MICROSCOPIC INVESTIGATIONS ON THE TRANSFORMATION OF METASTABLE INTO STABLE PHASES IN Al-Ge ALLOYS

Uwe Köster, Institut für Werkstoffe
Ruhr-Universität Bochum
Germany

A large number of metastable phases have been produced by rapid cooling from the liquid state. However few investigations have been made on the transition of these metastable phases into stable ones. Besides an analysis of the metastable phases in Al-Ge alloys obtained by rapidly quenching from the melt the purpose of our investigations is the transformation of the metastable phases into stable ones. Under equilibrium conditions Al and Ge form a simple eutectic system (fig.1). After slowly cooling an Al-Ge melt an eutectic structure is to be found besides Al or Ge primary crystals. After more rapidly cooling, i.e. by quenching of small amounts of melt (ca. 1g) in water or by splat cooling, this eutectic cannot be formed. According to the concentration of the melt and to the quenching rate one or two metastable phases can be found.

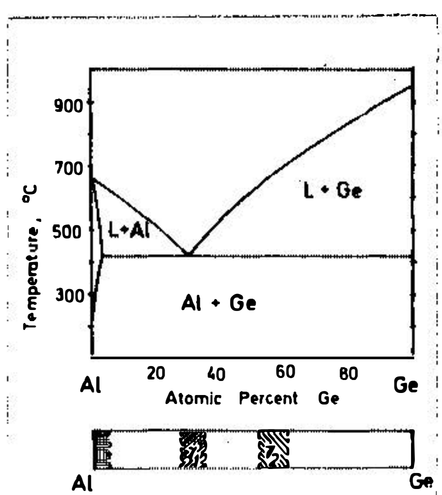

FIG. 1

Equilibrium phase diagram of Al-Ge with the composition range of the metastable phases

Splat cooling has been carried out with Al-20 wt.-% Ge and Al-50 wt.-% Ge after levitation melting. The melts were superheated to at least 400 °C above the liquidus temperature. Suitable parts of the foils were examined by transmission electron microscopy without any further thinning procedures. The microstructure of the Al-20% Ge alloy consists of a cell structure of Al primary crystals and a metastable phase lying between them. Thicker arrays of the splat had to be electropolished for electron microscopic investigations. These parts show the same structure except for a smaller diameter of the cells. The microstructure of the Al-50%Ge alloy consists mainly of large grains of the same metastable phase (fig. 2). In both alloys there are only a few dislocations in the Al crystals and none could be detected in the metastable phase. By electron diffraction we can determine the unit cell of this phase (γ_1):

γ_1: rhombohedral $a = 7{,}65$ Å
$\alpha = 96{,}5$ °

Fig. 3 shows the schematic electron diffraction pattern of a (001)-plane. In an additional produced X-ray diffraction pattern all lines can be identified accepting this unit cell.

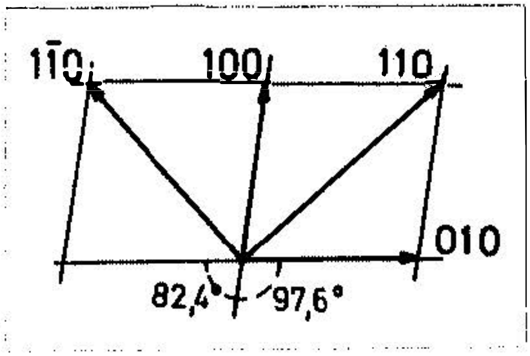

FIG. 3

Schematic electron diffraction pattern of a (001)-plane of γ_1

The combination of electron and X-ray diffraction seems extremely suitable for determining the unit cells of unknown metastable phases in splat cooled foils: It is possible to distinguish different states of the foil by transmission electron microscopy and especially selected area diffraction enables one to make diffraction of small areas with uniform structure. If one can select single crystallites, additional information about the angles between lattice planes can be obtained. This information makes it easier to determine the unknown structures. While this method is suitable for observing only small areas of the sample, by X-ray diffraction larger areas can be investigated resulting in a better knowledge of the overall conditions.

