EDITORIAL BOARD

CHIEF EDITOR
Prof. Dimitar Stavrev – Bulgaria

DEPUTY EDITOR:
Dr. Alexander Krugljakow, Germany
Prof. Sergey Dobatkin, Russia
Prof. Sergey Nikulin, Russia
Prof. Victor Anchev, Bulgaria

RESPONSIBLE SECRETARY:
Assoc. Prof. Tsanka Dikova, Bulgaria

MEMBERS:
Prof. Adel Mahmud, Iraq
Prof. Anna Proikova, Bulgaria
Prof. Bekir Sami Yilbas, Saudi Arabia
Prof. Dermot Brabazon, Ireland
Prof. Dipten Misra, India
Assoc. Prof. Eugeni Grigoriev, Russia
Prof. F. W. Travis, United Kingdom
Prof. Gennagiy Bagluk, Ukraine
Assoc. Prof. Ibrahim E. Saklakoglu, Turkey
Prof. Iis Sopyan, Malaysia
Prof. Ivan Parshorov, Bulgaria
Prof. Ivanja Markova, Bulgaria
Prof. Janez Grum, Slovenia
Prof. Jens Bergstrom, Sweden
Prof. Leszek Dobrzanski, Poland
Prof. Ludmila Kaputkina, Russia
Prof. Nikolai Dulgerov, Bulgaria
Prof. Omer Keles, Turkey
Prof. Plamen Danev, Bulgaria
Prof. Rui Vilar, Portugal
Prof. Rusko Shishkov, Bulgaria
Prof. Saleem Hashmi, Ireland
Dr. Sefika Kasman, Turkey
Prof. Seiji Katayama, Japan
Prof. Souren Mitra, India
Dr. Sumsun Naher, United Kingdom
Prof. Svetlana Gubenko, Ukraine
Prof. Sveto Cvetkovski, Macedonia
Prof. Ventsislav Toshkov, Bulgaria
Prof. Yovka Dragieva, Bulgaria
## CONTENTS

**CORROSION BEHAVIOR OF COMMERCIAL-PURE TITANIUM WITH DIFFERENT MICROSTRUCTURES**

**EFFECT OF NI ADDITION ON STRUCTURE FORMATION AT IN-SITU SYNTHESIS OF TiC HARDENED Fe-BASED POWDERED ALLOY**

**STRUCTURE, MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF MAGNESIUM ALLOY WE43 AFTER EQUAL-CHANNEL ANGULAR PRESSING**
PhD student Martynenko N.S., PhD Lukyanova E.A., PhD student Tokar A.A., Prof. Dr. Sci. Raab G.I., Prof. Birbilis N., Prof. Dr. Sci. Dobatkin S.V., Prof. PhD Estrin Yu.Z. ........................................................................................................................................ 176

**INFLUENCE OF STRUCTURAL AND PHASE TRANSFORMATION ON PROPERTIES OF SEVERELY DEFORMED DISPERSION-HARDENING ALLOYS**
S.N. Faizova, I.A. Faizov, V.I. Semenov, F.F Hizbullin ........................................................................................................... 180

**EVALUATION OF THE RESIDUAL STRESSES IN ADVANCED COMPOSITE CERAMIC COATINGS USING X-RAY DIFFRACTION AND FINITE ELEMENT TECHNIQUES**
Prof. Dr. Adel K. Mahmoud1, Dr. Zaid S. Hammoudi, M.Sc. Student Samah R. Hassan ....................................................... 184

**KINETICS OF FRONTS OF THE DEFORMATION PHASE TRANSFORMATION IN NITINOL**

**ONE-STEP SYNTHESIS OF NANOCRYSTALLINE OXIDES WITH UNUSUAL PHYSICAL PROPERTIES. MULLITE-TYPE SOLID SOLUTIONS SYNTHESIZED VIA MECHANOCHEMICAL/ THERMAL TREATMENT.**
Fabián Martin, Santiago T. Rafael, Klebso L. Da Silva, Kostová Nina, Šepelák Vladimír ....................................................... 191

**INFLUENCE OF THE BEAM DEFLECTION ON PROPERTIES OF THE ELECTRON BEAM HARDENED LAYER**
Matlák Jiří, Foret Rudolf, Dlouhý Ivo ........................................................................................................................................ 194

**CUTTING TOOL COMPLEX COOL SYSTEM BASED ON PHASE CHANGED MATERIALS FOR DRY MACHINING**

**MATHEMATICAL MODELLING OF HOT PLASTIC DEFORMATION OF MICROALLOYED STEELS**
Ph.D. Opiela M. ............................................................................................................................................ ............................. 200
CORROSION BEHAVIOR OF COMMERCIAL-PURE TITANIUM WITH DIFFERENT MICROSTRUCTURES

КОРРОЗИОННОЕ ПОВЕДЕНИЕ ТЕХНИЧЕСКИ ЧИСТОГО ТИТАНА С РАЗЛИЧНОЙ МИКРОСТРУКТУРОЙ


1SASI Institute for Strategic Studies, RB, Ufa, Russia
2Ufa State Aviation Technical University, Ufa, Russia
3National Taiwan University of Science and Technology, Taipei, Taiwan
4"Todor Kableshtov" Higher School of Transport, Sofia, Bulgaria
*corresponding author, e-mail: semenov-vi@rambler.ru

Abstract. This paper reports on the results of corrosion tests, using alternative methods, of Grade 4 CP Ti samples with coarse-grained (annealed) and ultrafine-grained structures after severe plastic deformation processing. The effect of microstructure on the corrosion of the material under study is demonstrated. It is revealed that the material with a UFG structure has a higher corrosion resistance, as compared to the samples with a CG structure.

KEY WORDS: CORROSION; COMMERCIAL-PURE TITANIUM; COARSE-GRAINED AND ULTRAFINE-GRAINED STRUCTURE; SEVERE PLASTIC DEFORMATION.

1. Gravimetric corrosion test

Introduction
Owing to a great interest in the production of high-strength implants for medical applications from commercially pure (CP) titanium, one turns, more and more often, to the technologies based on severe plastic deformation. These technologies enable producing a high-strength state due to the formation of an ultrafine-grained (UFG) structure that contributes to a significant enhancement of mechanical and functional properties [1, 2].

Promising is the use of high-strength long-length materials with a UFG structure [3], in particular, from CP Ti [4] which can be used for the production of medical implants that are, in particular, in frictional contact in saline medium.

Relatively recently, studies focused on a comparative evaluation of the corrosion resistance of materials with a coarse-grained and UFG structure were initiated [5]. For instance, it was demonstrated in [6] that in the investigated materials (low- and medium-carbon steels), having a UFG structure after severe plastic deformation (SPD) processing by equal-channel angular pressing (ECAP), an increase in corrosion resistance is observed. It may be assumed that a similar effect should be expected for CP Ti as well.

There are known works on the fabrication of semi-products from CP Ti for medical applications, having a UFG structure, processed by SPD [7-9] followed by deposition of coatings from titanium nitride [7, 8] and diamond-like carbon with zirconium [9].

At the current stage of research, an express evaluation has been performed, of the corrosion properties of CP Ti, depending on the structural state and the presence of a coating on the surface of the investigated material in the coarse-grained (CG) and UFG states.

1.1. Material and research procedure

As the material for the study, CP Ti Grade 4 was used, with a CG structure in the annealed condition, and with a UFG structure in the SPD-processed condition. Fig. 1 shows the principle of the SPD technique employed to process the material.

After SPD processing, specimens with a length of 25 mm were cut out from the produced rods, for the deposition of ion-plasma coating and surface treatment by microarc oxidation. One specimen was left uncoated. In a similar manner, specimens were prepared from the annealed samples having a CG structure.

Corrosion tests were performed by immersion in 3.5% sodium chloride aqueous saline solution. Fig. 3 shows the diagram of the unit used to perform the corrosion tests.

The immersion tests were carried out in a waterproof thermostat during 28 hours at a temperature of 40±0.2°C.

Fig. 1 Principle of the ECAP-Conform technique for the fabrication of long-length semi-products

Fig. 2. CP Ti samples after SPD processing

Metallographic studies were performed, using optical and transmission microscopes.

Fig. 3. Principle of the immersion tests
1.2. Research results

Given below are the results of the metallographic studies. Fig. 4 shows an example of microstructure transformation as a result of SPD processing.

![Image of microstructure transformation](image)

Fig. 4. Transformation of the material’s microstructure as a result of SPD processing: a) coarse-grained structure of the material in the initial state; b) ultrafine-grained structure of the material after SPD processing.

The results of corrosion tests are given in Table 1.

Table 1. Results of corrosion tests

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Coarse-grained structure (CG)</th>
<th>Ultrafine-grained structure (UFG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass loss, %</td>
<td>Uncoated</td>
<td>Ion-plasma coating</td>
</tr>
<tr>
<td>Mass, g</td>
<td>0.11104%</td>
<td>0.02232%</td>
</tr>
</tbody>
</table>

For the sake of visualization, the results of the corrosion tests are presented in the form of a bar chart in Fig. 5.

![Bar chart of corrosion tests](image)

Fig. 5. The results of comparative corrosion tests: CG denotes the coarse-grained material after annealing; UFG denotes the ultrafine-grained material after SPD processing.

As can be seen from this graph the specimens with a CG structure (curve 1) exhibit a much higher corrosion rate, as compared to the specimens with a UFG structure (curve 2) in the accepted time interval. The variation of mass loss for the CG material in the selected time range has a practically linear character. In contrast, for the specimens with a UFG structure there is observed an area with a small slope of the curve, which indicates a decrease in the corrosion rate. In addition, it is noted that for the specimens with a CG structure, the start of the corrosion process is recorded after the first hour of testing, whereas for the specimens with a UFG structure, the first signs of the starting mass loss are observed only after five hours of testing.

Presumably on the material with UFG structure in connection with more advanced and extended total grain boundary these layers form a dense, almost impermeable barrier, due to which corrosion is strongly inhibited or completely stopped. Passivation is carried out chemically or electrochemically. In the latter case, conditions are created when metal ions under the influence of current pass into a solution containing ions, the ability to form very slightly soluble compounds. This assumption requires further study of the corrosion behavior of commercially pure titanium with different microstructure in an aqueous solution of sodium chloride using electrochemical methods with the formation of anodic and cathodic curves.

As a result of metallographic studies, it has been established that in the initial state the microstructure of CP Ti represents an equiaxed structure with a mean grain size of 30 µm. The deformation processing by ECAP leads to an efficient grain structure refinement, with the mean grain size equal to 0.2 µm.

2. Electrochemical corrosion tests

2.1. Experimental procedure

The polarization curves were recorded according to the three-electrode scheme, using a silver-chloride reference electrode and a platinum auxiliary electrode. The samples were polished with abrasive papers of decreasing grit size and a diamond paste, afterwards they were degreased with a White Spirit solution and...
2.2. Results and discussion

In Fig. 7 the anodic reaction is displayed by the initial region of the curve, demonstrating a transition from active dissolution to the onset of passivation at the potential $E_p$ and full passivation at the potential $E_{pass}$; for the UFG samples passivation occurs at larger potentials than for CG samples, but the current of passivation onset for the CG sample is slightly higher.

![Polarization curves for CP Ti: (a) – with a CG structure; (b) – with a UFG structure](46x594 to 280x675)

The cathodic reaction of hydrogen evolution runs with a smaller overpotential. Consequently, the process of titanium's corrosion in a weak acid electrolyte takes place with anodic control.

