

## Chapter 3

# Ion-Beam Induced Formation of Nanoparticles with Predicted Structure

L. Kutsenko, L. Burlaka, A.E. Kiv, M. Talianker, and D. Fuks

**Abstract** The *ab initio* approach is developed that allows predicting structural changes, which can be induced by Plasma Immersion Ion Implantation (PIII) of Ag ions into Mg based alloys. The calculations are performed in the framework of the density functional theory. The approach is based on the assumption that the electronic properties of the irradiated parent phase predetermine the structural characteristics of a new implantation-induced phase. It is presumed that penetration of the implanted ions into the host lattice leads, firstly, to “immediate” excitation of the electronic subsystem of the parent phase. Then this initial stage is followed by changes of the atomic configuration so that the electronic subsystem transfers to the relaxed state. To characterize and to quantify how the initial non-equilibrium state is far from the quasi-relaxed state of the system, the energy parameter  $\Delta E$  is proposed. The behaviour of  $\Delta E$  plot vs. different concentrations of implanted ions correlates with the conditions of formation of the new phase. The correctness of the proposed approach was corroborated by *ab-initio* analysis of the experimentally observed phase transitions  $\text{Mg} + \text{Ag}_{\text{ions}} \rightarrow \text{MgAg}$  and  $\text{Mg}_{17}\text{Al}_{12} + \text{Ag}_{\text{ions}} \rightarrow \text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$  induced by PIII treatment.

**Keywords** Metallic nanoparticles • Mg alloys • Plasma immersion ion implantation

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### 3.1 Introduction

Nanotechnology is a fast growing industry producing a wide variety of manufactured nanomaterials with numerous potential applications. One of them is strengthening the construction materials enhanced with nanoparticles. Among the innovative construction materials, magnesium-based alloys take a special place due to their outstanding properties: they possess excellent specific strength and stiffness, exceptional dimensional stability and good recycle ability. Due to these superior properties magnesium-based alloys are a part of a constantly growing market of novel energy efficient, light and environmentally friendly materials [1–6].

In recent years, the research on magnesium alloys has been increasingly intensified aiming at the improvement of their properties and the enhancement of their further utilization in various industrial applications. The most effective technologies developed for the improvement of anticorrosion and mechanical characteristics of these alloys are associated with the surface engineering. A special advantage of this technique is that it substantially expands the possibilities of modifying the materials by creating nanoparticles with unique characteristics in the subsurface region. One of such techniques is known as Plasma Immersion Ion Implantation (PIII) technology [7–12]. Nowadays PIII has become a widespread technological tool in materials science and materials engineering.

In PIII technology, the target material is immersed in plasma, which contains ions of the species to be implanted. Repetitively pulsed high negative voltages are applied to the sample, thus, stimulating implantation of ions into the target. Due to the substantial progress in developing the ion implantation technology, metallurgists are now able to take almost any element in the periodic table and implant it into the subsurface region of any metal alloy. The important feature of the PIII-process is that the concentration of alloying elements in the implanted material can be much higher than the solubility limit. Despite the fact that the resulting modification of the structure is usually occurs only within the subsurface layer of approximately micron thick, the PIII metallurgy can have important technological applications [1, 6, 13, 14].

The fact that PIII process is athermal and independent of the usual thermodynamic constraints makes it possible to form new metastable phases and produce new structures with compositions never seen before. One of the most interesting aspects of the ion implantation metallurgy is its use in fundamental studies and high potential to contribute greatly to the fundamental research on metals and alloys. Investigations of structural changes induced by ion implantation provide valuable metallurgical data needed for developing theoretical models, which allow understanding the physical phenomena responsible for structural changes caused by implantation processes in a material.

In the present paper we describe a new approach based on *ab-initio* calculations which allows estimation of the implanted doses favouring formation of new intermetallic phases and even can predict their structural characteristics. The approach was tested on PIII process in which Ag ions were implanted into Mg substrate and into  $\text{Mg}_{17}\text{Al}_{12}$  intermetallic compound.

