JOURNAL OF MATERIALS SCIENCE 7 (1972) 627–630

Metastable phase formation in a laser-irradiated silver-germanium alloy

M. LARIDJANI*, P. RAMACHANDRARAO†, R. W. CAHN
Applied Science Laboratories, University of Sussex, Brighton, UK

The structure of laser-irradiated regions in a silver-21 at.% germanium alloy was studied by X-ray and metallographic techniques. A hexagonal close-packed metastable phase was detected in the irradiated zone. Its formation is explained in terms of the ultrarapid cooling of a thin molten zone in contact with a thermally highly conductive solid substrate.

1. Introduction

During the last decade very substantial progress has been made in the design and operation of high-energy lasers. The spectacular energy densities available with the present day lasers have prompted several investigations aimed at establishing the potentialities of these beams for cutting, machining, melting and welding of metallic materials [1-4]. While the importance of the rapid heating of localized regions in refractory metals has often been highlighted, relatively little attention has been paid to the stages of the process immediately following the heat pulse.

In general, only a small volume of the irradiated metal is affected by the laser and the high energy density achieved results in the formation of a crater. The physical processes involved in the formation of a crater are strongly dependent on the pulse length, peak power and hence on the mode of operation of the laser. A qualitative picture of the events has been proposed by Ready [5]. The temperature of the metal at the focal point of the laser beam rises rapidly and attains a magnitude sufficient to cause evaporation. In the case of a Q-switched laser, this initial vaporization sets up a recoil pressure in the regions below and raises the temperature of these regions well above their melting point. The vaporized metal is emitted as a plume. The molten material is quenched in at the base of the crater. In the case of a normal pulse laser of a longer duration, the vaporized material has enough time to leave the area of interaction and while doing so carries away some of the molten metal at the surface of the crater. In both cases, however, at the end of the laser pulse a small quantity of molten metal is in close contact with a semi-infinite mass of conducting material and can cool rapidly.

A theoretical analysis of the problem [5] indicates that rates of heating of the order of 10^{10} deg C/sec and post-irradiation cooling rates of comparable magnitude are possible. The latter effect is of particular importance in view of the recent results obtained by splat-quenching or rapid cooling of liquid alloys [6]. In a typical splat-quenching experiment, a very thin layer of liquid alloy is brought into close contact with a highly conducting substrate and results in the solidification of the alloy film at cooling rates of the order of 10^6 to 10^8°C/sec. Solidification of molten alloys at such cooling rates is now known to give rise to a number of metastable solid solutions and intermediate phases and even to lead to the formation of metallic glasses [7-9]. Most of these phases are metastable above room temperature and decompose to the equilibrium phases. The similarity between the solidification in splat-quenching experiments and at the base of the crater is striking. In both cases, cooling of a thin layer of liquid metal is brought about by conduction of heat through an efficient substrate at a lower temperature. This similarity has been pointed out and utilized by Jones [10] in his experiments on aluminium-iron alloys. He observed that the same metastable (supersaturated) solid solution and metastable new phase that were formed by splat-cooling could also be produced by laser-irradiation. This possibility of metastable phase formation by

---

*On leave from the Faculty of Engineering, University of Tehran, Tehran, Iran.
†On leave from the Department of Metallurgy, Institute of Technology, Banaras Hindu University, Varanasi, India.

laser-irradiation stresses the importance of an understanding of the structure and properties of laser-irradiated regions in alloys.

The present investigation was aimed at studying the structure of a laser-irradiated silver-germanium alloy by X-ray and metallographic techniques. Under equilibrium conditions and at room temperature, alloys of the silver-germanium system are made up of two terminal phases formed by a eutectic reaction at 651°C [11]. A metastable hexagonal close-packed phase was produced by Duwez *et al* [12] in alloys containing 10 to 26 at. % germanium. In a later investigation the metastable phase was shown to occur homogeneously in alloys with about 22 at. % germanium [13]. Laser-irradiation of a silver germanium alloy of appropriate composition may therefore be expected to yield the hcp phase.

2. Experimental

A silver-germanium alloy containing 21 at. % germanium was prepared by induction-melting the constituent elements (99.99 + %) in a "silver boat" apparatus. The alloy buttons were repeatedly remelted to ensure uniformity in composition. This was further verified by checking the microstructure over several sections of the alloy button.

