T6 - Materials Science - Metals and Alloys

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INCOMMENSURATE MODULATED STRUCTURE OF MSM Ni_2MnGa MARTENSITE

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Magnetic shape memory (MSM) Heusler Ni_2MnGa alloy shows very large strains induced by magnetic field. The mechanism at the basis of the magnetic shape memory effect is the reorientation of twin variants of martensitic phase activated by magnetic field. In spite of the research effort, the structure of the Ni_2MnGa martensite is still not completely understood. It is usually associated to a tetragonal lattice with unit cell $a_t = b_t = 5.90$ Å, $c_t=5.44$ Å. However the tetragonal lattice only represents an average structure which is affected by structural modulation [1]. Several investigations [1-4] interpreted this modulation in terms of a five-fold superstructure (i.e. a superstructure constituted by five unit cells along one of the fundamental crystallographic axes), while a recent study indicated for the same structure a seven-fold modulation [5].

In the present work, the structure determination of the thermally induced martensite in the stoichiometric Ni_2MnGa alloy, has been done on the basis of electron diffraction (ED) and powder neutron diffraction (PND) experiments. The combined analysis of the experimental data indicates an incommensurate modulated structure closely related to a five-fold layered structure, with a modulation vector $\mathbf{q} = 0.4248(2)\mathbf{c}^*$. The symmetry of the basic structure was found to be monoclinic with unit cell constants, $a_m=4.2198(2)\quad 2a_t$, $b_m=5.5541(1)$ Å, $c_m= 4.1903(1)$ Å $\quad 2a_t \quad = 90.12(5)°$. The complete structural determination, carried out within the superspace approach using the four-dimensional space group $P2_1/n(\ \ 0\ \ )$, was achieved with a Rietveld refinement performed on PND data (with Jana 2000 software [6]).

The results show that the modulation is mainly related to the periodic shuffling of the atomic layers perpendicular to the c axis of the monoclinic basic structure.

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STRUCTURE ANALYSIS OF $NiZr_2$ IN RECIPROCAL AND REAL SPACE

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Structure determination from powder diffraction using the Rietveld method are based on the analysis of the positions and intensities of Bragg reflections which allows to determine the long range average structure of the crystal. A method to reveal the local structure of a material is the analysis of the atomic pair correlation function. This methods is known for studying the short-range order in non-crystalline materials but has recently been applied to crystalline materials [1].

The aim of this paper is to compare the structural parameters and their temperature dependence for amorphous and polycrystalline $NiZr_2$ by the analysis of the diffraction data in reciprocal space with those data obtained from of the atomic pair correlation function in real space.

The temperature dependence of the structure of amorphous and crystallized $Ni_{33}Zr_{67}$ was investigated by means of in situ synchrotron X-ray diffraction at elevated temperatures. The (mean) crystal structure parameters of tetragonal NiZr$_2$ (S.G.140) were calculated by the Rietveld refinement of the X-ray diffraction patterns. The lattice parameters a_0, and c_0 increase linearly with temperature. Interatomic distances calculated from the crystal structure data behaves in a similar way.

The atomic pair correlation functions of amorphous and crystallized Ni$_{33}$Zr$_{67}$ show in both cases different behaviors. The nearest neighbor distances are found to be lower and decrease with temperature. The macroscopic thermal expansion is reflected by the behavior of the maxima of the atomic pair correlation at distances r > 0.6 nm. The analysis real space data with PDFFIT [2] confirms the presence of differences of the local and the average structure caused by to strong correlation of the thermal oscillation of neighbored atoms in amorphous and crystallized NiZr$_2$.

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SYNTHESIS AND X-RAY STUDY OF NON-EQUILIBRIUM SOLID SOLUTION Os$_{0.5}$Ir$_{0.5}$

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Os and Ir metals are of particular attention regarding their characteristics. For example, osmium has the highest bulk moduli value - 462 GPa [1] among all other materials. Furthermore Os and Ir possess the high values of density, melting temperature, etc. The phase diagram of Os-Ir system belongs to the peritectic type. Single-phase areas (a, b) with face-centered cubic (fcc) and hexagonal close packed (hcp) lattices are separated by a diphase area (a+b).

In [2, 3], several hcp phases Os$_x$Ir$_{1-x}$ with 0.65 < x <0.9 and a fcc phase with x 0.2 are discribed by X-ray analysis. The volume per one atom (V/Z) values are given in the picture. The single-phase area boundaries are marked with the dash lines. In some cases, upon thermolysis of binary complex salts one obtains non-equilibrium solid solution that is placed into the diphase area. For example, the hcp phase Re$_{0.5}$Ir$_{0.5}$ was thus obtained in [4].