### 3.2 *Ab Initio* Approach for Studying Ion-Induced Phase Transformations with Formation of Nanoparticles

At present, *ab initio* calculations are widely used for studying thermodynamic and structural properties of stable phases existing in alloys. The most stable phase is determined by the comparison of the total energies for competing phases. The values of the total energy for stable phases are employed to obtain the phase diagram. The studies are normally based on the knowledge of stable structures for initial and final phases. However, such information is not always available, for example, in the case of formation of new phases in conditions of plasma immersion ion implantation.

In this work we present an alternative approach which is based on *ab-initio* computations of the electronic characteristics of supersaturated systems in which phase transformations occur. Its basic ingredients include DFT [15], Green's function approach to the one-electron problem formulated within a LMTO basis [16], CPA corrected for charge transfer effects by the screened impurity model [17], and the atomic sphere approximation (ASA) corrected for the higher multipoles of the charge density [18].

As applied to modeling the implantation induced structural changes, this approach is based on the assumption that the electronic properties of the irradiated parent phase predetermine the structural characteristics of a new implantation-induced phase. According to this concept, a two-stage model of the ion-induced phase transition is proposed. The model is based on the adiabatic approximation, which means that the penetration of the implanted ions into the host lattice leads to "immediate" excitation of its electronic subsystem while the changes in atomic configurations occur later. As a result of spatial fluctuation of the density of implanted ions in the microscopic volumes of the parent phase, the quantitative relationships among the elements may correspond to the stoichiometric composition for some new phase. This leads to the change of electronic states according to the stoichiometric formula of the new phase.

At the first stage, the implanted system is in condition that can be defined as the intermediate state (IS) that corresponds to the strongly non-equilibrium state of the parent phase. We assume that at this stage the atomic lattice with the implanted ions still retains its original structure. The rearrangement of atoms occurs at the second stage of the phase transition. Such atomic rearrangement corresponds to the formation of a new phase. As a matter of fact, the IS is a virtual state and cannot be experimentally observed. Nevertheless, the proposed approach allows prediction of the structural characteristics of a new implantation-induced phase through the analysis of the electronic states describing the IS condition of the parent phase. This analysis also makes it possible to predict the dose of the implanted ions favouring the formation of a new phase.

Our approach is illustrated for two cases [19, 20]: (a)  $\alpha$ -Mg matrix implanted with Ag ions and (b)  $\text{Mg}_{17}\text{Al}_{12}$  compound implanted with Ag ions.

In accordance with our approach, the calculations were carried out for two states of the system:

- (a) The initial or starting state, which corresponds to the atomic configuration arising as a result of penetration of Ag atoms into the Mg target in the course of PIII processing. The system is considered as hexagonal closest packing of Mg atoms mixed with a controlled quantity of Ag atoms substituting for Mg atoms. Such a system is a non-equilibrium one (IS); its electronic subsystem is in an excited state.
- (b) The quasi-relaxed state, corresponding to a new atomic configuration, which would be adopted by the implanted system in the course of the relaxation process. Such a configuration can be found through the simulation of atomic displacements causing the system to come to some non-stable equilibrium state characterized by the relative energy minimum. Only those displacements that do not affect the symmetry of the parent matrix are tried. In fact, for each concentration of implanted ions, the total energy of the system was minimized by varying the lattice parameter.

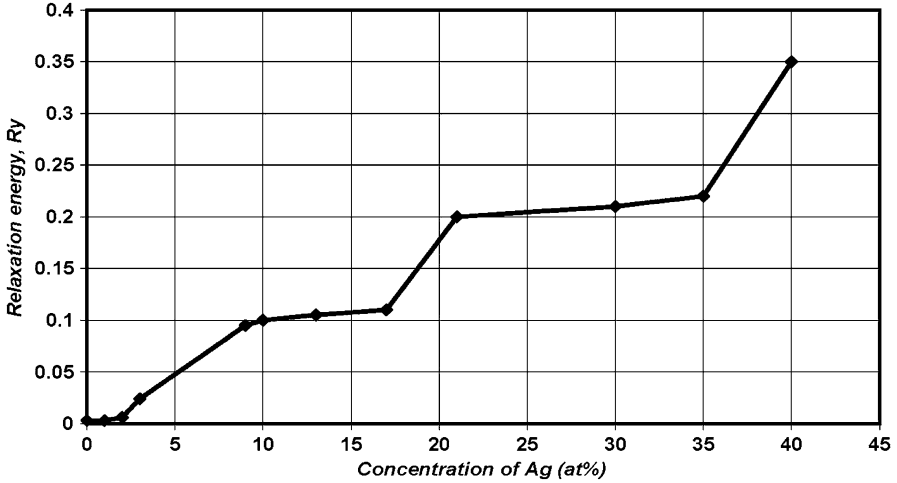
For both system states the values of total energy,  $E_t^{init}$  and  $E_t^{relax}$ , were computed and then used to get the difference  $\Delta E = E_t^{relax} - E_t^{init}$ . In addition, the total and partial densities of states (DOS) were calculated for different concentrations of implanted ions in the parent matrix. Considering  $\Delta E$  as a so-called “relaxation energy” showing how the initial non-equilibrium state is far from the quasi-relaxed state, it is reasonable to assume that there should be correlation between the values of  $\Delta E$  calculated for specific concentration of implanted ions and the corresponding possibility of formation stable phase .

