Radiation-induced Vacancies in B2 Intermetallic Compounds

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Abstract – On the basis of original authors and literary experimental data the review of characteristics of the vacancy defects induced by electron irradiation in the samples of aluminides, and also alloys on a base of titanium nickelide with B2 crystal structure is given.

Basic method of research is a positron annihilation spectroscopy (PAS) which may provide accurate information on vacancy-type defects in solids. The annealing kinetic of irradiation-induced vacancies and microscopical mechanism of vacancy migration in intermetallic compounds with B2 structure is considered. The correlation between frequency of phonons on boundary of a Brillouin zone in direction <110> and energy activation of vacancy migration in B2 intermetallics should been found. Effect of irradiation on thermoelastic martensitic transformations in TiNi-based alloys is considered.

1. Introduction

The B2 intermetallic compounds are the subjects of intensive investigation in connection with attractive high-temperature mechanical properties in transition-metal aluminides [1], shape memory effect and superelastic properties in B2 Ti-based alloys [2]. The formations of metastable and amorphous phase are observed in these alloys [3,4]. Lattice vacancies or vacancy-type defects play important role in forming of properties and have an appreciable influence on thermodynamic this alloys. The B2 structure is enough simple, but the mechanism of atomic diffusion in B2 alloys is still a subject of discussion [5]. The majority of researchers consider, that diffusion in B2 intermetallic alloys is carried out by atomic jumps on vacant lattice points, but the clear mechanism of diffusion and regularity of change migration energy of vacancy are understood insufficiently now. In order to understand this problem data obtained by PAS can be helpful.

2. Methodology

The positrons on entering in solids will rapidly lose their kinetic energy via dissipative processes like electronic excitation and ionization, electron-hole pair creation, and phonon interaction. The annihilation cross section becomes significant only at thermal velocities. As the lifetime positrons is a 1–2 hundred picoseconds in the metals, their diffusion through the solid will be decisive in their trapping at the specific sites. The positron lifetime and the positron-electron momentum distribution in solids depend upon the local electronic enviroment – the lower electron density in the defect, the longer positron lifetime and smaller average momentum electron-positron pair. The lifetime magnitude can be used to characterize defects of materials. When the vacancies concentration is about 10^{-4}, the all positrons will be annihilate from trapping states with the lifetime which is larger in 1,5–1,7 times in comparison the free positron lifetime. Positron trapping is described by standard model [6] in which trapping is limited by positron-capture cross-section (σ) and defect concentration (C_V), These defects are uniformly distributed vacancies. Average positron lifetime magnitude are determinated by:

$$\bar{\tau} = \tau_f \times \frac{1 + \sigma C_V \tau_V}{1 + \sigma C_V \tau_f}, \qquad (1)$$

where τ_f – the positron lifetime in the free state, τ_v – positron lifetime in the vacancy trapping state.

In general, behavior the vacancy defects may be obtained by PAS in temperature equilibrium measurements or from measurement by isochronous annealing of preliminary quenched samples [7,8].

3. Characterization of vacancy defects in B2 (CsCl) intermetallics.

In $L1_2$ (Ni_3Al) and $D0_{19}$ (TiAl) intermetallics with close-packed atomic cell positron lifetime in radiation-induced vacancies are higher then that in thermal vacancies. This difference is attributed to an atomic relaxtion in vacancy region or partial positron detrapping from vacancies at high temperatures.

On the other hand the data about the identity of characteristics of radiation-induced and thermal vacancies are obtained for the B2 intermetallics The same positron lifetime is observed in quenchen-in and radiation-induced vacancies in B2 NiAl, FeAl [6]. This agree with limits of experimental accuracy with *ab initio* calculations. Hence, the research of annealing kinetic of radiation-induced vacancies can give the useful information about migration energy of lattice vacancies.

For example in reference [6] had been studied isothermal annealing of electron irradiated vacancies in B2 $Fe_{61}Al_{39}$ alloy at temperatures 623 K and 723 K (E_e-=2.5; 2.6 MeV, $\Phi=(5{,}6–9{,}1)\times10^{22}m^{-2}$). Return kinetic to reference state was well described by monomolecular reaction. Disappearance of vacancies can be characterized by time constant:

$$t_E = t_0 \exp(E_m / k_B T_i), \qquad (2)$$

where T_i – annealing temperature and parameter t_0 determinated in [8]. Value t_E is equal to 42,4 and 0,7 hour for two above-mentioned annealing temperatures are vary close to magnitudes obtained from thermal vacancies.

