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ABSTRACT

The Albany Research Center of the U.S. Department of Energy used materials characterization and minerals beneficiation methods to separate and beneficially modify spent investment-mold components to identify recycling opportunities and minimize environmentally sensitive wastes. The physical and chemical characteristics of the shell materials were determined and used to guide bench-scale research to separate reusable components by mineral-beneficiation techniques. Successfully concentrated shell materials were evaluated for possible use in new markets.

INTRODUCTION

Investment casting, also called the lost-wax process or precision casting, is used to cast high-value and high-alloy parts that require maximum surface smoothness and rigid dimensional tolerances. The precise molds needed for this process are fabricated with a combination of zircon sand, zirconia, alumina, cristobalite, mullite, quartz, fused silica, and specialty face-coat metals or metal oxides.

Approximately 50,000 metric tons (mt) of zircon sand and 50,000 mt of silica and alumina are landfilled each year by the industry. The cost to dispose of used shell wastes is increasing because the number of landfill sites that accept such wastes is decreasing. The entire foundry industry, including the investment-casting companies, recognizes the need to recycle mold (shell) materials. Successful development of a process to recycle the investment-shell materials that are now disposed in landfills will conserve resources, lessen the importation of expensive and environmentally sensitive materials, and cause fewer hazardous materials to be landfilled.

Investment-mold materials are not currently reused in the casting process. These materials must have specific physical and chemical properties and acceptably low levels of contaminants. To date, attempts to reuse or recycle used spent shell materials have failed because the recycled products have not met these stringent requirements. Therefore, this project's objective was to investigate the potential for using minerals beneficiation processes to produce materials that may be recycled into new markets.

This study is based on an investigation of sample waste ceramic shell assemblies from alloy castings provided by a titanium investment-casting firm. The waste material studied was intended to typify investment-casting shell waste produced throughout the industry. Processes successfully demonstrated in this investigation would have to be customized for the shell components from individual investment-casting operations. However, the basic separation technology and information presented in this study is applicable to many shell-recycling concerns of the investment-casting industry as a whole.

CHARACTERIZATION

The samples were characterized with wet chemistry (fractions), optical and scanning-electron microscopy (SEM) with both energy-dispersive and wavelength-dispersive x-ray analysis (individual grains), and x-ray diffraction. The material contained ribbons of ceramic refractory-coated, woven-wire-cloth up to approximately 60 cm (2 ft) long and 5 to 7 cm (2 in to 3 in) wide, partially- and completely-liberated woven-wire cloth ribbons, 5 cm (2 in) bolts with nuts attached, pieces of ceramic refractory up to about 15 cm (6 in) in diameter and approximately 3 cm (1 in) thick with and without fine, steel wire inclusions, and titanium-alloy splash. The facecoat appeared as a thin, dark-gray layer on exposed surfaces of the ceramic refractory shell pieces.

The facecoat represented about 1 % of the shell materials. Recycling of the facecoat material depends upon how easily the spent facecoat is liberated and separated from the other shell components and its physical and chemical characteristics. Characterization of the facecoat studied (figure 1) indicated that most of the grains whould be liberated from the alumina and zirconia grains by grinding to approximately minus 75 μm (minus 200 mesh). Investment-casting operations may use such facecoat materials as alumina, calcia, columbium (niobium), erbia, molybdenum, tantalum, tungsten, yttria, zircon, and zirconia or a composite of more than one of these materials.

The zirconia and pure-alumina grains of the material studied (figure 1) made up approximately 1 % each of the waste material. The zirconia stucco layer, which was interlocked with both the facecoat and alumina, was approximately 200 to 400 μm thick. (The zirconia stucco is applied to the partially wet facecoat, and the shell is allowed to dry before the alumina slurry is applied). The alumina layer was interlocked with both the facecoat and zirconia on the inside of the shell and the alumina/silica refractory grains of the backup stucco. The alumina layer was approximately 500 μm thick, and the tabular alumina grains range from sub-micron flour to sand nearly 1 mm in diameter. These materials are fairly typical of stuccos/slurries used in many investment-casting shells although the thickness of the materials may vary greatly from operation to operation.