The *ab initio* calculations referred to the temperature  $T = 0^\circ\text{K}$ . The energy differences between various alloy phases are so large, that the possible contribution of entropy terms should not be significant. Therefore, entropy terms will not substantially influence the qualitative correlations between energies obtained for  $0^\circ\text{K}$ .

### 3.3 PIII-Induced Phase Transformation with Creation of MgAg Nanoparticles

We applied the *ab initio* technique to study phase transformation  $\text{Mg}_{(\text{hcp})} + \text{Ag}_{(\text{ions})} \rightarrow \text{AgMg}_{(\text{cubic})}$  which was experimentally observed in  $\alpha$ -Mg matrix subjected to implantation of Ag ions by PIII processing [20]. According to the method described in Sect. 3.2, the part of Mg atoms in the  $\alpha$ -Mg-matrix was substituted for Ag atoms followed by the analysis of the IS for this system. The *ab initio* calculations of “relaxation energy”  $\Delta E$  and DOS characteristics were performed in a wide range of concentrations of Ag in the  $\alpha$ -Mg-matrix [19–21].

A graphical representation of the computed  $\Delta E$  values for different Ag concentrations is shown in Fig. 3.1. One can see that at some Ag concentrations,



**Fig. 3.1** The experimental results showed that the  $\beta$ -phase AgMg begins to form at ion doses corresponding to concentrations of  $\sim 35$  at.% of Ag

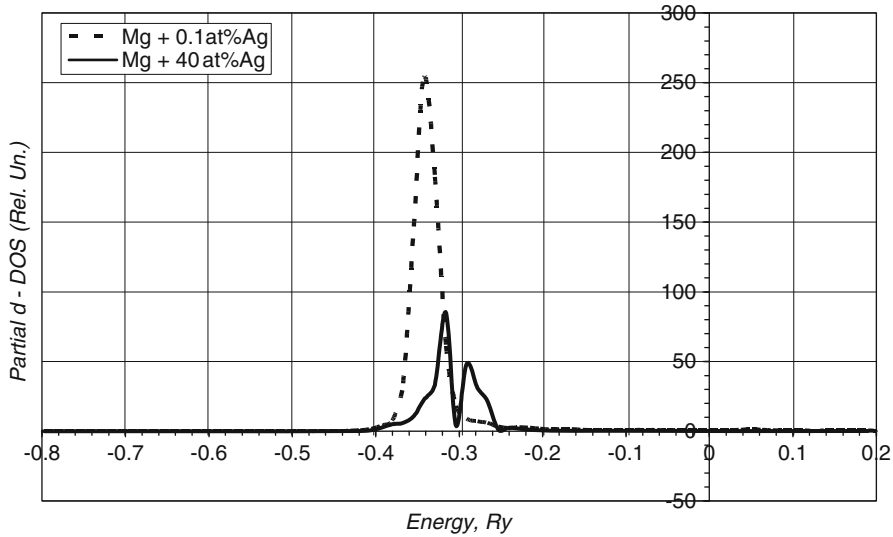
**Table 3.1** Binary phases existing in the Ag-Mg system

