Defect structure in non-stoichiometric CoTi with CsCl-type ordered structure

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Abstract

Positron lifetimes in CsCl-type intermetallic compounds Co\textsubscript{100–x}Ti\textsubscript{x} (X = 48–50.3) water-quenched and furnace-cooled from 1323 K have been measured to study their defect structures. Positron mean lifetimes in water-quenched specimens of both Co-rich and Ti-rich compositions are much longer than the calculated positron lifetime in the perfect lattice, and no matrix component is observed. The positron mean lifetimes in the furnace-cooled specimens of Ti-rich compositions do not have large difference from those for the water-quenched specimens, whereas the furnace-cooled specimens of Co-rich compositions show short positron mean lifetimes, which are almost equal to the calculated lifetime in the perfect lattice. These results indicate that Co-antistructure atoms and Co-vacancies are formed in CoTi as constitutional defects in accord with the model proposed by Bradley and Taylor.

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1. Introduction

The intermetallic compound, CoTi, is expected as a structural material at high temperature, because it maintains CsCl (i.e. B2)-type ordered structure up to the melting point of about 1600 K and exhibits positive temperature-dependence of yield strength; the yield strength increased from ambient temperature with increasing temperature [1].

The CoTi phase has a wide composition range from 49 to 55 at.% Co, extending across the stoichiometric composition [2], and hence constitutional defects have to be naturally introduced at non-stoichiometric compositions. Aoki et al. [3] have made magnetic studies on CoTi and found an appreciable increase in magnetic susceptibility at low temperature for Co-rich CoTi. This result suggests that the constituent Co and Ti atoms occupy their own correct sites, \( \alpha \)-sites and \( \beta \)-sites, respectively, and then the excess Co atoms over the stoichiometric composition occupy the \( \beta \)-sites, resulting in the Co-antistructure atoms, and constitutional vacancies are not formed. On the other hand, Takasugi and Izumi [4] have measured the lattice parameter, the density and the long-range-order parameter of Co-rich CoTi phase and drawn the same conclusion as Aoki et al. [3] However, the defect structure in Ti-rich CoTi has never been revealed and needs to be investigated in order to thoroughly understand CoTi. Furthermore, it should be noted that information on vacancy is not sufficiently obtained in the previous works. The magnetic and the long-range-ordering measurements adopted by Aoki et al. [3] and Takasugi and Izumi [4], respectively, are sensitive to Co-antistructure atoms, but cannot detect vacancies. Because the vacancy detection limit of the combination of XRD and density measurements performed in the study of Takasugi and Izumi [4] is of the order of \( 10^{-3} \) in atomic fraction at the best [5], even if there are vacancies of...
the fraction less than $10^{-4}$, which are sufficient to give great influence on the atomic diffusion and mechanical properties, it could not be detected in the previous works.

The positron lifetime spectroscopy is a powerful technique for sensitively detecting vacancies in alloys [6–11]. Its detection limit is of the order of $10^{-6}$ in atomic fraction, which is three orders of magnitude lower than that of combination of the XRD and density measurements [5].

Our research group has recently applied the positron lifetime spectroscopy to the study of defect structure in the intermetallic compounds NiAl [12] and CoAl [13] which have the same ordered structure as CoTi, and found out that numerous vacancies of the fraction more than $10^{-4}$ exist in Ni-rich NiAl and Co-rich CoAl in practice, where no constitutional vacancies are reported to be formed on the basis of the results of XRD and density measurements [14–16]. It is therefore worthwhile performing the positron lifetime study on CoTi, although the defect structure has been investigated by means of the XRD and density measurements. In this work, we have measured the positron lifetimes in Co-rich and Ti-rich CoTi water-quenched or furnace-cooled from $1323 \, \text{K}$ in order to reveal the defect structure in detail.

