	$-\Delta G_f^\circ$, kcal/g-atom of fluorine					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
AlF ₃	113	101	97	93	91	89
BF ₃	90	87	86	85	85	84
BaF ₂	137	125	122	119	117	116
CF ₄	40	36	35	34	33	32
CaF ₂	140	129	125	121	119	117
CdF ₂	77	66	63	56	53	50
CoF ₂	74	65	61	58	57	55
CrF ₂	86	77	74	70	69	68
CrF ₃	83	73	70	67	65	64
CuF	56	48	45	43	43	42
CuF ₂	59	50	47	45	44	43
FeF ₂	79	70	67	64	62	61
FeF ₃	73	63	60	57	55	54
HF	65	65	66	66	67	67
KF	129	114	109	102	99	95
LaF ₃	134	124	120	117	115	113
MgF ₂	128	116	112	108	106	103
MnF ₂	90	81	78	76	75	74
MnF ₃	74	64	61	58	57	56
MoF ₅	63	58	57	56	55	54
MoF ₆	64	58	56	54	53	52
NaF	129	115	110	104	101	97
NbF ₅	64	59	58	57	56	55
NiF ₂	74	64	61	58	57	55
PF ₃	54	50	48	47	46	45
PbF ₂	74	62	59	55	54	53
RF ₃ (a)	131	120	117	113	111	109
SF ₆	40	33	28	25	23	22
SiF ₄	94	89	87	86	85	84
SrF ₂	138	127	123	119	118	116
TiF ₃	100	90	86	83	81	79
TiF ₄	93	86	85	83	83	82
VF ₃	85	75	72	68	67	65
VF ₄	76	70	68	67	67	66
WF ₄	58	48	47	45	45	44
WF ₅	52	47	46	45	45	44
WF ₆	47	41	39	37	36	35
ZrF ₂	109	99	96	92	90	89
ZrF ₄	108	97	93	91	90	89

(a) RF₃ = Rare Earth Fluoride - Typically NdF₃

TABLE 6. Free Energy of Formation of Various Oxides

Compound	$-\Delta G_f^\circ$, kcal/g-atom of oxygen					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
Al ₂ O ₃	126	112	106	101	99	96
B ₂ O ₃	94	83	80	77	75	73
BaO	129	116	111	105	103	100
CO	33	45	49	53	56	58
CO ₂	47	47	47	47	47	47
CaO	144	131	126	121	118	116
CdO	54	41	36	25	20	16
CoO	51	41	36	34	33	31
Co ₃ O ₄	46	34	30	25	23	21
Cr ₂ O ₃	83	71	67	63	61	59
Cu ₂ O	35	24	21	18	16	14
CuO	30	19	15	11	9	7
FeO	58	49	46	43	42	40
Fe ₃ O ₄	60	49	45	41	39	38
Fe ₂ O ₃	59	48	43	39	37	35
K ₂ O	76	58	52	44	40	36
La ₂ O ₃	136	125	121	117	115	112
MgO	137	122	117	112	109	104
MnO	87	77	73	70	68	66
Mn ₃ O ₄	77	64	60	56	53	52
Mn ₂ O ₃	72	59	55	51	49	47
MoO ₂	64	52	46	44	42	40
MoO ₃	54	42	38	35	34	33
Na ₂ O	90	70	64	51	46	40
NbO	92	80	77	73	71	69
Nb ₂ O ₅	85	75	68	64	62	60
NiO	52	38	33	29	26	24
P ₂ O ₃	81	70	67	64	62	60
P ₂ O ₅	66	53	49	45	43	42
PbO	45	31	26	23	21	19
R ₂ O ₃ (a)	137	125	121	117	115	113
SO ₂	41	36	34	32	32	31
SiO ₂	102	90	86	81	79	77
SrO	134	121	116	111	108	106
TiO	116	103	99	93	92	90
Ti ₂ O ₃	113	102	98	92	91	89
TiO ₂	103	93	89	84	83	81
VO	97	90	86	82	79	77
V ₂ O ₃	93	82	78	74	72	70
WO ₂	64	54	50	46	44	42
WO ₃	61	49	46	42	40	38
ZrO ₂	123	110	105	101	99	97
H ₂ O	55	48	45	42	41	39

(a) Rare Earth Oxide - Typically Nd₂O₃

developed by Hildebrand and Scott.⁽⁵⁾ Since alloy compositions can vary significantly from heat to heat, particularly with the superalloys, the partial molar free energy of mixing for a given alloy component can vary somewhat depending on the actual concentration. This is especially true for alloy constituents which are present in low concentration. The partial molar free energy of mixing data presented in subsequent tables were calculated using the alloy compositions given in Table 3.