Phases		Pearson symbol	Composition, at.% Ag	Space group
(Ag)	$\alpha$	CF4	70.7–100%	$Fm\bar{3}m$
$Ag_3Mg$	$\alpha'$	CP4	75%	$Pm\bar{3}m$
$AgMg$	$\beta$	CP2	34.6–64.5%	$Pm\bar{3}m$
$Ag_{17}Mg_{54}$	$\epsilon'$	OI142	21.2–24.1%	$Immm$
$Ag_{7.96}Mg_{25.04}$	$\epsilon$	CF264	21.2–24.1%	$Fm\bar{3}$
$Ag_9Mg_{37}$	$\gamma$	HP92	19.6%	$P6_3$
(Mg)	$\delta$	HP2	0–8.9%	$P6_3/mmm$

the parameter  $\Delta E$  increases sharply, while within certain regions  $\Delta E$  is relatively constant. This may imply that the concentration ranges in which  $\Delta E$  is sharply increased correspond to conditions favoring the formation of a new phase. These considerations are corroborated by comparison of the plot  $\Delta E$  in Fig. 3.1 and Table 3.1 presenting the phases appearing in the Mg-Ag system [22]. It can be seen that the significant increase of  $\Delta E$  in the range 35–40 at.% Ag correlates well with the range 34–65 at.% Ag in which the cubic phase AgMg exists.

### 3.4 Electron Mechanisms of PIH-Induced Formation of AgMg Phase

To understand the electron mechanism of AgMg phase formation in Mg-Ag system, we studied DOS corresponding to the IS condition of the implanted Mg matrix. The total and partial DOS were calculated for concentrations of Ag atoms ranging



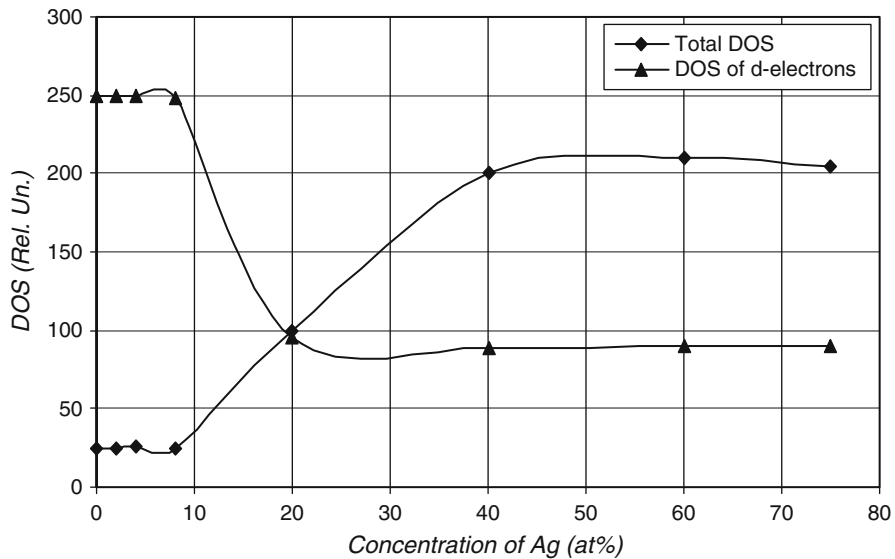
**Fig. 3.2** Partial DOS for  $d$ -electrons calculated for Mg + 0.1 at.% Ag and for Mg + 40 at.% Ag

from 0 to 75 at.%. Comparing DOS for pure Mg and for Mg + 0.1 at.% Ag and Mg + 40 at.% Ag, it was concluded that while a small increase of Ag content has no marked effect on the total DOS, significant changes in the total DOS occur for 40 at.% Ag.

