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Investigation on the Origin of Magnetization in Plastically Deformed $Ni_{51}Ti_{49}$ Alloy

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Abstract. The article deals with the investigation of structure and magnetic properties of plastically deformed $Ni_{51}Ti_{49}$ alloy. The magnetic hysteresis loops confirm the presence of ferromagnetic properties in the alloy. The transmission electron microscopy (TEM) detects the appearance of lenticular crystals with bending contours which indicate the large distortion of the crystal lattice. The crystal lattice curvature occurs due to the large atom displacement. As a result, icosahedral clusters with the Frank-Kasper (FK) structure can be formed. The spin-polarized density of electron states and the magnetic moments for both non-deformed (near-spherical structure) and deformed (elongated by 5% along the Z-axis) Ni_7Ti_5 (FK-12), Ni_8Ti_5 (FK-13), and $Ni_{10}Ti_6$ (FK-16) clusters are calculated for the explanation of possibility of magnetization appearance in $Ni_{51}Ti_{49}$ alloy. The calculations show the increase in the magnetic moments for the deformed clusters. The calculated spectra demonstrate the high density of electron states near the Fermi level which is a characteristic feature of ferromagnetic alloys.

Introduction

Ni-Ti is a unique material with the shape memory effect [1]. The products made from this alloy are widely used as structural elements of the apparatus and devices in mechanical engineering, aerospace, and instrumentation fields. In addition, as recent researches showed, these alloys have a fine biocompatibility with the human body tissues [2]. Therefore, they are used in medicine as the corrective devices and implants in dental, orthopedic, and cardiovascular surgery.

In previous work [3], the first mention of the occurrence of non-zero magnetization in $Ni_{51}Ti_{49}$ samples after plastic deformation or cyclic martensite transformations is observed. However, the magnetization origin has still not been investigated. In order to explain the non-zero magnetization appearance, it is necessary to identify the causes and mechanisms of the ferromagnetic phase formation in plastically deformed Ni-Ti samples. The combination of fine biocompatibility and discovered magnetic properties of this material can significantly expand the application area of Ni-Ti alloys in medicine. For example, the nanoparticles formed from this alloy can be used in cancer diagnosis [4].

In the present study, we investigated the $Ni_{51}Ti_{49}$ samples structure before and after plastic deformation by transmission electron microscopy (TEM). Based on the TEM data the clustered method was proposed for calculating the electronic phase transitions. Subsequently, the spin-polarized density of electron states and magnetic moments for both non-deformed (near-spherical structure) and deformed (elongated by 5% along the Z-axis) Ni_7Ti_5 (FK-12), Ni_8Ti_5 (FK-13), $Ni_{10}Ti_6$ (FK-16) clusters were calculated.

Methods

For the electron microscopy examination the samples of $Ni_{51}Ti_{49}$ were prepared from the deformed plates after elongation to break by mechanical and ion thinning, according to standard techniques. TEM study was performed on HT-7700 (Hitachi, Japan) at an accelerating voltage of 100 kV.

The scattered waves method (SW) [5] was used for calculation of the magnetic moments and spin-polarized density of electron states for Ni_7Ti_5 (FK-12), Ni_8Ti_5 (FK -13), and $Ni_{10}Ti_6$ (FK-16) clusters. The advantage of this method is that it does not require the condition of periodicity in the arrangement of the atoms. Therefore, it is possible to model the non-equilibrium systems and uneven distribution of the atoms, which is required to account for the strain.

In this method, the potential of molecule is divided into three regions: the atomic spheres (I), the intersectoral region (II), and the outer sphere (III). The appearance of magnetization in the clusters after plastic deformation is described on the basis of unrestricted Hartree-Fock (UHF) with the exchange-correlation potential Gunnarsson-Lundqvist [6, 7]. This potential can effectively describe the magnetic states of atoms as well as the entire cluster as a whole [8]. The calculated data obtained by solving the system of equations by UHF method, are used for construction of "Muffin-Tin" (MT) potential clusters [9]. This approach makes it possible to obtain the solution of one-electron equation for each region of molecule or cluster. The approximation of a spherical symmetry allows to separate the variables in the Schrodinger equation, and to represent the wave function of each one-electron state as the product of radial and angular parts. Using the "stitching" condition of the wave function at the border areas of section (I) - (III), the secular equation for calculation of the spectrum of molecule or cluster can be written as follows [9]:

$$\det \left\| \left[t_l^p \right]^{-1} \delta_{ll'} \delta_{mm'} - \sum_{\substack{q \neq p \\ l'm'}} G_{lm,l'm'}^{pq} \left(\varepsilon_i \right) \right\| = 0. \qquad (1)$$

