

Cermet Waste Forms for Waste Streams from Advanced Aqueous Processing of Spent Nuclear Fuels - 11348

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ABSTRACT

The nuclear fuel cycle options now under consideration in the U.S. include used nuclear fuel reprocessing to better utilize the energy content and to reduce waste. Aqueous reprocessing may use any of several separation strategies. Each will create different waste streams requiring an appropriate choice of waste forms to optimize subsequent management of these streams. Glass waste forms are a proven approach for high level waste immobilization, but these may not be the best choice for some of the separated waste streams. For example, if decay storage is to be used as a management option for separated Cs and Sr, the limited thermal conductivity of glass would impose severe constraints on the size of the glass canisters. Also, glass may not be the best choice for separated streams containing molybdenum and the noble metal fission products because these elements have limited solubility in glass. This paper describes development of a cermet waste form to immobilize separated Cs and Sr, and by tailoring the metal phases include other fission products such as molybdenum. In our cermet a copper tin alloy was chosen for the metal phase due to its low melting point and relative unreactive nature. The alloy was prepared from Cu and Sn (10 mass%) powders. These powders were mixed with pre-sintered ceramics consisting of alkali and alkaline earth elements in the form of aluminosilicates, then cold pressed to 300×10^3 kPa and sintered from 600° to 800°C under hydrogen. Cermets were also prepared which incorporated molybdenum carbide (Mo_2C) in the metallic phase. The cermet products were analyzed with scanning electron spectrometry coupled with energy dispersive analysis, X-ray powder diffraction, and the thermal properties were determined with the laser flash technique and differential scanning calorimetry. Cermet thermal conductivities increased over seven times compared to the ceramic alone.

INTRODUCTION

A modified open fuel cycle has the potential of generating various types of nuclear waste streams. The nuclear waste plan is yet to be determined, so a precise nuclear waste scenario is impossible to envision at this time. Designing a nuclear waste immobilization strategy that can accommodate diverse waste streams would have the flexibility necessary to be applicable to a wide range of waste types. Vitrification is a proven method which can handle most waste to various degrees of effectiveness. There are some waste streams which may be handled more successfully in a highly conductive waste form, Cs-137 and Sr-90 for example. These high heat generating isotopes could be formed into larger geometries if thermal conductivities are adequate to allow efficient heat removal. As a waste form becomes larger, center-line temperature increases, eventually reaching a level that may melt or soften the waste matrix. Efficient heat removal will lower the thermal gradient across the waste form, and lower overall temperatures which can reduce reaction rates such as corrosion, and reduce phase migration.

Cost analyses have shown that reducing the number and type of waste forms can save capital, as well as operating costs when compared to unique waste treatments for each type of waste [1]. The ability to consolidate waste streams and, for high-heat generating radionuclides, consolidate into waste forms of higher thermal conductivities are both desirable. A cermet may be capable of doing both. In this scoping study we investigate the potential for cermets as waste forms.

A cermet composed of a ceramic phase as well as metallic phase will have a dual nature that can be tailored to accommodate troublesome waste types. The ceramic can hold oxide wastes, while the metallic region may be used to immobilize metallic-forming waste elements. The noble metals and molybdenum have limited solubility in glass; these may be better managed in a metal matrix [2, 3]. Cesium and strontium create a different problem. These two elements contain most of the decay heat generated in spent nuclear fuel during the first few hundred years out-of-reactor [4]. A waste stream containing these elements will

cause substantial heating within any waste matrix. Any improvement in thermal conductivity will reduce the waste form centerline temperatures, thus allowing for larger waste form geometries and a lower number of packages. In addition, because the long-lived actinides will presumably be removed from the wastes and recycled in advanced burner reactors, the geological long-term performance assessment period for this waste will be reduced compared to TRU waste.

The metals used for the metal phase can either be virgin material, such as copper and tin to form an alloy, or they can be a combination of fresh metal and metal waste. Sources of metal that result from nuclear fuel reprocessing are the activated metals from the assembly hardware, zircaloy cladding, noble metals and transition metals in the TRUEX raffinate, and the noble metals in the undissolved solids. Oak Ridge National Laboratory has investigated the consolidation of most of these waste streams into a cermet waste form [5]. This path required high temperatures which may volatilize some of the lighter elements; we selected a bronze metal phase to avoid this complication. There are several potential waste streams in the various reprocessing scenarios which, if produced would require treatment. Most of these can be dealt with effectively within glass, zirconium and the lanthanides for example. We have selected waste streams which would benefit from improved thermal conductivity, or hinder glass waste loading. The cermet processing temperatures will vary depending on what metals are present in the waste, and the size of the metal powders used to form the matrix alloy. In the current work we used 10 mass% tin in copper to form bronze. Cermets were also prepared with molybdenum carbide added to pulverized ceramic (fully formed) and bronze precursor powders, these were mixed followed by cold pressing and sintering.

