Manufacturing of ultrafine-grained titanium by caliber rolling in the laboratory and in industry

G. Krállics\textsuperscript{a,*}, J. Gubicza\textsuperscript{b}, Z. Bezi\textsuperscript{c}, I. Barkai\textsuperscript{c}

\textsuperscript{a} Department of Materials Science and Engineering, Budapest University of Technology and Economics, H-1111, Bertalan L. str. 7, Budapest, Hungary
\textsuperscript{b} Department of Materials Physics, Eötvös Loránd University, H-1117, Budapest, Hungary
\textsuperscript{c} Institute for Logistic and Production Engineering, Bay Zoltán Nonprofit Ltd for Applied Research, H-3519, Miskolc, Hungary

\textbf{A R T I C L E  I N F O}

Article history:
Received 13 September 2013
Received in revised form 31 January 2014
Accepted 8 February 2014
Available online 18 February 2014

\textbf{Keywords:}
Grade 2 titanium
Severe plastic deformation
UFG microstructure
Strength
Ductility

\textbf{A B S T R A C T}

The mechanical properties and the microstructure of Grade 2 titanium semi-products processed by warm caliber rolling in both laboratory and industrial environments are studied. It is shown that this technology yields ultrafine-grained (UFG) microstructure with high tensile strength and good ductility at room temperature. Finite element modelling (FEM) suggests that the effectiveness of caliber rolling in grain refinement is mainly caused by the large, homogeneous imposed strain, similar to conventional severe plastic deformation (SPD) methods. It is proved that the mechanical and microstructural properties of titanium processed by the industrial equipment are similar to the characteristics of the material manufactured in the laboratory. This observation suggests that caliber rolling carried out in industrial environments may be a candidate technology in mass-production of UFG titanium with improved mechanical properties.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Titanium is an ideal material for medical implants in the human body since it is chemically inert, does not react with human body fluids, and after a proper surface treatment the bone is able to adhere to it. From a physiological viewpoint, pure titanium is the optimum choice as an implant material since it does not contain other elements which may be toxic for the body. Severe plastic deformation (SPD) techniques are capable to refine the grain structure to 100–200 nm in pure Ti, thereby providing high strength semi-products for the fabrication of implants. Different SPD methods, such as Equal Channel Angular Pressing (ECAP) (Gunderov et al., 2013), multiple forging (MF) (Zherebtsov et al., 2004), twist extrusion (TE) (Stolyarov et al., 2005), hydrostatic extrusion (Pachla et al., 2008), accumulated roll bonding (ARB) (Mílner et al., 2013), and asymmetrical rolling (Kim et al., 2011a) are used for production of ultrafine-grained (UFG) titanium. Most of these methods require special equipment and they are capable of producing only small quantities of materials. However, there is demand for UFG Ti in large amounts, therefore the objective of our research study is to develop an industrial production environment for UFG titanium. It is noted that high pressure torsion (HPT) is the most effective technique in refining grain structure of metals, but this method can process materials only in very small volumes, therefore HPT is out of the scope of this study.

SPD processing of materials with hexagonal closed packed structure (such as Ti) is often carried out at elevated temperatures due to the rigidity of the specimens at room temperature. However, warm SPD manufacturing processes are often followed by subsequent forming at room temperature or an annealing step in order to further improve the strength and the ductility of titanium. When very high strength is required, usually a final cold forming step is applied in the production procedure. The influence of these manufacturing processes on the microstructure and the mechanical performance of Ti is discussed in the literature overview presented below.