The alloy was cut into blocks of size 6 × 4 × 2 mm and one of the faces was ground and polished by the usual metallographic techniques. The polished surface was then irradiated by a normal pulse from a ruby laser for periods ranging from one to two milliseconds at power in the range 10 to 20 joule.* The focal length of the lens used for focusing the beam was 10 cm.

Sections of the resultant craters were prepared by spark-cutting the irradiated alloy blocks and polishing by mechanical means. Samples for X-ray diffraction analysis were obtained by carefully chipping off the rim of the crater. Diffraction patterns of the samples were recorded, using an 114.6 mm diameter Debye-Scherrer camera with CuKα radiation.

3. Results and discussion

A metallographic examination of transverse sections revealed the nature and extent of the irradiation damage. In all the sections the superheated and quenched-in layer was clearly demarcated and its thickness varied from 200 μm at the top of the crater to 20 μm at the base

Figure 1 Section of a laser-irradiated silver-21 at. % germanium alloy. Unetched (× 60).

---

*A normal pulse laser was preferred to a Q-switched laser in view of the greater volume of melt produced by the former.

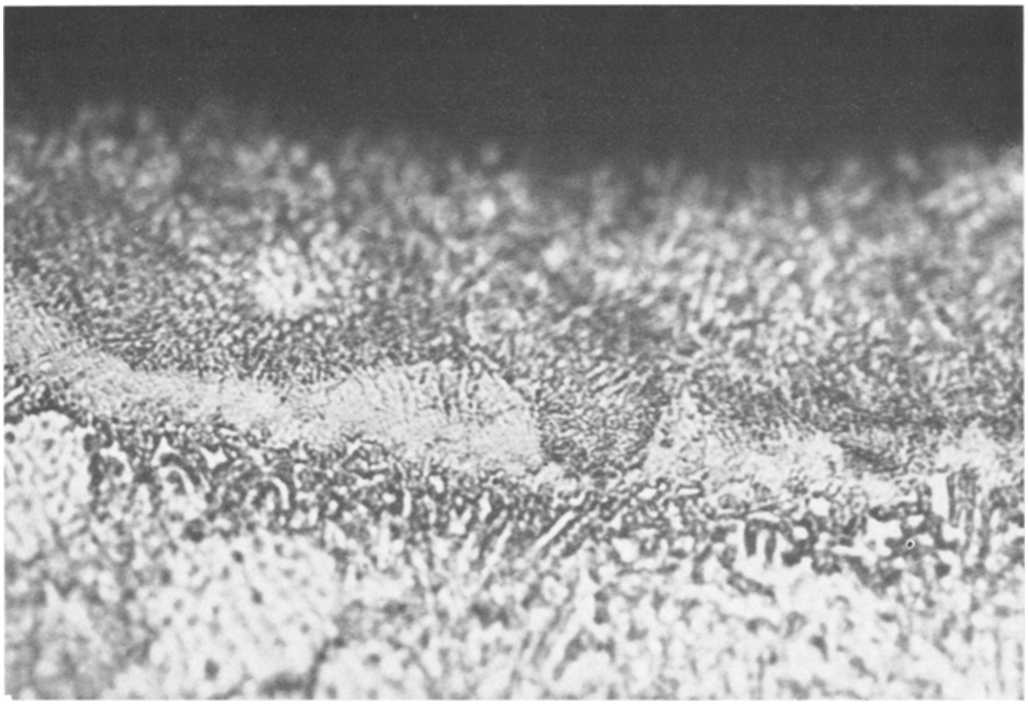

Figure 2 Micrograph of the laser-irradiated zone in a silver-21 at. % germanium alloy. Etched with 55% ammonia and 45% hydrogen peroxide (× 600).

(Fig. 1). This layer was metallographically clearly distinguished on etching with a solution of 45% ammonia and 55% hydrogen peroxide (Fig. 2).

X-ray diffraction patterns obtained from the material in the irradiated zone contained a number of extra reflections in addition to those from the equilibrium phases. These extra reflections could *all* be indexed in terms of a hcp structure with the lattice parameters $a = 2.890$ Å and $c = 4.712$ Å.

