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Prepared for the U.S. Department of Energy
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Synthesis of Trevorite to Capture Tc

C Tsui

September 2011

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Abstract

Spinel containing technetium can be used to prevent Tc volatilization during vitrification of radioactive waste. Spinel dissolves in glass at elevated temperatures. This study focuses on the synthesis of spinel and the retention of rhenium, a nonradioactive surrogate for Tc in the crystals. To produce trevorite, a nickel-iron spinel ($NiFe_2O_4$), Fe and Ni nitrates were mixed with alkali nitrates along with $Al(OH)_3$ and heated to 500 to 800°C. The trevorite content in samples (up to 40 mass%) was measured with x-ray diffraction. Viable samples were rerun with $KReO_4$. Scanning electron microscopy-energy dispersive spectroscopy detected that Re became partly immobilized in spinel-forming crystals.

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1.0 Introduction

Because of their physical flexibility and chemical stability, spinels are used in various applications. Spinel crystals were also observed to contain high concentrations of rhenium [1], which makes spinel crystals suitable for immobilization of technetium (Tc), a radioactive waste product chemically similar to rhenium (Re). Neither Tc nor Re can be directly retained in High Level Waste (HLW) glass because they volatilize before the glass is formed. However, Tc or Re-containing spinel crystals have a good chance of preserving these elements until a high temperature at which the crystals dissolve in molten glass [2].

This study focused on trapping Re in trevorite ($NiFe_2O_4$). Senthilkumar et. al [3] synthesized trevorite from molten salts. Unlike these authors, who produced trevorite at 900°C, trapping Re requires temperatures as low as possible, preferably below 500°C. Therefore, we selected Ni and Fe nitrates as starting chemicals mixed them with alkali nitrates in proportions close to the eutectic (Fig. 1). After the spinel was successfully produced at 500°C, we repeated the experiment with $KReO_4$ added to the mixture. The product is being chemically analyzed at this stage.

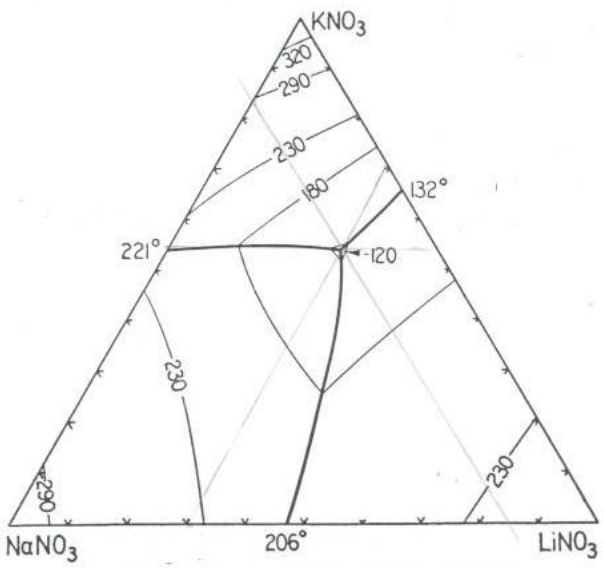

FIG. 1069.—System KNO_3–$LiNO_3$–$NaNO_3$.

H. R. Carveth, *J. Phys. Chem.*, 2, 216 (1898).

Figure 1. $NaNO_3$-$LiNO_3$-KNO_3 Phase Diagram [4]

2.0 Experimental Method

As Figure 1 shows, the $NaNO_3$-$LiNO_3$-KNO_3 ratio to achieve a melting point of 120°C is approximately 0.17:0.3:0.53 by mass. This mixture was prepared from analytical grade chemicals, blended with mortar and pestle and melted at 180°C in an oven. The melt was cooled down to room temperature. It turned to melt on reheat to 130°C. This alkali nitrate mixture was used as an additive in the spinel batches listed in Table 1.

The nitrate mixtures shown in Table 1 contain, in varying proportion, Fe and Ni nitrates, alkali nitrate eutectic mixture, and either B_2O_3 or $Al(OH)_3$, added to bond alkalis from decomposed nitrates. A batch of several known spinel-forming components, Table 2, was also tried. Table 3 shows a mixture of CT1.850 sample with chloride salts. This sample was heated to 900°C. Note that the maximum heat-treatment temperature was appended to the sample ID.