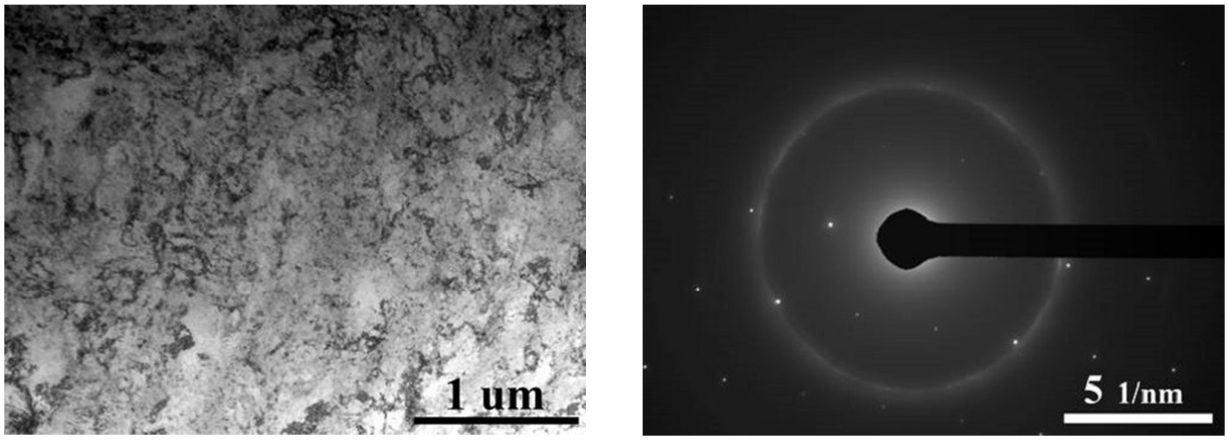
The notations in equation (1) are the same as in [8]. The zeros of determinant (1) give the values of one-electron energy levels of the cluster. It should be noted that the efficiency of this approach is illustrated by example of the study of magnetic properties of the clusters with the Frank-Kasper structure in iron and manganese [10].

Results and discussions

The results of TEM studies showed the appearance of lenticular crystals in $Ni_{51}Ti_{49}$ samples after plastic deformation (Fig. 2*a*). The lenticular crystals contain the bending contours with a high stress concentration and indicate a large distortion of the crystal lattice, which occurs due to the displacement of the atoms. Figs. 1 and 2 show the TEM images (*a*) and the electron diffraction (*b*) obtained before (Fig. 1) and after (Fig. 2) plastic deformation of $Ni_{51}Ti_{49}$ alloy samples. The deciphering of the electron diffraction patterns showed that the region with a lenticular crystal contained the fivefold symmetry (Fig. 2*b*) which is typical for icosahedral clusters with the Frank-Kasper structure. The lines indicate the exact orientation of reflexes for the symmetry axis of fifth-order. However, some reflections on the diffraction pattern are shifted, since the material is highly deformed and the crystal lattice is distorted.

