High resolution electron microscopic studies of HoAl_3 , $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ and $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$ in thin film form

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Abstract. Rare earth trialuminides (RAl_3) exhibit an interesting series of structures changing from 2H to 3C in the bulk form. Many of the rare earth trialuminides have been recently found to exhibit curious structural characteristics such as the occurrence of the modulated phases. A detailed investigation of the formation synthesis and characterization of some binary and ternary alloys of the rare earth-aluminium system has been carried out. High resolution microscopic technique has been employed to study the modulated phases for some alloys *e.g.* HoAl_3 , $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ and $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$. With the help of lattice imaging technique, several new modulated phases have been investigated. A possible mechanism for the formation of these phases has been suggested. The details of the results obtained by lattice imaging technique are discussed.

Keywords. High resolution electron microscopy; structural characterisation; modulated phases; Al–rare earth system; lattice imaging.

1. Introduction

About half a century ago a classic example of superlattice formation in CuAu was reported by Johansson and Linde (1936). Since then, several other modulated phases have been discovered in a variety of materials ranging from metallic to dielectrics through semi-metallics. The occurrence of modulated phases have been curious to crystallographers and also to materials scientists since these phases exhibit interesting properties and many times correspond to potentially important materials from the applied aspect. These alloys have drawn considerable attention in view of the fact that they absorb hydrogen exothermically, nonstoichiometrically and reversibly which has already been recognized as a future fuel. Rare earth metals and alloys are further known to exhibit interesting magnetic properties and are very promising materials for memory devices in computers.

The present communication deals with the occurrence and stabilisation of modulated phases in binary and ternary rare earth metal trialuminides such as HoAl_3 , $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ and $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$.

The modulated phases discovered in the present investigation originate in a novel way—they result as a consequence of amorphous to crystalline transformation. Often intergrowth of several modulated phases occurs. The profuse occurrence of random and ordered stacking faults suggests that the polytype-like modulated phases are formed through creating and ordering of stacking faults. Evidences and arguments have been put forward to show that the driving force for the modulated phases is the

lowering of electronic energies which offsets the increase in energy due to creation of stacking faults. It has been shown that even slight variations in electron concentration (size of the Fermi surface) may lead to the genesis of several modulated phases.

2. Experimental techniques and results

The binary and ternary rare earth metal trialuminides were made by homogenising the stoichiometric mixture of rare earth metal/metals and aluminium in vacuum ($\approx 10^{-6}$ torr) at a temperature ranging between 823 and 873 K for about 20 hr. The initial agglomerate of the alloys so formed were tested by x-ray diffraction through Guinier focussing camera. These agglomerates correspond to the reported bulk structure of the material, *e.g.* 15R for HoAl_3 . Thin films from these agglomerates were formed by vacuum ($\approx 10^{-7}$ torr) thermal vapour deposition. The as-grown thin films were amorphous as evidenced by the featureless electron micrographs and the diffraction patterns exhibiting haloes, obtained from them. These as-grown thin films underwent amorphous to crystalline transformation when they were heated with focussed electron beam at a temperature of about 500°K for about 30 sec. The resulting crystalline phase consisted of isolated crystals. These single crystal regions often contained heavy density of planar faults. An extensive analysis of electron diffraction patterns taken from the transformed phase revealed that the most abundant phase in thin film form for HoAl_3 and $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$, were their reported structural phases *viz.* 15R with $a = 6.052$ Å; $c = 35.93$ Å and 9R with $a = 6.185$ Å, $c = 21.14$ Å. However, in $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ the most abundant phase was 3C with $a = 4.1$ Å unlike its bulk phase 9R. In addition to their bulk structures in all the cases the non-basal diffraction patterns containing a^*c^* reciprocal lattice network revealed the presence of modulated phases where the a lattice periodicity was invariant but the c periodicity differed from one phase to the other. The c periodicity in all cases was integral multiples of interlayer spacing of close packed layers in their bulk structures *e.g.* 2.39 Å for HoAl_3 . The different modulated phases discovered are 4H, 5H, 15R, 30R, 42R and disordered 60R for HoAl_3 ; 3C, 4H, 6H, 9R, 12R, 15R, 16H, 24H, 42R and several other disordered structures for $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ and 9R, 4H and 16H for $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$. Although the characterisation of diffraction patterns revealed the presence of the modulated phases they alone could not lead to unambiguous results regarding the state of disorder and inter-growth of various phases. Also for the case of high period structures when the resolution of diffraction spots become questionable the diffraction analysis does not lead to an unambiguous structural characterisation. Keeping this in view high resolution transmission electron microscopy was resorted to unravel the details of the structural features of the modulated phases. Figure 1 shows the bright field high resolution electron micrograph employing direct beam and 00.3 spots. This figure clearly reveals the presence of a twin boundary at A. The two crystal regions were confirmed to correspond to 42R as was cleared from the crossed diffraction pattern of the region containing the boundary. The diffraction pattern is also shown and the spots 00.42 are indexed for both the crystals. The blocks of 42R were found to consist of two fringe spacings corresponding to 5 layers, followed by a fringe spacing corresponding to 4 layers. Several lattice images were recorded for the structural variants in $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ thin films. Figure 2 represents a dark field lattice image formed by 00.9 spot including two other neighbouring spots of 00.1 row. Here the fringe spacing comes out to be 7.04 Å. Since