The ceramic phase we tested was made from a simulated waste stream containing cesium, strontium, barium and rubidium nitrates dissolved in nitric acid. The alkali and alkaline earth metal ratios were typical of what is expected in spent nuclear fuel. The simulated waste stream was combined with bentonite clay, dried, and sintered to form a hard, dense ceramic. We have shown that when bentonite clay was added to the liquid waste stream, it provided the base material for the formation of alkali and alkaline earth aluminosilicates (e.g. pollucite). This method, done at relatively low temperatures, will reduce cesium volatilization during subsequent processes. The ceramics that result are comprised of cesium pollucite, and a rubidium pollucite analog, and feldspars of barium and strontium [6]. To form the cermet this ceramic was ground to a powder, mixed with the metallic powders, cold pressed into a puck, then sintered at 600-800°C under hydrogen.

We have investigated copper-tin alloys as potential cermet metal phases. The use of copper alloyed with tin was motivated by the low melting temperature, and the un-reactive nature of bronze. Bronze is a corrosion resistant metal in the absence of acids [7]. We have also investigated the feasibility of adding molybdenum in the form of molybdenum carbide to these metal and ceramic matrices. Molybdenum carbide was chosen because it will not change the melting temperature of the copper tin alloys; also, molybdenum carbide has a thermal conductivity of ~22 W/m•K [8], which is substantially greater than that of a glass or ceramic (~1 W/m•K)[9], thus increasing the total waste loading of the waste form.

METHOD

We combined a preformed ceramic with metal powders under moderate temperatures (600°C and 800°C) to form cermets. The ceramic phases were formed by mixing simulated Cs and Sr bearing liquid waste stream (nitrate salts Cs, Sr, Ba, and Rb dissolved in dilute nitric acid) and sodium bentonite (Volclay HPM-20, 425 mesh, American Colloid Company, Belle Fourche, SD). The mixture was dried, cold pressed to 45×10^3 kPa, and sintered 700°-1400°C. The resulting ceramic had a waste loading of up to 32 mass% metal ions (Cs+Sr+Rb+Ba). In the ceramic, the alkali and alkaline earth elements were found in crystals consisting of a Cs,Rb body-centered cubic pollucite phase, and monoclinic feldspars of Ba,Sr. The remaining waste elements were embedded within a glassy phase of the aluminosilicate ceramic. The density of the ceramic reached a maximum when sintered from 1100°C to 1200°C, and the mineralization was most pronounced at 1200°C, evident in the intense X-ray diffraction spectrum of the ceramic [6].

The crushed ceramic was mixed in an agate mortar and pestle with 10%Sn-90%Cu alloy the volume ratio was varied to assess its effect on resulting properties. The alloy powder precursors were supplied by Alfa Aesar, the copper was a 625 mesh with a 99% purity, and the tin was a 325 mesh with 99.8% purity. The

mixed powders were cold pressed at 300×10^3 kPa, and then they were sintered under hydrogen from 600° to 800°C. Experiments were carried out to assess the feasibility of incorporating molybdenum ions into bentonite clay derived ceramic directly. Molybdenum acetate ($\text{Mo}_2(\text{OCOCH}_3)_4$ Aldrich Co. 98% purity) was added to bentonite clay along with cesium, strontium, rubidium and barium nitrates in an aqueous solution, dried and sintered in air at 1200°C. Incorporation of molybdenum carbide (Mo_2C Strem Chemicals Inc. 99.5% purity) to the cermet was also tested by adding the carbide powder to the pre-sintered ceramic powder, as well as the copper, and tin powders, which were cold pressed and sintered in hydrogen at 600°C.

The resulting cermets were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). Cermet porosities were measured with a pycnometer. Thermal properties were measured by the laser flash technique, to obtain thermal diffusivity, and differential scanning calorimetry to measure specific heat (TPRL, Inc., West Lafayette, IN). The specific heat (c_p) and thermal diffusivity (α) were used to calculate the thermal conductivity (k) of the cermets (Eq. 1).

$$k = \alpha \rho c_p \quad (1)$$

RESULTS

The motivation to seek alternate methods to immobilize Cs and Sr bearing nuclear wastes was based on the immense heat dissipation that these elements will require; a higher thermal conductivity matrix is one method to deal with this concern. Other possible ways to mitigate the extreme activities would be to employ lower waste loadings, or to use active cooling systems. Without knowledge of future waste conditions, such as repository capacity or heat limitations, higher density options may be necessary. Another problem that may be addressed with a cermet waste form is the possible incorporation of waste types with limited solubility in glass, molybdenum and the noble metals for example. In this study we limited our investigation to the addition of molybdenum in the form of a carbide to the waste cermet. The preparation of the powder precursors, or direct incorporation of the waste into the cermet waste form will need to be done in a manner that minimizes the possibility of volatilizing any of the low vapor pressure elements, such as cesium.