The X-ray diffraction analysis clearly suggests the formation of a hcp phase in the irradiated zone. The observed lattice parameters of the hcp phase are in close agreement with the values given by Klement [14] for the metastable phase obtained by splat-quenching. The presence of silver and germanium reflections in the diffraction pattern suggests that the structure of the irradiated area is heterogeneous. Such an effect is to be anticipated owing to the variation in cooling rate resulting from variable thickness of the quenched-in layer. The heterogeneity of the structure was further confirmed by metallographic observations.

The silver-germanium alloy chosen for the present study is a hypo-eutectic alloy and accordingly the equilibrium microstructure exhibits dendrites of the silver-rich primary phase distributed randomly in a eutectic matrix (Fig. 1). An examination of Fig. 2 shows that the laser-affected area has a significantly different microstructure and is easily distinguishable from the unaffected regions. Within the affected area one can distinguish a light-etching phase with a massive morphology and areas of very fine eutectic structure. In the top half of the affected area the eutectic structure predominates while in the lower half the light-etching phase is most noticeable. X-ray analysis indicates the presence of only three phases, viz. a silver-rich solid solution, germanium and the metastable phase. The first two of these can be accounted for by the eutectic and fragments of primary dendrites. It is therefore to be concluded that the light-etching phase is the metastable phase. Such a conclusion is in accordance with the greater concentration of this phase at the interface between the affected and unaffected parts of the alloy, since the maximum cooling rate would be in the regions close to the unaffected part which acts as the substrate and conducts away heat of solidification. For the same reason, the areas far away from the interface and towards the surface of the specimen solidify predominantly as a eutectic. The resultant eutectic is finer than the equilibrium eutectic (as seen in the unaffected parts of the alloy) indicating that the cooling rate is still appreciably greater than under normal conditions of solidification.

An interesting observation of the present investigation is that there is no apparent influence of the presence of equilibrium phases on the nucleation of the metastable phase. The primary dendrites and the eutectic in the unmelted "substrate" at the interface do not act as effective nuclei for the growth of equilibrium phases into the laser-induced melt, even though there was occasional evidence for the nucleation of the equilibrium eutectic on the primary particles in the "substrate". This observation has important implications with reference to the growth velocities of metastable and equilibrium phases under conditions of drastic cooling.

4. Conclusions

The possibility of producing metastable phases by laser-irradiation has been established with reference to the behaviour of a silver-germanium alloy containing 21 at. % germanium. The observed metastable phase is identical to the phase obtained by splat-quenching the alloy. Metallography of the irradiated alloy suggests that the metastable phase forms predominantly at the interface between the affected and unaffected regions of the alloy and that the presence of the equilibrium phases has no undue influence on the nucleation of the stable or metastable phases.

Acknowledgements

Our thanks are due to Mr P. B. Withers for irradiating the samples and for helpful discussions. One of us (P.R.) is grateful to the Association of Commonwealth Universities, London, for the award of an Academic Staff Fellowship.

References

1. C. J. BAHUN and R. D. ENGQUIST, *Metals Eng. Quart.* **24** (1964) 27.
2. F. J. LAVOIE, *Mach. Design* **41** (1969) 136.
3. K. G. NICHOLS, *Proc. Inst. Elect. Eng.* **116** (1969) 2093.
4. J. F. READY, Paper presented at the Pennsylvania State University Seminar on New Industrial Technologies, July 1969.
5. *Idem, J. Appl. Phys.* **36** (1965) 462.
6. P. DUWEZ and R. H. WILLENS, *Trans. Met. Soc. AIME* **227** (1963) 362.
7. R. W. CAHN, *Fizika* (Belgrade) **2** (suppt. 2), paper 25, (Proceedings of the Brela Conference on Metastable Alloy Phases).
8. T. R. ANANTHARAMAN and C. SURYANARAYANA, *J. Mater. Sci.* **6** (1971) 1111.
9. P. FURRER and H. WARLIMONT, *Z. Metallk.* **62** (1971) 12. *Ibid*, p. 100.
10. H. JONES, *Mat. Sci. and Eng.* **5** (1969) 1.
11. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 23.
12. P. DUWEZ, R. H. WILLENS, and W. KLEMENT, *J. Appl. Phys.* **31** (1960) 1137.
13. P. RAMACHANDRARAO, P. RAMA RAO, and T. R. ANANTHARAMAN, *Z. Metallk.* **61** (1970) 471.
14. W. KLEMENT, *J. Inst. Metals*, **90** (1961) 27.

Received 11 November 1971 and accepted 7 January 1972.