Figure 1. A bright field electronmicrograph revealing the lattice image of 42R phase (HoAl_3) and corresponding diffraction pattern. Twin boundary can be noticed. Unit cell of 42R phase consists of fringes of 4H, 15R and 15R (i.e. $4\text{H} + 15\text{R} + 15\text{R}$). Unit cell width corresponds to $\approx 33.4 \text{ \AA}$.

Figure 2. Dark field lattice image of 9R phase of $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ alloy. Fringe spacing corresponds to $7.04 \text{ \AA}$.

the diffraction pattern revealed the phase to be 9R the actual periodicity of the lattice is $3 \times 7.04 = 21.12$ Å. This agrees very well with the known periodicity 21.14 Å of 9R phase. Figure 3 shows the lattice fringes of 4H. Fringe spacing directly gives the *c* periodicity of 4H modulated phase which corresponds to ≈ 9.4 Å. The heavy strips marked as *s* represent stacking faults. Figure 4 shows a typical lattice resolution in bright field from a disordered region. Growth of several modulated phases such as 6H, 15R and of 14 layer (42R) can be noticed. Random stacking faults are also clearly seen. The alteration of background intensity with lattice images of periodic structures yield evidence of the presence of twins. Several other modulated phases have been observed with the help of high resolution electron microscopy which could not be identified by means of electron diffraction alone. These results are summarized in the following table.

The electron microscopic studies of HoAl_3 , $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ and $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$ thin films reveal the existence of modulated phases in these films. The observed modulated phases for these trialuminides are given below:

Rare earth trialuminides	Modulated phases
HoAl_3	4H, 5H, 15R, 30R, 42R and disordered 60R
$\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$	3C, 4H, 6H, 9R, 12R, 15R, 16H, modulated phases with periodicity of 7, 9, 13, 18, 22, 24, 32 and 46 layers and some disordered structures.
$\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$	9R, 4H, 16H, some disordered structures and the existence of some high period modulated phases.

3. Discussion

The mystery behind the occurrence of modulated phases has been generally too intriguing to be unravelled in a satisfactory way. In the present case which is akin to the phenomenon of polytypism the already proposed mechanisms for the formation of polytypism which explains the formation of polytypes during growth is not applicable since in the present case the modulated phases are formed during an amorphous to crystalline transformation. However, as is well-known in metallic systems the electronic energy plays an important role in stabilising the modulated phases (Sato and Tooth 1963; Sato *et al* 1967). An explanation for the formation and stabilisation of the modulated phases has been proposed by Singh *et al* (1981) for GdAl_3 , on the basis of reduction of electronic energy elaborated in terms of contacts of Fermi surface and Brillouin-zone. In this the authors presume that slight variation in the Fermi surface scanning vector $2k_f$ may occur on the basis of valency fluctuations of rare earth metal involved and/or stoichiometric variation. It has been shown on the basis of geometrical scheme that even a slight variation in Fermi scanning vector may suffice to stabilise the modulated phases. The case of $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$ is shown in figure 5 (Singh *et al* 1981). The case of $\text{Y}_{0.91}\text{Er}_{0.09}\text{Al}_3$ is under consideration.

Figure 3. Lattice planes of 4H phase of $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$. Faults marked 's' can also be noticed. Fringe spacing corresponds to 7.04 Å.

Figure 4. Bright field lattice image revealing the inter-growth of different modulated phases such as 6H, 15R and 14H (42R) of $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$.

Figure 5. The Fermi surface Brillouin zone interaction exhibiting the stabilization of 4H, 6H and 9R modulated phases in $\text{Er}_{0.5}\text{Gd}_{0.5}\text{Al}_3$.

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