Local structure of TiNiCu(Hf) shape memory alloys: XAFS data analysis

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Abstract. The extended X-ray absorption fine structure spectroscopy (EXAFS) was applied to investigate the local structure peculiarities of TiNi-based shape memory alloys $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ and $\text{Ti}_{39.2}\text{Ni}_{24.8}\text{Cu}_{25}\text{Hf}_{11}$. Our experimental results demonstrate that the most significant changes in local crystalline structure under martensitic transformation arise in the Ni–Cu sublattice. The static disordering of the Ti coordination shell is more significant for Ni than for Cu environment. Such a conclusion is consistent with the refined values of atomic ν -shifts from the planar center of symmetry in (010) layers which are greater for Ni atoms than for Cu.

1. Introduction

TiNi-based alloys are some of the most widespread shape memory alloys (SMA). While being heated they are able to fully restore their pre-deformation shape as a result of reverse martensitic transformation (MT). Under such a behavior these alloys demonstrate considerable mechanical force. Due to their unique properties SMAs are of great interest to find the unusual ways in development of various important technical applications, such as electronics, power and machine engineering, instrument-making, space industry, medicine etc. [1–4]. However, the demand of micro- and nanodevices construction drives production of new types of SMAs as well as their further exploration on different scales.

Direct and reverse MTs occur in their own temperature ranges, therefore the material demonstrates hysteretic properties under phase transformation. Characteristic temperatures of MT depend on both the alloy grade and its chemical composition. The slight composition changes (intentional or as the result of flaw) lead to the shift of these parameters. The transformation properties undoubtedly have the connection with the fine effects taking place in the local crystalline structure upon cooling and heating the alloys. Therefore, SMA are also important for the under-

standing of chemical bonding and phase transitions in the intermetallics. In present work we made an attempt to investigate the peculiarities of Ni and Cu local environment in ternary $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ and quaternary $\text{Ti}_{39.2}\text{Ni}_{24.8}\text{Cu}_{25}\text{Hf}_{11}$ SMAs by means of extended X-ray absorption fine structure spectroscopy (EXAFS). Both alloys crystallize in cubic B2 structure in austenitic phase and orthorhombic B19 in martensitic phase [3, 5]. Such properties as the interatomic distances, local disordering factors, atomic shifts to define the character of distortion in unit cell etc. were examined.

2. Experimental

In initial state the samples are thin bands obtained by components melt extrusion from the quartz crucible through the thin nozzle on the surface of rotating copper disk, where the sample's cooling took place with the rate of 10^6 K/sec. Then samples were crystallized by annealing in the air at $\sim 500^\circ\text{C}$ for 4 min.

The EXAFS spectra were collected in transmission mode above K -Ni (8333 eV) and K -Cu (8979 eV) absorption edges in the temperature ranges covering martensitic and austenitic phase transformations. Spectra of quaternary $\text{Ti}_{39.2}\text{Ni}_{24.8}\text{Cu}_{25}\text{Hf}_{11}$ alloy were collected at beamline E4 of synchrotron center HASYLAB, DESY (Germany, Hamburg), spectra of ternary alloy $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ – at experimental station “Structural Materials Science” of KCSR and NT (Russia, Moscow) in transmission mode. Series of measures were carried out upon consistent sample heating and cooling through the temperature regions of direct and reverse MT. The samples were fixed in heating chamber and did not move during all the time of measurement. The processing of spectra was performed using VIPER [6] software with standard procedure of EXAFS-oscillations function $\chi(k)$ deconvolution and Fourier-analysis. Magnitudes and phases of back scattering were computed using the FEFF-8.20 code [7] within a model of martensitic phase crystalline structure, $Pmmb$ symmetry group.

Additional X-ray diffraction (XRD) was carried out at STM station at KCSR and NT in transmission geometry using Debye-Scherrer method to examine the phase composition of ternary alloy $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$.

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3. Results and discussion

XRD results demonstrate that $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy really has B2 type structure in austenitic phase and B19 in martensitic phase. No direct signs of frequently noted monoclinic B19' structure [8, 9] appear in this alloy. Up to $\sim 80\%$ of material undergo the phase transformation which occur in rather narrow temperature range $50\text{--}55^\circ\text{C}$. This result concerns only the long-range order of crystal-line structure.