The potential for a given fluoride-metal or oxide-metal to occur can be predicted very roughly by comparing the appropriate free energies of formation. In Table 7 the fluorides and oxides of interest are listed in order of decreasing free energy of formation at 25 and 1200°C. Theoretically any element should be capable of reducing the fluoride or oxide of any element below it on the table. In the WESF $^{90}\text{SrF}_2$ -alloy systems under consideration the problem is somewhat more complicated because of alloy solid solutions, and the partial molar free energy of mixing of alloy components must be considered in the free energy of reaction calculations.

For temperatures between 25 and 1200°C the ranking of the fluorides and oxides may vary somewhat from those given in Table 7 for 25 and 1200°C. These variations should not be significant, however.

Before discussing the individual $^{90}\text{SrF}_2$ -alloy systems there are certain factors to be considered which apply to all eight systems. If ZrF_2 is assumed to be present in the fluoride as a decay product of $^{90}\text{SrF}_2$ it would represent a powerful reducing agent. A comparison of the free energies of formation given in Table 5 shows that ZrF_2 could theoretically reduce many of the impurity fluorides present in WESF $^{90}\text{SrF}_2$ to the metallic state. Typical examples of such potential reactions are given in Equations 1-4.

TABLE 7. Fluorides and Oxides Listed in Order of Their Thermodynamic Stability at 25 and 1200°C

Fluorides		Oxides	
25°C	1200°C	25°C	1200°C
Ca	Ca	Ca	Ca
Sr	Sr	R(a)	R(a)
Ba	Ba	Mg	La
La	La	La	Sr
R(a)	R(a)	Sr	Mg
Na	Mg	Ba	Ba
K	Na	Al	Zr
Mg	K	Zr	Al
Al	Al	Ti(II)	Ti(II)
Zr(II)	Zr(II)	Ti(III)	Ti(III)
Zr(IV)	Zr(IV)	Ti(IV)	Ti(IV)
Ti(III)	B	Si	Si
Si	Si	V(II)	V(II)
Ti(IV)	Ti(IV)	B	B
B	Ti(III)	V(III)	V(III)
Mn(II)	Mn(II)	Nb(II)	Nb(II)
Cr(II)	Cr(II)	Na	Mn(II)
V(III)	H	Mn(II)	Nb(V)
Cr(III)	V(IV)	Nb(V)	P(III)
Fe(II)	V(III)	Cr	Cr
Cd	Cr(III)	P(III)	C(II)
V(IV)	Fe(II)	Mn	Mn
Co	Mn(III)	K	C(IV)
Mn(III)	Co	Mn(III)	Mn(III)
Ni	Ni	P(V)	P(V)
Pb	Nb	W(IV)	W(IV)
Fe(III)	Fe(III)	Mo(IV)	Mo(IV)
H	Mo(V)	W(VI)	Na
Mo(VI)	Pb	Fe	Fe(II)
Nb	Mo(VI)	Fe(III)	H
Mo(V)	Cd	Fe(II)	W(VI)
Cu(II)	P	H	Fe
W(IV)	W(IV)	Mo(VI)	K
Cu(I)	W(V)	Cd	Fe(III)
P	Cu(II)	Ni	Mo(VI)
W(V)	Cu(I)	Co(II)	S
W(VI)	W(VI)	C(IV)	Co(II)
S	C	Co(III)	Ni
C	S	Pb	Co(III)
		S	Pb
		Cu(I)	Cd
		C(II)	Cu(I)
		Cu(II)	Cu(II)

(a) R = Rare Earth - Typically Nd_2O_3

The calculated free energies of reaction (ΔG_R°) for Equations 1-4 (obtained using the data shown in Table 5) are presented in Table 8. Since the calculated ΔG_R° values for Equations 1-3 are strongly negative over the temperature range of interest (25 to 1200°C), ZrF_2 present in $^{90}SrF_2$ could theoretically reduce any iron, manganese, or nickel fluorides present to the corresponding metals. Fluorides of cadmium, copper, chromium, and lead could be reduced by the ZrF_2 in similar fashion. The metals formed by the reduction of the fluorides could, in turn, alloy with each other or the containment material to form solid solutions (or intermetallic compounds).