The corrosion currents determined by the extrapolation of the Tafel regions of the anodic and cathodic curves amount to $0.97 \mu A$ and $0.62 \mu A$, respectively, for the CG and UFG samples. Thus, the corrosion current of the CG sample in a weak acid electrolyte is 1.56 times higher than the corrosion current of the UFG sample (see table 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion current, $\mu A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFG</td>
<td>0.62</td>
</tr>
<tr>
<td>CG</td>
<td>0.97</td>
</tr>
</tbody>
</table>

The features of the corrosion behavior of CP Ti in the CG and UFG states may be associated with the self-passivation phenomenon. For instance, the perimeter of grain boundaries in the UFG sample is larger than the one in the CG sample, while the surface binding energy of atoms is lower. At the same time, on the surface there forms a continuous and thick oxide film due to a large amount of free enthalpy. As it can be seen in fig. 7, the equilibrium potentials of corrosion are more positive (-1.2 V) for the CG sample (Fig. 7, a) and less positive (-1.85 V) for the UFG sample (Fig. 7, b).

Proceeding from this, not taking into account the passivating properties of the oxide film on titanium, the CG sample is supposed to possess a lower corrosion activity than the UFG sample. However, as demonstrated by the analysis of polarization curves, the corrosion current of the CG sample is more than 1.5 times higher than the corrosion current of the UFG sample. In this connection, one may assume that the properties of the forming oxide film have a significant effect on the corrosion properties of CP Ti.

The differences in the formation of oxide passivating layer on Ti can be indirectly observed in the last third of the anodic branch of the polarization curves, displayed in fig. 7. As it can be seen in Fig. 7, a, the induced current continues to become further saturated, also after the overpotential of 0.2 V, and remains practically unchanged with increasing potential; this may indicate the maximum ionization current of Ti in this electrolyte solution. In Fig. 7, b the linear region is less expressed, but after it ends, the titanium, with increasing potential, continues to dissolve with growing induced current, its values being smaller than the ones for the CG sample; this may indicate larger diffusion limitations for the anodic process, created by the oxide film, in UFG Ti as compared to CG Ti.

In addition to the corrosion tests performed according to the two above-described procedures, clarifying tests in a salt spray chamber were conducted as an alternative method.

3. Corrosion tests in a salt spray chamber

3.1. Experimental procedure

The tests were performed in accordance with the ASTM G31 standard [10] in vapor atmosphere in a salt spray chamber, its schematic diagram being shown in Fig. 8. The size of the tested samples from CP Ti with CG and UFG structures was 9 x 25 x 9 mm. The concentration of the NaCl salt solution was 3.5%. The duration of the experiment was 10 days.

Corrosion resistance was evaluated on the basis of weight loss. The weight loss was recorded in accordance with the requirements of the ASTM G1 standard [11]. The samples were weighed on an analytical balance after withdrawal from a reservoir and careful washing in distilled water with a soft brush, followed by removal of water with filter paper.

![Schematic diagram of the salt spray chamber](378x469 to 479x603)

The salt spray chamber is a reservoir that can be used as a universal and convenient apparatus for conducting simple corrosion tests. The configuration of the reservoir's upper portion is such that more complex devices can be added to it, depending on the specific test type.

3.2. Test results

The area of corrosion damage was estimated in accordance with the recommendations set forth in CNS8886 [12]. According to the quantitative evaluation, the larger is the score, the smaller is the corrosion area, and vice versa. The corrosion evaluation is presented in table 3.

Table 3. Corrosion area on the basis of the corresponding sorting points [12]

<table>
<thead>
<tr>
<th>Estimate of corrosion area, A (%)</th>
<th>Numerical score of corrosion damage (score points)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.01$</td>
<td>$10$</td>
</tr>
<tr>
<td>$0.02 &lt; A \leq 0.05$</td>
<td>$9.5$</td>
</tr>
<tr>
<td>$0.05 &lt; A \leq 0.07$</td>
<td>$9.3$</td>
</tr>
<tr>
<td>$0.07 &lt; A \leq 0.10$</td>
<td>$9$</td>
</tr>
<tr>
<td>$0.10 &lt; A \leq 0.25$</td>
<td>$8$</td>
</tr>
<tr>
<td>$0.25 &lt; A \leq 0.50$</td>
<td>$7$</td>
</tr>
<tr>
<td>$0.50 &lt; A \leq 1.00$</td>
<td>$6$</td>
</tr>
<tr>
<td>$1.0 &lt; A \leq 2.5$</td>
<td>$5$</td>
</tr>
<tr>
<td>$2.5 &lt; A \leq 5$</td>
<td>$4$</td>
</tr>
<tr>
<td>$5 &lt; A \leq 10$</td>
<td>$3$</td>
</tr>
<tr>
<td>$10 &lt; A \leq 25$</td>
<td>$2$</td>
</tr>
<tr>
<td>$25 &lt; A \leq 50$</td>
<td>$1$</td>
</tr>
<tr>
<td>$50 &lt; A$</td>
<td>$0$</td>
</tr>
</tbody>
</table>
Fig. 9 shows the appearance of CP Ti samples with a coarse-grained microstructure after corrosion tests in a salt spray chamber.

Fig. 9. Appearance of the samples with a CG structure after corrosion tests

Fig. 10 shows the appearance of the CP Ti samples with an ultrafine-grained microstructure after corrosion tests in a salt spray chamber.

Fig. 10. Appearance of the samples with a UFG structure after corrosion tests

As it can be seen in Fig. 9, the corrosion damage of the samples with a CG structure is represented primarily by small, but densely spaced, point defects, as well as by rather extensive continuous areas. Apparently, such a difference is conditioned by a dissimilar surface preparation (polishing) prior to the experiment. In Fig. 10 visible are more extensive widely-spaced point defects, caused by corrosion damage. The most illustrative regions of corrosion damage are marked in red on the samples with different microstructures.

However, the weighing of the samples prior to and after the corrosion tests reveals that the weight loss for the material with a CG structure is much larger than the weight loss for the samples with a UFG structure.

Table 4 presents the experimental results of corrosion tests.

<table>
<thead>
<tr>
<th>Sample weight, g</th>
<th>CG structure</th>
<th>UFG structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prior to the tests</td>
<td>8.274</td>
<td>8.524</td>
</tr>
<tr>
<td>After the tests</td>
<td>8.2397</td>
<td>8.5112</td>
</tr>
<tr>
<td>Weight loss, %</td>
<td>0.415</td>
<td>0.150</td>
</tr>
<tr>
<td>Area of corrosion damage according to Table 3</td>
<td>0.07 &lt; A ≤ 0.10</td>
<td>0.05 &lt; A ≤ 0.07</td>
</tr>
<tr>
<td>Corrosion damage score</td>
<td>8.2</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Analysis of the table reveals that for CP Ti with a CG structure the corrosion damage under salt spray conditions is more than 2.5 times larger than the corrosion damage for the SPD-processed material with a UFG structure. This confirms the results obtained earlier.

Fig. 11 shows an electronic image of a corrosion damage region on the surface of CP Ti with a UFG structure, together with chemical analysis data.

Table 5 presents the chemical compositions corresponding to the spectra shown in fig. 11.

Table 5. Analysis of the chemical composition of the corrosion spot for CP Ti with a UFG structure.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>F</th>
<th>Na</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>96.85</td>
<td></td>
</tr>
<tr>
<td>Spectrum 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>24.87</td>
<td></td>
<td>0.33</td>
<td></td>
<td></td>
<td>74.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>25.51</td>
<td></td>
<td>0.31</td>
<td></td>
<td></td>
<td>74.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>20.30</td>
<td>0.82</td>
<td>0.31</td>
<td></td>
<td></td>
<td>76.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 7</td>
<td>23.00</td>
<td>1.18</td>
<td>0.79</td>
<td>0.28</td>
<td></td>
<td>74.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>28.91</td>
<td>0.79</td>
<td>1.02</td>
<td>0.33</td>
<td>0.24</td>
<td>0.37</td>
<td>68.00</td>
<td>0.33</td>
</tr>
<tr>
<td>Spectrum 9</td>
<td>27.96</td>
<td>1.57</td>
<td>0.94</td>
<td>0.20</td>
<td>0.20</td>
<td>69.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 10</td>
<td>25.64</td>
<td>0.99</td>
<td>0.42</td>
<td></td>
<td></td>
<td>68.47</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Spectrum 11</td>
<td>26.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70.70</td>
<td></td>
</tr>
</tbody>
</table>
Proceeding from the above, the following factors can be mentioned that influence the corrosion behavior of CP Ti: grain size, the oxide film thickness, composition and continuity, electrolyte composition.

**Conclusions**

1. The type of the used coating (applied by ion plasma spraying or microarc oxidation) has practically no effect on the corrosion damage value of CP Ti samples.

2. The studied material (CP Ti) without coating in the ultrafine-grained state after SPD processing has a much smaller degree of corrosion damage, approximately 3 times smaller, as compared to the initial (as-annealed) state having a coarse-grained structure.

3. For the studied material with a UFG structure, a much lower corrosion rate is revealed in a 3.5% aqueous solution of sodium chloride in the observed time interval.

4. It has been established that the corrosion currents of CP Ti in the CG and UFG states in a weak-acid chloride electrolyte are different. The smaller is the grain size, the smaller is the corrosion current, which may be related to the self-passivation phenomenon and the regularities in the growth and structure of oxide films.

5. The corrosion behavior of CP Ti is influenced by grain size, oxide film composition and continuity, electrolyte composition.

**ACKNOWLEDGEMENTS**

The authors gratefully acknowledge the financial support under the joint Russian-Taiwanese research project RFBR No. 15-58-52015 HHC_a and MOST No. 104-2923-E-011-003-MY3.

**REFERENCES:**


EFFECT OF Ni ADDITION ON STRUCTURE FORMATION AT IN-SITU SYNTHESIS OF TiC HARDENED Fe-BASED POWDERED ALLOY

Institute for Problems of Materials Science, National Academy of Science of Ukraine, Kyiv, Ukraine
E-mail: gbag@rambler.ru

Abstract: The features of structure and phase formation of TiC hardened Fe-based alloy at in-situ thermal synthesis from mixtures of TiH₂, Fe, graphite and Ni powders had been investigated. It was shown that after synthesis at 1200 °C the structure of the alloy is a skeleton of titanium carbide grains of various shapes and sizes from 1 to 20 µm cemented with Fe-based binding substance mostly located around the titanium carbide grains. The phase composition of the obtained alloy includes mainly phases of titanium carbide and α-Fe. In the case of using the initial mixture with the Ni in the composition of the alloy along with the titanium carbide solid solution of Ni in alpha-iron and Ni-based compounds were identified. When Ni is used instead of Fe in initial powder mixture it leads to a noticeable refinement of the alloy grain structure: the size of the carbide grains is generally not more than 5-7 microns. With the decrease in Ni content in the mixture and respectively increase of iron content at the same Ti and graphite content, the particle size increases markedly and approaches with 5 % of Ni to the particle size of the alloy obtained from the mixture containing no Ni.

Keywords: ALLOY, THERMAL SYNTHESIS, MICROSTRUCTURE, GRAIN, POWDER, TITANIUM CARBIDE, COMPOSITE

1. Introduction

Among the groups of wear-resistant materials that made by powder metallurgy methods, TiC reinforced ferrous based composites have gained widespread use in recent years. They consist of carbides with a mass fraction from 10 to 70% and the metal bonding i.e. alloyed steel [1-7].

Titanium carbide, as the carbide component of the TiC reinforced steels, is the most often used due to a combination of properties that exceed those of other carbides of transition metals (except tungsten carbide) [8]. Titanium carbide has a high melting point (3100 °C), Young’s modulus (451 GPa) and microhardness values up to 30 GPa. Titanium carbide has a satisfactory solubility in nickel (about 5% at 1250 °C) [9]. The low solubility of TiC in iron (about 0.5%) reduces the probability of "welding" between cutter and chip during processing steel parts, as a result titanium carbide-based alloys can be used at high cutting speeds. The advantage of using titanium carbide is also the relatively low cost of raw materials for its production. However, the main disadvantages of titanium carbide are low thermal conductivity and insufficient weldability by iron group metals during sintering.