A second metastable phase (γ_2) is seldom found in a splat cooled foil, but for the most part in water quenched alloys. By electron diffraction we found a hexagonal unit cell:

$$\gamma_2: \quad \text{hexagonal} \quad a = 13{,}45\ \text{Å}, \quad c = 7{,}25\ \text{Å}$$

This phase forms a lamellar eutectic with Al as can be seen by light and electron microscopy (fig.4). In Ge-rich alloys we also found γ_2 primary crystals.

The metastable states formed by rapid quenching from the melt tend to approach the equilibrium state, i.e. to decompose into Al and Ge. At room temperature both metastable phases are stable for longer periods of time. No significant decrease of volume fraction of the metastable phases could be detected after half a year. A complete transition from the metastable phases of the splat into the stable ones was achieved by an annealing treatment of 1 h at 200 ^{o}C. The disappearance of the X-ray lines of the metastable phases demonstrates this statement. In water quenched specimens only the beginning of this process could be observed after this annealing treatment. It seems that the large difference of the diffusion coefficients determines the kinetic of the transition (Al in Ge: $D_{200^oC} \ll 10^{-20}$ cm^2/sec, Ge in Al: $D_{200^oC} \approx 10^{-12}$ cm^2/sec).

Therefore the transformation of the metastable into the stable phases does not take place by a direct transition. The rate controlling mechanism by which equilibrium is approached is once the formation of Ge crystals in Al and on the other hand the diffusion of Ge from the dissolving metastable phases to the newly formed Ge crystals. Fig. 5 shows this mechanism schematically. It is the same for both metastable phases.

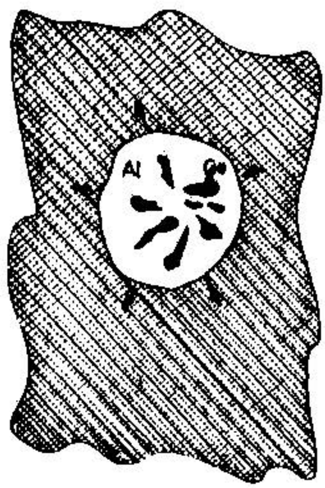

FIG. 5

Schematic sketch of the transformation of metastable phases into Ge and Al

By hot stage electron microscopy we can investigate this transformation of γ_1 into Al and Ge of a splat cooled foil (fig.6). Fig.7 shows the transition of γ_2 into Al and Ge of a water quenched sample, which was prepared for microscopy after annealing.

The apparent, different thermal stability of the metastable phases in the splat or in the water quenched sample can be explained by size and distribution of the metastable phases in Al. The splat shows a finer distribution of the metastable phases than the water quenched specimen. Therefore the metastable phases of splat cooled samples are much faster dissolved than those of water quenched ones.

By co-evaporation of Al and Ge amorphous films are obtained which crystallize after annealing. By isothermal or isochronal annealing equilibrium is approached by direct crystallization of the Al-rich or Ge-rich solid solutions as can be seen by hot stage electron microscopy. However pulse heating the specimen by the electron beam just below the melting point yields crystallization of the metastable phases described above. We suggest therefore these metastable phases to be high temperature phases.

