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$3Gd_2O_3 \cdot 5Fe_2O_3$ GLASS OBTAINED BY RAPID QUENCHING APPARATUS USING LASER BEAM

Seishi YAJIMA, Kiyohito OKAMURA, and Toetsu SHISHIDO
The Oarai Branch, The Research Institute for Iron, Steel and Other Metals,
Tohoku University, Oarai, Ibaraki-ken, 311-13

The oxide glass of $3Gd_2O_3 \cdot 5Fe_2O_3$ (GIG) was prepared using the piston and anvil technique incorporated into a laser melting furnace. The quenching apparatus provides higher quenching rates than an impact quenching apparatus already made. Crystallization and magnetization of the GIG glass have been examined by means of DTA method and magnetic balance.

Glasses essentially consisting of lanthanoid oxides have previously been produced by an impact quenching apparatus developed at our laboratory[1]. An attempt has been made to construct an apparatus which provides higher quenching rates. A new method of quenching is designed, using the conventional piston hammer and anvil technique incorporated into a laser melting furnace. The apparatus employed is shown schematically in Fig.1. The sample to be quenched as a scale of about ten

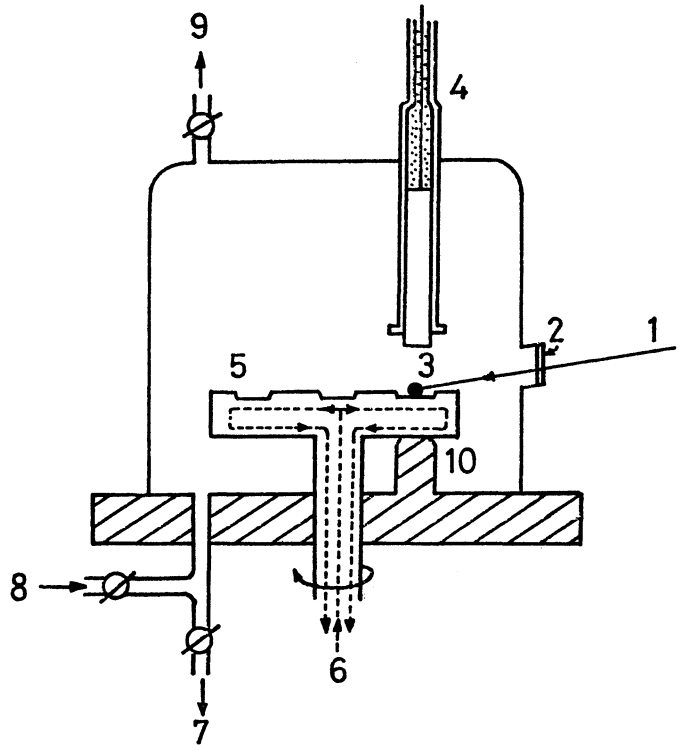

Fig. 1
Quenching apparatus incorporated into a laser beam system. Ten pellets can be set on the copper hearth which can be rotated about the vertical axis.

1. Laser beam
2. Germanium lens
3. Sample to be quenched
4. Pneumatic hammer
5. Copper hearth (Anvil)
6. Cooling water
7. To vacuum pump
8. Inert gas inlet
9. Inert gas outlet
10. Anvil support

milligrams is placed on a lapped flat depression which serves also as a cold anvil. A polished copper hearth attached to the head of a stainless steel hammer is positioned so as to be precisely in contact with the anvil. The piston is worked by compressed air (maximum 100 kg/cm^2). Neglecting friction, the terminal velocity is given by the formula of $V=(2\cdot P\cdot X_0/m)^{1/2}$ where P is the pressure, X_0 is the distance between the piston and the anvil, and m is the mass of the piston. The maximum terminal velocity attained is calculated to be about 100m/sec. The laser beam equipment made by Japan Electron Optics Laboratory (JEOL) was employed. This equipment has a maximum 250-watt output and is of a continuous wave (CW) CO_2 laser (10.6μm) with a gas mixture of CO_2:N_2:He=1:2:7 in molar ratio. The laser beam transmitted by germanium lens is focused on the sample position indicated in Fig.1.

The quenching apparatus was applied to produce the glass of Gd_2O_3-Fe_2O_3 system. The batch was prepared from oxide (purity 99.9%) with the molar ratio of Gd_2O_3:Fe_2O_3=3:5, corresponding to the chemical composition of garnet. The mixed powder was sintered in the form of a pellet by a method described previously[1]. The pellet placed in the sample setting position shown in Fig.1 was melted using the laser beam transmitted by germanium lens. The melt was rapidly quenched by applying the piston and anvil technique. The oxide foil obtained was about 5mm in diameter and about 1μ in thickness. The substance was identified as glass by an X-ray diffraction technique using CuKα radiation.