Samples were heated from 200°C until maximum temperatures at 5°C/min. Heat-treated samples were then analyzed by x-ray diffraction (XRD) and scanning electron microscopy—energy dispersive spectroscopy (SEM-EDS) for structure and composition. Based on XRD data (with 5% CaF_2 as an internal standard), composition CT4A was selected for mixing with $KReO_4$. Two samples were prepared, one with Re/Ni molar ratio 0.5 and the other 1. For SEM-EDS analysis, the Re containing samples were washed with hot water, dried, mounted in epoxy and polished.[1]

Table 1. Composition of Nitrate Mixtures in Mass Fractions[(a)]

	CT1	CT2	CT3A	CT3B	CT4A	CT4B
$LiNO_3$	0.0338	0.0215	0.0288	0.0257	0.0288	0.0257
$NaNO_3$	0.0597	0.0380	0.0508	0.0454	0.0508	0.0454
KNO_3	0.1054	0.0671	0.0898	0.0801	0.0898	0.0801
$Ni(NO_3)_2*6H_2O$	0.3353	0.2136	0.2835	0.2531	0.1793	0.1600
$Fe(NO_3)_3*9H_2O$	0.4658	0.2967	0.3939	0.3516	0.4982	0.4447
H_3BO_3	0.0000	0.3631	0.0000	0.0000	0.0000	0.0000
B_2O_3	0.0000	0	0.0000	0.2441	0.0000	0.2441
$Al(OH)_3$	0	0	0.1532	0	0.1532	0

(a) Sample CT1 was heated to 850°C, CT2 to 900°C, and the remaining samples to 600 and 800°C.

Table 2. Composition of SS-A spinel [5] Components in Mass Fractions

	CT5Li	CT5,2Li
$LiNO_3$	0.1281	0.2561
$Ni(NO_3)_2*6H_2O$	0.1401	0.1195
$Fe(NO_3)_3*9H_2O$	0.6509	0.5553
$Cr(NO_3)_3*9H_2O$	0.0656	0.0560
Mn_3O_4	0.0153	0.0130

[1] $KReO_4$; ρ = 4887 kg/m^3; $T_{melting}$ = 550°C, $T_{boiling}$ = 1360-1370°C; solubility in cold water 12.1 g/L and in hot water 140g/L.

Table 3. Nitrate Mixture with Chloride Salts in Mass Fractions

	CT6
$LiNO_3$	0.0169
$NaNO_3$	0.0298
KNO_3	0.0527
$Ni(NO_3)_2*6H_2O$	0.1676
$Fe(NO_3)_3*9H_2O$	0.2329
NaCl	0.2197
KCl	0.2803

3.0 Results

Table 4 lists the results of XRD analysis. Spinels, trevorite and magnetite (and possibly lithium iron oxide), occurred in CT4 samples, which contained B_2O_3 or $Al(OH)_3$ additions(it is possible that lithium-containing crystals can also carry Re into glass). Table 5 shows the XRD results of semi-quantitative analysis with JADE and TOPAS. Figure 2 shows Ni and Fe content in samples based on the stoichiometric compositions of the crystalline compounds. The data scatter is large, and no temperature effect can be discerned. The average yield is 42±17% for Ni, and 71±16% for Fe. As Table 6 shows, 48-71% of $KReO_4$ was retained in the sample. The rest, 29-52%, partly evaporated and partly became incorporated in spinel.

Table 4. XRD Results of CT1-CT6[(a)]

Sample	T	M	LF	LN	F	N	FNB	K
CT1.850				×	×	×		×
CT2.900					x		x	
CT3A600			x			x		x
CT3B600								
CT4A600	x	x						x
CT4A800		x						
CT4B600		x			x			
CT4B800	x				x			
CT5Li600			x			x		
CT5Li800			x	x		x		
CT5,2Li600			x			x		
CT5,2Li800			x			x		
CT6.900			x			x		

(a) F = Fe_2O_3, FNB = $FeNi_2BO_5$, K = KNO_3, LF = $LiFeO_2$, LN = $Li_{0.4}Ni_{1.6}O_2$, M = Fe_3O_4, N = NiO, T = $NiFe_2O_4$

Table 5. XRD Results of CT4A in Mass Fractions

Re/Ni	T, °C	T	M	LF	LP	LN	N	K
0	500	0.111	0.166	-	-	-	-	-
0	600	0.286	0.084	0.217	-	-	-	0.122
0	700	-	0.264	0.111	-	-	0.053	-
0	800	-	0.175	-	0.093	0.083	-	-
1	600	0.149	0.034	-	-	-	-	-
1	800	-	0.198	-	-	0.093	-	-
0.5	600	0.223	0.017	-	0.048	-	-	0.103
0.5	800	0.082	0.205	-	-	-	-	-

(a) F = Fe_2O_3, FNB = $FeNi_2BO_5$, K = KNO_3, LF = $LiFeO_2$, LN = $Li_{0.4}Ni_{1.6}O_2$, LP = $LiFe_5O_8$, M = Fe_3O_4, N = NiO, T = $NiFe_2O_4$