2. Experimental procedure

Five ingots were prepared by repeated arcmelting of pure cobalt (99.92%) and titanium (99.88%) in high purity argon gas atmosphere. They were annealed for 259.2 ks at 1323 K in argon atmosphere for homogenization and then cooled in a furnace. The alloy samples were cut into $10 \times 10 \times 1.3 \, \text{mm}^3$ plates with an electrodischarge machine and electrolytically polished using a solution of sulfuric acid and methyl alcohol. Some of the plates were annealed for 1.8 ks at 1323 K in argon gas atmosphere and then quenched in iced-water. After each heat treatment, the positron lifetime measurement was made at room temperature using a fast–fast timing coincidence system with a time resolution (FWHM) of 190 ps. A 30 $\mu$Ci positron source of $^{22}\text{Na}$ was sandwiched between two identical sample plates. The source contribution and the resolution functions were evaluated by using the code RESOLUTION [17]. The lifetime spectra were analyzed using the POSITRONFIT EXTENDED program [18,19].

3. Results and discussion

Fig. 1 shows the composition dependence of positron mean lifetime in water-quenched and furnace-cooled CoTi. The positron mean lifetime in water-quenched CoTi is in the range of 139–146 ps, and there is not appreciable difference in positron mean lifetime between Co-rich and Ti-rich CoTi. The first-principle calculation with the DV-Xα method by our research group [20] shows that the positron lifetime in the perfect lattice of CoTi with the CsCl-type ordered structure is 117 ps. As shown in Fig. 1, all the positron mean lifetimes measured for the water-quenched specimens with various compositions are at least 22 ps longer than the calculated positron lifetime in the perfect lattice [20].

$\chi^2 q^{-1}$ is proportional to the square of the difference between the experimentally obtained spectrum and the fitted decaying function of one lifetime component, and its magnitude represents the goodness of the fit [17–19]. If all the positrons are annihilated on only one kind of sites in the specimen, the $\chi^2 q^{-1}$ must be close to unity. On the other hand, if the positrons are annihilated on two or more kinds of sites, which have different positron lifetimes, the $\chi^2 q^{-1}$ must be significantly larger than unity. For all the specimens, the variance of the fit $\chi^2 q^{-1}$ for Co$_{52}$Ti$_{48}$, Co$_{50.5}$Ti$_{49.5}$ and Co$_{50.3}$Ti$_{49.7}$ is very close to unity. These results clearly show that the vacancy...
concentration in the furnace-cooled Co-rich CoTi is less than the order of $10^{-6}$, and Co-antistructure atoms are formed to compensate the deviations from the stoichiometry. The longer positron lifetimes obtained for the water-quenched Co-rich CoTi (see Fig. 1) are not owing to constitutional vacancies, but to quenched-in thermal-vacancies. This conclusion is consistent with both the result of magnetic measurement by Aoki et al. [3] and the result of the XRD and density measurements by Takasugi and Izumi [4].

On the other hand, the positron lifetime of furnace-cooled Co$_{49.9}$Ti$_{50.1}$ is 34 ps longer than the calculated positron lifetime in the perfect lattice [20] and does not have large difference from that of the water-quenched same specimen. Its variance of the fit $\chi^2$ is close to unity, which shows that the positron saturation trapping by vacancies occurs even in the furnace-cooled specimen, as in the water-quenched specimen. This means that many vacancies of more than $10^{-4}$ atomic fraction exist at room temperature and that vacancies are formed on the $\alpha$-sites to compensate the deviation from the stoichiometry.