Wetting improvement of carbide particles by a metal binder can be expected from a new technological approach for the synthesis of TiC reinforced steel powder which suggest that the carbide phase is not added into the initial powder mixture in the form of titanium carbide powder [1-4], while TiC is formed during the thermal synthesis of the alloy from powder mixtures of titanium, iron-carbon alloy and carbon powders [7, 10, 11]. Due to the presence of a low-temperature eutectic zone with a melting point of about 1085 °C [12] in the Fe-Ti system, interaction of Fe-Ti alloy with carbon, and high affinity of titanium to carbon at temperatures exceeding 1085 °C an active interaction of the components of the mixture occurs resulting into formation of titanium carbide particles [10].

In addition, J. Kubarsepp showed [2] that addition of nickel to the composition of the metal component of TiC-Fe composites reduces the wetting angle, and maximum hardness of the alloy is observed at a nickel content of 5 to 10%.

According to [13], nickel has a low diffusion coefficient in iron and increases the stability of austenite in powdered steels. It can be assumed that the binder in nickel-containing TiC-steel composites is most likely to contain γ-Fe based solid solutions, as well as titanium nikelide and intermetallics.

The aim of this work was to study the features of the structure and phase formation of alloys obtained by thermal synthesis from Fe-Ti-Ni-C powder mixtures.

2. Materials and experimental procedure

For experimental investigations of mixture composition influence the on the structure and phase composition of the pseudoolloys, five mixtures of iron, titanium hydride, nickel, and carbon powders were prepared (Table 1).

The initial powders were blended in a ball mill and pressed at 600 MPa into briquettes, which were then sintered at 1200 °C for 1 hour in vacuum to provide the thermal synthesis of the composite.

After the thermal synthesis the samples obtained from sponge of different compositions were cut, grinded and polished. The etching of the samples was carried out with an etchant based on a mixture of hydrofluoric and nitric acids.

Micro- and macrostructure analysis was carried out using a XJL-17 optical microscope and scanning electron microscope JEOL Supperprobe 733 with ultrasonic cleaning of fracture surface was used.

The size of titanium carbide grains was determined by the secant method on the samples studied. On each sample, at least 50 measurements were taken along arbitrarily chosen secants.

The X-Ray Diffraction (XRD) analysis of the samples was performed using DRON-3M diffractometer with CoKα radiation in the range of angles from 20 to 130 degrees. The sample during the analysis were rotated around its axis. The analysis of XRD data was performed by standard methods using the ASTM card index.

3. The results and discussion

To evaluate the influence of nickel on the structure, phase composition and properties of the synthesized alloy, the alloy
obtained from the initial mixture without nickel (No. 1, Table 1) was considered as the base material.

As can be seen from Fig. 1,a,c, the structure of this alloy is a skeleton of titanium carbide grains of various shapes and sizes with a binder located predominantly around the grains of titanium carbide. Carbide grains are distributed non-homogeneously. In the optical microphoto, titanium carbide has a white or light gray color, while the solid solution is a light, formless phase and metal binder is black and rims the light grains of titanium carbide. A large portion of the sample’s surface is occupied by large round pores formed mainly as shrinkage shells due to recrystallization during sintering in the presence of a liquid phase.

The structure of the alloy is not homogeneous. The size of predominantly rounded carbide grains varies from 1 μm to 20 μm (Fig. 1,c). The presence of rim zones around the grains of titanium carbide, which formed due to the interaction of carbide particles with the melt of the metal binder, is clearly observed. As the authors of [1, 2] note, the dissolution of titanium carbide in a metal binder is significantly influenced by the carbon content in carbide: the lower its content in carbide, i.e. the greater deviation from the stoichiometric composition, the higher its solubility in the steel binder.

The SEM data (Fig. 1,b,c) show that during thermal synthesis process, the partial sintering of titanium carbide powder is occurred. Melting of the particles and their mutual fusion with one another with following formation of colonies of fused carbide particles are observed too.

The replacement of iron with nickel in the initial powder mixture leads to a noticeable refinement of alloy structure (Fig. 2,a): the size of the carbide grains usually does not exceed 5-7 μm. It is noteworthy that the carbide skeleton becomes more disconnected (the carbide grains act as separate islands) (Fig. 2,b,c) in comparison with the alloy obtained from the mixture No.1 with iron as the metal binder.

As the content of nickel in the mixture decreases to 5%, the size of the particles (mixture No.5) increases noticeably (Fig. 4) and approaches the size of the particles of the alloy, obtained from the mixture No.1 without nickel.

In case of use of Fe-Ni alloy as the metallic binder of the composite with iron composition in the initial mixture of 5÷15% (mixtures No.3 and 4) a slight increase in size of carbide grains and somewhat larger grain size distribution can be noted in comparison with Fe-free alloy No.2. Internal fragmentation of carbide grains is observed too. Along with fine carbides of 1÷2 μm in size, the carbide grains are combined into large colonies with the size more than 25 μm (fig.3).
The XRD analysis of the sintered composites showed that in case of the alloy synthesized from the mixture of Fe, TiH₂, and C powders (mixture No. 1), the thermally synthesized alloy consists of TiC and solid solution of α-Fe (Fig. 5a). When the initial mixture with nickel is used (mixture No. 5), the solid solution of nickel in alpha-iron and nickel compounds with a lattice period of a = 4.3198 Å is observed along with the titanium carbide phase.

According to the Wulf-Bragg relation, the lattice period of titanium carbide in the obtained alloys is a = 4.3266 Å for cubic syngony (Fm3m), which corresponds to titanium carbide with TiC₀.₈₂ stoichiometry [8]. The size of the coherent scattering blocks for titanium carbide in the sample obtained from the mixture No. 5 is 217 Å, which is almost 20% less than that for the sample sintered from the mixture No.1 without nickel (259 Å). It seems that these are small titanium carbides (0.2÷0.3 μm) in the alloy, which are indistinguishable for optical microscopy but act as single crystallites for an X-ray radiation by scattering it coherently.

The average grain size of titanium carbide grains are in the range of 0.5 μm to 5 μm for all samples as was defined from the micrographs by the secant method (Fig. 6,a). At the same time, the highest amount of fine grains with sizes of 1÷2 μm was observed for alloys obtained from mixtures No.2 and 3 with high nickel content (20 and 15%, respectively), whereas grains of 8 μm to 17 μm in size were observed only in alloys obtained from nickel-free mixture (No.1) and mixture No.5 with a minimum (5%) Ni content.

The dependence of the minimum and maximum carbide grains size of on the nickel content in the initial mixture is also of interest. According to Fig. 6,b, the minimum grain size is 0.5÷1.0 μm, regardless of the nickel content in the mixture, while the maximum grain size (~17 μm) is substantially higher for nickel-free and low-nickel alloys (mixtures No.1 and 5). Whereas an increase of Ni content in the mixture to 10÷20% results in significant reduction of the maximum grain size to 6÷7 μm, which confirms the conclusion about the dispersive role of nickel additives.

**Conclusions**

1) It is shown that thermal synthesis is an efficient method for obtaining composite powders of TiC hardened steels from mixtures of iron, titanium hydride and graphite at relatively low temperatures and can be used for deposition of wear-resistant coatings and fabrication of bulk parts by powder metallurgy methods.

2) The structure of the synthesized alloy is a porous skeleton made of titanium carbide grains of various shapes and sizes and binder located predominantly around titanium carbide grains.

3) The phase composition of the alloy synthesized from the mixture of Fe, TiH₂ and graphite powders consists of titanium carbide and solid solution of α-iron, whereas in the case of using the initial mixture with nickel, a solid solution of nickel in α-iron and nickel compounds with a lattice period of a = 4.3198 Å is observed along with titanium carbide.

4) It is shown that the addition of 10÷20% Ni to the initial mixture leads to significant dispersion of the carbide phase (up to 1÷6 μm) in the synthesized alloy, whereas the maximum grain size of carbide phase reaches 17÷20 μm for nickel-free and low-nickel alloys.
Fig. 6. The relation of TiC grains size distribution of powder mixture content (a) and of Ni content in the mixture (b)

References

STRUCTURE, MECHANICAL PROPERTIES AND CORROSION RESISTANCE OF MAGNESIUM ALLOY WE43 AFTER EQUAL-CHANNEL ANGULAR PRESSING

PhD student Martynenko N.S.1,2, PhD Lukyanova E.A.1,2, PhD student Tokar A.A.1,2, Prof. Dr. Sci. Raab G.I.3, Prof. Birbilis N.4, Prof. Dr. Sci. Dobatkin S.V.1,2, Prof. PhD Estrin Yu.Z.1,4
1National University of Science and Technology "MISIS", Laboratory of Hybrid Nanostructured Materials, Moscow, Russia
2A.A. Baikov Institute of Metallurgy and Materials Science of Russian Academy of Sciences, Moscow, Russia
3Ufa State Aviation Technical University, Ufa, Russia
4Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia
E-mail: nataliasmartynenko@gmail.com, helenelukyanova@gmail.com, tokar2005@mail.ru, giraab@mail.ru, nick.birbilis@monash.edu, dobatkin.sergey@gmail.com, yuri.estrin@monash.edu

Abstract: ECAP was conducted using route Bc with an angle of 120° between the die channels and a stepwise decrease of temperature from the initial 425 °C to 300 °C at the final, 12th pass. The cumulative equivalent strain the ECAP billets underwent was about 7.8. The structure examination showed that ultrafine-grained structure with the grain size of 0.69 – 1 μm was formed during ECAP process. In addition, particles of the phase Mg2Nd with an average size of 0.45 μm were formed. The refinement of the microstructure resulted in an improvement of the mechanical properties of the alloy. After ECAP, the strength characteristics of the alloy increased to the levels of ultimate tensile strength of 300 and yield strength of 260 MPa to be compared to those for the initial state (220 MPa and50 MPa, respectively). At the same time, the ductility increased to 13.2 %, which compares favourably with the initial value of 10.5 %. The ECAP process does not affect the resistance to electrochemical corrosion. The rate of chemical corrosion was found to be reduced owing to the ECAP processing.

KEYWORDS: MAGNESIUM ALLOYS, SEVERE PLASTIC DEFORMATION, EQUAL CHANNEL ANGULAR PRESSING, ULTRAFINE GRAINED STRUCTURE, MECHANICAL PROPERTIES, CORROSION RESISTANCE

1. Introduction

The magnesium alloy WE43 (Mg-4%Y-3%(Nd+RE)-0.5%Zr) is a high-strength casting alloy, which finds successful applications in the aerospace and automotive industries. It is also a promising material for medical application due to its good biocompatibility [1, 2]. However, modification of the alloy is necessary for the successful use of the alloy by improving the strength characteristics, as well as corrosion resistance. There are a number of works devoted to severe plastic deformation (SPD) of WE43 alloy [3-14], including equal-channel angular pressing (ECAP) [15-17]. They demonstrated that the use of SPD process allows to refine the grain up to 30 nm [14], resulting in substantial hardening of the alloy. In addition, it was shown in [18, 19] that ultrafine-grained (UFG) and nano structure makes it possible to improve the corrosion resistance of magnesium alloys. Based on this, it can be concluded that the SPD is a promising treatment for increasing both strength and corrosion resistance. Therefore, the purpose of this work was to study the structure, mechanical properties and corrosion resistance of the magnesium WE43 alloy after equal-channel angular pressing.