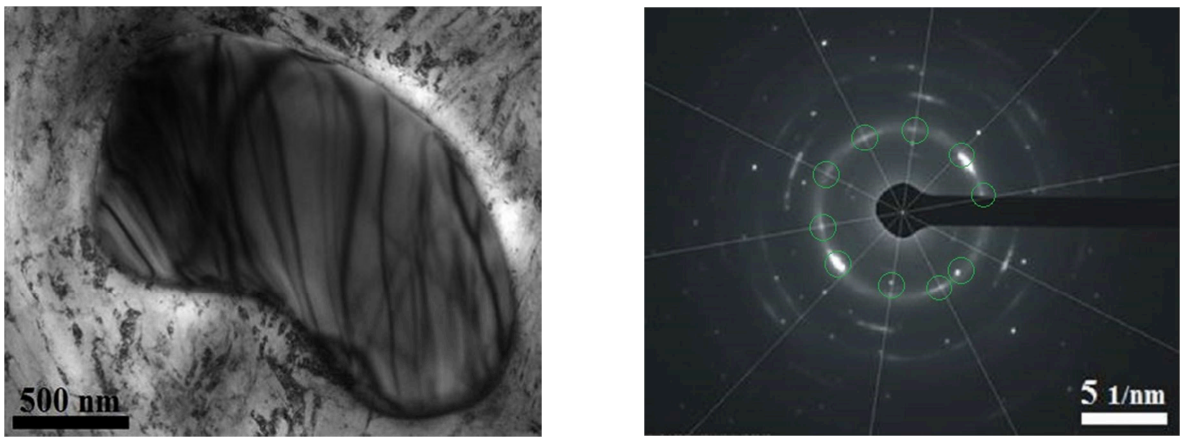
It is known that Ni-Ti alloy can exist in two phases: the high-temperature austenite phase with a BCC (body-centered cubic) lattice and the low-temperature martensite phase with a HCP (hexagonal close-packed) lattice. However, it was found that in the process of martensitic transformation and after plastic deformation, the intermediate phase with a FCC (face-centered cubic lattice) lattice can appear [3]. Also, it was shown that the interplanar spacings BCC_{110}, FCC_{111}, and HCP_{002} for the studied alloy have the values which demonstrate the possibility of their mutual polymorphic transformation. The curvature of the crystal lattice occurs due to the large displacement of atoms. As a result, the transformation of original BCC lattice into FCC lattice happens, which is shown in [3]. According to the clustered visualization of crystal structure [11], the unit cell of FCC lattice can be represented as a combination of regular octahedron surrounded by the regular tetrahedron, bounded by the common triangular faces. The shift and rotation of octahedrons and tetrahedrons induce the formation of hexagonal lattice. According to [12], the octahedron can transform into tetrahedrons. It makes possible the formation of icosahedral cluster with the Frank-Kasper structure. The icosahedron is a twelve vertex polyhedron, which is denoted by FK-12. Furthermore, other Frank-Kasper structures such as FK-13, FK-14, FK-15, FK-16 can

form in the crystal. For example, FK-16 is a fifteen vertex polyhedron with the atom located in the center of cluster. This structure is shown in [13]. The cluster method for calculation of the electronic phase transitions was proposed on the basis of the above information (Fig. 3). Fig. 3*a* shows the modular assembly of five octahedras of FCC lattice (I), forming a bowl, with the icosahedron, which is located in the center of the bowl. Fig. 2 *b* shows the modular assembly of the icosahedron (II), five octahedras of FCC lattice, and two octahedras of BCC lattice (III). Fig. 3 *c* shows the modular assembly of FK-16 structure.



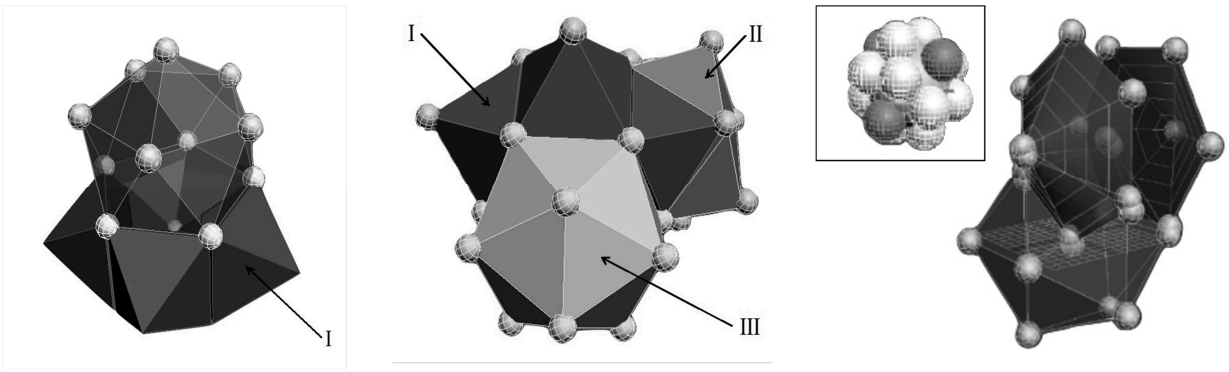
a *b*

Fig. 1. TEM image (*a*) and the electron diffraction (*b*) obtained from the $Ni_{51}Ti_{49}$ alloy samples before plastic deformation