The $3Gd_2O_3\cdot 5Fe_2O_3$ glass was obtained not by an impact quenching apparatus, but for the first time by the present apparatus.

Crystallization of the glass was examined by DTA. Sample handling in a DTA measurement was the same as described previously[2]. The powdered sample was heated or cooled at a rate of 10°C/min from room temperature to 1300°C under a flow of argon gas. The result is shown in Fig.2(a). An exothermic peak due to crystallization

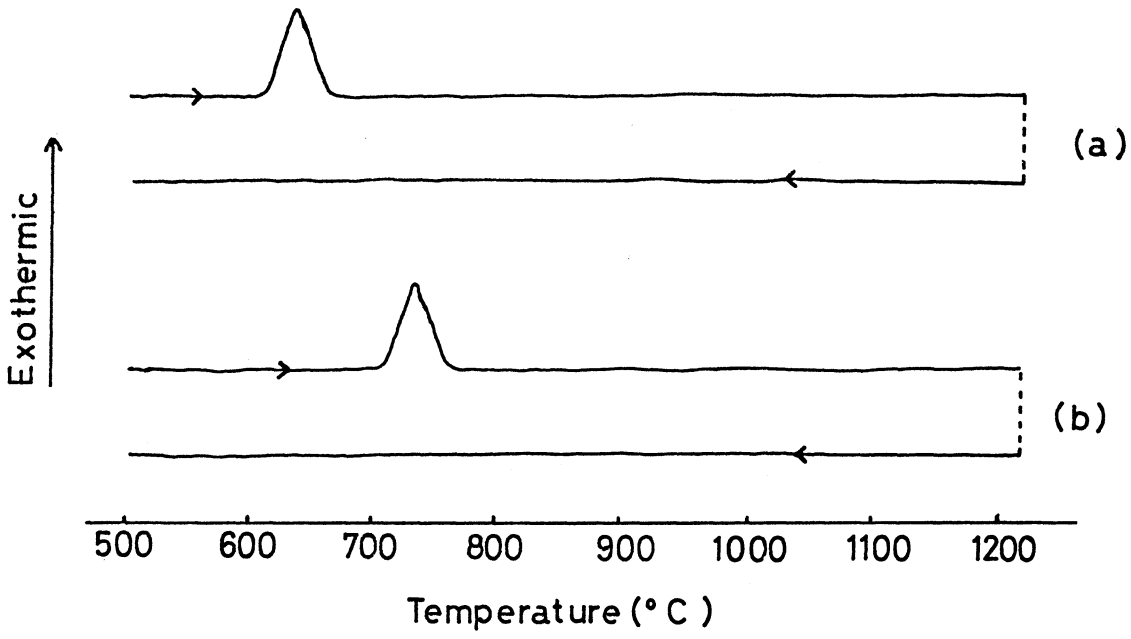

Fig. 2 DTA curve of the glass of the Gd-Fe-O system during heating and cooling.
(a) DTA measurement in a flow of argon gas.
(b) DTA measurement in air.

was observed at 642°C. The curve for the sample during cooling showed the absence of exothermic reaction. The sample, $3Gd_2O_3 \cdot 5Fe_2O_3$ glass, was heated for one hour at several temperatures above the exothermic peak and cooled down to room temperature. The X-ray diffraction pattern of the heat-treated sample showed the presence of the phase with the $GdFeO_3$ type structure. The exothermic peak was attributed to crystallization of this phase. The sample was further heat-treated for many hours at 1300°C in the atmosphere of argon gas. The X-ray pattern of the sample showed that the structure was of the $GdFeO_3$ type. After the above heat-treated sample was heated for several hours at 1300°C in air, the X-ray diffraction pattern indicates the presence of the compound $3Gd_2O_3 \cdot 5Fe_2O_3$ (garnet phase). On the other hand, the DTA curve measured in air is shown in Fig.2(b). The exothermic peak at 732°C due to the crystallization of the garnet phase was observed. The garnet phase appeared only in process of heating in air. In contrast with this, under a flow of argon gas, the phase with the $GdFeO_3$ type structure appeared. The crystallization temperature and the crystalline product associated with the exothermic peak differ depending upon the condition of measurement. This is interpreted such that the amount of oxygen in the glass obtained by the apparatus shown in Fig.1 is likely to be deficient comparing with the stoichiometric composition of garnet.

