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Effects of Zr and Nb on d electrons in NiAl alloy studied by coincidence positron annihilation spectroscopy

Wen Deng [a,*], J.T. Guo [b], R.S. Brusa [c], G.P. Karwasz [c], A. Zecca [c]

[a] *Physics Department, Guangxi University, 530004 Nanning, Guangxi Province, PR China*
[b] *Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China*
[c] *Istituto Nationale per la Fisica della Materia, Universita' di Trento, Dipartimento di Fisica, 38050 Povo, Italy*

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Abstract

The behavior of d electrons in pure Ni, Zr, Nb metals and NiAl-based alloys (NiAl, $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$) has been studied by two-detector coincidence system of Doppler broadening of positron annihilation radiation. It has been found that the probability of positron annihilation with 3d electrons in binary NiAl alloy is relatively low due to the Ni 3d–Al 3p interactions. The additions of Zr or Nb atoms to NiAl alloy lead to the enhancement of d–d interactions and thus the d electron signal in the spectrum. The d electron signal in the spectrum of $Ni_{50}Al_{48}Nb_2$ alloy is higher than that of $Ni_{50}Al_{48}Zr_2$ alloy, that is, the Nb addition is more effective in enhancing the d–d interactions in NiAl alloy compared with the Zr addition.

Keywords: Coincidence positron annihilation spectroscopy; d electrons; NiAl alloy

1. Introduction

The B2 compound NiAl has received considerable attention in recent years due to its attractive physical properties for aerospace application at high temperatures. These properties include high melting temperature (1638 °C), low density (5.86 g cm^{-3}), high modulus, high thermal conductivity and excellent environmental resistance. The two principal limitations of unalloyed NiAl are poor ductility at room temperature and inadequate strength at elevated temperature [1].

Considerable effort has been made in understanding these properties of binary NiAl and in improving the strength and ductility of NiAl alloy. The room temperature (RT) tensile ductility of polycrystalline binary NiAl can range from 0% to 2%, depending upon stoichiometry, grain size, and impurity content [2,3]. Among the problems actively studied in NiAl alloy, the role of the additions of ternary elements on the mechanical behavior of these compounds is of growing interest. Since their mechanical properties depend crucially on microalloying additions, this provides an important tool for controllable alloy design. Particularly important are the attempts to improve creep resistance, solid solution hardening and the room temperature ductility of NiAl due to ternary additions. Microalloying with Cr, Co, Fe and Mn has been shown to decrease the ordering energy of NiAl alloy and improve the room temperature tensile ductility of the alloys [4]. The large increase in the tensile ductility by the introduction of ternary elements provides the possibility of producing ductile NiAl alloys. For example, room temperature ductility as high as 6% has been produced in NiAl single crystals containing less than 0.5% (atomic) of Fe, Ga, or Mo [4].

The electronic structure of NiAl alloy plays an important role in the material's properties and it has been calculated using a variety of computational methods [5–10]. However, experimental investigations of the electronic structure of NiAl alloy and the role of ternary additions on the structural and electronic properties are very limited.

* Corresponding author. Tel.: +86 771 3236667 (Lab.); fax: +86 771 3237386.
E-mail address: wdeng@gxu.edu.cn (W. Deng).

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Positron annihilation techniques (lifetime and Doppler broadening) present some unique advantages and are well established to detect open volume and negatively charged centers in solids [11]. Doppler broadening spectrum presents information about the one-momentum distribution of the annihilating positron–electron pair. In particular, high resolution two-detector coincidence system of Doppler broadening of positron annihilation radiation allows reducing the background of the spectrum and pointing out the contribution of positron annihilation with core electrons that are fingerprints of the atoms [12–14].

In the present work, Doppler broadening spectra of single crystals of Si, Al, Ni, polycrystals of Zr and Nb, and NiAl, $Ni_{50}Al_{48}Zr_2$, and $Ni_{50}Al_{48}Nb_2$ alloys have been measured by a two-detector coincidence system. Current experiments are intended to study the high-momentum electrons in NiAl, $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$ as well as the effects of Zr or Nb on d electrons in NiAl alloy.

2. Experimental

The alloys with different chemical compositions $Ni_{50}Al_{50}$ (or NiAl), $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$ were prepared by non-consumable tungsten electrode arc melting in Ar atmosphere, using pure Ni, Al, Zr and Nb. The purity of raw materials used in this study was 99.95 wt.% Ni, 99.98 wt.% Al, 99.96 wt.% Zr, and 99.98 wt.% Nb. All button ingots were repeatedly melted (three times) by turning over to obtain chemical homogeneity. Since the weight losses after arc melting were less than 0.01wt.%, the alloys used in this study are expressed as the nominal chemical composition. The alloys were homogenized 12 h at 1000 °C and then cooled down to room temperature in a vacuum furnace. All samples were cut into pieces with a thickness of 1 mm (two pieces for each sample). The surfaces of the samples were polished. After cutting and polishing, all of the samples were annealed again at different temperatures (the NiAl, $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$ alloys at 900 °C, the Si, Ni, Zr and Nb samples at 1000 °C, and the Al metal at 500 °C) for 2 h in a vacuum furnace with a pressure of about 5×10^{-7} mbar and then were cooled down to room temperature in the furnace.