We used bentonite clay to immobilize the alkali and alkaline earths into hard dense ceramics, which had bulk densities from 2100 to 2300 kg/m^3 , with porosities from 15-17% [6]. The ceramic was crushed in a mortar and pestle then combined with metal powders to form the cermet. The metal phase for the cermet was required to be relatively inert with respect to the waste ceramic, and have a low enough melting point to allow consolidation without compromising the ceramic's integrity during processing. A bronze consisting of copper and 10 mass% tin was chosen for the metal phase. A bronze sample was prepared from the copper and tin powders in the same conditions the cermets were made, cold pressed and sintered under hydrogen at 800°C. The bulk density of the 10 wt.% Sn and Cu alloy was 5790 kg/m^3 with 2.3 % porosity. The volume ratio of ceramic to metal phase was varied, while the addition of molybdenum carbide was limited to only a few samples. The density of the cermet with 35 volume % ceramic was 5400 kg/m^3 , and the 45 volume % ceramic formed a cermet that was 4700 kg/m^3 . The cermet materials formed had porosities which were relatively high, ranging from 24% void space to over 50 volume %.

After preparing the cermets we characterized the solid products. The primary concern was to determine if the ceramic, composed of the alkali and alkaline earth metal minerals decomposed during processing. The integrity of the radioactive ion matrices within the ceramic should remain intact to mitigate any release of the elements of concern. In addition, to improve the thermal properties of the waste form, relative to a waste ceramic or glass, the cermet must have a continuous metal phase with minimal porosity within the cermet and the individual phases. The cermet's physical structure was determined by SEM and XRD. The elemental distribution was found with EDS, and the thermal properties were calculated from data obtained with differential scanning calorimetry, and flash diffusivity.

SEM and EDS Analysis

The low melting temperature of the bronze allowed for consolidation without compromising the structure of the ceramic phase. SEM and EDS analyses performed on the cermets found a distinct multi-phase structure. The metallic region became a continuous binding matrix with the ceramic phase embedded within (Fig. 1). The bronze was distributed throughout the material, filling cracks and voids between the ceramic particles. The elemental distribution determined by EDS did not find any ceramic to metal intermixing during cermet processing. The copper and tin were homogeneously mixed within the metallic region and the ceramic was found as isolated particles surrounded by metal. The bulk elemental distribution within the ceramic remained the same as it had been before being incorporated into the cermet (Fig. 2). The cesium and rubidium were in areas separate from those regions holding the barium and strontium. In previous work we have found monoclinic crystals of Cs-pollucite and the Rb analog were intimately mixed, while the strontium and barium feldspars coexisted in long crystals. These unique phases are held together within the ceramic in a silica rich glassy matrix [6]. This pattern is visible in the SEM imaging at the micrometer scale (Fig. 1), and to a few percent under EDS (Fig. 2).

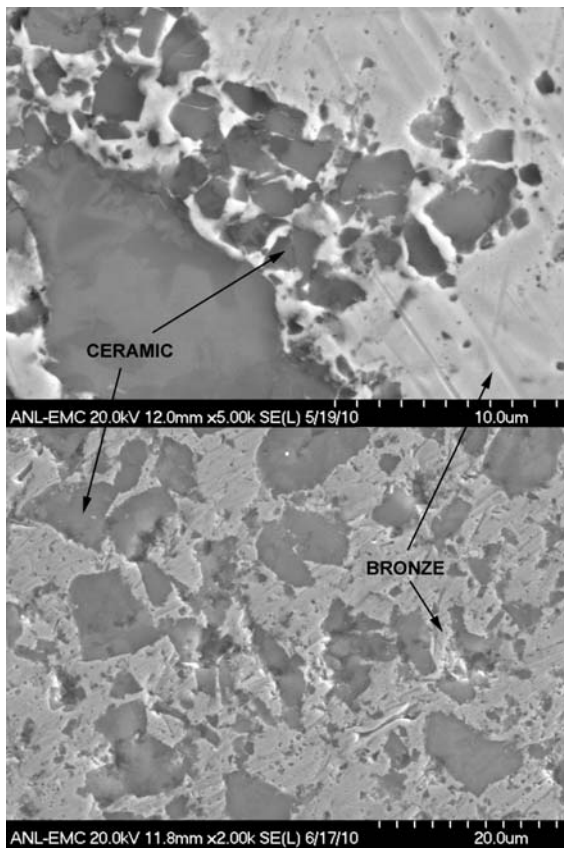


Figure 1 SEM backscatter images of cermets; **Top:** 30 mass% ceramic to 70 mass% bronze (90 mass% Cu 10 mass% Sn); **Bottom** 50-50 ceramic to metal mass ratio.