2. Materials and Methods

In this paper we used a commercial WE43 (Mg-4%Y-3%(Nd+RE)-0.5%Zr, wt.%) alloy. As an initial state, the ingot was homogenized at 525 °C for 8 hours. The samples of cylindrical shape with a diameter of 10 mm and a height of 80 mm were cut from the obtained rod for ECAP. Route Bc ECAP was conducted using a die with an angle of 120° between the channels for two regimes with different temperatures of beginning and finishing of treatment. For regime 1, the deformation temperature was reduced from 400 °C to 350 °C in increments of 50 °C. The alloy was deformed into 6 passes at each temperature. In case of the second regime the temperature was reduced from 425 °C to 300 °C in increments of 25 °C. The alloy was deformed into 2 passes at each temperature. The total number of passes was 12 for both regimes (Fig. 1), which corresponds to a true strain equal of 7.8. The microstructure was examined using an optical microscope Reichert MeF and a transmission electron microscope (TEM) JEM 1400 operating at 120 kV. Samples for TEM analysis after ECAP were cut in the longitudinal direction and then thinned to 150 μm. Further, the foil was subjected to electrolytic etching in an electrolyte consisting of 75% CH3COOH and 25% HNO3 at -35 °C using a Struers TenuPol-5 jet grinder.

The evaluation of mechanical properties was carried out by performing uniaxial tension tests at room temperature. The tests were carried out on an Instron1096 test machine at a strain rate of 1.5 mm/min on samples with a working length l equal to 15 mm and a working diameter d equal to 3 mm.

Corrosion resistance was evaluated by the potentiodynamic polarization, weight loss and hydrogen evolution methods in a 0.9% NaCl solution (pH = 7). All electrochemical tests were carried by VMP potentiostat controlled by EC-Lab software (Bio-logic). The setups were using PAR flat cell which has a “three electrode configurations” (working electrode, saturated calomel reference electrode and Pt-mesh counter electrode). Previously, the material was subjected to mechanical grinding on abrasive paper with gradually decreasing granularity (from P800 to P2500). Scanning was performed with a scan rate equal to 1 mV per second in the range from 100 mV below the open circuit potential (OCP) to -1000 mV. The dwell time prior to the commencement of the scan, which is necessary that the surface to form an electrical double layer (EDL) and associated redistribution of species in the electrolyte was 10 minutes [20]. The number of scan repetitions was 5 for each test sample. Before each scan, the sample was repolished. The weight loss and hydrogen evolution tests were carried out in a 0.9% NaCl solution (pH = 7) at room temperature and 37 °C [20, 21]. The test duration was 1 day for both methods of corrosion resistance assessment. Samples after weight loss tests were washed in a cleaning solution consisting of 200g Cr2O3, 10g AgNO3, 20g Ba(NO3)2 and distilled water to make 1 liter of solution for 1 minute to remove corrosion products, and then weighed on an electronic balance GR 200. Calculation of the corrosion rate was performed according to ASTM G1 (Standard Practice for Preparing, Cleaning, and Evaluation Corrosion Test Specimens).
3. Results and Discussion

There are equiaxed grains of a supersaturated magnesium solid solution of 70 μm in the alloy after homogenization at 525 °C and subsequent cooling in air. An ultrafine-grained structure with the average grain size of 1.00 ± 0.14 μm for regime 1 and 0.69 ± 0.13 μm for regime 2 is formed during the ECAP (Fig. 1). The occurrence of high-angle boundaries is confirmed by ring-like electron diffraction patterns with a number of point reflexes. Furthermore, the particles of the equilibrium Mg12Nd phase of 0.41 ± 0.18 μm and 0.45 ± 0.18 μm in size were observed in both cases (for regimes 1 and 2, respectively). It was shown in [14] that the HPT process accelerates the decomposition of a supersaturated magnesium solid solution, by forming a larger number of defects that act as a substrate for nucleation of particles. It should be noted that a similar effect appeared in case of ECAP, since the decomposition of the supersaturated magnesium solid solution occurred already during deformation and heating process of the treatment. It is also worth noting that we observed the deformation twins in the structure after ECAP in case regime 2 (Fig. 2 d). The smaller grain and the existence of twins in the structure of the alloy after deformation by regime 2 can be probably caused by the lesser end temperature of deformation compared with regime 1.

Fig. 2. Microstructure of WE43 alloy in initial state (a) and after ECAP for regime 1 (b) and regime 2 (c, d).

The refinement of the structure during ECAP process leads to strengthening of the WE43 alloy. For regime 1, the values of the yield strength increases up to YS = 180 MPa and the ultimate tensile strength – up to UTS = 250MPa compared with the initial state (150 MPa and 220MPa, respectively) with a slight decrease in ductility from 10.5 to 7%. However, the increase in ductility up to 13.2% occurs along with an increase in the ultimate tensile strength and the yield strength up to 300 and 260 MPa, respectively, for regime 2 (Tab. 1).

The high level of strength in case of regime 2 can apparently be explained by a more dispersed structure and also by the existence of deformation twins in the structure.

Table 1. Mechanical properties of WE43 alloy in the initial state and after ECAP treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>UTS, MPa</th>
<th>YS, MPa</th>
<th>EL, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state</td>
<td>220</td>
<td>150</td>
<td>10.5</td>
</tr>
<tr>
<td>ECAP Regime 1</td>
<td>250</td>
<td>180</td>
<td>10.0</td>
</tr>
<tr>
<td>ECAP Regime 2</td>
<td>300</td>
<td>260</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Fig. 3 and Table 2 demonstrate the results of potential dynamic polarization tests. The obtained results showed that deformation by ECAP practically does not influence on the resistance to electrochemical corrosion of WE43 alloy. For regime 1, the potential of corrosion remains equal within the error to the corrosion potential in initial state (-1622 ± 19 mV and -1630 ± 34 mV, respectively). In case of regime 2, a slight decrease occurs to the value of -1686 ± 8 mV. The values of the corrosion current density, corresponding rate of corrosion, are the same within experimental error for all three states of the alloy (21.30 ± 4.50 μmA/cm², 16.18 ± 3.14 μmA/cm² and 21.81 ± 6.50 μmA/cm² for initial state, ECAP regime 1 and ECAP regime 2, respectively).

Table 2. Results of PDP tests of the WE43 alloy in the initial state and after ECAP treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ecorr, mV SCE</th>
<th>jcorr, μmA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state</td>
<td>-1630 ± 34</td>
<td>21.30 ± 4.50</td>
</tr>
<tr>
<td>ECAP Regime 1</td>
<td>-1622 ± 19</td>
<td>16.18 ± 3.14</td>
</tr>
<tr>
<td>ECAP Regime 2</td>
<td>-1686 ± 8</td>
<td>21.81 ± 6.50</td>
</tr>
</tbody>
</table>

At the same time, the study of resistance to chemical corrosion revealed an improvement in corrosion resistance after ECAP. Fig. 4 shows the results of measuring the corrosion rate by weight loss (WL) and hydrogen evolution (HE) methods at room temperature and 37 °C. It can be seen that the corrosion rate after ECAP for both regimes is lower than the corrosion rate in the initial state, both for tests at room temperature and 37 °C. Laws of weight loss rate change and evolving of hydrogen are similar and identical to the experimental errors (Table 3). Increasing of the test temperature to 37 °C does not significantly affect the corrosion rate, but increases within the experimental error. Only samples processed by ECAP for regime 2, which demonstrate significant growth both the rate of degradation and the rate of evolution of hydrogen, and samples in the initial state, whose hydrogen evolution rate also increases, are the exception. Probably, the higher corrosion rate after the second regime of ECAP compared with the first regime ECAP is caused by the existence of deformation twins in the structure, which can have a negative effect on the corrosion resistance of the alloy.
The grain refinement during ECAP results in increasing of the tests both at room temperature and at 37 °C.

3. ECAP does not impair the resistance to electrochemical ductility increases up to 13.2%.

4. The corrosion rate, measured by the weight loss and hydrogen evolution methods, is reduced for both deformation regimes for corrosion.

ECAP leads to a significant refinement of the structure of the magnesium WE43 alloy. During the deformation process an UFG state is formed with an average grain size of 0.69 – 0.45 μm, as well as Mg12Nd phase particles with an average size of 0.41 – 0.45 μm.

The increase in corrosion resistance after deformation is apparently associated with a decrease in grain size caused by ECAP. The grain refinement affects the surface roughness parameters, which, in turn, affect the rate of degradation of the alloy.

4. Conclusions

1. ECAP leads to a significant refinement of the structure of the magnesium WE43 alloy. During the deformation process an UFG structure is formed with an average grain size of 0.69 - 1 μm, as well as Mg12Nd phase particles with an average size of 0.41 – 0.45 μm.

2. The grain refinement during ECAP results in increasing of the ultimate tensile strength of WE43 alloy up to 300 MPa while the ductility increases up to 13.2%.

3. ECAP does not impair the resistance to electrochemical corrosion.

4. The corrosion rate, measured by the weight loss and hydrogen evolution methods, is reduced for both deformation regimes for tests both at room temperature and at 37 °C.

Acknowledgments

Part of this work relating to studies of microstructure and mechanical properties was funded by the Ministry of Education and Science of the Russian Federation (grant #14.A12.31.0001).

Table 3. Results of weight loss and hydrogen evolution tests of the WE43 alloy in the initial state and after ECAP treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>WL, mg/cm²day</th>
<th>HE, ml/cm²day</th>
<th>WL, mg/cm²day</th>
<th>HE, ml/cm²day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state</td>
<td>0.93±0.20</td>
<td>0.87±0.21</td>
<td>1.09±0.24</td>
<td>1.34±0.26</td>
</tr>
<tr>
<td>ECAP Regime 1</td>
<td>0.40±0.17</td>
<td>0.38±0.04</td>
<td>0.56±0.09</td>
<td>0.60±0.04</td>
</tr>
<tr>
<td>ECAP Regime 2</td>
<td>0.52±0.09</td>
<td>0.37±0.16</td>
<td>0.87±0.08</td>
<td>0.95±0.07</td>
</tr>
</tbody>
</table>

Fig. 4. Results of weight loss (a) and hydrogen evolution (b) tests at room temperature and 37 °C.

Funding support of investigations of corrosion properties was provided by the Russian Science Foundation (project #17-13-01488).

5. Literature


INFLUENCE OF STRUCTURAL AND PHASE TRANSFORMATION ON PROPERTIES OF SEVERELY DEFORMED DISPERSION-HARDENING ALLOYS

S.N. Faizova1,2, I.A. Faizov3, V.I. Semenov3, F.F Hizbullin1
1Ufa State Petroleum Technological University
2Institute for Metals Superplasticity Problem RAS,
3ASI Institute for Strategic Studies, RR,Ufa,Russia
1 Kosmonavtov St., Ufa 450062 Russia
e-mail: snfaiz@mail.ru

Abstract: The effect of severe plastic deformation on the kinetics of second phases in a dispersion-strengthening Cu-Cr-Zr alloy is investigated. The observed set of phenomena indicates that during SPD processing there occurs a complex interaction between deformation mechanisms and the processes of dissolution and precipitation of second-phase particles in the copper matrix, influencing structure refinement and resulting in a change of the particle sizes and their distribution, and consequently, the material’s strength.

Keywords: SEVERE PLASTIC DEFORMATION, ECAP, MICROSTRUCTURE, DISPERSION PARTICLES, STRAIN HARDENING, PHASE TRANSFORMATIONS

1. Introduction

Copper-rich dispersion-strengthening chromium bronzes are widely used, for example, for the production of resistance welding electrodes. In spite of a great variety of electrode designs, all of them are intended for the supply of current and pressing force to the welded parts, and for the removal of heat from the parts. This determines the main requirements to the material they are made of, i.e. high electrical conductivity and hardness (wear resistance).