The alumina/silica refractory backup stucco, shown in figure 2, constituted approximately 88 % of the waste material. In forming the shell, the alumina/silica refractory was applied as an aluminum silicate sand and flour slurry. The resultant fired ceramic refractory contains cristobalite silica that crystallizes from the ethyl silicate binder. Some other investment-casting operations use refractories that contain significantly larger percentages of higher-worth alumina, zirconia, or zircon. Alumina/zirconia/silica (AZS), in various ratios, is a high-value refractory used in high-temperature environments such as glass-making operations.

Wire mesh screen and other wires constituted approximately 7 % of the waste material. The iron wire was magnetic, but a small amount of the wire was altered to a non-magnetic, black, iron-oxide product during the process. This iron-oxide residue concentrated in gravity and high-tension conductor concentrates. Large nuts and bolts were also magnetic and represented approximately 2 % of the spent material. These materials are similar to the structural metals commonly used in other investment-casting operations.

Titanium-alloy splash scrap made up only about 1 % of the waste material. Approximately one half of the splash was visually apparent as particles from about 850 μm (20 mesh) to 9 cm (3 ½ in) in length. The titanium alloy particles are generally coated on one side with a thin layer of the alumina/silica refractory where the molten metal splashed and fused. This refractory coating is not easily removed by standard comminution or beneficiation methods, and titanium-recovery processes would have to contend with this small amount of contamination. Chemical analyses indicated that approximately half of the Ti was in the recoverable plus-850-μm material. Other investment-casting operations may produce splash scrap from super-alloys, steel, or precious metals. The value, purity, and environmental nature of the cast metals/alloys will affect the desirability of stockpiling the splash as a possible marketable product.

COMMINUTION AND SCREENING

Standard mineral-processing equipment and techniques were used to shred, crush, grind, and size the waste materials.

Materials for this experimental process were initially broken with a hammer to expose structural wires and then hand-shredded with wire cutters into pieces with a largest dimension approximately 10 cm to facilitate feeding to the jaw and roll crushers used for the experiment. A mechanical shredder is used to perform this step

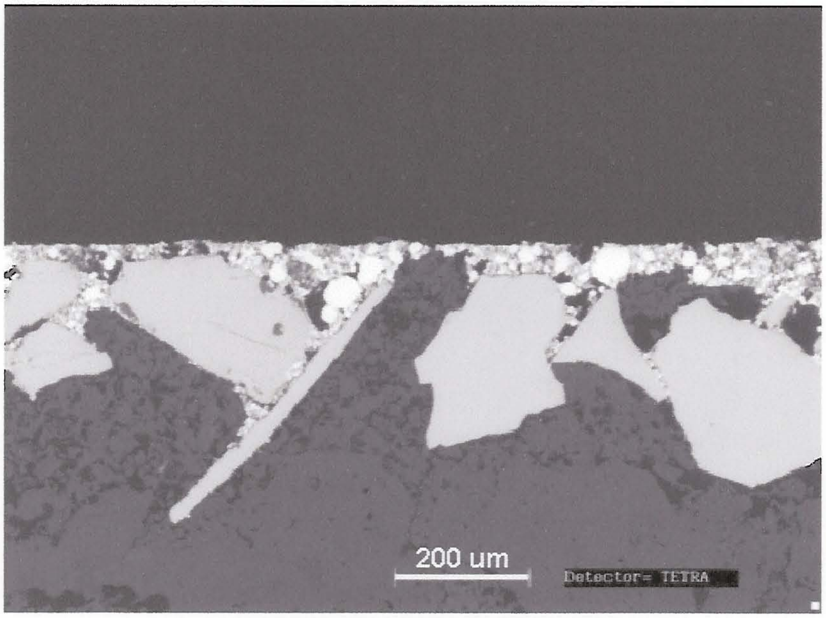

Figure 1. Backscattered-electron SEM image of near-surface, bright facecoat, light-gray zirconia, dark gray alumina, and black voids.