a *b*

Fig. 2. TEM image (*a*) and the electron diffraction (*b*) obtained from the $Ni_{51}Ti_{49}$ alloy samples after plastic deformation



a *b* *c*

Fig. 3. Different crystal structures in the cluster representation: *a, b* - the formation of icosahedral FC-12 structure from the clusters with BCC (III), FCC (I), HCP (II) lattice; *c* – the formation of FK-16 structure

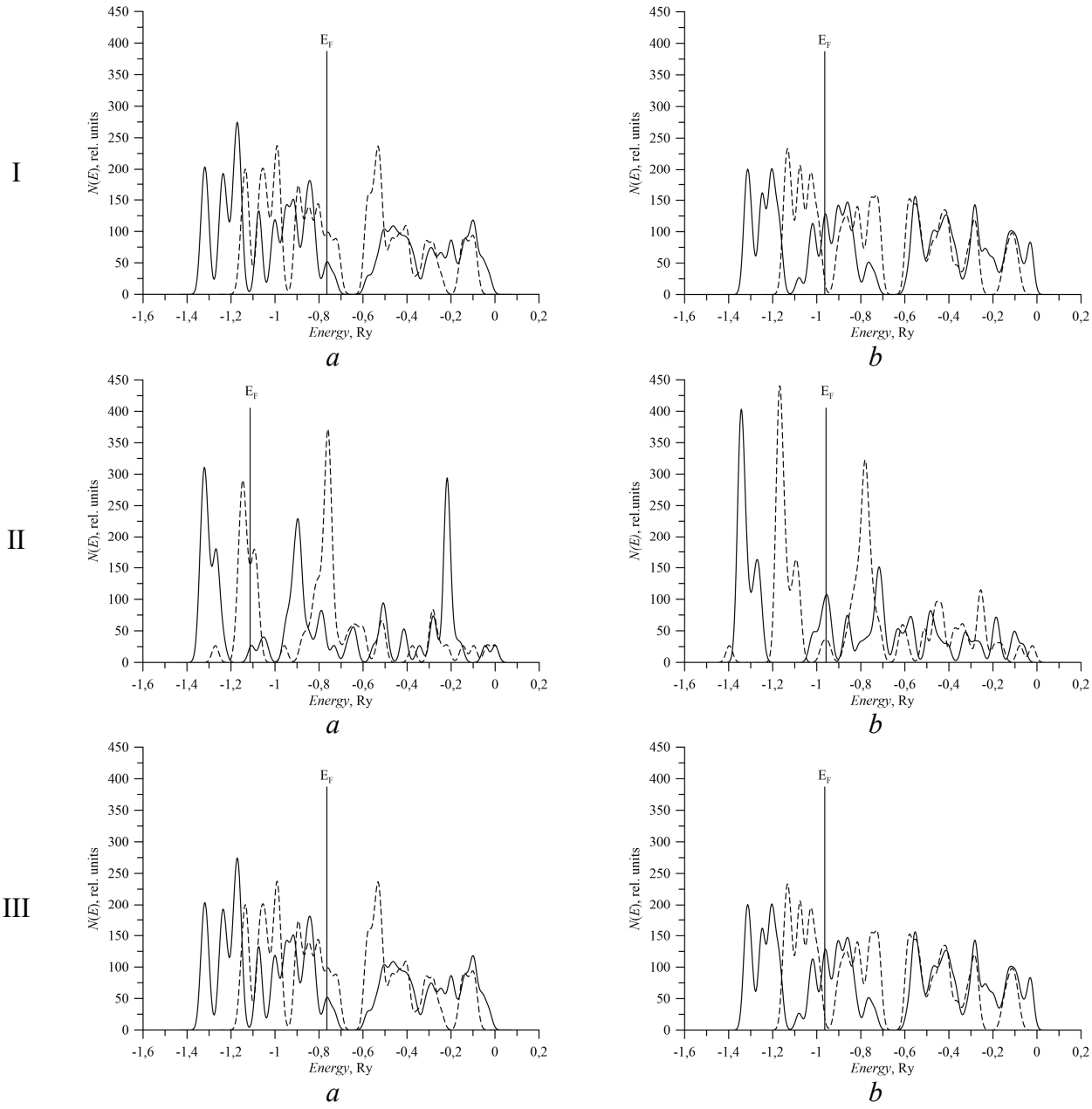


Fig. 4. Distribution of the density of electron states *N (E)* for Ni_7Ti_5 (I), Ni_8Ti_5 (II), $Ni_{10}Ti_6$ (III) clusters: a) deformed cluster; b) non-deformed cluster. Solid line indicates the density of electrons with an "up" spin (↑), dashed line – with a "down" spin (↓); E_F – the position of the Fermi level

Thus, the proposed cluster method showed the existence possibility of structures with pentagonal symmetry in plastically deformed samples of $Ni_{51}Ti_{49}$ alloy. In order to explain the appearance of magnetization in Ni-Ti alloy samples, the calculations of magnetic moments and spin-polarized density of electron states of the following clusters Ni_7Ti_5 (FK-12), Ni_8Ti_5 (FK-13), $Ni_{10}Ti_6$ (FK-16), in non-deformed (close to a spherical structure) and deformed (elongated by 5% along the Z axis) cases, were obtained. The calculations confirm an increase in magnetization of $Ni_{51}Ti_{49}$ alloy after plastic deformation. It was shown that the non-deformed clusters are also have a magnetic moment (the average magnetic moment per atom of Ni_7Ti_5 cluster, is about 1,0 μ_B, and for Ni_8Ti_5 and $Ni_{10}Ti_6$ clusters is about 0,5 μ_B and 0,3 μ_B, respectively). However, for the whole alloy the average magnetic moment is equal to zero, due to the absence of a common direction. In addition to that, if the cluster is tensioned, the compensation of the magnetic moments of clusters does not occur in the alloy, since the common direction for all atoms appears due to deformation. At the same time, the average magnetic moments of the atoms in deformed clusters increase to 1,6 μ_B, 0,6 μ_B, and 1,2 μ_B

