

**MASTER**

DEVELOPMENT AND CHARACTERIZATION OF CERMET FORMS FOR RADIOACTIVE WASTE\*

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INTRODUCTION

Cermets designed to isolate high-level wastes in a solid form are a composite consisting of various ceramic phase particles uniformly dispersed in and microencapsulated by an iron-nickel base alloy matrix. The metal matrix provides this waste form with many advantageous features including excellent thermal conductivity and mechanical strength. These cermets are formed by first dissolving the waste in molten urea, precipitating and calcining all the constituents, compacting the calcine, and sintering and reduction to form the final product. The exact formulation of cermets through additions to the waste is designed to fix most of the fission products in stable, leach resistant ceramic phases which are subsequently microencapsulated by an alloy matrix. The alloy matrix, which is derived primarily from the waste itself and includes the reducible fission and activation products from the waste, can be compositionally adjusted through additions to optimize its corrosion resistance under conditions existing in various disposal environments.

The processes by which cermets are formed include several new and unique materials preparation options that are being developed to permit engineering scale-up and to be compatible with remote operations. Cermets formed by alternate processing methods are being characterized. Simulated wastes, radiotracer-containing

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simulated wastes, and actual high level wastes have been studied. Until recently, investigations have been focused on NFS Thorex waste and SRP dried sludge and fresh acid wastes; however, the applicability of cermet processing to a widening variety of other waste types is also being investigated.

#### CERMET PROCESSING DEVELOPMENT

Initially, cermet samples were prepared using a laboratory scale, batch process developed for the preparation of special ceramics having high compositional uniformity and excellent sinterability.<sup>1,2</sup> The first step in this process involved the dissolution of the waste and additives in a molten urea solution. Upon heating dehydration and denitration of the solution occurred, and eventually a precipitate was formed containing the waste and additive ions distributed homogeneously throughout the precipitate. Calcination of this precipitate in air at 800°C decomposed the precipitate into its component oxides. Hydrogen reduction of this submicron size calcine powder at 800°C converted the reducible metal oxides to metal (Fe, Ni, Cu, etc.) from which the final alloy matrix was derived. Subsequent densification of this metal and oxide powder mixture by hot pressing or sintering formed the cermet samples for property evaluation purposes.<sup>3,4</sup>

The modification of this batch process to one suitable for scale-up and remote operation is the subject of this paper. Significant improvements in the precipitation and calcination steps have resulted from the development and use of a spray calciner. A 10-cm i.d. spray calciner with an 800°C wall temperature using simulated waste-additives-molten urea solutions has combined time consuming precipitation and calcination process steps into one very rapid unit operation with additional advantages. With spray calcination, a 1:1 molar ratio of urea to nitrate ion is used rather than the 5:1 to 40:1 ratio commonly employed in batch processing. This not only drastically reduces urea consumption, but also the effluent gases from the process are decreased and the exothermic nature of the urea-nitrate reaction improves the calcination of the material as it falls through the spray calciner. The off-gas resulting from spray calcination of a 1:1 urea-to-nitrate ratio is also more chemically inert than that generated over the course of comparable batch processing. Spherical calcine particles, composed of an intimate mixture of the oxides present in the waste-additives system, are produced in sizes up to approximately 10  $\mu\text{m}$  in diameter under these operating conditions. Further development and optimization of spray calcination operating parameters will be pursued following the completion of a larger, 20-cm i.d. spray calciner which will permit greater operating versatility and improved process monitoring.

Although facilities do not currently exist for waste component volatility loss studies using radiotracers in these calciners, it is expected that these losses would be even lower than those encountered during batch processing since exposure times of the material to elevated temperatures are greatly reduced in the spray calcination process. Maximum volatility losses encountered in batch processing were 0.27%, 0.23% and 0.0001% for Cs, Ru, and Sr, respectively.

A second major improvement in the process has been the development of liquid phase sintering as a densification technique. The calcine powder, consisting of an intimate homogeneous mixture of oxides, is first cold compacted into the desired shape using water as the binder. Under proper temperature conditions, a liquid phase can be developed by the simultaneous reduction and sintering of the cold compacted material, which greatly enhances its sinterability. Bulk densities comparable to those obtained by conventional sintering under a reducing atmosphere for periods up to 24 hours at temperatures of 1200°C or higher appear achievable by the liquid phase sintering method in less than one-half hour at a temperature of approximately 1100°C. More important, the microporosity typically produced by conventional sintering is greatly reduced by the liquid phase sintering technique. Micrographs in Figures 1.a and 1.b of samples prepared from actual high level waste clearly illustrate the microstructural differences resulting from conventional and liquid phase sintering. In Figure 1.a the rounded ceramic particles, although uniformly dispersed throughout the metal matrix, tend to be located within micropores without intimate metal encapsulation. This condition is undesirable because maximum density has not been achieved and more importantly because the leach and dispersion resistance provided by the metal matrix is of less than optimum quality. On the other hand, the microstructure developed by the presence of a liquid phase during sintering, as shown in Figure 1.b, has very little microporosity and excellent microencapsulation of the larger, angular particles of the various ceramic phases by the metal matrix. Refinements in the liquid phase sintering technique remain to be made; however, this densification technique appears to be very promising since it not only provides significant advantages in processing, but also improves the properties of the resulting cermet waste form. The development of this densification technique along with spray calcination has resulted in the improved basic flowsheet, shown in Figure 2, for cermet processing of sludge and acid wastes.