The desired set of required functional properties in chromium bronzes can be attained due to structure refinement to the nanometer scale as a result of severe plastic deformation (SPD) processing. Materials produced by nanostructuring exhibit combinations of functional properties, different from those formed by conventional industrial treatment. At the first stage – high-temperature treatment – the samples were subjected to holding for 1 hour at a temperature of 1050°C followed by water quenching in order to produce a solid solution of alloying elements in the copper matrix. Then the samples were subjected to cold deformation by equal-channel angular pressing (ECAP) followed by solid forging (SF) and drawing (D). Post-deformation ageing was performed at a temperature of 450°C for 1 hour. ECAP processing was conducted using a die set with a channels intersection angle of 90° via route  BC at room temperature, the number of ECAP passes was 8, the accumulated strain was ε = 1.1·8 = 8.8 [1-3]. Solid forging and subsequent drawing were conducted until the reduction of area reached 56% and 25%, respectively.

At all the stages, the material’s structure was studied by optical metallography (OM), scanning electron microscopy (SEM), including EBSD analysis, transmission electron microscopy (TEM) –foils and extraction replicas.

To study in detail the changes in particle sizes and their distribution during SPD, the method of extraction replicas was used. Taking into account the specific features of the separation of particles from the matrix, the acquired statistical data on the particle sizes and distances between them may contain errors concerning the largest and the smallest sizes observed. However, considering the substantial statistics of conducted measurements, at least 1000 particles for each state, the character of changes in these values can be evaluated with sufficient assurance. The particle size was estimated as the average value of two measurements made in two mutually perpendicular directions.

The average distance between particles in a plane was calculated according to the formula: \( L = \frac{\overline{N}}{\overline{S}} \), where \( S \) is the sample surface area, \( N \) is the number of particles in the area \( S \).

Study of the replicas by TEM made it possible to establish, while interpreting the electron diffraction patterns of individual particles, that the particles of certain compositions had a typical morphology. This fact was used for a further identification of particles, when statistical data were obtained.

Tensile mechanical test were performed on a universal Instron tensile testing machine at room temperature and a strain rate of 5.5×10⁻⁴ s⁻¹, and Vickers microhardness measurements (under a...
load of 1 N and a holding time of 10 seconds) were conducted on Micromet 5101 microhardness tester.

At each stage of processing, the contributions of different strengthening mechanisms into offset yield strength were estimated.

3. Results and Discussions

The average grain size after the high-temperature treatment of the alloy is 34±3 μm, a noticeable amount of particles is observed. Since the average particle sizes in this state are rather small, their presence is evidently related to an insufficient quenching rate.

SPD processing (ECAP+S+F+D) leads to a significant structure refinement – a banded, elongated along the rod, structure is formed (fig. 1, a). The transverse size of fragments is about 200-240 nm.

![Fig.1 (a) Banded structure of the Cu-1Cr-0.7Al-0.2Zr alloy after a complex SPD processing. (b) Small particles are clearly visible in the grain close to the fringes of extinction.](image)

The total density of particles decreases approximately two-fold as compared to the state after the high-temperature treatment. Although particles are observed both along boundaries and in grain interiors (fig. 1, 2), worth noting is the correlation of their location with the features of defect structure and the fragment boundaries. A large number of small particles are observed, as a rule, in dislocation pile-ups.

![Fig.2. Interaction between particles and dislocations (a, b)](image)

At each stage of processing, the contributions of different compositions changed at different stages of processing. Arrows show the direction in the changes of the average particle size.

It can be seen from Table 2 that the average sizes of particles with different compositions change at the stage of SPD processing in different directions. After the high-temperature treatment, the copper-aluminum particles that were present in the as-received state, are not observed. They appear again after SPD processing, and in this state their average size is even larger than in the as-received state. Such a behavior unambiguously indicates the deformation-induced decomposition of solid solution in the process of SPD.

The revealed correlation between particles and the elements of the material’s fragmented structure can be accounted for by the fact that particles, being efficient obstacles for dislocations (fig. 2, b), accumulate in their vicinity dense pile-ups, which are then transformed into fragment boundaries. An alternative mechanism, taking into account the presence of deformation-induced particle precipitation, could be that dislocation pile-ups and fragment boundaries are sinks for point effects and are therefore the preferred sites of new particles generation. In our opinion, most probable is the simultaneous synergic action of both mechanisms.

At the same time, SPD causes a significant decrease in the total number of particles, which indicates the domination of the inverse process, namely, deformation-induced particle dissolution, closely related to their mechanical fracture [12]. Under this processing, the mechanical fragmentation of particles may take place only via quasi-brittle fracture, since the cutting of dislocations under the attained accumulated strains cannot play a significant role.

In terms of their composition, the particles are intermetallics having a crystal lattice incoherent with copper, as a result of which the particle/matrix interface is hardly permeable for dislocations. Being an obstacle for dislocation motion, a particle accumulates on itself a pile-up creating stresses, sufficient for the development of internal shears inside it, and eventually for its destruction.

Table 1 lists the average distances between particles, reflecting their distribution densities, estimated for the whole particle ensemble. In view of the variety of chemical compositions, the task to determine the changes in the number of particles for each of the ensemble components is beyond the scope of this work.

Table 1. Dependence of the average particle size and the average distance between particles on the processing stage

<table>
<thead>
<tr>
<th>Processing stage</th>
<th>The average particle size, nm</th>
<th>The average distance between particles, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>80</td>
<td>960</td>
</tr>
<tr>
<td>Solid solution treatment</td>
<td>40↑</td>
<td>460↑</td>
</tr>
<tr>
<td>SPD</td>
<td>50↑</td>
<td>680↑</td>
</tr>
<tr>
<td>Age hardening</td>
<td>20↑</td>
<td>360↑</td>
</tr>
</tbody>
</table>

Table 2 demonstrates how the average size of particles with different compositions changed at different stages of processing. It can be seen from Table 2 that the average sizes of particles with different compositions change at the stage of SPD processing in different directions. After the high-temperature treatment, the copper-aluminum particles that were present in the as-received state, are not observed. They appear again after SPD processing, and in this state their average size is even larger than in the as-received state. Such a behavior unambiguously indicates the deformation-induced decomposition of solid solution in the process of SPD.

Table 2. Dependence of the average particle size on the processing stage

<table>
<thead>
<tr>
<th>Processing stage</th>
<th>The average particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>80</td>
</tr>
<tr>
<td>Solid solution treatment</td>
<td>40↑</td>
</tr>
<tr>
<td>SPD</td>
<td>50↑</td>
</tr>
<tr>
<td>Age hardening</td>
<td>20↑</td>
</tr>
</tbody>
</table>

Arrows show the direction in the changes of the average particle size.

![Table 2. Dependence of the average particle size on the processing stage](image)
Table 2. Changes in the average sizes of second-phase particles with processing stages in the Cu-1Cr-0.7Al-0.2Zr alloy. Each particle type is characterized by its typical morphology, electron diffraction pattern and chemical composition.

<table>
<thead>
<tr>
<th>Processing stage</th>
<th>Cu3Al, Cu4Al, CuAl, Al2Zr; ZrAl5, Zr2Al15, Cr</th>
<th>ZrAl5, Cu3Zr14</th>
<th>AlCrZr, Al2Zr5, CuZr, CuCr</th>
<th>CuCr4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial state</td>
<td>125±4</td>
<td>88±5</td>
<td>83±4</td>
<td>60±4</td>
</tr>
<tr>
<td>Solid solution treatment</td>
<td>–</td>
<td>67±4</td>
<td>53±3</td>
<td>35±3</td>
</tr>
<tr>
<td>SPD</td>
<td>155±5</td>
<td>69±3</td>
<td>38±4</td>
<td>60±4</td>
</tr>
<tr>
<td>Age hardening</td>
<td>32±3 ↓</td>
<td>27±4 ↓</td>
<td>18±3 ↓</td>
<td>38±3</td>
</tr>
</tbody>
</table>

The formed fragments have areas with a high surface curvature (ribs), which makes thermodynamically possible their partial dissolution. The progress of dissolution is influenced by diffusion acceleration in the process of SPD [13]. The drift of impurity atoms in the field of dislocation pile-ups, relaxing after particle destruction, can also make a contribution into accelerated mass transfer. The efficiency of this process depends on the metastability degree of a specific intermetallic, which accounts for the complex changes in the sizes of particles of different compositions. The reduction in the average size of particles, caused by the dissolution process, makes some of them undetectable by TEM, which explains the observed decrease in their number after SPD processing.

Another indicator of kinetically multidirectional processes of dissolution and precipitation, running during SPD, can be the behavior of the lattice parameter of the copper matrix, depending on the concentration of the solid solution of alloying elements. Figure 3 shows the XRD data on the lattice parameter values after different numbers of ECAP passes, complete SPD processing and post-deformation ageing. It can be seen that this value changes non-monotonically. Since at the stage of deformation there are no grounds to expect the non-monotony of the contribution from stresses created by the defect structure, the main cause for such a behavior should be considered to be the changes in the concentration of solid solution as a result of phase transformations.

![Fig.3. The copper lattice parameter of the Cu-1Cr-0.7Al-0.2Zr alloy at different stages of treatment](image)

All of these changes indicate that under SPD there occur deformation-induced decomposition of solid solution and deformation-induced dissolution of second-phase particles.

Table 3. Mechanical properties of the alloy at different stages of processing

<table>
<thead>
<tr>
<th>Processing stage</th>
<th>Microhardness, MPa</th>
<th>Tensile strength σ, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial stage (after industrial treatment)</td>
<td>1450</td>
<td>550</td>
</tr>
<tr>
<td>Solid solution treatment</td>
<td>660</td>
<td>220</td>
</tr>
<tr>
<td>SPD</td>
<td>1400</td>
<td>550</td>
</tr>
<tr>
<td>Age hardening 450°C 1 h</td>
<td>1980</td>
<td>700</td>
</tr>
</tbody>
</table>

During post-deformation ageing, solid solution decomposition is finalized and, correspondingly, there appear many small, ~20 nm, particles, which determine eventually the high strength attained in this alloy – 700 MPa (Table 3). For comparison, after industrial treatment the average size of particles and the average distance between them is 80 and 960 nm, respectively, and strength is 550 MPa.

The high strength characteristics after a comprehensive processing of the alloy are possible only due to the interaction of two basic strengthening mechanisms – structural strengthening and dispersion strengthening. As demonstrated by the results described in this work, an important role in the interaction of these mechanisms is played by phase transformations observed under SPD.

Conclusions:

The obtained experimental results indicate that under the equal-channel angular pressing of chromium-zirconium bronze there occur not only refinement of the matrix structure, but also complex phase transformation involving the second-phase particle sizes and their distribution.
Analysis of the whole aggregate of experimental results, obtained at different structural levels, allows us to assume that two multidirectional processes are realized simultaneously: deformation-induced decomposition of the solid solution of alloying elements and deformation-induced dissolution of second-phase particles.

References

12. V. V. Sagaradze, Diffusion transformations in steels due to cold deformation, Metal Science and Heat Treatment, Vol. 50, No. 9-10, pp. 422-429, 2008.
EVALUATION OF THE RESIDUAL STRESSES IN ADVANCED COMPOSITE CERAMIC COATINGS USING X-RAY DIFFRACTION AND FINITE ELEMENT TECHNIQUES

Prof. Dr. Adel K. Mahmoud1, Dr. Zaid S. Hammoudi2, M.Sc. Student Samah R. Hassan3
Faculty of Engineering, Diyala University, Diyala-Baqouba – Iraq1,2,3

Email: adel_alkayali@yahoo.com, zshaaa@yahoo.com, samahrasheed217@gmail.com

Abstract: The aim of this work is to evaluate the residual stresses in advanced composite ceramic coatings (60wt% Al2O3 – 40wt% SiO2) produced by thermal spraying coating (flame spraying) on the mild steel substrate (AISI 1050) steel. The bond coat used in this work was AlNi alloy to reduce mismatch of thermal expansion coefficient between substrate and composite ceramic coating as a top coating. The thickness of bond coating was (150㎛) and for composite ceramic coating was (450 χm). The residual stresses evaluated by X-Ray diffraction technique were compressive residual stresses (~62.6099), while by finite element method were compressive residual stresses (~68.491). The percentage of agreement between the residual stresses evaluated by X-Ray diffraction technique and finite element technique was (91.509%).