The other case represents equatomic intermetallic compound TiNi. The electron irradiation was made at 150 K in martensitic state, but isochronous annealings it was made in B2 (austenitic) state. The experimental data about the peak height of angular distribution annihilation photons, N(0), vary in dependence on isohronous annealing temperature are presented in Fig. 1.

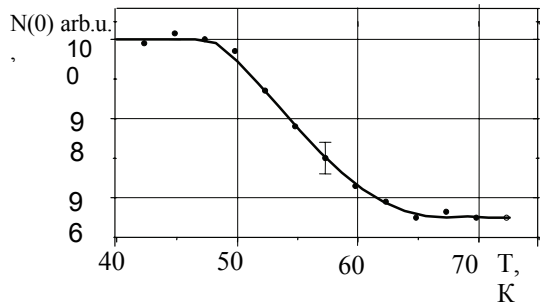

Fig. 1. Dependence of peak height of angular distribution annihilation photons N(0) on annealling temperature. Annealing time at T_i equal 20 minutes. (E_e-=2.0 MeV $\Phi=2\times10^{22}m^{-2}$)

It is visible, that largest change of N(0) occur in 473–623 K temperature range. Then process annealing of vacancies finishes and N(0) becomes typical for unirradiate sample. It is necessary to note, there is no growth stage connected with the agglomeration radiation defects during annealing. Conditions of an irradiation and temperature interval of defects annealing (~0,33 $T_{melting\text{-}point}$) allow to suppose that monovacancies had been formed during irradiation predominantly. Similar results have been received by us earler after electron irradiation TiNi with E=17 MeV [9]. But in [9] the defect annealing was observed at more elevated temperatures that had been probably connected with formation of defects with higher migration energy.

The additional information on the nature of radiation defects may be obtained from the activation energy of defect annealing process. For definition of this energy we used the trapping model for positrons in solids. The trapping parameter K for annealing process will be determinates by the next expression:

$$K = \frac{1}{\tau_0}\frac{N(0) - N_{min}(0)}{N_{max}(0) - N_0(0)}, \qquad (3)$$

where $N_{max}(0)$ – value of N(0) parameter, when defect concentration is maximum; $N_{min}(0)$ – N(0) value, when defects are removed completely;
$N_T(0)$ – current value N(0) at annealing temperature T.

For monomolecular reaction model of annealing process the interconnection between K and E_a is given by eq. (4):

$$\ln[\pm\ln K_{i-1} \mp \ln K_i] = \ln C't - \frac{E_a}{k_B T_i} \qquad (4)$$

Assumed that E_a is equal to energy of migration vacancies E_m, it is possible to calculated selfdiffusion energy in TiNi, using value E_V from [7]. If diffusion occurred by jumps of atoms on vacant lattice sites and, considering, that diffusion goes mainly nickel sublattice, it may be obtained:

$$E_D = E_V + E_m \qquad (5)$$

For TiNi E_D = 0.78 eV+ 0.7 eV = 1.48 eV. This value practically identical E_D obtained from [10].

In Table 1 integrate information about energetic characteristic of vacancies in B2 intermetallic and BCC metals, obtained by PAS.

Table 1. Systematic data of energetic characteristic vacancy defects

Intermetallic	Em, eV	Ev, eV	Em / Ev	Reference
FeAl (B2)	1,7	1,08	1,57	[6,8]
AuCd (B2)	0,58	0,39	1,5	[11]
NiAl (B2)	2,14	1,05	2	[6,14]
CuZn (B2)	0,4	0,47	0,85	[12]
TiNi (B2)	0,72	0,78	0,9	[7]
Nb (OLI[K)	1,4	2,6	0,54	[13]
Mo (OLI[K)	1,5	3	0,5	[13]
Ni_3Al (L12)	1,2	1,8	0,67	[6,14]

It is visible in usual BCC metals $E_V > E_m$, and $E_m/E_V \sim 0,5$, but the vary low E_V and $E_m/E_V \geq 1$ are observed in B2 intermetallics. These differences are connected with pecularities of interatomic interaction in B2 intermetallics. It is to note that "anomaly" characteristics of vacancy defects come to light as well in comparison with intermetallic with density packing of atoms (compare data for Ni_3Al and NiAl).

