LASER- SYNTHESIS OF METAL SULPHIDES IN SULPHUROUS LIQUIDS

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Laser processing of materials in chemically reactive surrounding mediums has been marked with growing interest, using a pulsed laser in conjunction with a proper liquid makes it possible to induce rapid and often non - equilibrium reactions at the solid-liquid interface. It is believed that temperature, pressure and phase transformations in the liquid are the key parameters necessary to understand the interface reactions.

Introduction

Recent research into laser processing of materials in a chemically reactive surrounding medium has been marked with growing in lets /1-3/. In most of the studies on laser- induced reactions the main emphasis has been laid on the interaction at the vapour-solid interfaces and hardly any attempts have been made to explore the possibilities of synthesizing new materials by pulsed-laser-induced reactions at liquid-solid interfaces. Using a pulsed laser in conjunction with a proper liquid makes it possible to induce rapid and often non-equilibrium reactions at the solid-liquid interface and consequently to form compound layers with metastable phases and desirable properties.

Experimental results

The basis processes in the liquid at the interface affected by pulsed laser irradiation are still largely unknown, but it is believed that temperature, pressure and phase transformations in the liquid are the key parameters necessary to understand the interface reactions /4/. The purpose of the present investigation is to determine the effects of pulsed laser processing in different power density regimes and, particular, to study the formation of several phases in circumstances where violent shock waves are generated causing great transient pressures.

We have chosen the In- sulphur containing liquid interface as a model system for the pulsed processing experiments both because the In -S phase diagram has been described in sufficient detail and because a considerable number of In - sulphide phases have already been discovered /2,5/. Sulphur and sodium sculpted were simultaneously dissolved in a water-glycerin mixture (1:2) to form a sodium polysulphide solution used as a chemically reactive liquid. The radons and concentrations of the components were calculated to insure a high transparency of the solution for a laser wavelength of λ= 1.06 μm. The solution contained 80 g per litter of sulphur element in the form of sodium polysulphide. Its transmittance value was equal to 56% for a wavelength of λ = 1.06 μm in a layer of l cm in depth.

An Nd-glass laser used in experiments (λ=1.06 μm). The beam was collimated to sensure a homogeneous energy density and focused to a spot size which corresponded to the incident power density required by the experiments. While processing the samples in a liquid ambient, the depth of the liquid covering the sample surface was maintained at 1,0-1,5 mm. The experimental arrangement is shown in figure 1.

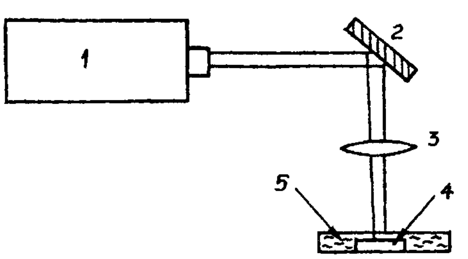

Fig. 1. Schematic illustration of the experimental set-up for liquid mediated pulsed laser processing: I, Nd-glass laser, 2, mirror; 3, lens; 4, substrate; 5, reactant liquid.

The growth of the chemical compound layer in the sample causes the initial conditions of the pulsed event to change within nanoseconds of high intensity irradiation /8/. Samples were therefore irradiated by a single pulse to obtain comparable results. The incident intensities of single pulsed varied from 2.5 10^8 to 4-10^9 W/cm^2 for a pulse width of 50 ns in the Q-switched mode and from 1.3 10^5 to 3.1 10^5 W/cm^2 for a pulse width of 0.23 ms the free-running mode to determine the effect of such variatiation on the composition of the surface compounds. The temperature in the laser-induced area was calculated from the non-stationary equation of heat conduction with a source of heat and the corresponding initial and marginal values. The computation techniques have been described in greater detail in [3].

To detect the formation of the compounds, the laser irradiated nickel samples U were analyzed using X-ray diffraction in glancing Iangle geometry's. The glancing angle X-ray patterns were obtained on a DRON-3 (USSR) machine by keeping the glancing angle of incidence fixed at 1°. For the results of the X- ray analysis of the laser processed nickel samples see figures 2.