Keywords: Advanced Composite Ceramic Coatings, X-Ray Diffraction Technique, Finite Element Method

1. Introduction

Increased use of thermal spray coatings, especially for high-temperature environmental resistance, requires confidence in coating durability, i.e., resistance to cracking, debonding, and spallation, both during application and in service. Residual stresses are known to play an important role in coating durability; for example, tensile residual stresses typically increase the susceptibility to cracking and debonding. Many studies have been devoted to the measurement of residual stresses in coatings [1-4]. Residual stresses develop during cooling of a thermal spray coating due to the mismatch of thermal expansion coefficients of the coating and substrate. Depending on the relative magnitudes of the thermal expansion coefficients of the coating and substrate [5-7] residual stress can be either tensile or compressive. Parameters that strongly affect the magnitude of residual stresses are coating and substrate temperature during spray deposition and properties of the coating such as thickness, roughness and porosity. Experiments have shown that residual stress increases with coating thickness and deposition temperature [8]. Thermal barrier coatings (TBCs) are the best way to protect components of gas turbine engines and the demand for such coatings is becoming more important as higher temperature engines are being developed [9-14]. Generally, the residual stresses of thermally sprayed coatings are induced by different mechanisms and sources [15-17]. In a thermal spray process with a high flame temperature, such like flame spray, plasma spray, or arc spray, fully and partially molten particles striking onto the surface of the substrate, are flattened, solidified, and cooled down in a very short period of time (few microseconds). After their solidification and adhesion onto the surface of the substrate, the contraction of the splats can be hindered by substrate material or the underlying solidified coating material, which results in tensile stresses which are called intrinsic, deposition, or quenching stress. Due to an extremely high temperature difference, a high theoretical residual stress in the order of up to 1 GPa can be induced. However, due to the many relaxation mechanisms, such as the sliding of the splats, micro cracks, plastic deformations, and material creep, the experimentally measured values are much lower (<100 MPa) [18]. X-ray diffraction was used as a complementary technique; it can determine stress only in a thin surface layer, whereas the penetrating power of neutrons enables through-thickness stress profiling without any material removal [19].

This work aims to evaluation of the residual stresses in advanced composite ceramic coating (60%wt Al2O3 - 40%wt SiO2) using X-ray diffraction technique (XRD) and the residual stresses calculated by finite element method (FEM).

2. Materials and method

2.1 Materials and parameters of the spraying processes

The coatings were applied by thermal spraying method (flame spraying) in air on the plain-carbon steel (AISI 1050), cylindrical substrate that’s dimensions were 15 mm in diameter and 10 mm in height. The flame spraying system is designed and implemented in the welding laboratory of Mechanical Engineering Department, College of Engineering, University of Diyala, Iraq using spray gun the heat flame is produced by the burning of oxygen and acetylene, where the molten powder is carried out in the gas mixture and is attached to the surface to be coated by the high temperature of the torch which can raise to 3000 C°. It is required to control the pressure of the gases to obtain the flame equal to the speed of the powder rush. The oxygen pressure should be adjusted according to the spray gun used no more than 4 bar and the acetylene pressure not more than 0.7 bar before spraying process. Two coating layers were used in this work are the bond coat from (AlNi) alloy to reduce mismatch of thermal expansion coefficient between substrate and composite ceramic coating as a top coating layer. The conditions of deposition process are listed in Table1.
### Table 1 Operating parameters during coating deposition process

<table>
<thead>
<tr>
<th>Operating Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen pressure</td>
<td>4 bar</td>
</tr>
<tr>
<td>Acetylene pressure</td>
<td>0.7 bar</td>
</tr>
<tr>
<td>Distance</td>
<td>20 cm</td>
</tr>
<tr>
<td>Powder feed rate</td>
<td>7 cm³/min</td>
</tr>
<tr>
<td>Particle size</td>
<td>Mish (100-300)</td>
</tr>
<tr>
<td>Temperature substrate</td>
<td>(300 - 450) °C</td>
</tr>
</tbody>
</table>

### 2.2 Residual stress analysis

#### 2.2.1. X-Ray stress evaluation

XRD-based residual stress measurements were made using standard d-spacing vs. sin²ψ techniques using Shimadzu X-Ray Diffractometer type XRD-6000 and CrKα radiation. The sin²ψ method [20, 21] was used to determine the residual stresses in this work, the change of a lattice plane distance (d spacing) of a phase, i.e., the peak shift of the corresponding reflection, was measured for tilt ψ-angles between 0° and 45°. To calculate the residual stresses the linear regression of the plot (d spacing) versus sin²ψ and the X-ray elastic constants. The coating and substrate physical properties (elastic modulus, Poisson’s ratio, and coefficient of thermal expansion), thickness of the top coating, bond coat and substrate are shown in the table 2. The deposition temperature used in the present work during coating process for the top coat and bond coat was 850°C.

### Table 2 The physical properties of substrate, bond coat and top coat [22-25]

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Substrate</th>
<th>Bond coating</th>
<th>Top coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yong’s modulus (Gpa)</td>
<td>200</td>
<td>105</td>
<td>64.167</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.33</td>
<td>0.315</td>
<td>0.206</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>10</td>
<td>150μm</td>
<td>400μm</td>
</tr>
<tr>
<td>Thermal expansion coefficient, μE⁻¹</td>
<td>12.6</td>
<td>11.9</td>
<td>7.6</td>
</tr>
</tbody>
</table>

From Shimadzu X-Ray Diffractometer XRD-6000 chart, will be getting on the following values are shown in the table 3.

### Table 3 Shows the relationship between 2Θ & ψ to the topcoat (60%Al₂O₃+40%SiO₂)

<table>
<thead>
<tr>
<th>2Θ</th>
<th>ψ</th>
</tr>
</thead>
<tbody>
<tr>
<td>156.966</td>
<td>0</td>
</tr>
<tr>
<td>156.825</td>
<td>15</td>
</tr>
<tr>
<td>157.007</td>
<td>30</td>
</tr>
<tr>
<td>157.483</td>
<td>45</td>
</tr>
</tbody>
</table>

By Brag Law (nλ = 2d sinθ) may be calculated (d), where n=1, λ=2.28970 Å and θ (0, 15, 30, 45) degree. From the figure 1 may be calculated the linear slop of the plot $d_{spacing}$ versus sin²ψ.

The stress can then be obtained from the following equation:

$$\sigma = \left(\frac{E(1+\nu)}{d_{o}}\right) \times \frac{1}{d_o} \left(\frac{\Delta d}{\Delta \sin^2 \psi} \times 2 d\right)$$

From figure 1 the slop $\Delta d$/($\Delta \sin^2 \psi$ $\times 2 d$) ≈ 0.00239,

$\Delta d = 2.02712$ Å

from Eq. (1), the value of the Residual stresses is:

$\sigma = -62.6099$ Mpa
3. Results and discussion

3.1. Residual stress measurement—XRD results

It can be referred from Eq. (1) that in topcoat (60%wt Al₂O₃-40%wt SiO₂) was subjected to compressive residual stresses (-62.6099 Mpa). This residual stresses were evaluated in the surface layer of coating adherent to the substrate. Thickness of topcoat layer conforming to the X-ray penetration was observed 450 µm. The study was carried out at several sites of each coating and the residual stresses were always determined along two perpendicular directions corresponding to azimuth angles of 0º and 120º. The results showed for each sample characteristics of a plane-equiaxial and compressive stress state, with constant values at sites far from the borders or irregularities. The results presented in the remainder of the study confirm this feature.

The level of the residual stresses in the topcoat surface was related to characteristics of composite ceramic coating (60%wt Al₂O₃-40%wt SiO₂) deposited by flame spraying technique. The parameters considered were the substrate material (AISI 1050), the substrate thickness (10 mm), and a bond coat of NiAl (150µm). As can be observed, the level of the residual stresses remains constant for all the samples inside the error bars. This behavior can be related to the stress relief by extensive micro-cracking during spraying. The coating flaws, porosities and microcracks have an important effect on the stress release and only quenching stresses remain in the finished deposit [18].

3.2. Residual stress measurement—FEM results

Figures 3, 4 show the results of FE simulation of residual stresses on the topcoat surface can be seen. The figures show the residual stresses in plane plastic strain within the composite ceramic coating (60%wt Al₂O₃ - 40%wt SiO₂) layer and the steel substrate. In this case, the maximum plastic strain is induced into the coating (60%wt Al₂O₃ - 40%wt SiO₂) layer. However, the bond coat is significantly affected as well, while only a minor influence on the steel substrate can be found.

Acknowledgements

Authors wishing to acknowledge assistance and encouragement from colleagues in the Production Engineering Department & Metallurgy and Materials Engineering Department, University of Technology, Baghdad-Iraq, special work by technical staff in this University. Also acknowledge assistance from Mechanical Engineering Department, University of Diyala-Iraq.

References

KINETICS OF FRONTS OF THE DEFORMATION PHASE TRANSFORMATION IN NITINOL

Prof. dr. phys.-mat. sci. Danilov V.1,2,a, Cand. phys.-mat. sci. Gorbatenko V.1,b,
Prof. dr. phys.-mat. sci. Zuev L.1,3,c, Cand. phys.-mat. sci. Orlova D.1,2,d
Institute of Strength Physics and Material Science Siberian Branch of Russian Academy of Sciences1,
Tomsk Polytechnic University2, Tomsk State University3
4dvi@ispms.tsc.ru, 5gvv@ispms.tsc.ru, 6lbz@ispms.tsc.ru, 7dvo@ispms.tsc.ru

Abstract: In this study, we investigated the localization of the macroscopic deformation during tensile test of nitinol at room temperature. The specimens were fully austenitic and therefore, the martensitic phase transition under deformation had place. It is established that the deformation phase transformation is realized by the formation and motion of fronts of localized deformation. Fronts moves at constant velocities and annihilated at the meeting. The velocities of their movement are determined by crosshead velocity and the duration of stress plateau. In this respect, the behavior of the phase-transition fronts is completely similar to the kinetics of the Lüders bands fronts observed in mild steel, but distinctive feature of this phenomenon is that the level of localization of the deformation at the phase transition front is an order of magnitude smaller than at the front of the Lüders band. In addition, the phase transition front has a more complex structure than the front of the Lüders band. These features of the kinetics and morphology of the transformation front lead to the fact that its motion takes place under hardening conditions, and inclined strain plateau is observed on the deformation curve.

KEYWORDS: LOCALIZED PLASTIC DEFORMATION, LÜDERS BANDS, NITINOL, DEFORMATION PHASE TRANSFORMATION, FRONTS OF PHASE TRANSFORMATION

1. Introduction

At the initial stages of plastic deformation, a macroscopic heterogeneity of the plastic flow known as Lüders band (LB) is observed in some materials. Investigation of this phenomenon has received a new impetus owing to development of modern methods for recording and analysis of strain distribution in loaded objects [1-3]. Processes of LB formation in iron, copper, magnesium, etc. based polycrystalline alloys, where plastic flow at the micro level is realized by dislocation sliding, were studied in detail [2, 4, 5]. Study of Lüders band fronts kinetics and morphology, both at their generation and propagation, is of special interest. It has now been established that deformation heterogeneity in the form of LB is observed in single crystals, too. Moreover, deformation at the microscopic level is not necessarily presented by dislocation sliding. Movement of localized deformation fronts was recorded and studied in nickel bronze single crystals, twinning austenite manganese steel single crystals and Ni$_3$Mn ordered alloy [6]. In all these cases deformation curves commonly featured a yield plateau.

