Rare-earth Information Center INSIGHT

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Rare Earths Shape Up Diamond

Diamond films are one of the current hot technological materials, because of its optical transparency, hardness, high thermal conductivity, low thermal expansion, chemical inertness and semiconducting properties. Diamond films are prepared by a chemical vapor deposition (CVD) process. However, after deposition the films generally must be shaped into the desired form and thickness for most applications. Most processes used today, e.g. polishing by reaction with oxygen atoms or ions, or high temperature and/or high pressure reaction with solid transition metals, have serious drawbacks, such as grain boundary pitting or difficult processing conditions. In late April, S. Jin and co-workers from the AT&T Bell Laboratories, Murray Hill, New Jersey, reported the use of molten lanthanum or cerium for thinning and shaping CVD diamond films [**Nature, 362,** 822 (April 29, 1993)]. Free standing diamond films (~275µm thick) were placed between two lanthanum (or cerium) sheets (~250µm thick) and heated at ~920°C for 4 hours in an argon atmosphere. The reacted and unreacted metal was dissolved using aqua regia (3 HCl:1 HNO_3). The thinned diamond film was examined by a variety of techniques and the resultant material was found to be superior to the as-deposited CVD film.

Rutherford back-scattering analysis, which can detect the presence of a monolayer of lanthanum or cerium, indicated that no lanthanide metal was present on the diamond surface. The surface roughness was reduced by a factor of ten by removal of the rough growth facets on the top of the diamond film. The molten lanthanum (or cerium) also removed the fine grains at the bottom of the film. This surface modification led to a considerable improvement (by more than 40%) in the thermal conductivity through the thickness of the film, and a slight improvement in the in-plane thermal conductivity. The authors found that etching in molten lanthanum left a slightly smoother surface than etching in molten cerium.

For many diamond-based semiconductor devices, heat treatment in the molten lanthanide metal at ~900°C is still too high to carry out the thinning, polishing and patterning processes. These processes must be done at as low a temperature as possible to minimize the temperature- or diffusion-induced damage to doped regions, metallizing and interconnection portions of the device. They found that by using a lanthanide-transition metal alloy near the eutectic composition on the lanthanum (or cerium) side of the phase diagram, the thinning temperature could be reduced by nearly a factor of two. An alloy of the composition 89 wt.% Ce - 11 wt.% Ni was reported to work as well at ~500°C as pure cerium.

Jin *et al.* thought that their technique could be adopted to process many diamond films simultaneously. They also believe that the molten lanthanide etching process could be used to fabricate diamond wires, needles, lenses, and other shapes from CVD diamond films. For

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complicated shapes, they suggested that a solid state reaction could be used with the preshaped metal acting as a negative mold for the diamond body, however, the etching times would be considerably longer. For example, preshaped molds with concave cavities could be used to shape diamond films into an array of microlenses for optical device applications.

Although this application will not lead to large tonnage uses of lanthanum or cerium, it should be a good steady market for the better grade, commercial, light lanthanide metals.

Market Projections

Several marketing projections by various organizations have appeared in a variety of trade journals, and all indicate that steady growth can be expected in a number of areas, which will have a favorable impact on the rare earth market. The advanced materials markets are predicted to exhibit rapid growth between now and the turn of the century, and rare earth permanent magnets are expected to be one of the advanced materials leading this growth. Another study estimates that the U.S. permanent magnet market will grow annually by about 11% between 1992 and 1997. But within this category the rare earth permanent magnet materials will at least double this growth rate. The last marketing study was concerned with the worldwide growth of zirconia, which was predicted to increase at a rate of 5% above the overall world economy growth rate. Since yttrium oxide is added to many zirconia products, this bodes well for the yttria market, especially since the thermal barrier coatings, and electronic and structural ceramics products are expected to lead this growth, and these are materials to which yttria is added.

Advances in Extraction and Processing

Two papers, one by H. Y. Sohn and W. D. Cho and the other by F. M. Doyle and S. Duyvesteyn, reviewed the developments that occurred during 1991 and 1992 on the extraction and processing of materials and industrial minerals [**J. Metals 45**, [5], 40 and 46, respectively, (April 1993)]. The paper by Sohn and Cho covered developments and basic principles, and the review by Doyle and Duyvesteyn dealt with hydrometallurgy and aqueous processing. Both reviews included numerous citations to rare earth materials. Included are the papers published on solvent extraction and ion exchange, physical properties and metallothermic reduction in the former, and solvent extraction in the latter.

RE-Ru Cryocooler Alloys

Mitsubishi Materials Corporation has reported that their Ho-Er-Ru alloys are being used as cryocooler alloys in magnetic resonance imaging (MRI) units. The cryocooler alloys are used to cool the liquid helium to ~2K to reduce the loss of helium gas by evaporation. This means that the lost liquid helium needs to be replaced only once or twice a year instead of monthly. The liquid helium is required to keep the superconducting magnets, which are necessary in the MRI units, in the superconducting state. The most likely used alloys in the MRI cryocooler units are $(Ho_{1.5}Eu_{1.5})Ru$ and/or $(Ho_{2.5}Er_{2.5})Ru_2$ or some slight modifications thereof. The main competition to these lanthanide-ruthenium alloys are the Er_3Ni-base alloys used by Toshiba Corporation in their cryocooler units {see **RIC Insight, 4** [11] (November 1, 1991)}.

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