Doppler broadening spectra were measured using a two-detector coincidence system. The main detector was a high purity Ge (HPGe) detector with a resolution of 1.3 keV at 511 keV. The auxiliary detector supplying the coincidence signal was a NaI(Tl) scintillator. The NaI(Tl) detector was placed in collinear geometry with the Ge detector in order to detect the two 511 keV γ rays from the e^+–e^- annihilation pair. With this setup, we get a peak to background ratio of about 1.5×10^4 on the high-energy side of the peak. About 10^7 counts had been accumulated in the peak of each spectrum. The Doppler broadening spectra of single crystals of Si, Al, and Ni, polycrystals of Zr and Nb, and NiAl, $Ni_{50}Al_{48}Zr_2$, and $Ni_{50}Al_{48}Nb_2$ alloys have been measured.

Doppler broadening measurements were carried out by sandwiching a 0.6 MBq ^{22}Na radioactive source, supported by two kapton films, between two pieces of the same sample.

3. Results and discussion

Lifetime measurements have been performed in annealed single crystals of Si, Al, and Ni and polycrystals of Zr and Nb and the results have shown that these samples are defect-free, as seen by positron.

The 511 keV annihilation line is Doppler-broadened ($511 \pm \Delta E$) due to the longitudinal momentum p_L component of the annihilating positron–electron pair. In a Doppler experiment the longitudinal momentum component p_L in the direction of the detector is measured. The momentum component p_L is correlated to the Doppler shift ΔE by the formula $p_L = 2\Delta E / c$, where c is the light velocity. Only the high-energy side of the annihilation peak is analyzed and shown because in the low-energy side the effects of Compton scattering, incomplete charge collection, and 3-γ positronium decay cannot be overcome by the coincidence technique.

To observe the differences among different spectra, we have constructed ratio curves, dividing every spectrum by the spectrum of a reference specimen [15,16]. As a reference specimen Cz–Si p(100) was chosen. Before the ratio is taken, all of the spectra have been normalized to a total area of 10^6 from 511 to 530 keV (p_L from 0 to $74.3 \times 10^{-3}\ m_0c$) and a smoothing routine on 9 points was applied.

Fig. 1 shows the ratio curves for: (a) pure Al, Ni, Zr, and Nb metals; (b) Al, Ni, and NiAl alloy; and (c) NiAl, $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$ alloys.

The detailed shape of the high-momentum part of the Doppler spectrum depends on the different contributions coming from the positron annihilation with the electrons of each shell of the atom. Comparing the Al, Ni, Zr, and Nb ratio curves in Fig. 1(a), it can be found that the Ni ratio curve shows a very high peak at about $15 \times 10^{-3}\ m_0c$ and it is due to positron annihilation with 3d electrons of Ni atom according to the calculation results of positron–electron momentum distribution on Ni metal [17]. The Zr and Nb ratio curves show a peak at about $11.2 \times 10^{-3}\ m_0c$ which is due to positron annihilation with 4d electrons according to the calculation results [17]. The Nb ratio curve is higher than the Zr ratio curve; this may be correlated with the increase in the number of 4d electrons of the Zr and Nb elements, as it is known that Zr and Nb atoms have 2 and 4 electrons in the 4d orbital, respectively. The Al ratio curve is almost flat, for the Al atoms without d electron.

For comparison and discussion, an artificial ratio curve, NiAl(Cal) ratio curve, was constructed as the sum of 50% of the Ni and 50% of the Al ratio curves. The NiAl(Cal) ratio curve was also shown in Fig. 1(b).

We start from the assumptions that the bonding nature in a binary NiAl alloy is metallic bond and the injected positrons are homogenized distribution in the alloy. These assumptions lead us to conclude that the probability of positrons located at Ni sites will be 50%, which is the same as that located at Al sites, and the NiAl ratio curve should be similar to the NiAl(Cal) ratio curve. However, our experimental result shows that the binary NiAl alloy