To get the single Ir$_{0.5}$Os$_{0.5}$ phase we have synthesized a precursor complex [Ir(NH$_3$)$_5$Cl)][OsBr$_6$]. Thermolysis of this complex was held at 700 °C in hydrogen atmosphere. Finally, according to X-ray analysis data, a single-phase product with the hcp lattice was obtained. The lattice parameters are: a = 2.729(2) Å, c = 4.361(3) Å, V/Z = 14. 064 Å^3, D$_x$ = 22.576 g/cm^3. The V/Z value obtained fits well a line connecting the values for pure metals.

Sample of meta-stable Ir$_{0.5}$Os$_{0.5}$ was soldered up into capsule, vacuumized and then heated up to 800 °C. X-ray analysis showed that after heating sample became diphase. The lattice parameters of hcp phase: a = 2.729(2)Å, 4.357(3) Å, V/Z = 14.051 Å^3. These values are close to Ir$_{0.5}$Os$_{0.5}$. The lattice parameter of fcc phase is a = 3.837(2) Å and close to pure iridium.

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T6 - P124

X-RAY DIFFRACTION INVESTIGATIONS OF THE CRYSTALLIC STRUCTURE CHANGES IN THE Ni-BASED ALLOY AT THE THERMAL CYCLING

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X-ray diffraction investigations of the Ni-based alloy (1,3% W; 3,2% Mo; 5,6% Al; 4,5% Ti; 12-15% Co), which is wide using in aviation enginebuilding, was shown a presence of the two same structure matrix and intermetallic ‘-phase Ni$_3$(Al,Ti) with disaccordance of the parameters of the crystalline lattices approximately 0,1%. Thus a ‘-phase has more perfect crystalline structure, than the matrix -phase.

In the mode of thermal cycling the exposure at the maximal tempetrature of the cycle 1173 K (= 2-4 hour) there is disintegration of matrix -solid solution with the extraction of the intermetallic ‘-phase Ni$_3$(Al,Ti). The parameter of crystalline lattice of the intermetallic ‘-phase Ni$_3$(Al,Ti) have been decreased. Except for it the change of parameter takes place at the thermal cycling by means of substitution of matrix hard solution by the atoms of other elements. Because of and ‘-phases have the crystalline lattice of the same type with close value parameters, diffraction peaks of these phases are together on the Bregg reflection. Because of the contents of more perfect intermetallic ‘-phase Ni$_3$(Al,Ti) is increased with the increase of number of the thermal cycles, the semiwidth of resulting diffraction peaks is diminished.

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THE INFLUENCE OF ALUMINUM ON THE PROCESSES OF CARBONIZATION IN STEELS

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The X-ray and Mössbauer investigations [1] have shown, that the main factor which influences the structure and properties of high-carbon steels alloyed with Al is the presence of coherence ordered carbide phase $Fe_{4-y}Al_yC_x$ (K-phase) with antiperovskite structure over a wide concentration and temperature range. This structure has high temperature stability to the phase transformations. Depending on the concentration of Al and C as well as on the external influences the K-phase can exist in different modifications. These crystalline modifications correspond to different symmetries and have various composition. It has been proposed to study the set of model configurations of the K-phase both of the stehiometrical composition and with an essential shortage in compounds (Fe_3AlC, Fe_3Al, Fe_4C, Fe_7Al, Fe_7AlC_2, $Fe_{14}Al_2C_4$, $Fe_{25}Al_7C_4$ $Fe_{28}Al_4C_4$). The X-ray spectrums for all the above modifications with different concentration of Al and C have been theoretically obtained. The simulated spectrums can be compared with experimentally observed X-rays powder diffraction pictures of extracted K-phase. It can give a possibility to estimate the mainly probable configuration of the K-phase in alloys with different concentration of alloyed elements.

The total and partial densities of states for all the above configurations have been calculated using the linear MT-orbital method (LMTO). We have found that for the stehiometrical configuration density of states at the Fermi level is very high. This indicates that such a structure is unstable and is influenced by the lattice distortions and concentration variations [2]. This fact is in agreement with the experimental results according to which the K-phase does not exist in its stehiometrical configuration, but only with the lack of C.

From the partial densities of states one can note the binding role of Al and its influence on Fe carbonization. There is a strong hybridization of Al 3s- and C 2p- states. One can note a considerable addition of Al 3p-states to the lower part of the Fe 2d- band. It can be interpreted as the formation of direct Fe-Al and Fe-C bindings. The same result has been observed during the calculation of valence electron charge density plots in (001), (011), (111), (020) planes for the stehiometrical configuration using the FLAPW (full-potential linear augmented plane waves) method. The calculated plots approve the density polarization in carbon direction which occurs due to the transport of the part of charge density from the metal (transitional and not transitional) to the areas of carbon atoms.

