Chapter 3

DEPARTMENT OF METAL PHYSICS

3.1 STAFF

3.1.1 Scientific staff

Kornel Csach (head of department), Alena Juríková, Viktor Kavečanský, Jozef Miškuf, Václav Ocelík (temporary employed at the University of Groningen, Netherlands)

3.1.2 Technical staff

Technicians: Vladimír Hajko, Ivan Jurčo and Valéria Štammová

3.2 SCIENTIFIC ACTIVITIES

3.2.1 Introduction

The activities of the department are concentrated on the experimental study of metals, mainly their mechanical properties, in a wide temperature range. The scientific interest is focused on the homogeneous and inhomogeneous plastic deformation of amorphous metals. Creep and creep recovery processes in these materials are studied in detail. The fractography of amorphous alloys is often used for describing the materials structure and their failure mechanisms. Mechanical testing, fractography, thermomechanical investigations and structure examinations are the basic experimental methods of experiments. The assumption about the existence of activation energy spectrum is the common approach for characterizing the homogeneous deformation and crystallization processes. New numerical methods for calculating of activation energy spectrum from isothermal and non–isothermal experimental measurements were used.

Crystal structure and relation between the structure and other physical properties (mainly magnetic) of materials has been studied by means of diffraction techniques. New mathematical methods of measured data processing which enable the investigation of the crystal structure details were used.

The scientific group cooperates with the Institute of Physics SAS in Bratislava, B. Verkin Institute of Low Temperature Physics and Engineering in Kharkov, University of Groningen, University of Voronezh, Technical University of Vienna, Hahn Meitner Institute, Berlin. The department is equipped with the thermal analysis laboratory (differential scanning calorimeter, thermogravimetry and thermomechanical analyzer), X–ray diffractometer and melt-spinning method apparatus.

3.2.2 Projects

Projects of Slovak Scientific Grant Agency VEGA:

G–2101 Deformation and failure mechanisms in metastable metallic materials

Principal investigator: Kornel Csach

3.3 RESULTS

3.3.1 Low-temperature deformation and fracture of bulk nanostructural titanium obtained by intense plastic deformation

Bulk polycrystals of metals and alloys with ultrasmall grain size of the order of $10^2$ nm, which are called nanostructural (NS) materials, are finding increasing applications as structural materials in modern technology. The mechanical properties of nanograined metals look like superposition of properties of crystalline and amorphous metals.
The character of the temperature (in temperature range 4.2 K – 300 K) dependence $\sigma_y(T)$ remains the same as the grain size varies: for samples with grain size 15 $\mu$m, 300 nm and 100 nm the yield stress increases monotonically with decreasing temperature. This dependence shows that the elementary acts of plastic shear in NS titanium are thermally activated.

The quantitative differences of the yield stresses and the temperature dependences of the deforming stress show that the intragrain and intergrain slipping and also twinning make different contributions to the deformation of the structural modifications of titanium. At low temperatures the fracture of NS titanium under uniaxial compression is due to propagation of unstable plastic shear, which is accompanied by local adiabatic heating of the material. Examination of the morphology of the surface of shear fracture of NS titanium under an electron microscope shows the specific vein pattern, analysis of which yields an estimation of the local heating temperature about 800 °C. Cold-brittleness for NS titanium was not observed down liquid-helium temperatures.

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3.3.2 Creep of bulk metallic glass

Tensile creep tests of bulk and ribbon samples of Zr$_{52.5}$Ti$_5$Cu$_{17.9}$Ni$_{14.6}$Al$_{10}$ metallic glass have been performed in a wide range of heating rates.
It has been found that a change of the quenching rate at least by three orders of magnitude exerts little influence on the shear viscosity below the glass transition temperature $T_g$. In all cases, a linear dependence of the viscosity on the inverse heating rate is observed. The viscosities of bulk and ribbon samples are nearly the same at temperatures $T < 500$ K while at $500$ K $< T \leq T_g$ the viscosity of ribbon samples is somewhat lower. This fact can be explained within the framework of the Directional Structural Relaxation model as a result of irreversible structural relaxation with distributed activation energies occurring below $T_g$.

Temperature dependencies of the shear viscosity on the inverse heating rate at $T = 450$ K (a) and $T = 550$ K (b). The straight and dotted lines are drawn as the least square fits through the origin.

An increase of the quenching rate by three to four orders of magnitude results in a 30%-rise of the volume spectral density of relaxation centers in the high-energy part of activation energy spectrum of irreversible structural relaxation (AES) while the low-energy part of the AES remains unchanged. Above $T_g$, the viscosity of bulk samples is always lower than that of ribbons and the viscosity difference increases with temperature. This phenomenon is supposed to be due to phase decomposition above $T_g$.

3.3.3 Neutron diffraction study of Re[Fe(CN)$_6$] · $n$H$_2$O structure, $Re =$ Pr, Dy

The design of materials exhibiting new physical properties represents significant course of solid state physics research. In the field of molecular magnetism among main challenges belong reaching high values of such parameters as transition temperatures, coercive fields and magnetization. Knowledge of crystal and magnetic structures can significantly contribute to solve the problem. Rare-earth ferrocyanides Re[Fe(CN)$_6$] · $n$H$_2$O ($n=4,5$), as a member of Prussian blue family, represent the type of materials that can be used for this purpose. Depending on chemical composition and preparation conditions they form tetrahydrate and pentahydrate complexes.