The variation in the magnetization (σ gauss$\cdot$cm^3/g) with the transition from the glass to the crystalline phase has been measured by a magnetic balance over the range from liquid nitrogen temperature to 1073°K. The sample was heated at the rate of 10°C/min in helium gas atmosphere. The magnetization curve plotted against temperature is shown in Fig.3. Curve (A) shows magnetization of the glass including the process of the transition from glass to crystalline phase; curve (B) shows magnetization for the sample with the $GdFeO_3$ type structure after the glass crystallized. Further, the magnetic susceptibility (χ cm^3/g) of the $3Gd_2O_3 \cdot 5Fe_2O_3$ glass was measured in the range from liquid nitrogen temperature to about 800°K. The relation between $1/\chi$ and temperature is shown in Fig.4. From the result, the glass follows the Curie-Weiss law over the above temperature range. The critical point near 830°K corresponds to the Curie point in

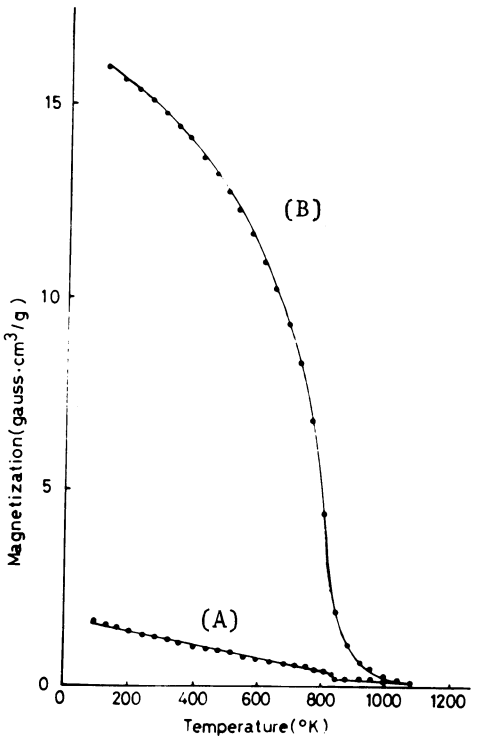

Fig.3 Temperature dependence of magnetization of $3Gd_2O_3 \cdot 5Fe_2O_3$ glass

A: glass
B: after crystallization

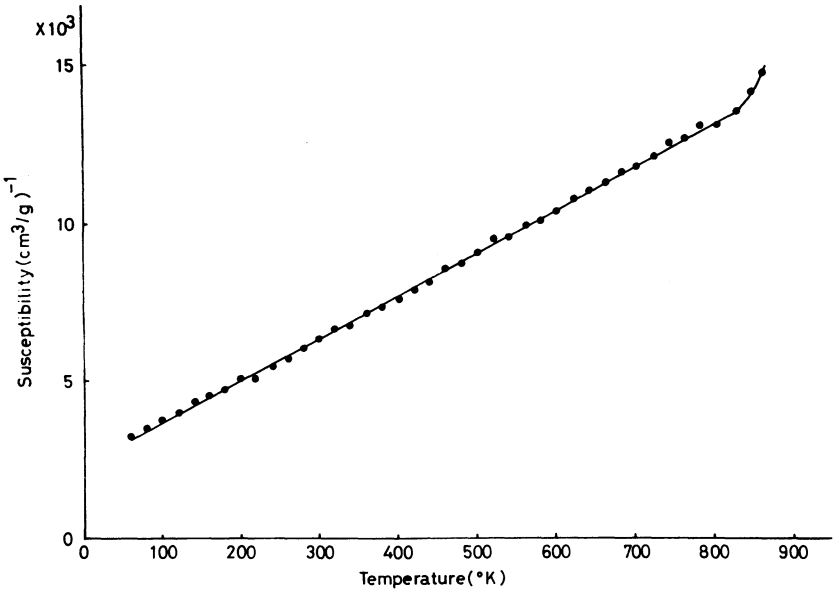

Fig.4 The variation of the reciprocal susceptibility with temperature for $3Gd_2O_3 \cdot 5Fe_2O_3$ glass

crystalline state. The $3Gd_2O_3 \cdot 5Fe_2O_3$ glass is thus considered to crystallize microstructurally at a temperature near 830°K.

The relationship between magnetic property and atomic arrangement of $3Gd_2O_3 \cdot 5Fe_2O_3$ glass will be reported elsewhere in detail.

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