The positron mean lifetime of furnace-cooled Co$_{49.9}$Ti$_{50.1}$ is about 14 ps shorter than that of quenched specimen, but is about 10 ps longer than the calculated positron lifetime in the perfect lattice [20]. The variance of the fit $\chi^2$ for the furnace-cooled Co$_{49.9}$Ti$_{50.1}$ is larger than 1.6 indicating that the measured spectrum consists of two components. From these results, it follows that some positrons are trapped in vacancies and annihilate there, but the other positrons annihilate in the matrix. Because the composition of the specimen is nearly equal to the stoichiometry, slight microsegregation of 0.1 at.\% easily produces two regions of Co-rich and Ti-rich concentrations across the stoichiometry. The positrons injected into the slightly Ti-rich composition region, where constitutional vacancies exist, must be mostly trapped in vacancies and give the longer lifetime, must be long, as shown in furnace-cooled Co$_{49.7}$Ti$_{50.3}$. On the other hand, positrons injected into the slightly Co-rich region, where Co-antistructure atoms are formed as constitutional defects, annihilate in the matrix and have the shorter lifetime, as shown in furnace-cooled Co$_{49.7}$Ti$_{48.5}$ and Co$_{50.5}$Ti$_{49.5}$. As a result, the mean positron lifetime measured for furnace-cooled Co$_{49.9}$Ti$_{50.1}$ must take a middle value between the furnace-cooled Co$_{50.5}$Ti$_{49.5}$ and Co$_{49.7}$Ti$_{50.3}$, and its $\chi^2$ is larger than those for the furnace-cooled Co$_{50.3}$Ti$_{49.5}$ and Co$_{49.7}$Ti$_{50.3}$.

Bradley and Taylor [14] have carried out the XRD and density measurements of NiAl and proposed a model of defect structure in CsCl-type intermetallic compound, AB, which is called the BT model; at the stoichiometric composition all the cube centers (\(\alpha\)-sites) and the cube corners (\(\beta\)-sites) are filled with A and B atoms, respectively; on the A-rich side of the stoichiometry, the excess A atoms are substituted on the \(\beta\)-sites, resulting in the antistructure atoms; on the B-rich side, instead of the substitution of the B atoms on \(\alpha\)-sites, a substantial number of vacancies on the \(\alpha\)-sites are created. Before now, on the basis of XRD and density measurements, many researchers have reported that, besides NiAl, several CsCl-type intermetallic compounds, for example CoAl [15,16] and CoGa [21,22], obey the BT model.

Our research group [12,13] have recently applied the positron annihilation technique to study on constitutional vacancies in NiAl and CoAl. In the works [12,13], it has been found that the positron saturation trapping, which indicates the existence of vacancies of more than $10^{-3}$ atomic fraction, takes place even in furnace-cooled Ni-rich NiAl [12] and furnace-cooled Co-rich CoAl [13] where only antistructure atoms and no constitutional vacancies have been expected to exist, according to the BT model [14]. These positron annihilation studies revealed that vacancies are formed even on the \(\beta\)-sites in Ni-rich NiAl and Co-rich CoAl, which had been considered to obey the BT model on the basis of XRD and density measurements [14–16].

Differing from the cases mentioned above, no indication of the existence of vacancies was obtained in Co-rich CoTi in this work in spite of the high sensitivity of positron annihilation technique. It follows that only antistructure atoms are formed on the $\alpha$-sites as constitutional defects in Co-rich CoTi. On the other hand, the result of this work shows the existence of constitutional vacancies in Ti-rich CoTi. The defect structure in CoTi well corresponds to what the BT model describes, differing from NiAl and CoAl.

4. Conclusion

The positron lifetimes in Co$_{100-x}$Ti$_x$ (\(x = 48–50.3\)) were measured and the following results were obtained:

1. The saturation trapping of positrons by quenched-in vacancies occurs in the water-quenched Co$_{52}$Ti$_{48}$ and Co$_{50.5}$Ti$_{49.5}$, but there is no indication of existence of vacancies in furnace-cooled Co$_{52}$Ti$_{48}$ and Co$_{50.5}$Ti$_{49.5}$.

2. The saturation trapping of positrons by vacancies was observed not only for water-quenched Co$_{49.7}$Ti$_{50.3}$ but also for furnace-cooled Co$_{49.7}$Ti$_{50.3}$.

These results show that Co-antistructure atoms and $\alpha$-vacancies are formed in CoTi to compensate the deviation from the stoichiometry in accord with the BT model.

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