Among the warm SPD methods ECAP is the most frequently used technique. Stolyarov et al. (1999) processed a titanium rod by seven passes of ECAP in the temperature range of 500–450 °C (referred to as case A throughout this manuscript), which yielded a refined mean grain size of ~300 nm. Stolyarov et al. (2003) applied a two-step SPD procedure in order to obtain UFG Ti with significantly enhanced strength. Eight passes of warm ECAP via route B\textsubscript{c} at 450 °C was first used, resulting in a grain size of ~350 nm (case B). The Ti billets were further processed by repetitive cold rolling and annealing at 300 °C (case C). Latysh et al. (2006) used a combination of warm ECAP with warm drawing to produce Grade 2 UFG titanium. In this process four (case D) and eight passes (case E) of ECAP at 450 °C led to grain sizes of 500 and 350 nm, respectively.
The thermo-mechanical treatment after 4 and 8 ECAP passes further refined the grain size to 350 and 250 nm, respectively. Kang and Kim (2010) investigated the microstructure of Ti processed by a combination of warm multi-pass ECAP and cold extrusion. A T-type ECAP apparatus was developed in order to improve the efficiency of the common ECAP procedure in grain refinement and the mechanical performance of the finished products. After 5 passes of ECAP an average grain size of 960 nm was reached (case F), which did not change during subsequent cold extrusion (case G). While the strength of Ti usually increased due to ECAP technique and further thermo-mechanical treatments or cold forming processes, in many cases the ductility of the material decreased. The yield strength, the ultimate tensile strength and the elongation to failure obtained for Ti processed by warm ECAP-based SPD procedures are shown in Fig. 1. The highest strength achieved by the combination of warm ECAP and conventional processes is 2.5 times higher than that in the initial state. High strength is accompanied by sufficient ductility.

Besides ECAP other SPD processes, such as asymmetric and symmetric rolling, TE and ARB, can also improve the mechanical performance of Ti. The mechanical properties of samples processed by these techniques are shown in Fig. 2.

Li et al. (2012) produced nano-grained Grade 2 titanium with an average grain size of 80 nm by the combination of asymmetric and symmetric rolling at room temperature (case H). The rolled Ti samples possessed UFG microstructure, and the grain size remained smaller than 200 nm even after annealing the specimens at 400 °C for 30 min. Kim et al. (2011b) examined the effect of the roll speed ratio (SR) on the microstructure, texture and mechanical properties of commercially pure Ti during differential speed rolling at 400 °C for SR = 3 (case I) and SR = 5 (case J). Kim et al. (2011a) produced pure titanium sheets with UFG microstructures by high-ratio differential speed rolling at different SR values and temperatures. The strengthening was increased by either increasing SR or decreasing the processing temperature. In warm rolling, the samples were preheated to 400 °C and the roll surface temperature was maintained at 200 °C. The rolling procedures resulted in mean grain sizes between 180 and 500 nm (case K). Milner et al. (2013) processed sheet samples of Grade 2 titanium by seven consecutive ARB cycles at 450 °C (case L). At the end of the procedure the grain size was about 100 nm. Stolyarov et al. (2005) tested the microstructure and the mechanical properties as well as the thermal stability of commercially pure titanium subjected to TE. A combined manufacturing process (TE and rolling, case M) resulted in an additional refinement of the microstructure, which remained thermally stable up to 300–350 °C. Subsequent low-temperature annealing increased the ductility of the SPD-processed titanium, retaining its enhanced strength. It should be noted that the strength achieved by rolling, TE and ARB techniques was slightly lower than that obtained by ECAP-based processes. At the same time, outstanding ductility was achieved by the TE method.

Multi-pass caliber rolling is a continuous multiple forging process, known as one of the most powerful SPD methods (Inoue et al., 2007). For instance, the warm caliber rolling process has been used to produce UFG steels (Oh et al., 2011). In the present paper the microstructure and the mechanical properties of Grade 2 Ti processed by caliber rolling are investigated. The rolling process was carried out both in laboratory and industrial environments. It will be shown that caliber rolling carried out in an industrial environment might be a candidate technology for mass-production of UFG titanium with improved mechanical properties.

2. Experimental and modeling procedures

2.1. Rolling experiments in laboratory

Grade 2 titanium specimens with 200 mm in length and 30 mm in diameter in an annealed condition (annealing at 650 °C for 2 h, then cooling in air) were used for the laboratory rolling tests. The initial mechanical properties were as follows: yield strength, YS = 332 MPa, ultimate tensile strength, UTS = 439 MPa, reduction in area, Z = 58%, elongation to failure, A = 22%, strain energy density to fracture, Wf = 412 J/cm². A twin motor rolling mill with the power of 2 × 7.5 kW was used in the experiments. The diameter of the roll was 180 mm. The roll stand can be used in both symmetrical and asymmetrical modes (Fig. 3).

The first mode enables both flat and caliber rolling processes. The caliber rolls used in the present study are shown in Fig. 4.