TABLE 8. Calculated Free Energy of Reaction for Equations 1-4

Equation	ΔG_R° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
1	-210	-192	-180	-198	-210	-210
2	- 34	- 28	- 24	- 28	- 30	- 30
3	- 66	- 62	- 58	- 64	- 66	- 68
4	36	36	42	18	6	0

In the case of Equation 4, ΔG_R° is positive at the lower temperatures and reaches a value of zero at 1200°C. Therefore, the ZrF_2 would react with AlF_3 only at the higher temperatures.

The ZrF_2 would not react with any of the other impurity metal fluorides present in WESF $^{90}SrF_2$ to any appreciable extent up to 1200°C in a closed system.

If zirconium metal is present in the $^{90}SrF_2$ as a decay product, it could react with impurity fluorides in the $^{90}SrF_2$ in the same manner as the ZrF_2 . It could, theoretically, reduce the same fluorides to the metallic state. The zirconium could also alloy directly with the containment material.

Analyses show the strontium fluoride contains small amounts of water. The water could react with certain of the impurity fluorides to form HF and the corresponding oxides. For example:

The calculated free energies of reaction for Equations 5-9 are presented in Table 9, and show that theoretically water should react appreciably with the metal fluorides at the higher temperatures. In a closed system the reactions would proceed until an equilibrium partial pressure of HF is established or until one or more of the reactants is completely consumed. The water could also react with the lead, chromium, and cadmium fluorides in similar fashion, but would not react with the alkali, alkaline earth or rare earth fluorides to any appreciable extent in a closed system.

TABLE 9. Calculated Free Energy of Reaction for Equations 5-9

Equation	ΔG_r° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
5	36	-12	-30	-45	-60	-66
6	13	- 1	- 8	-11	-14	-16
7	18	3	- 4	- 8	-11	-13
8	21	8	2	- 3	- 5	- 9
9	75	24	3	-15	-30	-39

In analyzing the various fluoride-superalloy systems, it soon becomes obvious that, on a thermodynamic basis, the systems are very similar. The alloys contain a number of common components, and even though the concentrations vary, the potential molar free energies of mixing of the common components vary only slightly. This being the case, most reactions involving common components which are potentially possible in one system are also possible in the other systems.

WESF $^{90}\text{SrF}_2$ - TZM System

The alloy TZM is being tested as a potential containment material for WESF $^{90}\text{SrF}_2$. Potential reactions between the components of the TZM and WESF $^{90}\text{SrF}_2$ were evaluated based on thermodynamic considerations using the assumptions discussed earlier.

The partial molar free energies of mixing for the components of TZM were calculated using the composition given in Table 3. The values obtained are shown in Table 10 for temperatures from 25 to 1200°C.

TABLE 10. Calculated Partial Molar Free Energies of Mixing for TZM Alloy Components

Component	<u>$-\Delta G_m$, kcal/mole</u>					
	<u>25°C</u>	<u>600°C</u>	<u>800°C</u>	<u>1000°C</u>	<u>1100°C</u>	<u>1200°C</u>
Mo	0	0	0	0	0	0
Ti	3	8	10	12	13	14
Zr	7	13	16	19	21	23

Molybdenum is reported to form several fluorides, but on a thermodynamic basis the pentafluoride (MoF_5) and hexafluoride (MoF_6) appear to be the most stable. Since the free energy of formation (per atom of fluorine) is almost the same for both compounds, only the pentafluoride was considered in the analysis of the system. In the case of titanium and zirconium, TiF_4 and ZrF_4 were assumed to be the only potential reaction products. With regard to the oxides only MoO_2 , TiO , and ZrO_2 were considered as potential reaction products.

Free energy of reaction calculations, using the data given in Tables 5 and 10, predict the molybdenum present in the TZM would react with only a few of the fluorides present in the WESF $^{90}\text{SrF}_2$ at temperatures from 25 to 1200°C.

The calculated free energies of reaction for Equations 10-26 are presented in Table 11. They predict that only the fluorides of copper and iron could react with molybdenum throughout the entire temperature range, while the lead and cadmium fluorides would react at the higher temperatures. None of the other metal fluorides in the WESF $^{90}\text{SrF}_2$ should react with the molybdenum to any appreciable degree in a closed system. If any HF were present in the system, due to hydrolysis reactions between water and the fluorides, it would not react with the molybdenum to any measurable degree.

The titanium and zirconium in the TZM would be stronger reducing agents than the molybdenum (even allowing for substantial partial molar free energies of mixing). They could react, therefore, with some additional fluorides in the WESF $^{90}\text{SrF}_2$ which do not react with the molybdenum.