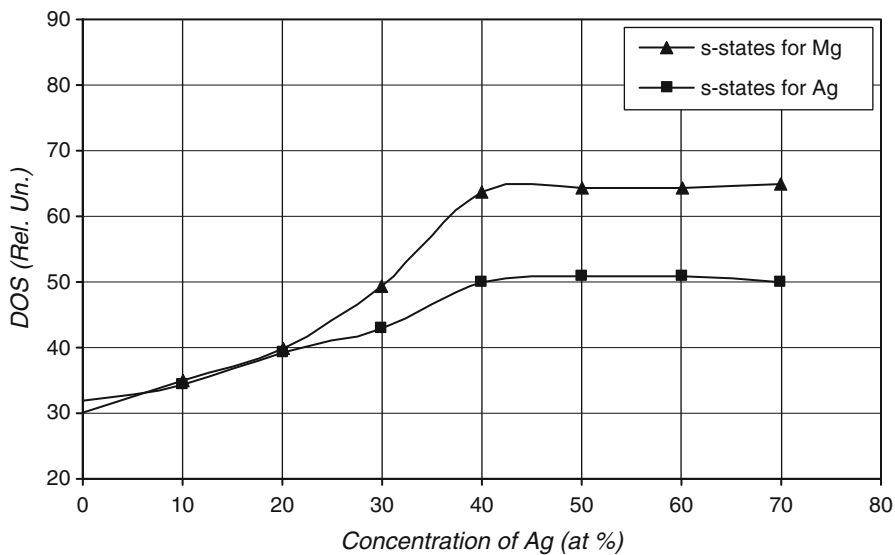
Concomitantly, the partial density of  $d$ -electrons of Ag atoms also changes substantially when the concentration of implanted atoms increases from 0.1 to 40 at.% (Fig. 3.2). It can be said that the characteristic dependence of partial DOS on the Ag concentration is associated primarily with the electronic states in the energy region from  $-0.25$  to  $-0.45$  Ry. It was reasonable, therefore, to integrate within this energy range the total DOS and the partial densities of  $d$ -states and calculate them for different concentrations of Ag. The comparison between concentration dependence of the integrated total DOS and the partial density of  $d$ -states is presented in Fig. 3.3. It can be seen that a correlation exists between changes of the integrated total and partial DOS: the total DOS tends to increase with the increase of Ag concentration and, in contrast to this, the partial DOS for  $d$ -electrons of Ag decreases.

Similar calculations were performed for integrated (in the energy interval  $-0.25$  to  $-0.45$  Ry) partial DOS for  $s$ - and  $p$ -electrons of Mg and Ag. The corresponding plots of the concentration dependence of the partial DOS for  $s$ -electrons and  $p$ -electrons are shown in Figs. 3.4 and 3.5, respectively.

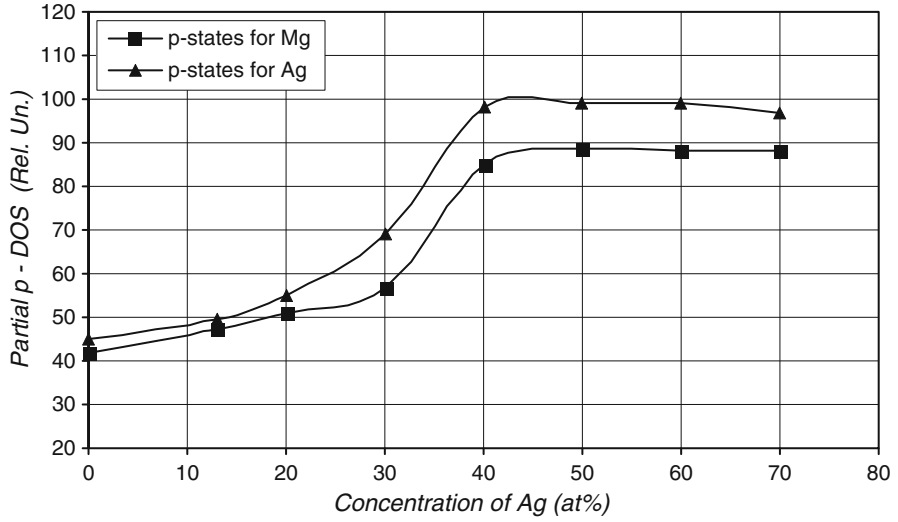
From the comparison of the plots in Figs. 3.3, 3.4, and 3.5, it can be surmised that the increase of a number of states in the total DOS can be ascribed mainly to the decrease of a number of  $d$ -states of Ag. Obviously,  $d$ -electrons of Ag promote more symmetrical  $s$  and  $p$  states, thus, favouring the formation of intermetallic phases with higher symmetry. This exactly corresponds to the general trends manifested in Table 3.1: the structures with a larger Ag content possess a higher symmetry.