#### CERMET CHARACTERIZATION

General properties and characteristics which were determined for cermets formed primarily from SRP and NFS wastes using various formulations and processing methods are shown in Tables 1 and 2. Presented are typical ranges for cermet materials which have been found to be representative for a wide variety of compositions and



Fig. 1.a. Microstructure resulting from conventional sintering methods.

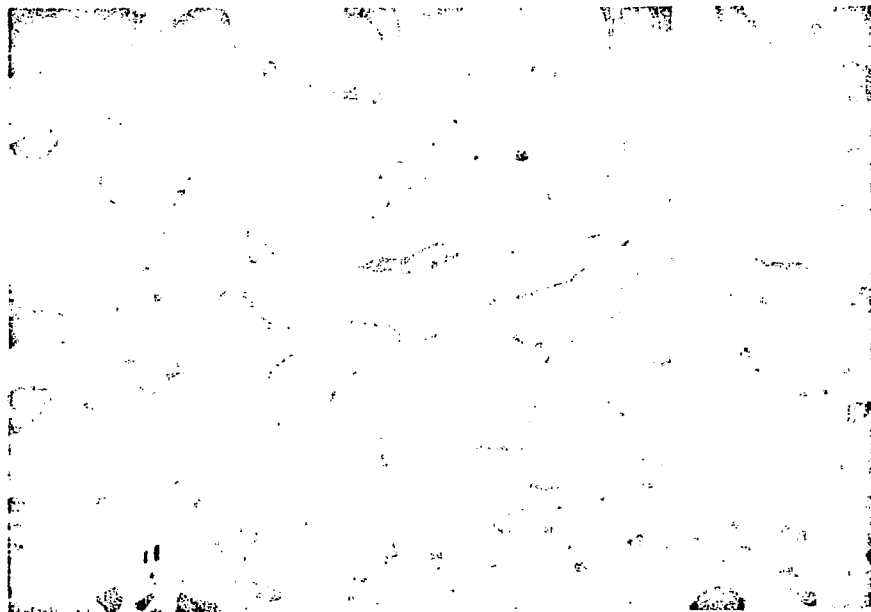


Fig. 1.b. Improved microencapsulation and minimized microporosity resulting from liquid phase sintering.

Fig. 1. Microstructural comparison of cermets densified by conventional and liquid phase sintering.

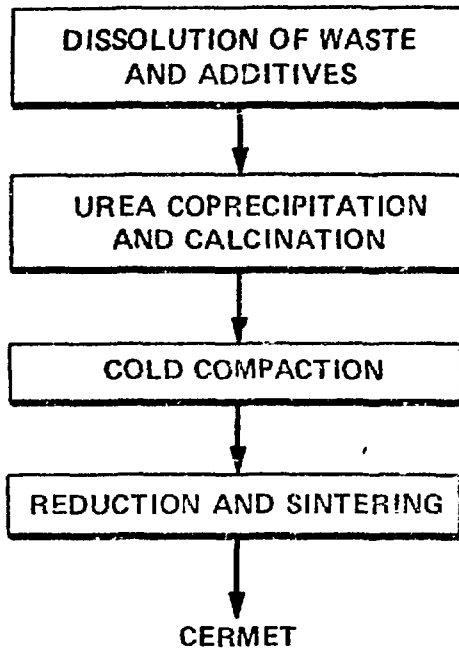


Fig. 2. Improved basic flowsheet for cermet processing of high level wastes.

processes and are expected to remain valid in spite of future changes in the process or the wastes considered. The distinction between cermet characteristics related to processing methods and those related to the cermet formulation is somewhat ambiguous; however, characteristics related most closely to cermet formulations can vary over a wide range while intrinsic cermet properties are less variable and essentially determined by the general ceramic-to-metal ratio.