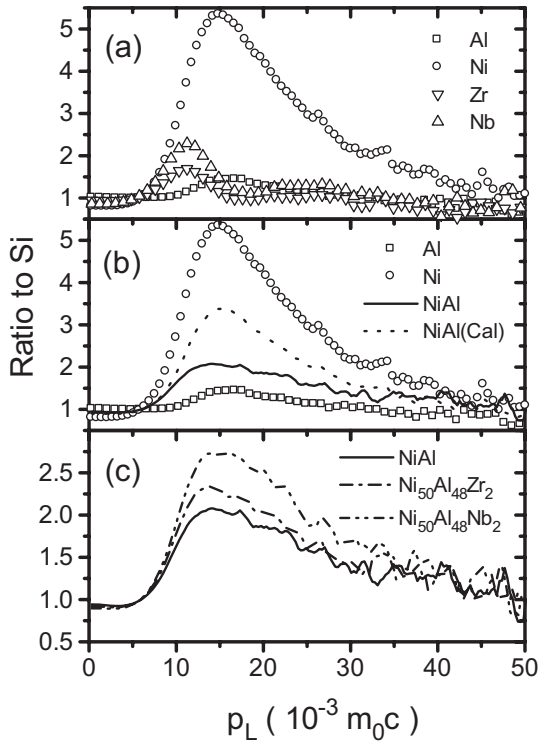

Fig. 1. The ratio curves for the samples; the reference sample is Si. (a) The Al, Ni, Zr, and Nb ratio curves. (b) The Al, Ni and NiAl ratio curves. (c) The NiAl, $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$ ratio curves.

ratio curve is obviously lower than the NiAl(Cal) ratio curve as shown in Fig. 1(b), that is, the probability of positron annihilation with 3d electrons of Ni atoms is relatively low in the binary NiAl alloy. Our experimental result is in disagreement with our previous assumptions. The evidence we obtained implies that some of the 3d electrons of Ni atoms and 3p electrons of Al atoms in NiAl alloy are localized to form strong covalent bonds due to strong Ni d–Al p hybridization along <111> directions between nearest neighbor Ni–Al atom pairs, thus decreasing the probability of positron annihilation with 3d electrons of Ni atoms. Our result is in agreement with the calculations of electronic structure of undoped NiAl [10].

Comparing the NiAl, $Ni_{50}Al_{48}Zr_2$ and $Ni_{50}Al_{48}Nb_2$ ratio curves in Fig. 1(c), it can be found that the NiAl ratio curve is the lowest curve; the additions of 2 at.% Zr or 2 at.% Nb atoms into NiAl alloy lead to the increase of d electrons signal in the spectrum and the $Ni_{50}Al_{48}Nb_2$ ratio curve is higher than that the $Ni_{50}Al_{48}Zr_2$ ratio curve. The above findings can be interpreted as follows: the addition of small amount of Zr or Nb atoms to NiAl alloy may weaken the tendency of the nearest neighbor Ni–Al atom pairs to form strong Ni d–Al p covalent bonds and enhance the d–d interactions, thus increasing the probability of positron annihilation with d electrons. The fact that d electrons signal in the spectrum of $Ni_{50}Al_{48}Nb_2$ alloy is higher than that of $Ni_{50}Al_{48}Zr_2$ alloy can be correlated with the increase in the number of 4d electrons, for Zr and Nb with 2 and 4 electrons in the 4d orbital, respectively.

The effects of ternary additions on the mechanical properties of intermetallics are rather complicated and include the variation of phase equilibrium, alloy microstructure and solid solution hardening. In addition, a general understanding of the role of ternary additions in strongly ordered B2 intermetallics is complicated by so-called “stoichiometric effects”. However, the electronic factor appears to be one of the crucial factors to control the ductility of aluminide intermetallic compounds. Calculations of electronic structure of undoped NiAl has shown that the 3d electrons of Ni atoms and 3p electrons of Al atoms are localized to form strong covalent bonds due to strong Ni d–Al p hybridization along <111> directions between nearest neighbor Ni–Al atom pairs [10] and experimental observations have shown a weak ionic repulsion between second-nearest neighbor atoms along <100> directions [18]. The strong atomic bond along <111> and the weak bond along <100> are suggested to cause this compound to be brittle. Therefore, it could be expected to obtain plasticity enhancement by weakening the p–d interactions and enhancing d–d interactions. Our experimental results indicate that the addition of Zr or Nb elements to NiAl will enhance d–d interactions and weaken the p–d interactions. This implies that both Zr and Nb are beneficial elements in improving the ductility of the NiAl alloy. Furthermore, the Nb addition is more effective in enhancing the d–d interactions in NiAl alloy as compared with the Zr addition.

4. Conclusions

(1) The probability of positron annihilation with 3d electrons of Ni atoms is relatively low in binary NiAl alloy. This implies that some of the 3d electrons of Ni atoms and 3p electrons of Al atoms in NiAl alloy are localized to form strong covalent bonds, thus decreasing the probability of positron annihilation with 3d electrons of Ni atoms.

(2) The addition of small amount of Zr or Nb atoms to NiAl alloy will weaken the tendency of the nearest neighbor Ni–Al atom pairs to form strong Ni d–Al p covalent bonds and enhance the d–d interactions, thus increasing the probability of positron annihilation with d electrons.

(3) The d electrons signal in the spectrum of $Ni_{50}Al_{48}Nb_2$ alloy is higher than that of $Ni_{50}Al_{48}Zr_2$ alloy, that is, the Nb addition is more effective in enhancing the d–d interactions in NiAl alloy compared with the Zr addition.

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