(a) Rare Earth Fluoride - Typically NdF_3 .

TABLE 11. Calculated Free Energy of Reaction for Equations 10-26

Equation	ΔG_R° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
10	750	645	600	555	540	525
11	740	670	650	630	620	620
12	770	710	680	650	640	630
13	140	80	60	0	-20	-40
14	70	35	25	25	10	10
15	-40	-80	-100	-110	-110	-110
16	-10	-45	-55	-65	-70	-70
17	330	280	260	230	220	205
18	650	580	550	520	510	490
19	270	230	210	200	200	200
20	330	285	265	240	230	215
21	110	60	40	20	20	10
22	110	40	20	-10	-10	-10
23	1020	930	900	855	840	825
24	750	690	660	630	630	620
25	460	410	390	360	350	350
26	20	70	90	100	120	130

The calculated free energy of reaction for Equations 27-34 are shown in Table 12. While not all of the equations and ΔG_R° values have been shown, the thermodynamic calculations predict that the titanium and zirconium in the TZM could react with all of the fluorides in the WESF $^{90}\text{SrF}_2$ except AlF_3 and the alkali metal, alkaline earth and rare earth fluorides.

TABLE 12. Calculated Free Energy of Reaction for Equations 27-34

Equation	ΔG_R° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
27	-231	-252	-270	-276	-297	-294
28	-9	-12	-18	-16	-19	-18
29	-73	-80	-86	-88	-91	-94
30	-109	-76	-66	-56	-51	-46
31	-65	-51	-44	-41	-39	-37
32	-279	-249	-228	-231	-237	-239
33	129	87	96	81	75	69
34	91	85	84	71	65	55

Although the concentration of metal oxides in the WESF $^{90}\text{SrF}_2$ would be very low, they could have an effect on $^{90}\text{SrF}_2$ containment and should be considered in the thermodynamic analyses of $^{90}\text{SrF}_2$ -alloy systems. Assuming MoO_2 , TiO and ZrO_2 are the possible reaction products, the thermodynamic calculations predict that molybdenum in TZM would react with the oxides of cadmium, copper, iron (III), manganese (III), nickel and lead if they are present in the fluoride. The molybdenum could also react to some degree with any water that might be present. The titanium and zirconium in the TZM could react with any of the oxides present except those of aluminum and the alkaline earth and rare earth elements.

In summary, the thermodynamic calculations predict that the components of the TZM alloy could react with some of the impurity fluorides (and oxides) present in WESF $^{90}\text{SrF}_2$, particularly those of the polyvalent ions such as copper, iron and manganese. Fortunately those impurities which the calculations predict should react with TZM are present in the WESF $^{90}\text{SrF}_2$ in low concentrations (≤ 0.2 wt%). The calculations also indicate that no reactions should occur between the TZM components and those fluorides present in high concentrations ($^{90}\text{SrF}_2$, ZrF_4 , ZrF_2 , NaF , CaF_2 , BaF_2 , MgF_2).

It is interesting to compare the results of the thermodynamic calculations with the results of the compatibility studies in which TZM was

tested with high purity SrF_2 containing controlled levels of added impurities. The results of the experimental tests involving TZM are shown in Table 13 (a detailed description of the tests is given in BNWL-1845-6). The only TZM couples showing appreciable attack were those in which the SrF_2 contained CuF_2 or FeF_3 , and the thermodynamic calculations indicate such attacks should occur. However, the calculations also show that the TZM in couples containing MnF_2 , PbF_2 and H_2O should be attacked, but this was not the case. The TZM couples containing MnF_2 , PbF_2 and H_2O showed relatively little attack. There are several possible explanations for this disagreement:

1. The thermochemical data used in the calculations are incorrect,
2. The thermodynamic calculations are in error because of the assumptions that were used,
3. The reaction kinetics are relatively slow,
4. The reaction rates are limited by diffusion of the reactants to the reaction zone.