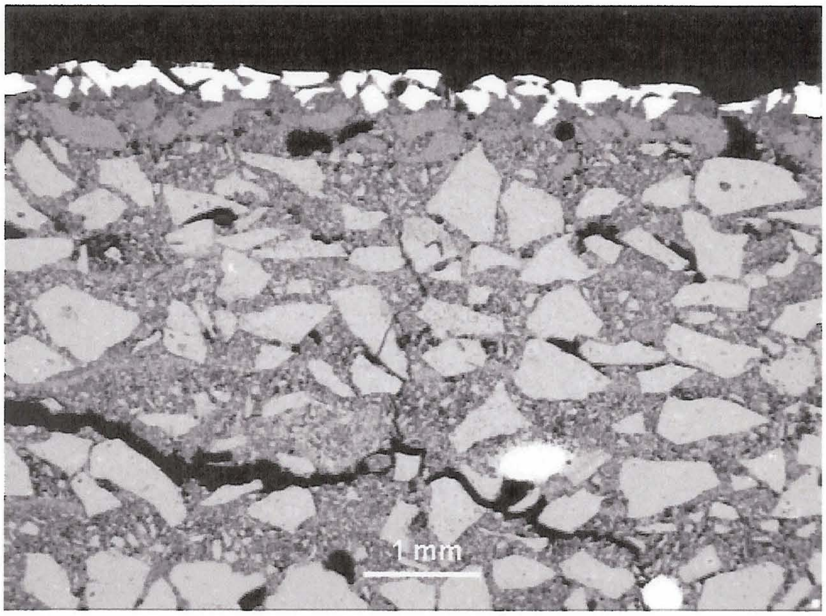

Figure 2. Backscattered-electron SEM image of bright zirconia and facecoat (top), darker gray alumina (below zirconia), and alumina/silica refractory (remaining material). Bright circular areas in the alumina/silica layer are reinforcing wires.

in some metal-recycling operations. The necessity for a shredding step depends upon the size of the crushing equipment chosen for the shell-recycling process. If the material can be fed directly to crushers, then the shredding step could be eliminated from the flowsheet.

Shredded pieces of refractory with unliberated and liberated wires and small metal scrap were fed into the jaw crusher. The nuts and bolts and other large metal scrap were removed by hand prior to this step. The operation produced significant breaking and cracking of the refractories and compression of the wire cloth. The pieces were then fed into a roll crusher, and the resulting products were a relatively clean concentrate of larger wires and titanium-alloy splash, and a concentrate of smaller pieces of easily-crushed refractory material.

After crushing, the material was sized on a 0.6 cm (¼ in) screen. The oversize products included woven-wire cloth, long wires broken from the wire cloth, titanium alloy splash fragments, 5 cm (2 in) steel bolts with attached nuts, and a small amount of large pieces of refractory as shown in figure 3.

The oversize metal fragments were magnetically hand-separated into iron and titanium concentrates. Magnetic separation was also done on the minus 0.6-cm sample. The magnetic fraction consisted of small fragments of fine steel reinforcing wires with a very minor amount of attached refractory. This material is considered unrecoverable waste due to its mixed nature and insignificant volume.

The nonmagnetic, minus 0.6-cm sample was further screened on 300-μm (48 mesh), 150-μm (100 mesh), and 75-μm (200 mesh) screens. The plus 300-μm fraction was ground dry in a 18 cm x 23 cm (7 in x 9 in) rodmill in several stages to minimize fines. After the first grind, most of the brittle refractory materials passed 300 μm, with the exception of a concentrated residue of small pieces of titanium-alloy splash and remnant iron wires that were not removed during the magnetic-separation step. Seven grinding stages reduced all of the refractory material to minus 300 μm. The ground and sized samples were prepared for chemical analyses and microscopy studies. The iron and titanium concentrated in the plus 300-μm fraction, the zirconia and alumina and silica/alumina refractory in the 300 μm x 150 μm fraction, and the facecoat in the minus 75-μm fraction.