The laboratory caliber rolling was carried out on samples preheated to 450 °C. Four reductions were performed in the first part of the process. The roll speed was 6 rpm. After the first part of the rolling procedure the specimen was reheated to 450 °C. The second part of the rolling process was performed in six passes using the same heating procedure between subsequent passes as applied in the first part of the process. In the first and second parts of the procedure different roll pairs were used, as shown in Fig. 4. After the last pass in the second part a final diameter of 8 mm was achieved. The shape and the size of the roll cavities for the ten passes are shown in Fig. 5. The basic parameters of the process are listed in Table 1.
The experimental roll stand used in laboratory caliber rolling. (a) Control unit, (b) twin motor drive, (c) roll stand.

The pairs of rolls used in laboratory caliber rolling. (a) The first pair of rolls (four cavities), (b) the second pair of rolls (six cavities).

The shape and the size of the roll cavities for the ten passes applied in laboratory caliber rolling. The first and second rows in the figure are related to the first and second pairs of rolls respectively.

### Table 1

<table>
<thead>
<tr>
<th>Reduction No.</th>
<th>Stretching factor (SF)</th>
<th>Maximum roll force [kN]</th>
<th>Maximum roll torque [Nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.15</td>
<td>145</td>
<td>1550</td>
</tr>
<tr>
<td>2</td>
<td>1.15</td>
<td>130</td>
<td>1400</td>
</tr>
<tr>
<td>3</td>
<td>1.25</td>
<td>170</td>
<td>2000</td>
</tr>
<tr>
<td>4</td>
<td>1.35</td>
<td>153</td>
<td>1750</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>175</td>
<td>2150</td>
</tr>
<tr>
<td>6</td>
<td>1.35</td>
<td>125</td>
<td>1260</td>
</tr>
<tr>
<td>7</td>
<td>1.4</td>
<td>130</td>
<td>1300</td>
</tr>
<tr>
<td>8</td>
<td>1.3</td>
<td>85</td>
<td>750</td>
</tr>
<tr>
<td>9</td>
<td>1.4</td>
<td>110</td>
<td>800</td>
</tr>
<tr>
<td>10</td>
<td>1.25</td>
<td>65</td>
<td>450</td>
</tr>
</tbody>
</table>

* SF = the ratio of the rod cross-sections before and after caliber rolling.

### 2.2. Industrial production of UFG titanium rod

Warm caliber rolling of titanium was performed using the rolling mill system of OAM Özsd Steelworks Ltd. ( Özsd, Hungary). First, the material was heated up to the rolling temperature of \( \sim 300^\circ \text{C} \) in an induction furnace. This temperature is lower than that applied for laboratory milling, since the heat production rate during industrial rolling was larger due to the higher rolling speed. During rolling process the so-called “elongation section” was executed in the first six mill stands. The speed of the first pair of rolls was 8 rpm. The finish rolling was performed in the next six stands. The diameter of the rolls was 415 mm. The oval piece is rotated by an angle of 90° at each stand in order to arrive in the next mill position. The bars with 1000 mm in length were continuously moved through the six mill stands. The temperature was measured by contact thermometers. The cross section of the bar was reduced from 70 mm to 34 mm during the elongation section of rolling. The process parameters are listed in Table 2. The rolled bars were cut to smaller pieces with 2000 mm in length. They were heated to \( \sim 300^\circ \text{C} \) before the finish rolling. In this final step of processing the diameter of the bars was reduced from 34 mm to 20 mm. The process parameters for finish rolling are listed in Table 3. The speed of the first pair of rolls in the finish rolling process was 40 rpm which is larger than in the case of the elongation section of rolling.

It should be noted that the shape and size of cavities in the laboratory rolling procedure were designed in order to obtain similar deformation and thermal conditions as in the industrial environment. For instance, the average equivalent strains calculated for the
whole volume of the material after the laboratory and the industrial procedures were 2.64 and 2.5, respectively. It should be also noted that both rolling processes satisfy the conditions given in the patent developed for producing UFG microstructure in titanium (Krállics et al., 2009).