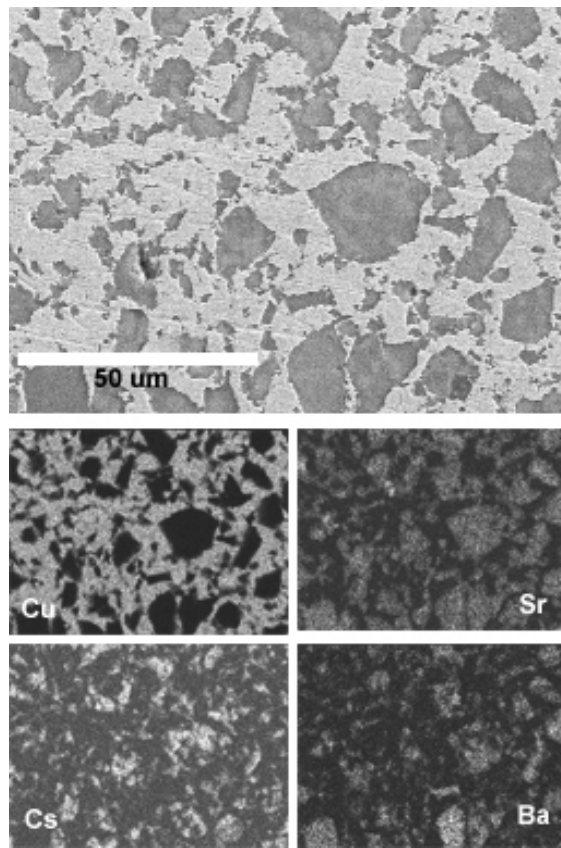


Figure 2 **Top:** SEM backscatter image of 30 mass% ceramic to 70 mass% bronze (90 mass% Cu 10 mass% Sn) cermet; **Bottom:** EDS maps where light areas represent higher relative concentration of the elements.

In another experiment, molybdenum carbide (Mo_2C) was mixed with the ceramic and metal powders, cold-pressed and sintered to 600°C under hydrogen. The resulting cermet had a three-phase structure, where the molybdenum remained as inclusions within the copper alloy (Fig. 3).

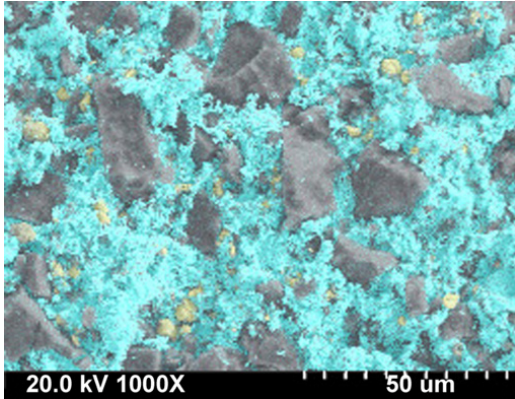


Figure 3 False color composite of SEM and EDS analyses of cermet consisting of ceramic, bronze and molybdenum, where the blue regions are copper, yellow molybdenum, grey ceramic; Precursors were 40 mass% ceramic, 10 mass% Mo₂C, 50 mass% bronze (10 mass% Sn and Cu).

X-ray Diffraction

The X-ray diffraction analysis of the cermet products found that the mineral forms that existed within the ceramic before cermet processing remained after cermet formation. The diffraction spectra of the cermets had copper or alloy patterns which overlapped the pollucite and feldspar signatures of the ceramic. Alumino-silicates of copper, tin, or molybdenum were not observed under XRD analysis.

