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NOTE

Laser Evaporation and Condensation of Er in Hydrogen and Inert Atmosphere*

Er, condensing under Ar at room temperature after exposure to laser pulses, forms with particle sizes of approximately 1.25×10^{-8} to 5.0×10^{-8} m. When this process is carried out under hydrogen atmosphere the dihydride is formed.

Introduction

With this note we explore the behavior of a rare earth element (Er) when condensing from plasma temperatures reached on exposure to laser beams. It was of interest to see whether amorphous or crystalline materials would condense under inert atmosphere. In addition, we were interested to study possible hydride formation when processes are carried out under hydrogen atmosphere. Er was chosen as a representative rare earth as in this case the dihydride and the cubic oxide are relatively easily distinguishable in their diffraction patterns.

Experimental

Targets for laser bombardment were prepared to present a relatively flat, smooth face to the laser pulse of at least 3 × 3 mm. All targets were at least 1 mm thick. Targets were taped to aluminum stubs and held vertically inside of a cylindrical Pyrex vacuum chamber 8 cm in diameter by 19 cm long. The chamber, charged with a sample, was pumped to a vacuum of better than 1 μm of mercury before introducing the fill gas; Ar or H_2 (Matheson Research grade) with less than 1 ppm O_2. In all experiments, the chamber was flushed once with the appropriate gas and reevacuated before the final gas charge was introduced. Experiments were carried out at 1-atm gas pressure. The laser pulse from a solid state laser (Nd^{3+} in glass or ruby) operating in the normal (non-*Q* switched) mode was incident horizontally, approximately perpendicular to the target face. The main pulse consisted of a series of random pulses, each of 1–2 μsec in duration, with a pulse envelope lasting about 5 μsec. The energy of each pulse was ~5 J. The laser was focused onto the target by a lens. The resulting craters were 1 mm^2 corresponding to a calculated flux density of about 10^6 W m^{-2}. The material is evaporated from the target, at a temperature near the normal boiling point, accompanied by a shock wave (*1*), and cools by expansion and collisions with the cold ambient gas molecules. Condensation takes place near the target without interaction with the cell walls. The condensate in some cases is seen as a fine smoke with a settling time of $\frac{1}{2}$ hr. The chamber is entirely filled with floating particles immediately after the laser pulse, as evidenced by strong scattering of a low-powered continuous laser beam. The condensed material settled onto carbon planchets as well as transmission electron microscope grids placed near the bottom of the chamber. More experimental details of this technique will be given elsewhere (*2*).

Results and Discussion

Er exposed to laser pulses under 1 atm Ar condenses in chains of globular particles with sizes from about 125 to 100 Å as shown by

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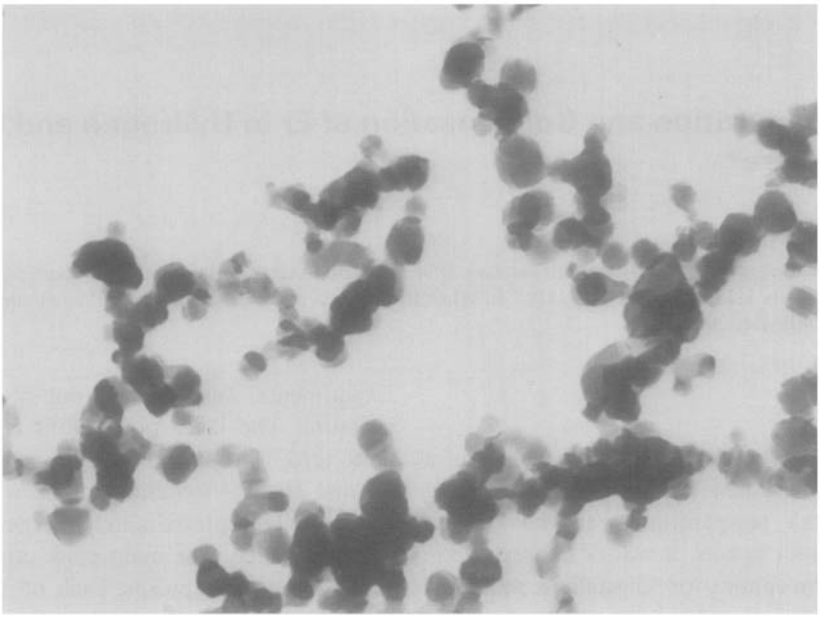

FIG. 1. Er vaporized in Ar atmosphere; 1 cm in the figure corresponds to 800 A.

electron microscopy (Fig. 1). The resulting particles were collected on a gold grid and analyzed by electron diffraction at an energy of 80 keV, yielding a wavelength $\lambda = 0.04032$ Å. Accordingly, only reflections of Er are observed.