It is possible to suggest that the applied strain dependence on a material with yield drop and yield plateau is mutually consistent with the formation of localized deformation space-time structure in the form of switching autowave [7]. In this case, the micromechanism of plastic flow shall not play a decisive role, and occurrence of such feature as the yield plateau on the deformation curve may be an attribute of macroscopic deformation localization in the form of mobile fronts.

On the other hand, deformation curves with yield plateaus are typical of materials in which plastic flow at the micro level occurs due to phase transformation, like in nitinol, for instance. Phase transformation front in nitinol deformation was captured [8], however, the morphology and kinetics of these fronts were not studied. All these items are subjects of this paper.

2. Material and experimental procedures

The investigations declared were carried out using nitinol composed of 55.76 wt. % Ni + 44.24 wt. % Ti. The tensile specimen was flat dog-bone specimen with a 40 mm of the gauge length, 6 mm width and 1 mm thickness. Prepared specimens were annealed in a salt-bath furnace at 450 °C and cooled down in water. After the heat treatment, nitinol of this composition demonstrated the following characteristics.

1. Temperature of cubic (B2) to rhombohedral (R) phase transition, $T_R = +31^\circ C$;
2. Start temperature of martensitic rhombohedral (R) to monoclinic (B19') phase transition, $M_r = -13^\circ C$;
3. End temperature of martensitic rhombohedral (R) to monoclinic (B19') phase transition, $M_f = -54^\circ C$;
4. Start temperature of reverse monoclinic (B19') to cubic (B2) phase transition, $A_1 = +10^\circ C$;
5. End temperature of reverse monoclinic (B19') to cubic (B2) phase transition, $A_2 = +24^\circ C$.

Thus, the specimens were in R phase at room temperature and were supposed to have $R \rightarrow B19'$ deformation phase transition at uniaxial tension. When the load is removed, the reverse $B19' \rightarrow B2$ transition is not possible without cooling; therefore, superelasticity diagram at room temperature can’t be obtained. However, it is fairly suitable for studying macroscopic features of deformation-induced phase transformation kinetics and morphology. The specimens were tested at a constant rate of $V_{mach} = 3.3 \times 10^{-3}$ mm/s.

Deformation localization fronts were visualized using digital image correlation (DIC) method [1]. It was implemented by recording and digitizing a sequence of speckle images at a 10 Hz frequency. A flat grid of 1×1 mm or 0.5×0.5 mm square cells is applied on each recorded image, and displacements of grid nodes for 6 s time shift are determined that corresponds to the absolute displacement by 1 pixel, at most. The measured field of displacement vectors, $r$, was numerically differentiated by coordinates that allows determination of distortion tensor $\delta_{ij}$ components for the flat case [8]. In this study, distribution of local elongations $\varepsilon_{xy}$ and local rotations $\omega_{xy}$ is analyzed.

3. Results and discussion

The analysis of the stress-strain diagram curves of the above samples showed that their initial parts contain a well-defined linear section in the range of 0.022 < $\varepsilon$ < 0.058 with a minor strengthening
$\theta_I \approx 816 \text{ MPa}$ equal to 2 to 4% of the material shear modulus (see fig. 1).

Fig. 1. Nitinol specimen stress-strain diagram at room temperature

It is obvious that the deformation-induced phase transformation takes place at this section, therefore, it was selected for deformation localization zones DIC visualization attempt. By sensitivity to displacements, this method is comparable with the classical double-exposure speckle photography [9]. However, both these methods have insufficient spatial and temporal resolution, which prevented us from studying deformation-induced transformation band formation process and transformation front morphology details. Nevertheless, the fronts proper are fairly well revealed [Figs. 2, 3]. In all studied cases, two transformation bands were formed at ends of the specimen. Each transformation front is characterized by a maximum of local elongations $\varepsilon_{xx}$ (Fig. 2). Mobile band fronts moved towards each other and annihilated. The incline of both fronts to axis of elongation is $\approx 60^\circ$, on average. Front velocities are the same, constant and equal to 0.044 mm/s. This correlates well with the relationship (1) previously determined for LBs front velocities in steels [10].

Fig. 2. Movement of deformation-induced phase transformation fronts in nitinol. Times are indicated from the start of recording (see Fig. 1).

$$\sum |v_i| = \frac{V_{max}}{\varepsilon_{pl}}, \quad (1)$$

were $|v_i|$ is velocity modulus for each of the moving fronts; $\varepsilon_{pl}$ is yield plateau length in deformation units.

It is important to note that characteristic changes in distortion tensor rotation component $\omega_{ij}$ are associated with transformation fronts (Fig. 3). The front itself is represented by a negative rotation which spatially coincides with the local elongations maximum. As the fronts approach, the amplitude of this rotation increases and reaches its maximum when the fronts meet (annihilate). Two local areas of positive rotations are located ahead and behind each front during movement. As the fronts come closer, the entire space between them is occupied by the positive rotation area. After annihilation of the fronts, i.e. after completion of the deformation-induced phase transformation, deformation localization at the macroscopic level is stopped, and positive and negative rotations disappear. A short-term stress decay, similar to that occurring when LB fronts meet in low-carbon steel, is observed on the deformation curve [10]. Plastic deformation of the formed B19' martensite occurs rather homogeniously, with the strain-hardening coefficient $\theta_{II} \approx 4 \text{ GPa}$.

4. Conclusion

Based on the data presented, it can be asserted that deformation-induced phase transformation in nitinol does develop in a manner similar to LB propagation in iron-carbon alloys. Mobile transformation fronts are formed, where the entire deformation is localized. The phase transformation fronts orientation and velocities follow patterns established for LB fronts. Like LB fronts, phase transformation fronts annihilate when they meet.

However, some distinctive features were also identified. The degree of deformation localization at phase transition fronts is an order of magnitude lower than at the LB front, therefore, they are not detected by digital statistical speckle photography method [3, 10]. Not only elongation is localized at the deformation-induced phase transformation front. Movement of the front goes with meaningful rotation processes. As a result, transformation can’t take place at constant stress, and the load curve features a inclined yield plateau. This may be explained by the fact that transformation at the microscopic level follows martensitic mechanism which is known to be self-locking due to internal stress occurrence [11].
Acknowledgments

The work was carried out within the framework of the Program of Fundamental Scientific Research Russian State academies of sciences for 2013-2020.

References


Abstract: The one-step synthesis using high-energy ball milling can be used in preparation of many complex/doped oxides. In this work we report, as an example, on synthesis and characterization of mullite-type solid solutions. Mullite type $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ solid solutions with $0.1 \leq x \leq 1.0$, were synthesized by combination of mechanochemical and thermal treatments of the $\text{Bi}_2\text{O}_3/\alpha-\text{Fe}_2\text{O}_3/\text{Ga}_2\text{O}_3$ stoichiometric mixture. The microstructure of the as-prepared materials on the long-range and local atomic scales was investigated by X-ray diffraction and $^{57}\text{Fe}$ Mössbauer spectroscopy, respectively.

Keywords: Mullite-type solid solution; Bismuth-bearing complex oxide; Rietveld analysis; Mössbauer spectroscopy

1. Introduction

In recent years, the mullite structured bismuth-bearing complex oxides with the general formula of $\text{Bi}_2\text{M}_n\text{O}_{3n+1}$ ($\text{M} = \text{Fe}^{3+}$, $\text{Ga}^{3+}$ and $\text{Al}^{3+}$) and their substituted derivatives of the type $\text{Bi}_2(\text{M}_2\text{A}_2)\text{M}_n\text{O}_{3n+1}$ (e.g., $\text{A} = \text{Sr}^{2+}$) have become attractive subjects in materials research and applications [1]. It is due to their high thermal stability, good creep resistance, low thermal conductivity, low thermal expansion, anionic conductivity, high emission in the infrared region, etc. [2]. As shown in Figure 1, their structure is characterized by columns of edge-sharing $\text{MO}_6$ octahedrons parallel to the $c$ axis, which are interconnected by double $\text{MO}_4$ tetrahedrons. Tetrahedrally coordinated ($\text{T}$) and octahedrally coordinated ($\text{O}$) sites can accept both transition and main group metal cations [3].

![Crystal structure of mullite-type $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$, $x = 0.5$.](image)

It is well known that functional properties and microstructure of complex oxides are closely related to the processes used for their preparation [4]. In fact, in recent years, several methods have been reported to synthesize bismuth-bearing complex oxides with mullite structure. For example, Zha et al. [5] and more recently Voll et al. [6] used a glycine-nitrate process to synthesize mullite-type compounds. Giagininta et al. [7] applied a conventional ceramic route to bismuth-bearing oxides, based on the annealing stoichiometric amounts of oxides at 1125 K in air for two weeks with frequent grindings. Gesing et al. [8] reported on glycerine- and the EDTA/citric acid synthesis method. In both cases samples were heated at 1023 K for several tens of hours. Pure [9] and doped [10] $\text{Bi}_2\text{Al}_4\text{O}_9$ samples were also prepared by the combustion synthesis route using the glycine-nitrate process and followed by high-temperature annealing at $1323 – 1363$ K. In another powder syntheses of $\text{Bi}_2\text{Al}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$, annealing temperatures in the range from 1123 K to 1273 K were used [11-13].

In this manuscript, the synthesis of mullite-type $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ solid solutions ($0.1 \leq x \leq 1.0$) prepared by mechanochemical treatment of stoichiometric mixtures of the $\text{Bi}_2\text{O}_3/\alpha-\text{Fe}_2\text{O}_3/\text{Ga}_2\text{O}_3$ precursors, followed by their annealing at the reduced temperature (1073 K), is reported. Although the similar preparation method of mullite-type complex oxides has already been described in our previous work [1,14,15], it should be noted that the precise structural study of the above-mentioned solid solutions has not been performed yet. Based on our previous experience [see e.g., 4,16,17], the simultaneous use of diffraction techniques sensitive to medium- and long-range structural order, and spectroscopic methods, which make possible observations on a local atomic scale, is crucial to reveal structure of the as-synthesized complex oxides properly. In this work, information is provided on the local structure of the as-prepared $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ ($0.1 \leq x \leq 1.0$) solid solutions, including coordinates of the atoms, the unit cell dimensions and the atom occupation factors derived from the Rietveld refinements of X-ray diffraction (XRD) data. Moreover, due to the ability of $^{57}\text{Fe}$ Mössbauer spectroscopy to reveal local environment of Fe nuclei, the effect of iron concentration on the variation in site occupancy, isomer shift and quadrupole splitting in $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ solid solutions is also discussed.

2. Experimental material and method

$\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ ($0.1 \leq x \leq 1.0$) solid solutions were prepared from the stoichiometric mixture of $\text{Bi}_2\text{O}_3$ (Alfa Aesar, 99.999 %), $\alpha-\text{Fe}_2\text{O}_3$ (Alfa Aesar, 99.999 %) and $\text{Ga}_2\text{O}_3$ (Alfa Aesar, 99.99 %) powders by the mechanochemical/thermal synthesis using a high-energy planetary ball mill Pulverisette 6 (Fritsch, Germany). The precursors were milled for 3 h at 600 rpm in ambient atmosphere using the chamber (250 cm$^3$) with 22 balls (10 mm in diameter) both made of tungsten carbide. The ball-to-powder mass ratio was 22:1. After milling, the powdered mixture was calcined at 1073 K in air for 24 h.