In Table 1, the waste loading levels are primarily determined by the waste composition, more specifically the metal and sodium contents of the waste. As the metal content increases, waste loading levels can be increased since this metal is used in the formation of the alloy matrix requiring lower additions of metals from other sources. On the other hand, as sodium content increases, greater additions of aluminosilicate formers are required to fix the sodium and thus maintain the integrity of the cermet body. If it is desired to maintain a particular metal-to-ceramic ratio, increased metal additions may be required to compensate for the aluminosilicate additions, thus further reducing the maximum possible waste loading. The waste volume reduction factor is primarily dependent on the waste loading level and to a smaller extent, the final cermet density. As greater amounts of materials additions are made, especially in the lower density ceramic phases, the waste volume reduction factor is reduced.

Table 1. Processing Related Cermet Characteristics

Waste loading	2-75 wt. %
Waste volume reduction	1:1-100:1
Ceramic phase loading	20-50 wt. %
Metal phase loading	50-80 wt. %
Metal phase composition	70 Fe-20 Ni-5 Cu-5 Misc.

Table 2. Typical Cermet Property Ranges

Density	6.0-8.2 g/cc
Thermal conductivity	3-20 W/m · °C
Decay heat loading	0.02-0.2 W/cc
Oxidation	
8 hr - 500°C air	~2 μm thick oxide layer
2 hr - 800°C air	~5-7 μm thick oxide layer
Thermal shock	
3 cycles: 900°C → water quench	No damage detected metallographically
Leach rate	
Soxhlet test (72 hr)	7.1 x 10 <sup>-6</sup> g/cm <sup>2</sup> · d, 0.024% Cs loss

As would be expected, the ceramic and metal phase loadings are dependent on the waste composition and the amount and type of additives used in each particular case. The upper limit for ceramic loading while maintaining continuity of the metal and satisfactory microencapsulation has not yet been determined. A trade-off does exist between the amount of ceramic phase in a cermet and the level of retention of the advantageous properties supplied by the metal matrix, such as thermal conductivity, mechanical strength, etc.

Finally, although little investigation of alternative metal matrices has been performed, it appears that an iron-nickel base alloy will most likely be chosen for cermets because of the amount of these metals in typical wastes. The metal matrix is composed of those metals which can be reduced during processing by hydrogen or carbon-monoxide-containing atmospheres. These include reducible fission or activation products in the waste which result in some degree of variability in the alloy composition as the waste composition (type) changes. In cases examined up to this point, no detrimental effects from this variation have been observed.

In Table 2, property measurements taken from various simulated and/or actual waste cermets are shown. The composite cermet densities achieved are dependent upon the densification technique used and the relative amounts of low density ceramic phases and high density metal present. Thermal conductivity is likewise dependent on the density (more properly the porosity) and the ceramic phase loading. As both porosity and ceramic phase loading of the cermet increase in magnitude, the bulk thermal conductivity is decreased. Decay heat loading of cermet waste samples is strictly determined by the type, age, and loading level of the waste in a particular cermet sample. The 0.02 W/cc (cermet) was obtained from a sample prepared from actual NFS acid Thorex waste at a waste loading level of approximately 28 wt. %. The value of 0.2 W/cc or 31 W/kg of cermet was determined for a sample formed from fresh SRP acid waste at a loading level of only 2.1 wt. %.

Some tests on the oxidation resistance and thermal shock performance of cermets have been performed. These properties are almost exclusively dependent on the alloy matrix. As shown in the table, upon exposure to air at elevated temperatures, thin oxide layers were formed on the surfaces of the cermet samples. Further testing for longer periods and over wider temperature ranges will be required to more definitely ascertain the oxidation behavior of cermets.

Again in limited testing of the thermal shock performance of cermets, no detrimental effects (except oxidation) could be found in samples cycled three times from 900°C to room temperature by water quenching. Here also, further testing will be required to better define the resistance of cermets to thermal shock degradation.

Significantly more leach testing of cermets is required to determine the performance of this waste form under the variety of disposal environments that might be encountered. A variety of leach tests, reported in detail elsewhere<sup>5</sup>, have been performed both at ORNL and PNL. Testing difficulties were encountered that, in most cases, prevented the quantification of leach rates for cermets. Galvanic coupling effects between the cermet samples and



test apparatus, except the Soxhlet test (see Table 2), were chiefly responsible for the problems encountered in these radiotracer leach tests. Indications are, however, that the cermet waste form possesses a leach resistance comparable to or greater than various alternate waste forms currently under evaluation.

Since significant changes have occurred in the process by which cermets are formed and subsequently are expected to change a few of the properties of the final cermet, detailed studies of these properties, especially leach resistance, have been delayed until samples representative of the products from these new processes can be produced repetitively. At this point, quantitative in-depth characterization of cermets will be undertaken.

#### FUTURE DIRECTIONS

The cermet program is of recent origin and more development of the process and characterization of the product must be performed to permit quantitative evaluation of this alternate for nuclear waste disposal. As indicated above, such studies are being actively pursued. A previously unconsidered disposal option, space disposal, is now being considered as an application for cermet waste forms. Engineering and economic feasibility analyses have been initiated.

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