for Ni_7Ti_5, Ni_8Ti_5, $Ni_{10}Ti_6$ clusters of $Ni_{51}Ti_{49}$, respectively. It should be noted that the part of the magnetic moments of surrounding atoms is transferred to the atom located in the center of the cluster and, in general, the magnetic moment of the cluster decreases.

Fig. 4 presents the results of calculations of the spin density of electron states $N(E)$ of the clusters with the Frank-Kasper structure in the case of "up" and "down" spin projections of the electrons. The spectra calculated in this work are in a qualitative agreement with the spectra obtained in [14]. Unfortunately, the authors of [14] did not give any information about magnetization of the alloy.

In Fig. 4 the spectra show a high density of the states near the Fermi level which is the characteristic feature of metals. The calculated spectra demonstrate that the density of electron states after plastic deformation increases at the Fermi level which leads to the increase in magnetization of $Ni_{51}Ti_{49}$ alloy.

Summary

1. The experimental and theoretical research has shown the origins of the ferromagnetic phase appearance in the plastically deformed samples of $Ni_{51}Ti_{49}$ alloy.
2. The origin of the ferromagnetic phase appearance in the samples of $Ni_{51}Ti_{49}$ alloy is the displacement of atoms caused by plastic deformation which leads to the reduction of the crystal lattice symmetry and appearance of the icosahedral clusters with the Frank-Kasper structure.
3. The reduction of the crystal lattice symmetry leads to uncompensated magnetic moment in neighboring clusters and, as a result, the ferromagnetism appears.
4. The calculation carried out using the scattered-wave method showed the formation of the high density of electron states at the Fermi level when the clusters with the Frank-Kasper structure are deformed.

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