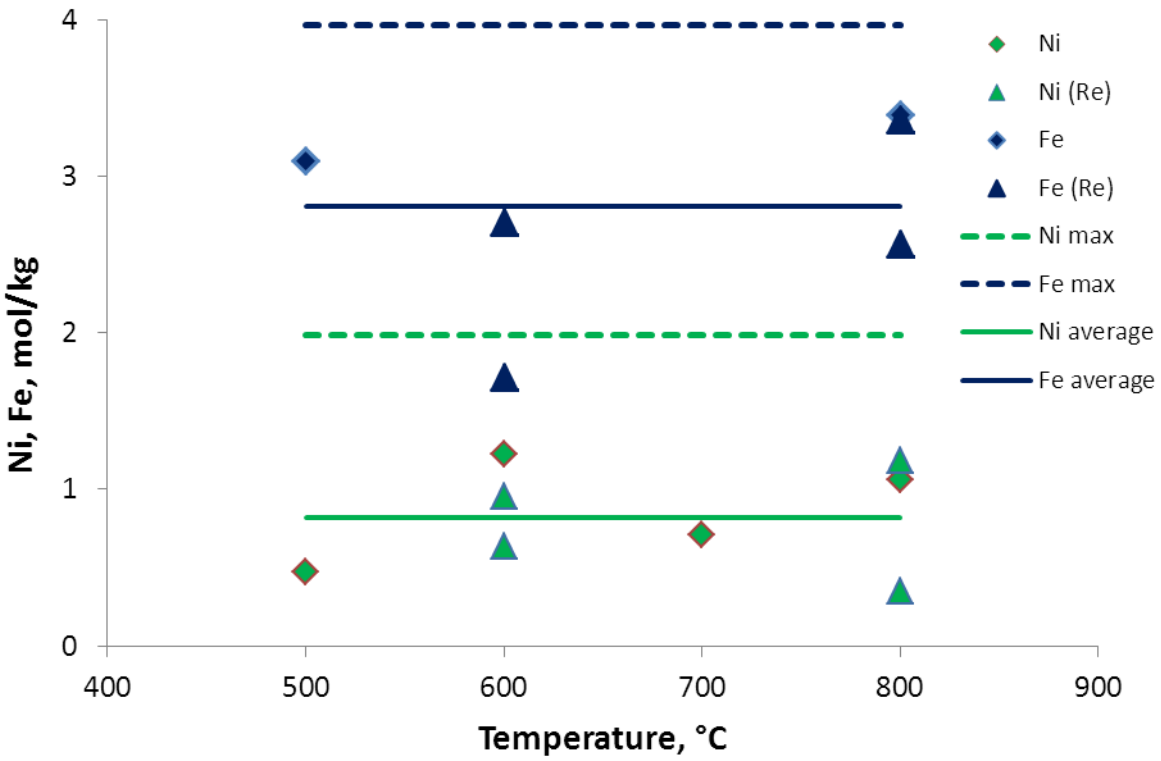

Figure 2. Spinel Yield vs. Temperature

Table 6. $KReO_4$ Content in CT4, XRD Data

T, °C	Mass fraction	Fraction retained
600	0.2578	0.708
800	0.2107	0.578
600	0.1476	0.663
800	0.1065	0.478

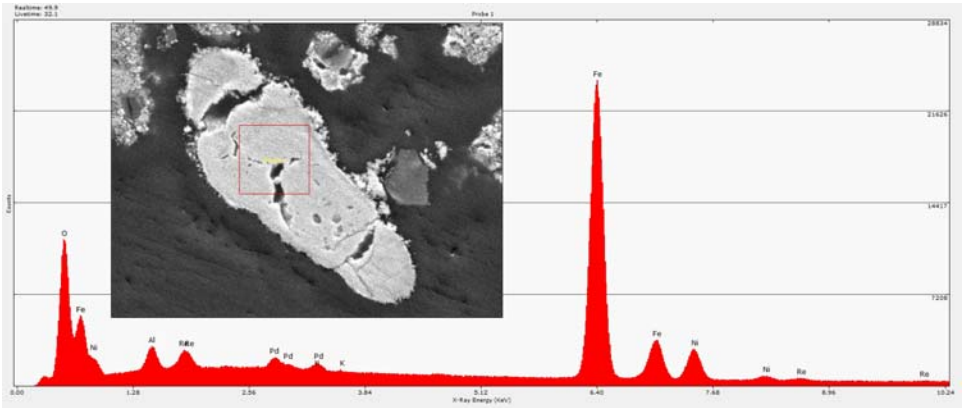

Figure 3. SEM-EDS of CT4A600R (Re/Ni = 1)

Table 7. SEM-EDS Data (atomic fraction)

Average	Fe	Ni	Re
600	0.329	0.100	0.0079
800	0.256	0.085	0.0059
total	0.297	0.093	0.0070
Standard deviation			
600	0.148	0.036	0.0032
800	0.127	0.010	0.0004
total	0.132	0.028	0.0030
Spinel cation fraction			
600	0.754	0.228	0.018
800	0.738	0.245	0.017
total	0.748	0.235	0.018

4.0 Discussion

This study is part of a larger project to immobilize Tc in HLW glass. While we are in the initial stages of this study, there is a high probability that Re will be found in satisfactory concentration in spinel. If so, we can expect that satisfactory amounts of Re will be carried by spinel into HLW glass.

5.0 Conclusions

Trevorite and other spinels can be produced from a nitrate mixture at temperatures as low as 500°C. Spinel crystals can contain several percent of Re. For future work, the Re-containing spinel will be added to HLW feed to determine the fraction of Re retained in glass.

6.0 References

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