The hexagonal structure ($P6_3/m$) of La[Fe(CN)$_6$] · 5H$_2$O was worked out by Bailey et al. in 1976. However, the structure contains a water molecule with $C_2v$ symmetry localized on a three-fold axis. The arrangement, which is rather unusual, represents possible conflict between molecular and crystal symmetry. Crystal structure of tetrahydrate complexes has been described as orthorhombic ($Cmcm$) where no such possible conflict occurs. However, the data often indicate pseudohexagonal symmetry. Detailed analyze of Pr[Fe(CN)$_6$] · 4H$_2$O revealed that the single crystal was twinned with three components. The structure consists of FeC$_6$ octahedra located along screw axis. Pr atom is coordinated by six N atoms lying at the apices of a trigonal prism. The polyhedron is completed by two coordinated water molecules (O1). The next two water molecules (O2) occupy holes in the structure above and below the trigonal prism faces and are obviously less strongly bonded.

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Figure A: Low angle part of diffraction patterns of Dy[Fe(CN)$_6$] · 4H$_2$O at different temperatures. The shifted curves document gradual development of magnetic moment as temperature decreases.
The crystal structure of powder sample was characterized by X-ray diffraction and next studied by neutron diffraction methods. However, neutron diffraction experiments require substitution of hydrogen by deuterium atoms. As, in contrast with X-ray diffraction experiments, contribution of the deuterium atoms to the neutron scattering intensity is significant, their positions in the unit cell must be determined. Knowledge of the complete crystal structure allows to subtract its contribution to the diffraction pattern and the pure magnetic part can be determined and analyzed.

Diffraction patterns were indexed by McMaille, program based on Monte Carlo simulation. Localization of deuterium atoms was performed by the direct-space method using reverse Monte-Carlo approach (Fig B). For the structure simulation building units (FeC₆ octahedra, D₂O water molecules and other atoms that were taken as isolated) were used. After deuterium positions in Pr[Fe(CN)₆]·4H₂O were localized, the complete crystal structure was refined using Rietveld method (Fullprof, GSAS).

Indexing procedure has confirmed the orthorhombic symmetry of the phase Pr[Fe(CN)₆]·4H₂O. The structureless (profile matching) fit gave refined values of lattice parameters a=7.4968(2) Å, b=12.9582(4) Å, c=13.8253(4) Å, α=β=γ=90. In accordance with the single crystal analysis of Pr[Fe(CN)₆]·4H₂O the Cmcm space group was suggested. The final fit of the structure including localized deuterium atoms (Rwp = 5.69, reduced χ²= 4.64) is shown in Fig C. All atoms were refined isotropically, deuterium atoms with a common atomic displacement parameter. The refined structure was validated by Platon.

The deuterium atoms were directly implemented during the preparation process into the compound instead of hydrogen. The neutron diffraction experiments were carried out at the BER II reactor in HMI in Berlin. The powder sample has been investigated at room temperature at E9 instrument (λ=1.7972 Å) covering an angular range 2θ from 6° to 156°. The possible magnetic ordering was studied at E6 instrument (λ=2.45 Å). The diffraction patterns were taken in the temperature range 1.6 – 40 K (Fig A).

Selected bond distances are listed in Table 3.1. The crystal structure was found to be analogue
to the structure formerly described. The uncoordinated water molecule (O2) is bonded to O1 and to three N atoms through hydrogen bonds (O1-D1· · ·O2, O2-D21· · ·N2 and to two N1 atoms by symmetrically bifurcated O2-D22· · ·N1 bond)(Fig D).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance [Å]</th>
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<tbody>
<tr>
<td>Pr – O1</td>
<td>2.432(13)</td>
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<tr>
<td>Pr – N1</td>
<td>2.560(7)</td>
</tr>
<tr>
<td>Pr – N2</td>
<td>2.575(8)</td>
</tr>
<tr>
<td>Fe – C1</td>
<td>1.929(7)</td>
</tr>
<tr>
<td>Fe – C2</td>
<td>1.931(8)</td>
</tr>
<tr>
<td>O1– O2</td>
<td>2.822(6)</td>
</tr>
<tr>
<td>O1– D1</td>
<td>0.951(11)</td>
</tr>
<tr>
<td>O2– D21</td>
<td>0.926(16)</td>
</tr>
<tr>
<td>O2– D22</td>
<td>0.938(11)</td>
</tr>
</tbody>
</table>

Table 3.1: Selected bond distances (in [Å]).

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3.4 SELECTED PAPERS


3.5 OTHER ACTIVITIES

3.5.1 Organized scientific conferences and workshops

In cooperation with the Institute of Anorganic Chemistry SAS in Bratislava, Department of Physics, Military Academy in Liptovský Mikuláš, Faculty of Chemical Technologies, Slovak Technical University in Bratislava and the Czech and Slovak Crystallographic Association we organized the XIIIth (2004) Regional Powder Diffraction Conference (RPDK).

The scientific topic of the conference, which took place each year at the end of September in Demänovská dolina, is crystal structure investigation mainly by means of x-ray and neutron diffraction methods.

(V. Kavečanský)

3.5.2 Educational activities

On the basis of the cooperation agreement between the Department of Experimental Physics, Faculty of Sciences, University of P. J. Šafárik and the Department of Metal Physics, a course for students of the University of using x-ray diffraction methods for crystal structure investigation was read. Lectures concerning some special problems of x-ray diffraction physics were presented for post-graduated students within the scope of their doctoral study.

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