TABLE 13. Metal Attack Observed in TZM- SrF_2 Couples Containing Controlled Levels of Added Impurities - After Testing at 1000°C

Impurity Added	Depth of Metal Affected, mils			
	Chemical Attack		Change in Microstructure	
	1500 hr	4400 hr	1500 hr	4400 hr
NaF	<<1(a)	<<1	0(a)	0
MnF_2	<<1(a)	<1	0(a)	0
PbF_2	<1	<1	0	0
CuF_2	2(a)	6	2(a)	6
FeF_3	2(a)	3	2(a)	3
AlF_3	<<1	<1	0	0
$(\text{Ca-Ba-Mg})\text{F}_2$	<<1	<<1	0	0
SrO	<1	<1	0	0
$\text{Sr}(\text{NO}_3)_2$	<<1(a)	<<1	0(a)	0
H_2O	<1	<<1	0	0

(a) Indicates couples accidentally overheated to 1200°C for about 4 hr

WESF $^{90}\text{SrF}_2$ - Hastelloy C-276 System

This system is considerably more complex than the fluoride-TZM system because of the greater number of components in the Hastelloy C-276. Because of the additional components, far more reactions are potentially possible.

The partial molar free energies of mixing for the components of Hastelloy C-276 were calculated using the alloy composition given in Table 3. The calculated values from 25 to 1200°C are shown in Table 14.

TABLE 14. Calculated Partial Molar Free Energies of Mixing for Hastelloy C-276 Alloy Components

Component	$-\Delta\bar{G}_M$, kcal/mole					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
C	4	10	14	17	19	20
Co	2	6	8	9	10	11
Cr	1	3	4	4	5	5
Fe	2	5	6	7	7	8
Mn	3	9	11	13	14	15
Mo	1	4	5	6	6	7
Ni	0	1	1	1	1	2
P	5	13	16	19	20	22
S	5	16	19	23	25	27
Si	4	12	15	18	19	20
V	4	10	12	15	16	18
W	3	3	10	12	13	13

A comparison of the free energy data given in Tables 5, 6, and 14 makes it apparent that a number of reactions are potentially possible between constituents of the Hastelloy C-276 and impurity fluorides and oxides in the WESF $^{90}\text{SrF}_2$. Typical examples of fluoride reactions that could take place in the system are provided by Equations 35-46.

The calculated free energy of reaction values for Equations 35-46 from 25 to 1200°C are given in Table 15.

TABLE 15. Calculated Free Energy of Reaction for Equations 35-46

Equation	ΔG_r° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
35	-28	-24	-20	-19	-16	-13
36	-24	-26	-22	-21	-22	-19
37	-17	-19	-20	-24	-27	-29
38	-23	-27	-26	-26	-25	-25
39	-38	-35	-34	-31	-29	-28
40	-8	-8	-7	-6	-4	-6
41	-23	-23	-21	-17	-22	-21
42	-30	-27	-27	-25	-25	-22
43	-120	-156	-159	-174	-183	-180
44	-32	-26	-24	-18	-20	-15
45	-58	-58	-54	-48	-46	-36
46	15	12	6	4	-3	-3

Typical examples of oxide reactions that are potentially possible are listed in Equations 47-54. The calculated free energies of reaction for Equations 47-54 are listed in Table 16.

TABLE 16. Calculated Free Energy of Reaction for Equations 47-54

Equation	ΔG_R° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
47	+6	-11	-14	-18	-21	-24
48	32	11	12	-5	-10	-13
49	-112	-114	-115	-112	-110	-110
50	-4	-7	-8	-8	-10	-10
51	-56	-40	-40	-37	-35	-31
52	-32	-32	-33	-30	-31	-32
53	-32	-33	-29	-20	-16	-10
54	-21	-12	-12	-6	-3	-3

From the examples given above it is obvious that, on a thermodynamic basis, a number of reactions are potentially possible between components of the Hastelloy C-276 and some components of the WESF $^{90}\text{SrF}_2$. However, the thermodynamic calculations also show that the only components of the WESF $^{90}\text{SrF}_2$ which will react with the alloy are those which are present in low concentrations. Conversely, none of the fluorides which are present

in relatively large concentrations (i.e., SrF_2 , NaF , ZrF_4 , CaF_2 , BaF_2 , MgF_2 , R_2F_3) will react with alloy components to any measurable degree.

Because of the similarity of the superalloys (on a thermodynamic basis), most of the reactions which the calculations predict would occur between fluoride-Hastelloy C-276 would also occur in the other superalloy systems.

WESF $^{90}\text{SrF}_2$ -Hastelloy X System

On a thermodynamic basis the WESF $^{90}\text{SrF}_2$ -Hastelloy X system is very similar to the WESF $^{90}\text{SrF}_2$ -Hastelloy C-276 system. This is to be expected because the two alloys contain, with two exceptions, the same components (Hastelloy C-276 contains some vanadium not found in the Hastelloy X while the latter contains a trace of boron not found in the former). Since the two systems contain almost identical components one would predict the same reactions would occur in each system. The only differences one would expect (other than the reactions involving vanadium and boron) would be due to differences in partial molar free energies of mixing resulting from component concentration differences in the two alloys.