**Fig. 3.3** The concentration dependence of integrated total DOS and partial DOS for  $d$ -electrons in the region from  $-0.25$  to  $-0.45$  Ry



**Fig. 3.4** The concentration dependence of integrated partial DOS of  $s$ -electrons for Mg and Ag in the region from  $-0.25$  to  $-0.45$  Ry



**Fig. 3.5** The concentration dependence of integrated partial DOS of  $p$ -electrons for Mg and Ag in the region from  $-0.25$  to  $-0.45$  Ry

### 3.5 Concentration Dependence of Parameter $\Delta E$ for PIII-Induced Formation of New Phase from $\text{Mg}_{12}\text{Al}_{17}$

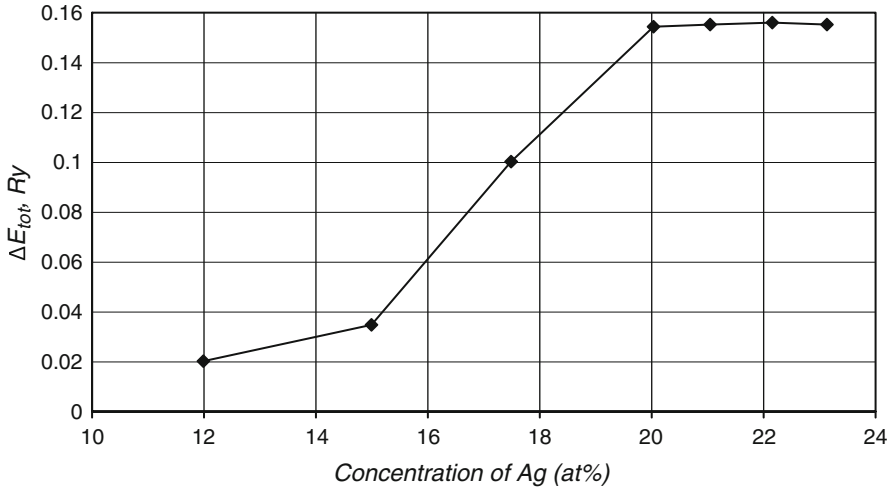
TEM examination of the implanted grains of  $\text{Mg}_{17}\text{Al}_{12}$  compound revealed that  $\text{Mg}_{17}\text{Al}_{12}$  transformed into a new phase with a composition  $\text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$ . Attempts to identify the new structure on the basis of the ternary phases known in the literature for the Mg-Al-Ag system were unsuccessful; therefore, crystallographic characterization of the new phase was performed using electron diffraction methods [23].

In order to study the implantation induced transition  $\text{Mg}_{17}\text{Al}_{12} \rightarrow \text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$ , we applied the approach described in Sect. 3.2. In accordance with this approach, the requirement that the parent structure is retained at the IS stage should be satisfied. This means that since the unit cell of the parent  $\text{Mg}_{17}\text{Al}_{12}$  phase consists of 58 atoms (34 atoms of Mg and 24 atoms of Al), the ratio between Mg and Al atoms in the implanted unit cell at IS condition can be expressed as:

$$\frac{34 - N_{\text{Mg}}}{24 - N_{\text{Al}}} \quad (3.1)$$

where  $N_{\text{Mg}}$  and  $N_{\text{Al}}$  represent, respectively, the number of Ag atoms replacing Mg atoms and Al atoms in the parent unit cell. On the other hand, the ratio (3.1) should correspond to the ratio between the Mg and Al atoms in the new structure





**Fig. 3.6** Dependence of  $\Delta E$  on the atomic fraction of implanted Ag ions

$\text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$  formed by implantation. Hence, it can be stated that for the compound  $\text{Mg}_x\text{Al}_y\text{Ag}_z$  we can formulate two equations to determine  $N_{\text{Mg}}$  and  $N_{\text{Al}}$ :

$$\frac{34 - N_{\text{Mg}}}{24 - N_{\text{Al}}} = \frac{x}{y} \quad \text{and} \quad x + y + z = 1 \quad (3.2)$$

where  $x = \frac{34 - N_{\text{Mg}}}{58}$ ,  $y = \frac{24 - N_{\text{Al}}}{58}$ , and  $z$  are, respectively, the fractional content of Mg, Al, and Ag atoms in the implanted parent unit cell with the stoichiometric relations corresponding to the new phase.