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THE CHANGES OF -MARTENSITE ORIENTAL RATES AT THE HIGHCARBON Fe-Al-C ALLOYS AND MODELING OF THESE ORIENTAL RATES BY MEANS OF MATRIX ANALYSIS

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The general matrix analysis was used for mathematical description of the changes of pole figures after martensite transformation at the highcarbon Fe-Al-C alloys. Is was calculated and built pole figures á-martensite with anomalous high tetragonality. The matrix which corresponded to oriental rates by Nishijama (OR N) was transformed by auxiliary matrix which take into account of the corners of turns and rate of tetragonality of á-martensite. It was received the calculated pole figures for the variants of oriental of Greninger-Trojano (G-T) and Kurdyumov-Zacks (K-Z). It was established that only at the particular sequence of matrix transformations the calculated shifts of the martensite <001> poles about <001> and <011> poles was coincided with analogous shifts of the experimental poles. These shifts are explained by coherent stresses which appear at the martensite by existing of carbon and ordered carbide particles (K-phase).

Alignments of martensite poles in alloys of Fe-Al-C system are investigated in a broad temperature and concentration intervals. Also variation of these alignments during the low-temperature tempering is studied.

It was established, that changing structure, velocity of cooling, time of the low-temperature tempering it is possible to receive an - martensite with anyone known orientational ratio. The tempered martensite has no irrational Greninger-Trojano OR. Half of poles 24+24 OR (G-T) appears as though grouped two by two, half - as though disappears (diffraction reflects are not fixed). The martensite as though tends to orient according to OR N.

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SUBMICROCRYSTALLINE IRON, COPPER AND MAGNESIUM OBTAINED BY SEVERE PLASTIC DEFORMATION – MICROSTRUCTURE AND ITS THERMAL STABILITY

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Thermal stability of fine microstructure of the selected samples of iron magneisum and copper with addition of different amount of Al_2O_3 prepared by high-pressure torsion deformation under 6 GPa is investigated by X-ray powder diffraction (PXRD), positron life-time spectroscopy (PL) and transmission electron microscopy (TEM).

Conventional powder diffraction studies were carried out in order to analyse lattice parameters, texture coefficients and line broadening. In simplified analysis, the profiles were fitted with analytical functions and analyzed in terms of integral breadths an dmodified Williamson-Hall plot. More sophisticated analysis was performed by total powder diffraction pattern fitting as proposed by Ungar et al [1] and Scardi & Leoni [2]. The crystallite size in the order of 50-300 nm and dislocation densities of $1\ \ 10^{14}$ m^{-2} to $1\ \ 10^{15}$ m^{-2} were determined by all the methods.

Typical line broadening anisotropy was well accounted for by the dislocation orientation (contrast) factors. The agreement was not so good for annealed samples. In some cases strong anisotropy remaines even after the dependence on diffraction vector magnitude (strain) disappear.

PL spectra shown two major components – one comes from positrons trapped at dislocations inside the distorted regions and another that can be attributed to positrons trapped in microvoids with the size of 4-5 vacancies.

Obtained values of crystallite size and dislocation density agree quite well with the estimations made from TEM for Cu + 0.5 wt. % of Al_2O_3 and Fe samples. On some of the TEM pictures of the former sample the Al_2O_3 droplets were found. It was found that the addition of at least 0.5 wt. % Al_2O_3 prevents grain growth and keeps the dislocation density high and crystallites small up to about 400 C. The amount of 0.3 wt. % is insufficient for that and rapid grain growth is observed at about 200 C.

For iron samples continuous strain recovery is observed in the range 130-200 C.

Valuable results were obtained by old and simple back-reflection method. For as-prepared samples, continuous rings were observed while after annealing a few dots were clearly distinguished on them indicating fast growth of only a few grains. This appeared at lower temperatures, before any significant changes of line broadening and PL spectra and it was only detected for copper samples while for iron and magnesiumthe grain growth seems to be homogeneous. In-plane inhomogeneity was also detected by the technique. In margin regions of disc specimens, larger grains were detected than in their centers. The effect appeared only after annealing above 200 C and only for copper samples. With increasing annealing temperature such effects can be seen also on diffraction profiles.

The bimodal crystallite size distribution is a typical structural feature after annealing of the HPT deformed copper and copper with addition of Al_2O_3.

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