Qualitative analysis of spectra was performed using wavelet transform of EXAFS oscillation functions $\chi(k)$ with IGOR PRO (WaveMetrics, Lake Oswego, OR, USA). Results of wavelet transform for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy K -Ni spectrum are shown in Fig. 1. They demonstrate three clear resolved maxima, *i.e.* three scattering acts are registered on different elements situated in approximately same distances from the absorbing atom. Thus, the closest local environment of Ni and Cu atoms consists of 3 atom types.

Ni and Cu atoms occupy equivalent positions in lattice. In ternary alloy $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ the closest coordination shell contain 8 Ti atoms and 6 atoms which can be Ni or Cu (in our study we implied there were 3 Ni and 3 Cu atoms in these shells). Parameters of Ni and Cu atoms local environment in ternary alloy were investigated in temperature range $30\text{--}70^\circ\text{C}$. EXAFS-functions of spectra above K -Ni edge at the temperature of martensitic phase 30°C , austenitic phase 70°C , and in the region of phase transition at 58°C are shown in Fig. 2. There is a notable difference in the region $4.2\text{--}4.8\text{ \AA}^{-1}$, where two oscillations maxima are situated. Amplitudes ratio of these maxima changes with temperature, and besides, their shape at 58°C is not the same under heating and cooling. Modules of Fourier transforms (FT) of EXAFS-functions above K -Ni absorption edge at various temperatures are shown in Fig. 3. The first large peak corresponds to the first Ti shell and doesn't change much with temperature. Whereas several smaller peaks in the region $3.5\text{--}5\text{ \AA}$ beyond the first one change significantly and their shape depends on circumstances the spectra was measured under. To support

Fig. 1. Wavelet transforms of K -Ni-EXAFS-functions for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy at 30°C . Wave vector k , $\text{\AA}^{-1}$ is set along the horizontal axis; distance R , $\text{\AA}$ is set along the vertical axis.

Fig. 2. K -Ni-EXAFS-functions for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy at various temperatures.

current observation the back Fourier transform (BFT) of FT region is presented in Fig. 4. It is clearly seen that in case of sample heating at 58°C the oscillation shape is close to one at 30°C . On the contrary, under cooling it is much similar with the shape at 70°C , hence we can consider the change of EXAFS line shape hysteretic. Discussed FT region beyond the first Ti shell peak corresponds to the variety of shells containing Ni and Cu atoms and also multiscattering path Ni–Ti–Ti. However, magnitude of the latter is rather low, therefore we suppose that the general reversible changes in local crystalline structure upon MT take place in the sublattice of Ni and Cu atoms.

Fig. 3. Fourier transforms of K -Ni-EXAFS-functions for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy at various temperatures.

Fig. 4. Back Fourier transforms of *K*-Ni-EXAFS-functions FT region beyond Ti-shell peak for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy at various temperatures.

EXAFS-functions fitting reveal that the interatomic distances Ni–Ti and Cu–Ti don't change much with temperature, but the average degree of their local disordering expressed by the Debye-Waller factor σ^2 increases. Besides, Ti atoms in the Ni local environment are characterized by considerably higher static disordering than in the Cu environment. Situation with the Ni–Ni, Ni–Cu and Cu–Cu distances is more complicated. Their average values at room temperature are $R_{\text{Ni–Ni}} \sim 2.80$ Å, $R_{\text{Ni–Cu}} \sim 3.00$ Å, $R_{\text{Cu–Cu}} \sim 3.05$ Å and reversibly increase by 0.04–0.05 Å upon heating and cooling. The character of this change is approximately the same if we consider Ni or Cu local environment. Disorder of these distances also increases with temperature and within the error of technique employed might be considered the similar for heating and cooling. It is notable, that changes upon reversible MT in short-range order of our SMA crystalline

Fig. 5. Modules of *K*-Ni and *K*-Cu EXAFS-functions Fourier transforms for the $\text{Ti}_{39.2}\text{Ni}_{24.8}\text{Cu}_{25}\text{Hf}_{11}$ alloy at temperature 5 K.

structure occur gradually in compare with drastic changes in long-range order examined by the X-ray diffraction.

Parameters of Ni and Cu atoms local environment in quaternary alloy $\text{Ti}_{39.2}\text{Ni}_{24.8}\text{Cu}_{25}\text{Hf}_{11}$ were also investigated in a broad temperature range 5–300 K, covering the direct and reverse MTs occurring at 168–200 K. However, unlike the case of the ternary alloy, analysis of heating and cooling spectra didn't yield any signs of hysteretic effects near the transformation temperature. Only monotonous increase of EXAFS-oscillations magnitude with temperature is observed. The spectral compositions of EXAFS-oscillations are notably different around Ni and Cu atoms (Fig. 5) but do not change considerably with temperature. The lack of visible hysteretic effects in EXAFS-spectra can be caused either by small amount of material undergoing MT or by insufficiently precise temperature following over MT region during the experiment.