### 2.3. Finite element modeling

Marc-Mentat 2011 nonlinear finite element (FE) software was used for modeling the thermo-mechanical processes in laboratory and industrial rolling procedures. The rolling passes were prepared in separate models, where the initial geometrical, stress and deformation states were the results of the previous calculations. When it was necessary to reduce the calculation time, the length of the workpiece was shortened, making use of the steady-state character of the process. In the model, the rolls were perfectly rigid, while the deformed material was assumed to be isotropic elastic-plastic.

The scheme of FEM analysis is shown in Fig. 6. The workpiece was modeled by a three-dimensional mesh of four-node tetrahedral elements. The initial mesh consisted of 18,250 elements and 21,900 nodes. Re-meshing was performed after each rolling step. The Updated Lagrange formulation was used in the FEM analysis. The constitutive equation used in FEM for the description of the dependence of flow stress on strain, strain rate and temperature was determined from compression tests performed on titanium at different strain rates and temperatures. These experiments were carried out on specimens predeformed by laboratory rolling. A detailed description of the applied constitutive equation has been given elsewhere (Zeng et al., 2009).

The temperature dependence of the material parameters were taken into account in the FEM analysis. The temperature rise due to the heat generated by plastic deformation and friction, as well as the cooling of the sample due to heat-transfer between the billet and the environment (rolls and air) were considered. The heat generated by plastic deformation was calculated as the product of the plastic work and a conversion factor of 0.9. The heat generated by friction was also calculated using the friction coefficient between the workpiece and the rolls given in terms of their relative velocities. In the calculation of the heat-transfer the rolled material was considered to be in contact with two rigid surfaces of the rolls, which have constant temperatures of 20 °C and 65 °C in laboratory and industrial rolling, respectively. The larger temperature of the industrial rolls was obtained from direct temperature measurements during rolling and caused by the higher speed of the rolls, as compared to the laboratory process. Additionally, the heat-transfer between the sample and the air at the temperature of 20 °C was also taken into account. The heat-transfer coefficients from the workpiece to the rolls and the air were selected to be 20 and 0.02 Ns/mm°C, respectively.

### 2.4. Mechanical testing

The mechanical properties of the rolled materials were investigated by tension using an Instron universal mechanical testing machine (type 8809) at room temperature and a cross-head velocity of 6 mm/min. The tests were carried out on cylindrical specimens with the length and diameter of 25 and 5 mm, respectively, machined out from the rolled bars. For both laboratory and industrial rolling 3–3 samples were tested.

### 2.5. Microstructural examination

The grain structure in the initial and the rolled specimens was examined by a Tecnai G2 X-TWIN transmission electron microscope (TEM). The TEM foils were prepared from both the cross- and longitudinal sections of the rods which were thinned by mechanical grinding to a thickness of 20–40 μm. The foils were further thinned by Ar-ion milling using a Gatan Model 691 precision ion polishing system.

The microstructures of the initial and the rolled samples were also examined by X-ray line profile analysis. Before measurements the surface was mechanically polished to a mirror finish with diamond paste. The surface layer distorted during polishing was removed by chemical etching using hydrogen fluoride. The measurements of the X-ray diffraction lines were performed on the longitudinal sections using a special high-resolution diffractometer with CoKα1 radiation (wavelength: λ = 0.1789 nm). The scattered intensity was detected by imaging plates. The line profiles were evaluated using the Convolutional Multiple Whole Profile (CMWP) fitting procedure. In this method, the diffraction pattern is fitted by the sum of a background spline and the convolution of the instrumental pattern and the theoretical line profiles related to the crystallite size, dislocations and twin faults. The details of the procedure are available elsewhere (Ribařík et al., 2004).

### 3. Results and discussion

The results of the mechanical tests are shown in Fig. 7. Caliber rolling performed in laboratory resulted in a slightly higher
Fig. 7. Mechanical properties of Grade 2 titanium in the initial state and after caliber rolling in the laboratory and industry. YS: yield strength, UTS: ultimate tensile strength, A: elongation to failure, Z: reduction in area, $W_f$: strain energy density to fracture. The experimental error of the values is about 8%.

strength and a similar ductility compared to the process carried out under industrial conditions.