The discrete ceramic phases remained when we formed the cermet from pre-sintered ceramic and metal powders. In a separate experiment to test the incorporation of molybdenum waste to the cermet, bentonite clay and the aqueous solution of metal ions, nitrates of the alkali and alkaline earths, along with molybdenum from acetate were dried to a powder and sintered. The Mo²⁺ reacted with the simulated waste to form a strontium molybdate (SrMoO₄), thus altering the formation of the alumino-silicates. Less pollucite formed, evidenced by a lower intensity of the reflections and formation of a competing cesium zeolite (Cs₄Al₄Si₂₀O₄₈) phase. In another experiment molybdenum carbide was combined with the sintered ceramic and the bronze alloy. X-ray diffraction analysis of the cermet product found reflections of the molybdenum carbide along with the alumino-silicates present in the original sintered bentonite clay. Molybdenum metal reflections were also present, evident of carbide reduction during processing, the bronze alloy reflections were also found in the spectrums. The inclusion molybdenum waste to the cermet may be possible if the molybdenum is converted to a carbide then added during cermet processing, rather than attempting to add the molybdenum ions directly to the ceramic.

Thermal Properties

The continuity of the conductive metal made a substantial improvement in the thermal conductivity of the cermet. The addition of 70 mass % metal to the cermet increased the thermal conductivity over 7 times that of the 50 mass % metal cermet (Fig. 4). The 50:50 mass % metal and ceramic cermet was porous, with over 40 % void space making its thermal conductivity particularly low, comparable to the ceramic alone. Porosity reduction will improve thermal properties of ceramics [10]. Our analysis has shown that an increase in thermal conductivity will exponentially reduce a waste form centerline temperature (unpublished). Higher metal content is not the only way to improve thermal properties. The cermets' thermal conductivity may be improved using processing methods which can reduce porosity such as hot pressing, hot isostatic pressing, or minimizing the size of the powder precursors. An improved thermal conductivity will transfer heat more effectively, reducing waste form temperatures, thus making higher loadings possible.

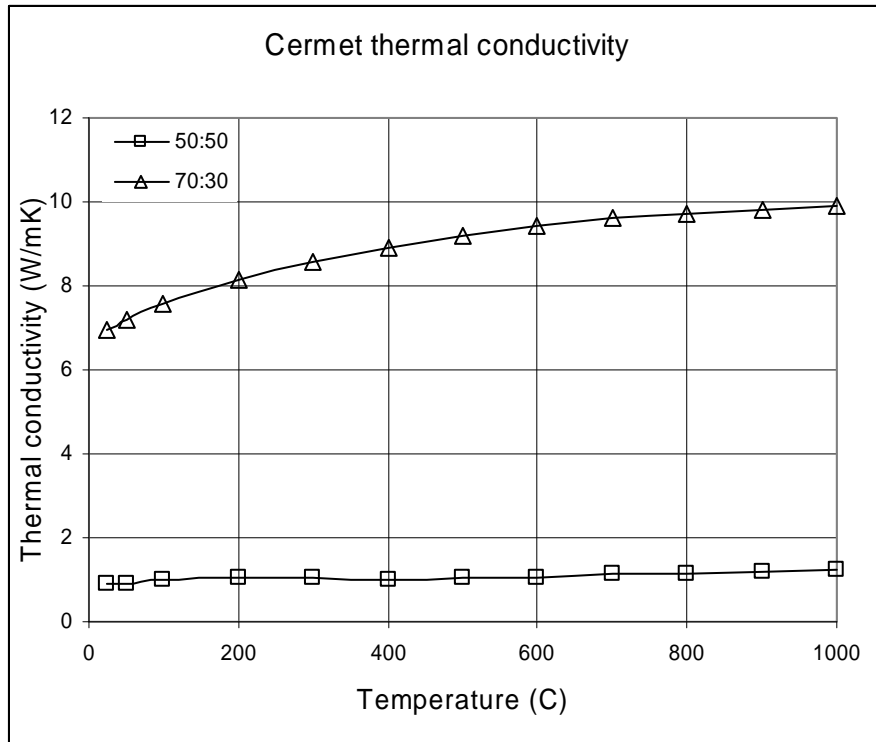


Figure 4 Thermal conductivity of cermets consisting of 50 mass% and 30 mass% ceramic with the remainder bronze.

CONCLUSIONS

Cermets consisting of alloys of copper and tin mixed with ceramics loaded with alkali and alkaline earth metals were tested for thermal conductivity and their structural properties. The bronze matrix formed a continuous matrix when the volume fraction metal was 70%, which led to improved thermal conductivity. Chemical interaction between the metal and ceramic constituents was not observed by EDS analysis, which indicates that volatile Cs and Sr were well contained in the stable pollucite and feldspar; thus if the cermet metal is corroded the Cs and Sr will not be released from the metal.

Nuclear waste storage or disposal in a future where space and volume are limited, a waste form with efficient heat removal may be a desirable option. Cermets could complement nuclear waste glass which has limited capacity to hold certain elements, molybdenum and the noble metals for example, and a poor thermal conductivity. A two phase waste form may hold the potential to incorporate oxide and metallic types of waste with improved thermal properties.

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