It follows from the conditions (3.2) that the value  $z_{\min}$  of the minimal concentration of the implanted Ag atoms which may cause transition to the product phase with composition  $\text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$  should be equal to 0.11.

The *ab-initio* calculations applied to the “excited” IS condition of the implanted  $\text{Mg}_{17}\text{Al}_{12}$  phase were performed for  $z = 0.12, 0.13, 0.15, 0.17, 0.20, 0.21, 0.23, 0.25, 0.27$ , and  $0.30$ . The LMTO ASA-CPA approach was used for computation of the total energy,  $E_{\text{tot}}$ , DOS characteristics and construction of the plot of “relaxation energy”  $\Delta E$  vs. concentration of Ag.

The analysis of the plot  $\Delta E(z)$  (Fig. 3.6) reveals that a slow increase of the parameter  $\Delta E$  begins at 12 at.% Ag, while a marked increase of  $\Delta E$  takes place within the range of 15–20 at.% Ag; the change of  $\Delta E$  in the range 20–23 at.% is negligible. This implies that the ion doses corresponding to a 0.15–0.22 range of  $z$  should favour the formation of a new phase. The experimentally observed implantation dose that provides the formation of the new compound  $\text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$  was determined as  $\sim 6 \cdot 10^{15}$  to  $\sim 10^{16} \text{ cm}^{-2}$ . This range corresponds to  $z = 0.15$ – $0.22$ , which is in a good agreement with the prediction obtained by *ab-initio* calculations. Regarding the concentration range from 20 to 23 at.% Ag, where parameter  $\Delta E$  does not depend on the Ag content, we may suggest that this interval corresponds to Ag content when the new phase is already formed.

The concentration behaviour of the parameter  $\Delta E(z)$  correlates well with the behaviour of total and partial DOS profiles calculated for different concentrations of implanted Ag ions larger than 0.15. In accordance with the sluggish behaviour of parameter  $\Delta E$  in the range 20–23 at.% Ag, we do not observe the marked changes in the partial DOS plots for  $d$ -states of Ag within this interval.

The analysis of the partial DOS profiles for  $s$ -,  $p$ - and  $d$ -electrons of Ag atoms in the implanted  $\text{Mg}_{17}\text{Al}_{12}$  structure has shown that  $d$ -states of the Ag atoms are mainly responsible for the changes of profile of the total DOS, when the parent  $\text{Mg}_{17}\text{Al}_{12}$  phase transforms to a new  $\text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$  compound. This means that the chemical bonds in the new  $\text{Mg}_{54}\text{Al}_{28}\text{Ag}_{18}$  structure are formed primarily by the  $d$ -electrons of Ag atoms. Moreover, the areas under partial DOS plots for  $d$ -states of Ag increase in the direction of 13%  $\rightarrow$  15%  $\rightarrow$  17%  $\rightarrow$  20%, indicating a greater involvement of  $d$ -electrons in the formation of chemical bonds of the new phase. It was also shown that, in addition to  $d$ -electrons of Ag atoms that, obviously, are dominant in the formation of chemical bonds in the new phase, the  $s$ -electrons of Mg may also contribute to chemical bonds. Possibly, the effect of  $s$ - $d$  hybridization may take place in this case.

### 3.6 Conclusions

The *ab initio* approach described in the present paper has been applied for the prediction of structural changes induced by Plasma Immersion Ion Implantation of Ag ions into Mg based alloys. The calculations are based on the density functional theory. According to the proposed approach, a correlation exists between the structural parameters of a new implantation-induced phase and the electronic properties of the irradiated parent phase. The model is based on the adiabatic approximation assuming that penetration of the implanted ions into the host lattice leads to the “immediate” excitation of its electronic subsystem while the changes in atomic configurations occur later. The parameter  $\Delta E$  has been introduced that shows how far is the initial non-equilibrium state from the quasi-relaxed state of the system. It has been demonstrated that correlation exists between the value  $\Delta E$  calculated for different concentrations of implanted ions and the conditions of formation of the new phase in the form of nanoparticles. As a result of the analysis of the dependence of  $\Delta E$  parameter and DOS characteristics on the concentration of implanted Ag ions, the conditions favouring the formation of nanoparticles of a new phase have been determined.

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