The reason for the slightly better mechanical performance of the material rolled in the laboratory can be attributed to a more rigorous control of the thermo-mechanical conditions (e.g. the temperature of the sample) during the manufacturing process. Caliber rolling both in laboratory and industrial environments yielded about twice the strength as for the initial annealed state. The parameters characterizing the ductility do not show uniform tendencies. The elongation to failure slightly decreased due to rolling while the reduction of area remained unchanged within experimental error. At the same time, the strain energy density to fracture increased to more than twice the value characteristic to the initial state. This can be attributed to much larger flow stress values for the rolled specimens.

The progress of the forming process obtained by FEM analysis is illustrated in Fig. 8, where the equivalent plastic strain is shown for each rolling pass. In order to keep the spherical cross-section of the rolled rod, the contact surfaces between the workpiece and the

Fig. 8. Distribution of equivalent plastic strain after different passes of caliber rolling, as obtained by FEM analysis.

Fig. 9. Distribution of strain components after the first and the second passes of caliber rolling, as obtained by FEM analysis.
rolls were varied cyclically. For instance, in Fig. 8 the top-bottom or the left-right surface pairs of the rod are in contact with the rolls during the odd or even number of rolling passes. In practice, in laboratory the rolls were in fixed positions and the workpiece was rotated, while for industrial experiments the rod orientation was unchanged and the rolls were rotated. From the results presented in Fig. 8 it is clear that at the end of the forming process the local plastic strain is about three, similar to SPD-processing by three passes of ECAP, which should be large enough for producing UFG microstructure. Another important result is that a relatively uniform strain distribution is achieved at the end of the forming procedure. Additionally, caliber rolling yields a cyclic deformation process. This leads to more effective grain refinement. The cyclic nature of caliber rolling is illustrated in Fig. 9 where the normal components of the logarithmic strain tensor are shown. The dark and bright areas in the figure correspond to volumes with compressive and tensile stress components, respectively. It is clearly visible that dark areas in the first pass became bright in the second pass and vice versa.

Figs. 10 and 11 show the temperature as a function of rolling time obtained by FEM for some selected points in the cross section located in the middle of the rod during the first and second parts of the rolling procedure, respectively. During rolling the temperature increased at points inside the pre-heated rod due to the generation of heat by plastic deformation. At the same time, the temperature of the pre-heated surfaces decreased due to the contact with the cool rolls. As the orientation of the contact surfaces changes cyclically by increasing the number of passes, at surface points A and C the temperature decreased and increased periodically. After the first part of rolling, the workpiece was heated up again to the initial temperature (450 °C in the case of laboratory rolling). The equivalent strain values versus the rolling time for these points in the cross-section are shown in Figs. 12 and 13, for the first and second parts of rolling. A similar FEM analysis was also performed for the case of industrial rolling, but the results of this calculation are not shown here. It should be noted that the latter FEM analysis revealed a larger temperature increment for industrial rolling due to a higher rolling rate, in accordance with experiments.

The results of the microstructural investigations can be summarized as follows. TEM images (not shown here) revealed that the grain size in the initial Ti material was between 1 and 4 μm. Rolling in the laboratory yielded significant grain refinement in the UFG regime, as illustrated in the TEM images of Fig. 14 obtained at the end of the manufacturing process. In the cross-section the average grain size was about 300 nm. In the longitudinal section the grains
were elongated with an average width and length of 300 nm and 1 μm, respectively. Electron diffraction patterns for the specimen rolled in the laboratory are also presented in the insets of Fig. 14. The transition from a spotted to a ring-like diffraction pattern due to rolling also confirms the strong grain-refinement.

After industrial rolling the grains are also elongated in the longitudinal section, as revealed in Fig. 15. The average width and the length of the grains are 500 nm and 1 μm, respectively. In the cross-section, considerable elongation of the grains was not observed. In this section the mean grain size is 500 nm. It can be concluded that both laboratory and industrial rolling procedures resulted in UFG microstructures, but the grain refinement was slightly stronger in the former case, as also indicated by the electron diffraction pattern. The smaller grain size can explain the slightly higher strength of the material rolled in the laboratory.