BENEFICIATION

Standard mineral beneficiation schemes may employ comminution; screening; gravity concentration; differential settling; flotation; electrostatic, high-tension, and magnetic separation; scrubbing; grease tabling; thermoadhesion; flocculation; thickening; filtering; agglomeration; and other physical processing operations. Hydrometallurgical processes may include leaching, precipitation/crystallization, biomineral processing, and solvent extraction. Thermal treatments may include drying, calcination, combustion, and roasting processes. Pyrometallurgy covers

Figure 3. Plain-light image of a representative split of the oversize fractions of shell components after hand-sorting, jaw- and roll-crushing, initial screening and magnetic separation. At top right are typical pieces of titanium-alloy splash. At bottom center are 5-cm (2-inch) bolt and nut sets and at bottom right is the relatively small amount of oversize pieces of refractory that remain after crushing.

smelting processes.

The applicable operations chosen to concentrate the marketable components of the investment-casting shell studied were comminution, screening, and magnetic, gravity, and high-tension separations. The facecoat concentrate was treated by roasting, leaching, and crystallization steps to recover the facecoat material in a desired form. Details of the specific thermal and hydrometallurgical treatment of the facecoat material studied is not covered in this paper and it is doubtful that recovery of most facecoat materials would, generally, be a practical option. A conceptual flow diagram of the comminution, beneficiation, and hydrometallurgical steps developed is shown in figure 4.

The three sized fractions (300 μm x 150 μm, 150 μm x 75 μm, and minus 75 μm) were each separated on a laboratory shaking table equipped with a slime deck. Concentrate (heavy facecoat , zirconia, and alumina), middlings, coarse tailings (those that settled and banded on the table), and very-fine tailings (those that washed off the deck before they had a chance to settle) were collected; the coarse and very-fine tailings in the minus 75-μm fraction were combined for analysis. Besides