FIG.2: Electronmicrograph of the metastable phase γ_1

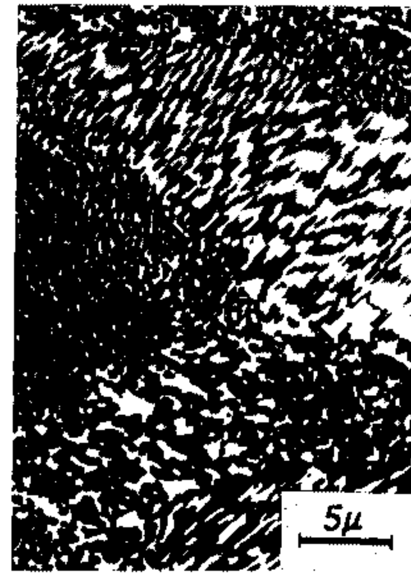

FIG.4: Metastable eutectic γ_2-Al. Deeply etched in KOH. γ_2 - white

FIG.6: Electronmicrograph of the transformation γ_1 into Al + Ge

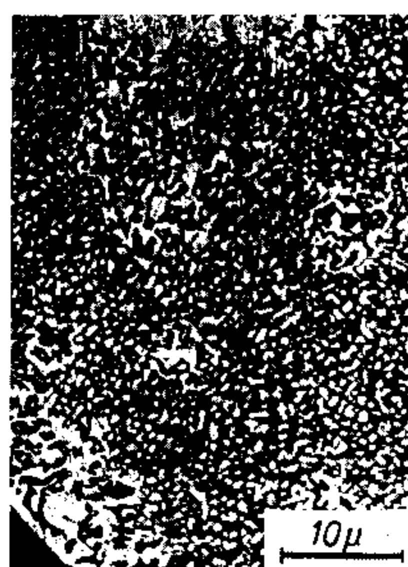

FIG.7: Transformation of γ_2 into Al + Ge white - Al, grey - γ_2, dark - Ge

DISCUSSION :

K. Lõhberg : 1. What are the specific volumes or mean atomic volumes of the metastable phases ?
2. Is the process of decomposition of the metastable phases similar to that of the decomposition of Fe_3C ?

U. Köster : 1. We have not yet estimated the specific volumes of the two phases.
2. Typically the process of decomposition of these metastable phases is such that there is in the most part no connection of the growing g-crystals with the reaction front.

R.W. Cahn : Prof. Anantharaman (Banaroas Hindu University) and co-workers recently completed a thorough study of the whole Al/Ge system, with 3 different cooling rates. The paper is in process of publication in Journal of Materials Science. They include details of the atomic volumes of the γ_1 and γ_2 phases as a function of composition. Incidentally they also include a kind of "meta-equilibrium diagram": here, composition is plotted horizontally and log (cooling rate) vertically the various single and two-phase fields are drawn relative to these coordinates, extrapolating to very low and very high cooling rates. It seems to me that the presentation of such diagrams would be most useful as a matter of routine in the study of splat-cooled alloys.

R. Maddin : I as well as my colleagues at Pennsylvania, and indeed in the USA, are puzzled by the reports of the lack of defects, e.g.collapsed vacancy aggregates, dislocations, voids, in freshly quenched specimens not subjected to deformation as with the piston/anvil technique. Concentration of vacancies of 10^{-4} are considered to exist just below the melting point in pure metals and one would believe that metals quenched from the liquid state should show evidence of defects. Yet a few, if any, are in electron micrographs published to date. Why is this so?

U. Köster : In Al-Ge we found after quenching from the α -region (ca.550°C) no dislocation loops formed by precipitation of excess vacancies. The binding energy between vacancy and germanium atoms is considerably larger than the corresponding value for most other Al-alloys and larger than the binding energy vacancy-vacancy. Ge-atoms and vacancies stay in random distribution during the cooling or after annealing at temperatures at which in other alloys precipitation of vacancies occurs.

A. Guinier: The dislocation may be invisible because of the imperfections distributed in the matrix which decrease the contrast between the dislocation lines and the surrounding matrix.

N.J. Grant: High concentrations of vacancies have been found in Cu-Zr alloys splat cooled as fine films. Concentrations as high as 25 at% are regarded as probably the highest value reported to date. The Zr content was about 20%. The alloys are stable at 20°C for long periods of time. How this high concentration of vacancies can be maintained is an interesting question.

J. Dixmier: In what range of concentration did you have an amorphous phase by coevaporation and what is the exact shape of the diffraction pattern of this phase?

U. Köster : If we cooled the substrate to the temperature of liquid nitrogen, we could obtain amorphous films in the composition range from Al-30 at% to the pure Ge. The electron diffraction patterns are in the shape of those from amorphous pure Ge.

G.W. Lorimer: If a large number of vacancies are present in splat cooled alloys as very small clusters which are invisible in the electron microscope, as suggested by prof. Guinier, then it should be possible to grow these defects to a size which is visible in the electron microscope by a critical annealing treatment.