The crystallite size and the dislocation density were determined in the longitudinal sections by X-ray line profile analysis. As an example, fitting for the sample processed by industrial rolling is shown in Fig. 16. The open circles and the solid line represent the measured data and the fitted curves, respectively. The intensity is plotted on a logarithmic scale. The inset shows a part of the diffractogram with larger magnification. In the inset the intensity is plotted on a linear scale and the difference between the measured and the fitted patterns is also shown at the bottom. The crystallite size and the dislocation density obtained for the initial material and the samples processed by laboratory and industry rolling are listed in Table 4. The crystallite size determined by X-ray line profile analysis is smaller than the grain size obtained by TEM, which has already been observed for other plastically deformed metals (Gubicza and Ungár, 2007). This phenomenon can be attributed to the fact that the crystallites are equivalent to the domains in the microstructure which scatter X-rays coherently. As the coherency of X-rays breaks even if they are scattered from volumes having quite small misorientations (1–2°), the crystallite size corresponds

---

**Table 4**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size [nm]</th>
<th>Dislocation density $[10^{14}$ m$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>220 ± 20</td>
<td>0.5 ± 0.3</td>
</tr>
<tr>
<td>Laboratory rolling</td>
<td>62 ± 8</td>
<td>4.9 ± 0.5</td>
</tr>
<tr>
<td>Industrial rolling</td>
<td>127 ± 15</td>
<td>3.7 ± 0.4</td>
</tr>
</tbody>
</table>

---

Fig. 14. Dark field TEM images illustrating the grain structure in laboratory-rolled Ti. (a) Cross- and (b) longitudinal sections. The rolling direction is vertical in figure (b). The insets show the corresponding diffraction patterns.

Fig. 15. Dark field TEM images illustrating the grain structure in industrially rolled Ti. (a) Cross- and (b) longitudinal sections. The rolling direction is horizontal in figure (b). The insets show the corresponding diffraction patterns.
rather to the subgrain size in severely deformed microstructures (Gubicza and Ungár, 2007). Table 4 reveals that the crystallite size decreased while the dislocation density increased due to rolling. The reduction in the crystallite size and the increment in dislocation density are stronger in the laboratory rolling procedure, but the difference between the dislocation densities obtained by the two types of rolling is not very large. It is noted that the grain size obtained on the cross-section of the sample rolled in the laboratory (300 nm) is close to the value (265 nm) determined for Ti processed by eight passes of ECAP at 400–450 °C and subsequently rolled at room temperature to a total strain (reduction in cross-section area) of 73% (Zhu et al., 2003). At the same time, the crystallite size (40 nm) and the dislocation density (3 × 10^14 m^-2) in the specimens rolled after ECAP were smaller and larger, respectively, than the values obtained in the present experiments.

Finally, caliber rolling procedures applied in laboratory and industry are placed on the map illustrating the relationship between grain size and mechanical properties for Grade 2 Ti processed by different warm SPD methods. Fig. 17 shows the yield strength and the elongation to failure as a function of the grain size determined for UFG Grade 2 titanium after warm SPD-processing (Pachla et al., 2008). It can be seen that the mechanical properties of the present caliber rolled samples fit the general trends obtained from fitting the data given in the literature (represented by the curves in Fig. 17). Some literature data obtained on Ti processed by warm SPD without additional forming procedures are also shown in the figure. It can be concluded that caliber rolling both in laboratory and industrial conditions results in similar mechanical properties to those obtained by conventional warm SPD processes. However, industrial caliber rolling yields one or two orders of magnitude larger volumes of UFG Ti per unit time than other SPD routes, therefore this procedure may be a candidate in mass-production of titanium with improved mechanical behavior.

4. Conclusions

1. It was shown that warm caliber rolling carried out on Grade 2 titanium at about 450 °C in the laboratory yielded an UFG microstructure with high strength and good ductility. The grain size and the mechanical properties were similar to values characteristic of samples processed by conventional SPD methods, such as ECAP.

2. Finite element modeling proved that caliber rolling yielded large and nearly homogeneous plastic strain in the material, which is an important condition for effective grain refinement throughout the material. The cyclical nature of the process was also revealed which might also contribute to evolution of the UFG microstructure.

3. Caliber rolling carried out in industrial environment yielded similar small grain size and improved mechanical properties as the process performed in the laboratory. It was proposed that this technology might be a candidate process for mass-production of UFG titanium with high strength and good ductility. This may open a new gate to commercialization of SPD-processed materials.

Acknowledgement

This study was supported by the Hungarian Scientific Research Fund, OTKA, Grant nos. K-100500 and 109021.

References