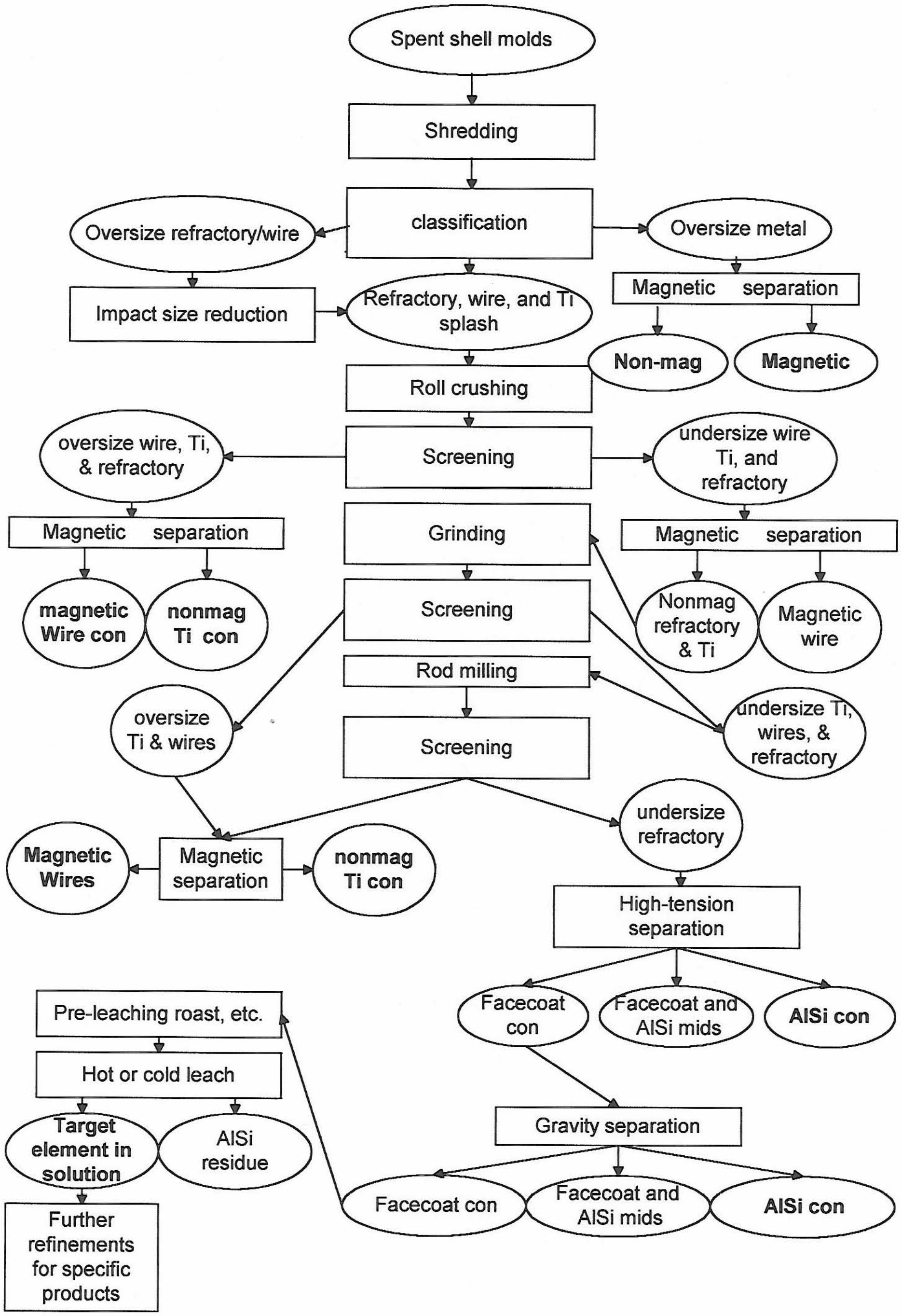

Figure 4. Conceptual beneficiation and hydrometallurgical flow diagram.

tabling, gravity separations of particles may be done on a variety of apparatuses that control settling through manipulation of gas or liquid media through gravitational or centrifugal force.

A pilot-scale electrostatic and high-tension drum separator was used for high-tension separation tests. Separation of dry granular materials may be accomplished based on differences in particle-surface conductivity. At settings of 20 kV potential and 100 rpm rotor speed, a 150-μm x 75-μm fraction of refractory mixed with facecoat was separated into conductor (facecoat concentrate, 24 % of the weight), middlings (58 %), and non-conductor (refractory concentrate, 18 %) fractions in one pass. The first-pass middlings and non-conductor fractions were removed for chemical analysis. The first-pass conductor concentrate was put through a second pass at the same settings. The resulting second-pass conductor (26 %), middlings (54 %), and non-conductor (19 %) fractions were chemically analyzed. This concentration method may be used to separate a conductive material from a non-conductive material.

A simple gravity-separation test was also performed on the conductor concentrate from high-tension separation. The facecoat material tested was readily separated from the other conducting materials by vanning. Vanning is a highly effective laboratory gravity-separation technique that does not fully predict the results of a commercial-grade gravity separator. However, considering the promising results, a gravity separation step following high-tension concentration would likely be very effective.

RECLAIMED PRODUCT SPECIFICATIONS AND POTENTIAL MARKETS

The literature suggests that reusing waste shell components in new shells is feasible[1], and attempts have been made by some of the major investment-casting companies to do so. However, due to contamination problems, there is no major reuse presently done in the industry. The emphasis of this study, therefore, was to identify potential new markets for spent shell components.

All recycling options in this study involved breaking the spent shell materials down into major, recoverable components (not necessarily single compounds or elements) and surveying markets for these components separately. The components in the material studied that were found to be physically recoverable by standard mineral beneficiation methods were concentrates of facecoat, iron (woven wire, nuts, and bolts), titanium-alloy scrap, and alumina/silica (with cristobalite) ceramic refractory. The facecoat and the alumina/silica refractory were successfully recovered by grinding, sizing, high-tension separation, and gravity concentration in concentrations high enough to be potentially recycled into other products. Other components may or may not be potentially marketable materials due to their low volume. A detailed economic analysis of a complete recycling program was beyond the scope of this study. Proceeds from the sale of the recycled products alone probably would not make the recycling circuit economical. However, recycling may be less expensive than steadily increasing landfill costs, especially if local markets for the refractories exist.

Facecoat materials may be of high value and, in some instances, may be recovered for resale either by physical beneficiation methods and/or by hydrometallurgical extraction methods.

Refined, ground, and fused alumina sells for about $575/metric ton. Although there are markets for each of these commodities when available in bulk quantities, the low volume and difficult cleaning of these materials did not warrant a market analysis or an individual separation strategy for this particular shell composition. In the conceptual flowsheet (figure 4), these materials remain part of the alumina/silica refractory ceramic grain concentrate.