The same experiments carried out under 1 atm of H_2 yield materials of similar microstructure. Because electron diffraction patterns usually exhibit different intensities than X-ray diffraction patterns, an intensity calculation for electron diffraction patterns was performed using computer techniques. Table I shows the calculated values for ErH_2 and Er_2O_3, with lattice constants of $a_0 = 5.12$ and 10.55 Å, respectively. ErH_3 (hexagonal) yields a significantly different diffraction pattern and can be easily distinguished (*3*). Table II shows the electron diffraction pattern of the laser treated Er in hydrogen. The *d* values are obtained by

TABLE I

CALCULATED INTENSITIES FOR ErH_2 AND Er_2O_3 FOR ELECTRONS OF WAVELENGTH 0.04032 Å[a]

ErH_2			Er_2O_3		
hkl	*d*	I/I_1	*hkl*	*d*	I/I_1
111	2.96	1000	211	4.29	129
200	2.56	384	222	3.03	1000
220	1.81	301	400	2.63	222
311	1.54	274	411	2.47	38
222	1.48	65	332	2.24	43
400	1.28	36	431	2.06	56
331	1.18	88	440	1.86	378
420	1.15	69	622	1.58	208

[a] *d* values are in angstrom units; intensities are relative.

TABLE II

ELECTRON DIFFRACTION DATA FOR LASER-TREATED Er IN HYDROGEN

d (Å)	I/I_1
2.96	v.st.
2.53	m
1.83	st
1.55	m
1.23	v.w.
1.16	w
1.04	w

calibration against a gold standard. Intensities are reported on a relative scale. The results show conclusively that the dihydride was formed with a lattice constant of approximately $a_0 = 5.09$ Å, in good agreement with the literature value $a_0 = 5.12$ Å.

It is not surprising to find the Er condensate in crystalline form because the cooling rate of the condensate particles (10^6 K°sec^{-1} around 1800°K, calculated by assuming the particles as black bodies) is an order of magnitude lower than for the formation of glassy materials (*4*). Further studies should show whether cooling the sample chamber will have an effect on the nature of the crystallographic state of the materials possibly resulting in amorphous rare earths. The fact that the cubic hydride was formed, and not the hexagonal trihydride, is perhaps somewhat surprising. A conventional method of preparation (*3*) of rare earth trihydride involves synthesis at pressures of 1 atm hydrogen (or greater) and a temperature of 570°K (or lower). The dihydride is stable above ~570°K and 1 atm H_2 and prepared by desorption of the trihydride at high temperatures (<1070°K) and low pressures (<10 mm Hg). At the melting point of Er, 1795°K, the equilibrium pressure of the dihydride may be calculated, using a value $\Delta H = -54$ kcal/mole H_2 (*3*), to be 0.96 atm. Therefore the dihydride would form at this temperature at 1 atm hydrogen. However, as the material cools below 570°K under 1 atm H_2, one could have expected that the trihydride would form in a second reaction step. It is obviously the rapid quenching rate of the fine particles of ErH_2, connected with an activation energy barrier, which precludes trihydride formation. Metastable condensates of glassy olivine, Y–Al_2O_3 and some metals obtained by this method have been attributed to the fast cooling rate of the submicron particles (*2*).

Generally speaking the somewhat unconventional mode of hydride formation of the present study should also open a new route to synthesis of more complex hydrides. In particular it should be of interest to explore the possibility of creating complex hydrides of the type $A_xB_yH_z$ by coevaporation of elements A and B under hydrogen, elements which do not form stable compounds with each other. In addition, it should then be of interest to explore the possibility of subsequent removal of H_2-yielding metastable compounds A_xB_y.

It should finally be mentioned that compound formation under conditions similar to the ones described above can also take place under other reactive gases. For example evaporation of Fe in O_2 or H_2S atmosphere produces condensates of iron oxides or iron sulfides respectively (*2*).

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References

1. S. I. Anisimov, A. M. Bonch-Bruevich, M. A. El'yashevich, Ya. A. Imas, N. A. Pavlenko, and G. S. Romanov, *Sov. Phys. Tech. Phys.* **11**, 945 (1967).
2. J. R. Stephens and B. R. Kothari, unpublished.
3. W. Mueller, J. P. Blackledge, and G. G. Libowitz, "Metal Hydrides," Academic Press, New York (1968).
4. P. Duwez, *Ann. Rev. Mater. Sci.* **6**, 83 (1977).

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