The calculated partial molar free energies of mixing for the components of Hastelloy X (obtained using the composition given in Table 3) are given in Table 17. Comparing the data given in Table 17 with that given in Table 14 for Hastelloy C-276 it is apparent that the partial molar free energies of mixing of the common alloy components do not vary by more than a few kcal/mole between 25 and 1200°C. Therefore, most of the reactions which are potentially possible in the fluoride-Hastelloy C-276 system would also be possible in the fluoride-Hastelloy X system, and vice versa.

Comparing the data in Tables 5, 6, and 17 it is apparent that, of all the components in the Hastelloy X, silicon provides the greatest potential for reacting with the WESF $^{90}\text{SrF}_2$. Potential reactions of silicon with fluorides in the WESF $^{90}\text{SrF}_2$ are given in Equations 55-70 and the calculated free energies of reaction are given in Table 18.

TABLE 17. Calculated Partial Molar Free Energies of Mixing
for Hastelloy X Alloy Components

Component	$-\Delta\bar{G}_M$, kcal/mole					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
B	6	17	81	24	26	28
C	3	9	12	14	15	16
C _o	2	7	8	10	11	12
Cr	1	3	3	4	4	4
Fe	1	3	4	4	4	4
Mn	3	9	11	13	14	15
Mo	2	5	6	7	8	9
Ni	0	1	2	2	2	2
P	5	14	17	20	22	24
S	5	16	19	23	25	27
Si	3	8	10	12	13	14
W	4	11	14	17	18	19

TABLE 18. Calculated Free Energy of Reaction for Equations 55-70

Equation	ΔG_p° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
55	237	168	150	120	111	102
56	175	152	150	144	141	142
57	187	168	162	152	149	146
58	-65	-84	-86	-108	-115	-122
59	-123	-156	-174	-192	-201	-198
60	-137	-148	-150	-152	-151	-150
61	-247	-300	-306	-328	-337	-338
62	143	108	98	76	69	58
63	139	116	110	100	95	90
64	-19	-42	-48	-54	-55	-56
65	143	112	102	84	77	66
66	-77	-94	-98	-104	-105	-106
67	-77	-100	-102	-112	-111	-110
68	453	396	390	360	351	330
69	179	160	154	144	145	142
70	59	40	34	32	33	34

The calculations show that the silicon will react with those fluorides which are present in low concentrations (≤ 0.2 wt%), but will not react appreciably with the fluorides which are present in relatively high concentrations. Since the reaction product SiF_4 is a gas at the temperatures in question each reaction will proceed until the equilibrium partial pressure of SiF_4 is established (assuming no complex compound formation such as Na_2SiF_6). Similar reactions can be written involving silicon and impurity oxides. The thermodynamic calculations show that the silicon could potentially react with all of the oxides except those of aluminum, the alkaline earth and rare earth elements, and zirconium.

The other components of the Hastelloy X would show less potential to react with $\text{WESF}^{90}\text{SrF}_2$ than silicon, but even so most of the reactions which were potentially possible in the Hastelloy C-276 system would also

be possible in the Hastelloy X system. The boron in the Hastelloy X is a relatively strong reducing agent but because of its large partial molar free energy of mixing would react with fewer components of the fluoride than the silicon.

WESF $^{90}\text{SrF}_2$ - Hastelloy N System

On a thermodynamic basis this system would be very similar to the two previous Hastelloy systems. The Hastelloy N differs from the other two Hastelloys in that it contains small amounts of aluminum, copper and titanium. The calculated partial molar free energies of mixing for the components of Hastelloy N (calculated using the composition from Table 3) are presented in Table 19.