Although the alumina content of the alumina/silica refractory studied was relatively modest (~40 %), the high volume produced could make the product attractive as a single-source, stable-composition feedstock. Major refractory recycling companies would be interested in purchasing such a feedstock if it came from a local supplier. Due to the bulk nature of this material, a local market would be needed to offset the relatively high cost of transport. Companies that buy materials for recycling generally require the materials to be shipped at the expense of the seller. This may involve transportation fees on the order of $0.10/mile/ton, a significant limiting cost for recycling a high-volume, low-value alumina/silica refractory but would be less of a problem for low-bulk, high-value concentrates.

Other possible markets for alumina/silica refractory materials include concrete, asphalt, mineral wool, grog, pottery, porcelain, flowable fill materials, topsoil additives, landscape paving stones, glass industry tanks, kiln and furnace fireclay linings, bricks, and cements.

Some investment-casting operations use refractories that contain significantly larger percentages of higher-valued alumina, zirconia, or zircon that may be economically shipped longer distances. An example would be materials suitable for producing AZS.

If the alumina/silica refractory is cleaned of other shell components, landfill operators may consider it a desirable cover material and the casting company may be able to negotiate lower landfill fees for a cleaned refractory material.

Recoverable wire screen and structural wires constituted approximately 7 % of the waste material. Woven-wire steel scrap is bought for $15-$25/ton by small recycling operators who compact the material into bales for resale. If the number and weight of the large nuts and bolts found in the sample is representative, then an additional 2 % of the waste was recoverable metal. In quantity, this material may also be saleable to local recyclers. The magnetic susceptibility of reinforcing metals is an important characteristic to ascertain in a recycling study and an operation considering recycling would be advised to only use magnetic structural metals.

Some titanium-alloy splash scrap was recovered from the steel wires by crushing, screening, and magnetic concentration to the non-magnetic fraction. Most of this material has a very-thin crust of alumina/silica. If stockpiled to collect marketable quantities, this type of scrap may be recyclable. There was approximately ½ % titanium alloy in the waste material, of which about half was in recoverable form.

DISCUSSION

The results of this investigation suggest that mineral beneficiation (and hydrometallurgical processes) can separate spent investment shell components into potentially marketable concentrates. Concentrates of facecoat, iron, titanium, and alumina/silica ceramic refractory were successfully produced by the experimental processes on the spent shell studied. The preliminary conceptual process flowsheet (figure 4) was developed based on the findings of the investigation.

A recycling scheme must be considered in light of a number of economic, regulatory, and environmental concerns, in addition to technological feasibility[2]. The following should be considered before a recycling operation is attempted:

- the target markets and products for each reclaimed material
- the present and projected market prices for each reclaimed material
- viable and dependable production levels
- efficiency of the reclamation system and individual processes
- equipment size, type, and level of sophistication
- capital investment, training, operating, and maintenance costs
- potential savings or costs in transportation and/or disposal
- the integration of recycling with existing or future plant processes and layout
- other businesses that may be interested in performing part or all of the recycling processes
- beneficial or detrimental impact of recycling on the physical and chemical makeup of the shell components (both products and waste)
- environmental or safety considerations of equipment or reagents used
- present and future environmental, safety, regulatory, tax, or political benefits or costs
- present and future disposal costs
- partial reclamation as a viable option

A preliminary study, as was done for this project, provides general answers to some of these questions. More detailed guidance for cost analysis of mineral-processing operations may be found in the literature[3,4] and there are some commercial concerns that have the expertise to assist in developing individualized flowsheets. A number of experiments have been done on recycling of sand-casting foundry waste that have produced materials suitable for recycling at a net benefit to the foundry[5-10]. As is true for any significant change in operations, a company must complete an analysis based on estimates of all current and projected costs and gains. If such an analysis of spent investment-shell waste indicates a net positive outcome to the operation, then recycling of waste components may be a viable option. At that point, bench-scale laboratory work can optimize beneficiation and/or hydrometallurgical processes and provide samples for marketability studies, and pilot-plant tests can determine if scaled-up processes work efficiently.

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