The outlines of the roentgenograms apparently depend on the processing mode.

The results of the roentgenogram calculation are shown in the fig. 2 a, b. As is obvious, the processing mode of the samples has an essential influence on the structure of roentgenograms obtained. Only a-In_2S_3 reflections were detected after a 230 ms irradiation of the sample by a single pulse with an incident intensity in the range from

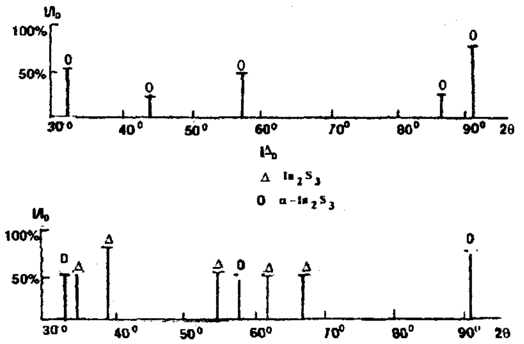

Fig. 2 Glancing angle XRD pattern of nickel disc laser-treated in a sulphur containing liquid at a power density value of 1.710^4 W/cm^2 and a pulse duration of 0.23 ms, Glancing angle XRD pattern of a In disc laser-treated in a sulphur containing liquid at a power density value of 3 10^9 W/cm^2 and a pulse duration of 50 ns.

1.10^4 to 1.10^5 W cm^{-2}. The irradiation of the sample with a 50 ns single pulse of a power density of 2.8 10^9 W cm^{-2} and more leads to the formation of an In_2S_3 modification interpreted as a high pressure phase [6-9].

$$P=\sqrt{\frac{\gamma-1}{\gamma}}\sqrt{q\frac{\rho_1 D_1\cdot\rho_2 D_2}{\rho_1 D_1+\rho_2 D_2}}$$

where γ- is the varoup adiabatic index, ρ- density , D - velocity of sound.

We connect the formation of this phase with increasing of the chemical reaction rate by high pressures. Such a conclusion is suggested by the date on low temperature synthesis of some metal sulfides affected by high pressure with applied shear action.

Conclusions

1. Formation of high pressure In_2S_3 phase occurred when indium samples were processed in a sulfur-containing liquid medium with laser pulses of 3 10^9 W/cm^2 power density. This phase forms due to generation of a shock wave in the reactive liquid medium.

2. Processing of indium samples with a laser pulse of 1.7 10^4 W cm^2 power density leads to the formation of a-In_2S_3 phase in the diapason of sulfur concentrations from 80 to 150 g l^{-1} .

References

1. *Bauerle D.* Chemical processing with lasers (Springer series in material sciences; V.I) // Springer-Verl.,Berlin-Hheidelberg.- 1986.- P. 112.
2. *Ogale S.B.* Pulsed laser-induced and ion-beam-induced surface synthesis and modification of oxides, nitrides and carbides // Thin Solid Film. - 1988. - V.3.- P.215-227.
3. *Hansen M., Anderko K.* Constitution of binary alloys // McGraw-Hill Book Co .- New-York. - 1958.
4. US Patent 4814259.
5. *Podoltsev A.S, Zheltov G.I.* Effects of infrared rariation on the cornea // Sov. J. Qquantum Electron (USA).- 1989. - №19. - P.1376-1378.
6. *Preiffer I.* Attack of sulphur on nickel and nickel alloys/ / Z. Metallkunde. - 1958. - №49. - P. 267-275.
7. *Zhiryakov B.M, Obesnyuk V.F.* Effect of transparent coatings on the generation of laser-induced shock waves in metals // Phys. Chem. Mater. Treat.(GB). - 1984. - №.8. - P.487- 489.
8. *Ivanov E.E., Simakov Yu.M., Yanushkevich V.A.* Laser-induced formation of pores in aluminium samples // Fiz. Khim. Obrab. Mater. - 1985. - № 5. - P. 35-27.
9. *Zubova E.V., Korotaeva L.A.* Chemical transformations in the solid phase at pressures of 50.000 kg/sq. cm with applied shear action // Zhur. Fiz. Khim. - 1958. - V.2. - P. 1576-1579.