TABLE 19. Calculated Partial Molar Free Energies of Mixing for Hastelloy N Alloy Components

Component	$-\Delta\bar{G}_M$, kcal/mole					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
Al	3	10	12	14	15	16
B	4	13	16	18	19	21
C	3	10	12	14	15	16
Co	4	11	14	16	17	18
Cr	2	4	5	6	7	8
Cu	4	10	13	15	16	17
Fe	2	5	6	8	8	9
Mn	3	9	11	13	14	15
Mo	1	4	5	6	6	7
Ni	0	0	1	1	1	1
P	5	14	18	21	23	25
S	5	14	17	21	22	24
Si	3	7	9	10	11	12
Ti	3	10	12	15	16	17
W	4	11	14	17	18	19

While the partial molar free energies of mixing for common alloy components vary somewhat for the Hastelloy N compared to the other two Hastelloys, thermodynamics predict that reactions involving common components which occur in the other two systems would also occur in the Hastelloy N system. In addition, several reactions involving aluminum and titanium are possible in the Hastelloy N system. Both the aluminum and titanium in the Hastelloy N represent strong reducing agents, even allowing for substantial partial molar free energies of mixing. They would react with the same components of the fluoride as does the silicon in the Hastelloy N and Hastelloy X. The copper in the Hastelloy N would be essentially unreactive with any of the components of the fluoride.

WESF $^{90}\text{SrF}_2$ - Haynes 25 System

Haynes 25 differs from the Hastelloy alloys discussed earlier in that it is a cobalt base rather than a nickel base alloy. However, it contains the same elemental constituents as Hastelloy C-276 except for molybdenum and vanadium. Concentration differences of the common components result in somewhat different partial molar free energies of mixing as can be seen by referring to Tables 14 and 20. These differences amount to, at most, a few kcal/mole and do not affect the free energy of reaction calculations

TABLE 20. Calculated Partial Molar Free Energies of Mixing for Haynes 25 Alloy Components

<u>Component</u>	<u>$-\Delta\bar{G}_M$, kcal/mole</u>					
	<u>25°C</u>	<u>600°C</u>	<u>800°C</u>	<u>1000°C</u>	<u>1100°C</u>	<u>1200°C</u>
C	3	9	11	13	14	15
Co	0	1	1	2	2	2
Cr	1	2	3	3	4	4
Fe	2	6	7	9	9	10
Mn	2	7	9	10	11	12
Ni	1	4	5	6	6	7
P	4	13	16	19	20	22
S	4	13	16	18	19	21
W	2	5	6	7	8	8

to any appreciable degree. Therefore, reactions involving common components which occur in the fluoride Hastelloy C-276 system should also occur in the fluoride-Haynes 25 system and vice versa.

WESF $^{90}\text{SrF}_2$ - Haynes 188 System

Haynes 188 is another cobalt base alloy. It differs from Haynes 25 principally in its nickel content (much higher) and in the fact that it contains a small amount of lanthanum. The partial molar free energy of mixing for components of Haynes 188 are given in Table 21 (values were calculated using the composition given in Table 3).

TABLE 21. Calculated Partial Molar Free Energies of Mixing for Haynes 188 Alloy Components

Component	$-\Delta\bar{G}_M$, kcal/mole					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
C	3	9	11	13	14	16
Co	1	2	2	2	2	3
Cr	1	2	3	3	4	4
Fe	2	7	8	10	11	12
La	5	14	17	20	22	23
Mn	2	7	9	11	12	12
Ni	1	2	3	4	4	5
P	5	14	17	20	22	23
S	5	15	18	21	23	24
Si	3	9	11	12	13	14
W	2	5	6	8	8	9

These values are quite similar to those calculated for Haynes 25. Therefore, reactions involving common components which occur in the fluoride-Haynes 25 system (and the fluoride-Hastelloy C-276 system) should also occur in the fluoride-Haynes 188 system.

The lanthanum in the Haynes 188 is a very strong reducing agent, even allowing for a sizable partial molar free energy of mixing. It could react with all of the fluorides in the WESF $^{90}\text{SrF}_2$ except those of the alkaline earth elements and some of the rare earth elements. For example:

The calculated free energies of reactions for Equations 71-74 are given in Table 22. They predict that the lanthanum would react with NaF, ZrF_4 and AlF_3 in the WESF $^{90}\text{SrF}_2$ in addition to the less stable fluorides. They also indicate the lanthanum would not react with CaF_2 and the other alkaline earth fluorides present.

TABLE 22. Calculated Free Energy of Reaction for Equations 71-74

Equation	ΔG_R° , kcal/equation as written					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
71	- 10	- 13	- 13	- 19	- 20	- 25
72	-292	-260	-256	-232	-212	-196
73	- 58	- 55	- 52	- 52	- 50	- 49
74	41	44	47	44	46	47

The thermodynamic calculations also indicate that the lanthanum would react with all oxides present in the WESF $^{90}\text{SrF}_2$ except for CaO, SrO, MgO and some rare earth oxides. The lanthanum would react with BaO at the lower temperatures (<600°C) but not at the higher temperatures.