From the temperature dependences of disordering factors σ^2 for the first titanium coordination shells around Ni and Cu atoms (Fig. 6) we obtained the characteristic Einstein temperatures for the average distances Ni–Ti ($\Theta_E \sim 303$ K) and Cu–Ti ($\Theta_E \sim 300$ K). The Θ_E values as well as line shapes in Fig. 6 are almost similar, hence Ni–Ti and Cu–Ti interatomic bonds are approximately of the same rigidity. Whereas, the curve for the Ni–Ti bond lies above the one for the Cu–Ti bond, and therefore the static disordering of the first titanium shell is more significant for Ni than for Cu environment. This effect is the same as in the ternary alloy.

The values of Cu–Ti and Ni–Ti distances allowed us to refine the positions of Ni and Cu atoms in unit cell of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy. The first Ti shell around Ni or Cu atoms in martensitic phase, space group *Pnmb*, is divided into 3 “subshells” containing 2, 4 and 2 Ti atoms respectively. The first 2 Ti and the third 2 Ti atoms lie in (010) layer while the second 4 Ti atoms lie in orthogonal (001) layer. In paper [5] authors reveal that the structure differs from the standard B19 type and demonstrates a ν -shift of Ni and Cu atoms from the planar centro-symmetric position along *c*-axis inside the (010) layers similar to that observed in the B19' monoclinic martensite structure. Our

Fig. 6. Temperature dependences of Ni–Ti and Cu–Ti interatomic distances local disordering factors in the $\text{Ti}_{39.2}\text{Ni}_{24.8}\text{Cu}_{25}\text{Hf}_{11}$ alloy.

Fig. 7. Schematic of the atomic shifts in (010) layers in $Pmm\bar{b}$ space group for the $Ti_{50}Ni_{25}Cu_{25}$ alloy.

examinations also demonstrate this shift, moreover, for Ni and Cu atoms it is not similar. The distances between absorbing atom and Ti atoms in these 3 subshells obtained at room temperature turned out to be $R_{1Ni-2Ti} \sim 2.51$ Å, $R_{2Ni-4Ti} \sim 2.63$ Å, $R_{3Ni-2Ti} \sim 2.86$ Å around Ni atom and $R_{1Cu-2Ti} \sim 2.61$ Å, $R_{2Cu-4Ti} \sim 2.61$ Å, $R_{3Cu-2Ti} \sim 2.75$ Å around Cu atom (the error of technique is ~ 0.02 Å). ν -shift determined from these values is -1.9% for Cu atom and -4.6% for Ni atom in coordinates of conventional unit cell (Fig. 7), while in [5] the “universal” shift for both types of atoms is -2.7% . The difference between values is obtained due to the EXAFS’s selectivity to the type of chemical element in contrast to XRD employed in [5]. Such an inhomogeneity of Ni and Cu atomic shifts in (010) layers is consistent with our conclusion that Ti atoms are more disordered in Ni local environment.

4. Conclusion

Results of EXAFS spectroscopy study demonstrate that the changes in short-range order of investigated TiNi-based SMAs crystalline structure, unlike the long-range order, occur gradually and can be modeled using B19 structure or $Pmm\bar{b}$ symmetry group both in austenitic and martensitic phases. Hysteretic discrepancies in X-ray absorption spectra of ternary alloy $Ti_{50}Ni_{25}Cu_{25}$ generally result from the changes in coordination shells of Ni and Cu atoms around

the absorbing atom. Apparently, the most significant changes in local crystalline structure under MT occur in the Ni–Cu sublattice. No hysteretic effects in the region of phase transformation were found in quaternary alloy $Ti_{39.2}Ni_{24.8}Cu_{25}Hf_{11}$. However, in both alloys average static disordering of Ti atoms in coordination shell around Cu atom is less than around Ni. This assertion is consistent with the refined values of the Ni and Cu atomic ν -shifts from the planar centro-symmetric position in the (010) layer. The value of ν -shift, which in itself is not typical for general B19 orthorhombic structure, for Ni atoms turned out to be greater than for Cu atoms. Such a distortion may drive the further local deformation and affect the parameters of the phase transition under certain conditions.

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