As for analyzed intermetallics, The mechanism of selfdiffusion is conditioned by atom-vacancy exchanges in analyzed intermetallics because the (5) relation is carried out. Recently it is shown by neutron experiments that the elementary diffusion event occurs by atom jump in nearest neighbors sites in B2 intermetallics. However atom lifetime in this state extremely short and finally diffusion process looks as atom jumps on second nearest neighbors [15].

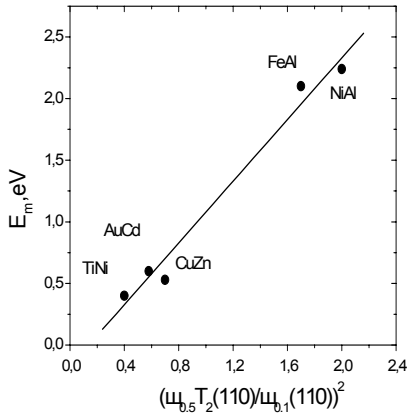

Fig. 2. Dependence of migration energy of vacancies from normalized phonon frequency in <110> direction for intermetallics with B2 structure

The barrier heights (i.e. atom position in the saddle point) defining Em depend on the character interatomic interaction. This becomes apparent in the frequency normal phonon mode. The second nearest neighbors, which are the atoms of the same type are locate in <110> direction in B2 structure. So, the frequency of phonon branch on boundaries Brillouin zones in these directions must be correlated with the E_m in B2 intermetallics. It is known that T_2 1/2 [110] phonon frequency is vary low in B2 phase of AuCd, CuZn and TiNi alloys and values of E_m and E_D is very low too [16]. For intermetallics FeAl, NiAl frequency this phonons branch and E_D and E_m values are considerably larger then for above-mentioned alloys [17].

4. Influence of radiation-induced defects on the thermoelastic martensitic transformations

Character of influence on temperatures martensitic transformation (MT) in TiNi B2 alloys of the electron irradiation, which creates only simple Frenkel defects, and neutron irradiation which creates cascades of atomic collisions are different strongly. Neutron damage sharply reduces all characteristic temperatures of MT. At the same times electron irradiation does not change or can slightly raise ones [18,19]. Simultaniously, the magnitude of accumulation and recovery of inelastic strain (shape memory effect) decrease [9].

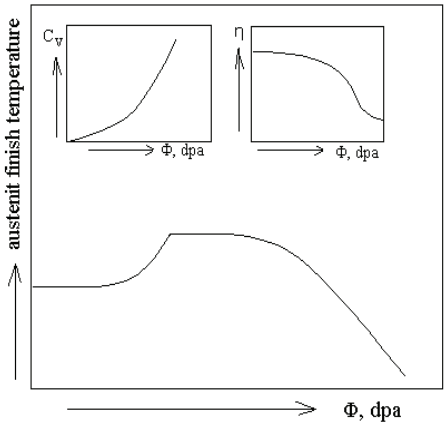

Fig. 3. Vacancy concentration C_V, longe-range orderng parameter η and austenit finish temperature depending on irradiation parameter Φ. Schematic representation model results from [20]

Thermodynamic model [20] is proposed for explanation of radiation induced non-monotonous change of MT temperatures in shape memory alloys. Based on this model austenit finish temperature can be raised slightly for electron irradiation with small fluence. This implyies that radiation-induced point defects (vacancies) enhances mainly the non-chemical term in change of free energy during of MT. Strong decrease martensit start and austenit finish temperatures after irradiation with large fluence are caused by the irradiation-induced chemical disordering which reduces predominantly the chemical term in free energy change.

Both terms depend on energies of formation (E_V) and migration (E_m) of vacancy defects. It needs for predicted functional properties shape memory alloys and high temperature structural materials behavior under irradiation exposure.

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