WESF $^{90}\text{SrF}_2$ - Inconel 600 System

On a thermodynamic basis Inconel 600 is a less complex alloy than the other superalloys under consideration since it contains only eight constituents. It is essentially a nickel-chromium-iron alloy with minor amounts of other components.

The partial molar free energies of mixing for components of Inconel 600 (based on the composition given in Table 3) are presented in Table 23. A comparison of the data in Table 23 with corresponding data for the other superalloys shows that partial molar free energies of mixing for components of the Inconel 600 are quite similar to those for the same components in other superalloys. Therefore, reactions involving common components which occur in the Hastelloy and Haynes systems should also occur in the WESF $^{90}\text{SrF}_2$ - Inconel 600 system. The only component of the alloy which would not react with at least one component of the fluoride would be the copper.

TABLE 23. Calculated Partial Molar Free Energies of Mixing for Inconel 600 Alloy Components

Component	$-\Delta\bar{G}_M$, kcal/mole					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
C	3	10	12	14	16	17
Cr	1	3	4	4	4	5
Cu	4	10	12	15	16	17
Fe	2	4	5	6	6	7
Mn	3	9	11	13	14	15
Ni	0	0	1	1	1	1
S	5	15	19	22	24	26
Si	3	9	11	13	14	15

WESF $^{90}\text{SrF}_2$ - Inconel 625 System

The WESF $^{90}\text{SrF}_2$ - Inconel 625 system is more complex than the corresponding Inconel 600 system because of the added components in the Inconel 625. However, potential reactions in the Inconel 625 system are similar to those in the other superalloy systems. The only component in Inconel 625 not found in the other superalloys is niobium. Considering the free energies of formation of its fluorides and oxides and its partial molar free of mixing (see Table 24) the niobium in the Inconel 625 would react with only a few of the impurity fluorides and oxides present in the WESF $^{90}\text{SrF}_2$.

TABLE 24. Calculated Partial Molar Free Energies of Mixing for Inconel 625 Alloy Components

Component	$-\Delta\bar{G}_M$, kcal/mole					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
Al	3	9	11	13	14	15
C	3	10	13	15	16	17
Cr	1	2	3	3	3	4
Fe	2	5	7	8	9	9
Mn	4	13	16	19	20	23
Mo	2	5	6	7	8	8
Nb	2	6	8	9	10	11
Ni	0	1	1	1	1	1
P	5	14	18	21	23	24
S	5	15	19	22	24	25
Si	3	9	11	13	14	15
Ti	3	9	12	14	15	16

SUMMARY

The WESF $^{90}\text{SrF}_2$ contains a number of fluoride impurities. Fortunately, the fluorides which are present in relatively high concentrations (>0.2 wt%) are the most stable of the metal fluorides (i.e., SrF_2 , ZrF_4 , NaF , CaF_2 , etc.). The thermodynamic analysis of the WESF $^{90}\text{SrF}_2$ - alloy systems indicates a large number of reactions are possible between alloy components and impurity fluorides. With one exception, however, the potential reactions are restricted to impurity fluorides which are present in low concentrations (≤ 0.2 wt%). The only possible reactions involving fluorides present in large concentrations are limited to those involving lanthanum (which is found in trace levels in Haynes 188 alloy).

A number of reactions involving oxides are also possible in each of the fluoride-alloy systems. However, the concentration of oxygen in the

fluoride is very low (<0.05 wt), and most of the oxygen is present as water or nitrate. Therefore, the concentration of metal oxides in the fluoride should be very low.

Based on the thermodynamic calculations, TZM and tungsten (reported previously) should provide the greatest resistance to attack by WESF $^{90}\text{SrF}_2$. Because of the similarity in composition of the superalloys, it is impossible to predict, on a thermodynamic basis, the relative resistance of the superalloys to attack by WESF $^{90}\text{SrF}_2$. All of the superalloys will be attacked by the fluoride to some degree. The extent of attack of each alloy, under a given set of conditions, would depend to a large degree on reaction kinetics and diffusion mechanisms. These factors are almost impossible to estimate because of a lack of reliable data. A realistic evaluation of WESF $^{90}\text{SrF}_2$ - alloy reactions can only be obtained by experimental studies.

The thermodynamic analysis of fluoride-alloy systems discussed above was based on a number of simplifying assumptions. A rigorous analysis which ignores these assumptions could provide significantly different results. Such an analysis is limited by the lack of thermochemical data, however, and is not warranted at this time.

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