XRD patterns were recorded with a PW 1820 X-ray diffractometer (Philips, Netherlands), operating in Bragg configuration, using Cu–$\text{K}\alpha$ radiation ($\lambda = 1.54056$ Å). XRD data were collected in the range of 10–$80^\circ$ 20 with a step size of 0.02$^\circ$ and collection time of 5 s. Rietveld refinements of XRD data of the as-synthesized solid solutions were performed in $\text{Pbam}$ space group with orthorhombic structure using $\text{Fullpro} \text{f}$ software [18]. The XRD line broadening was analyzed by refinement of regular pseudo-Voigt function parameters.
$^{57}$Fe Mössbauer measurements were carried in the transmission mode at room temperature. $^{57}$Co in Rh was used as γ-ray source. Recoil spectral analysis software was employed for the quantitative analysis of the Mössbauer spectra [19]. The velocity scale and isomer shifts were calibrated using a metallic α-Fe foil absorber at room temperature.

3. Results

The representative XRD patterns of the Bi2(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions with 0.1 ≤ x ≤ 1.0 are shown in Figure 2a. The as-synthesized samples are characterized by narrow diffraction peaks indicating their well-crystallized nature. All diffraction peaks correspond to the orthorhombic mullite-type phase with $Pbam$ space group; no spurious or minority phases have been observed. It should be highlighted that in relatively low annealing temperature (1073 K) was applied in the present case. In this context we can conclude that the combined mechanochemical/thermal treatment used in the present study represents an effective, simple, lower-temperature processing route, and thus, a low-cost protocol to synthesize Bi2(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions.

To gain quantitative information on the structure of the as-synthesized Bi2(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ (0.1 ≤ x ≤ 1.0) solid solutions, their XRD data were refined by Rietveld analysis. The representative Rietveld refinement of the XRD data for the Bi2(Fe$_0.5$Ga$_{0.5}$)$_4$O$_9$ sample with x = 0.5 is shown in Figure 2b. Here, the observed data are represented by the open circles and the solid curve represents the result of fitting. The bottom line shows the difference between observed and calculated intensities. The derived crystal structure parameters and the exact atomic positions for the Bi2Fe$_2$Ga$_2$O$_9$ sample are listed in Table 1. The crystal structure parameters and the goodness parameters of the fits resulting from the Rietveld analyses of the as-prepared solid solutions are listed in Table 2. Rietveld refinements revealed that the cell volume of the as-synthesized samples increases with iron content as expected according to the Vergard’s law (see Figure 3) [1,7]. In order to reveal the short-range local structure of the as-synthesized solid solutions, in the following we will present and discuss the results obtained by $^{57}$Fe Mössbauer spectroscopy. The representative $^{57}$Fe Mössbauer spectra of the samples (for x = 0.1, 0.5 and 0.9) are shown in Figure 4. They demonstrate very clearly the presence of two coordination sites for iron cations in the mullite-type structure of Bi2(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions; i.e., two well-resolved doublets are characteristic for tetrahedrally coordinated (IS = 0.2 mm.s$^{-1}$, external doublet in Figure 4) and octahedrally coordinated (IS = 0.3 mm.s$^{-1}$, internal doublet in Figure 4) ferric cations.

Table 1

<table>
<thead>
<tr>
<th>Atomic position</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_1$ – 4f</td>
<td>0.50000</td>
<td>0.00000</td>
<td>0.2609(7)</td>
</tr>
<tr>
<td>Fe$_2$ – 4h</td>
<td>0.3547(4)</td>
<td>0.3411(5)</td>
<td>0.50000</td>
</tr>
<tr>
<td>Ga$_1$ – 4f</td>
<td>0.50000</td>
<td>0.00000</td>
<td>0.2609(7)</td>
</tr>
<tr>
<td>Ga$_2$ – 4h</td>
<td>0.3547(4)</td>
<td>0.3411(5)</td>
<td>0.50000</td>
</tr>
<tr>
<td>O$_1$ – 2b</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.50000</td>
</tr>
<tr>
<td>O$_2$ – 8i</td>
<td>0.3794(9)</td>
<td>0.2147(13)</td>
<td>0.2474(18)</td>
</tr>
<tr>
<td>O$_3$ – 4h</td>
<td>0.1365(12)</td>
<td>0.380(3)</td>
<td>0.50000</td>
</tr>
<tr>
<td>O$_4$ – 4g</td>
<td>0.1708(18)</td>
<td>0.4303(12)</td>
<td>0.50000</td>
</tr>
<tr>
<td>R-values</td>
<td>$R_p$ = 11.4</td>
<td>$R_{wp}$ = 14.3</td>
<td>$R_{wp}$ = 7.88</td>
</tr>
<tr>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_2$ – 4f</td>
<td>0.50000</td>
<td>0.00000</td>
<td>0.2609(7)</td>
</tr>
</tbody>
</table>

They demonstrate very clearly the presence of two coordination sites for iron cations in the mullite-type structure of Bi2(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions; i.e., two well-resolved doublets are characteristic for tetrahedrally coordinated (IS = 0.2 mm.s$^{-1}$, external doublet in Figure 4) and octahedrally coordinated (IS = 0.3 mm.s$^{-1}$, internal doublet in Figure 4) ferric cations.

Table 2

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>7.930</td>
<td>8.325</td>
<td>5.908</td>
</tr>
<tr>
<td>0.2</td>
<td>7.940</td>
<td>8.335</td>
<td>5.919</td>
</tr>
<tr>
<td>0.3</td>
<td>7.949</td>
<td>8.348</td>
<td>5.930</td>
</tr>
<tr>
<td>0.5</td>
<td>7.955</td>
<td>8.375</td>
<td>5.950</td>
</tr>
<tr>
<td>0.7</td>
<td>7.967</td>
<td>8.406</td>
<td>5.975</td>
</tr>
<tr>
<td>0.8</td>
<td>7.964</td>
<td>8.416</td>
<td>5.983</td>
</tr>
<tr>
<td>0.9</td>
<td>7.969</td>
<td>8.432</td>
<td>5.995</td>
</tr>
</tbody>
</table>
Fig. 3. Lattice parameters (a, b, c) and lattice volume (V) of the Bi$_2$(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions as a function of iron content (x).

Fig. 4. $^{57}$Fe Mössbauer spectra of selected Bi$_2$(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions (for x = 0.1, 0.5 and 0.9) measured at room temperature. The open circles represent measured data and solid lines (red) represent the fitting curves. The subspectra corresponding to tetrahedrally and octahedrally coordinated ferric cations are denoted as Fe$_3^+$($T$) and Fe$_3^+$($O$), respectively. Subspectral area fractions Fe$_3^+$($T$)/Fe$_3^+$($O$) are also indicated.

4. Conclusion

Mullite-type Bi$_2$(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ solid solutions with 0.1 ≤ x ≤ 1.0 were synthesized by high-energy ball milling of Bi$_2$O$_3$/α-Fe$_2$O$_3$/Ga$_2$O$_3$ stoichiometric mixtures followed by subsequent annealing at 1073 K for 24 h. Relatively short time and lower temperature of the combined mechanochemical/thermal synthesis of the Bi$_2$(Fe$_x$Ga$_{1-x}$)$_4$O$_9$ mixed crystals is ascribed to the pre-activation of the reaction precursors. The long-range and short-range structures of the as-prepared samples were characterized by XRD and $^{57}$Fe Mössbauer spectroscopy. Rietveld refinements of the mixed crystals revealed that their lattice parameters vary linearly with iron content and change in accordance with Vegard’s law. $^{57}$Fe Mössbauer spectra of all investigated samples distinguished tetrahedrally and octahedrally coordinated Fe$^{3+}$ cations.

Acknowledgments

This work was supported by the Visegrad Group (V4) – Japan Joint Research Program on Advanced Materials “Structure-Function Relationship of Advanced Nanoxides for Energy Storage Devices (AdOX)”; the VEGA (projects 2/0128/16 and 2/0097/14) and by the APVV (project SK-BG 2013-0011). M.F. thanks FA/CAPES agency (project 12/2013-FA).

References

INFLUENCE OF THE BEAM DEFLECTION ON PROPERTIES OF THE ELECTRON BEAM HARDENED LAYER

Matěj Jiří, Foret Rudolf, Dlouhý Ivo

Faculty of Mechanical Engineering – Brno University of Technology, the Czech Republic

xcmatlajk@vutbr.cz

Abstract: The usage of the high-energetic source of the electron beam enables a repeated surface quenching of the chosen areas of an engineering part surface. Different techniques of the electron beam deflections allow the creation of hardened layers of different shapes and above all the thicknesses. The deflection was tested at one point, six points, a line and a field on the material 42CrMo4 (1.7225). The effect of the process speed and defocusing of the electron beam was studied. The electron beam surface quenching resulted in a very fine martensitic microstructure with the hardness over 700 HV0.5. The thickness of the hardened layers depends on the type of deflection and depends directly on the process speed. The maximum observed depth was 1.49 mm. The electron beam defocusing affects the width of the hardened track and can cause an extension of the trace up to 40%. The hardness values continuously decrease from the surface to the material volume.

Keywords: Electron beam, hardening, quenching, 42CrMo4, deflection

1. Introduction

An electron beam (EB), together with laser, is one of the most modern technologies used for the local surface heat treatment. Both of the methods have some similar characteristics; however there are clear differences predetermining which of them will be chosen. The fast beam deflection characteristic for the EB allows a different distribution of the supplied energy at an adequate programming of the quenching equipment. A deflection of the EB can be realized both in a direction perpendicular to the direction of the components movement and also in a parallel direction.[1-5]

The properties of the quenched layer can be directly controlled by process parameters. The total supplied power rate is controlled by a combination of the accelerating voltage \( U_{\text{EB}} \) and the electron current \( I_{\text{EB}} \). This energy is distributed to the components surface depending on the selected type of the EB deflection. The scanned area is determined by dimensions \( \text{SWX} \), \( \text{SWY} \) and is set together with the scanning frequency in the individual directions \( \text{FRQ} \), \( \text{FRQ}^2 \) (Fig. 1). Usually some beam defocusing \( \text{Offset} \) is set up, which can be realized by a shift of the focal plane above the quenched surface (a positive value) or below the surface (a negative value). The last very important parameter is the quenched component movement rate \( \text{vs} \) below the quenching beam \( \text{EB} \).

![Fig. 1 The EB surface quenching parameters scheme.](image)

2. Experimental material and methods

Experiments were carried out on the high grade steel 42CrMo4 (1.7225) with the chemical composition of (wt%): C 0.41, Mn 0.69, Si 0.25, Cr 1.04, Mo 0.20), which is a suitable material for the surface quenching. It finds an application where there is a requirement for an elevated strength in a combination with a defined and high level of toughness. The tested material was in a state tempered at the temperature of 600 °C with a fine sorbitic structure and an average hardness 300 HV0.5.

The surface quenching was performed on the PROBEAM K26 equipment adopting the electron beam technology with a maximum beam power of 15 kW and an accelerating voltage from 80 to 150 kV. The width of the EB hardened traces were set to \( \text{SWX} = 10 \text{ mm} \) except of one point deflection. The constant accelerating voltage \( U_{\text{EB}} = 80 \text{ kV} \) was used for the experiments and the electron beam current \( I_{\text{EB}} \) was subsequently optimized for each machines configuration. One point, six points, a line (consisting of 1,000 points) and a field were tested as the EB deflection modes and many more inflences of a defocusing degree and a movement rate in each mode on the quality of the hardened layer were observed. A common “Offset” values for each mode were 50, 100, 200 and 300 mA and common \( \text{vs} \) were 5, 10, 15, 20 and 25 mm s\(^{-1}\).

The field deflection mode was programmed to allow a local energetic intensity increase within a given area. This is used for an intense heating at the surface of a treated material during the progressive quenching. The rest of the area, with the lower beam intensity, contributes to the heating of the material deeper to the volume. The length of the field SWY was determined for each movement rate based on the change of a temperature across the affected area on the sample measured with a pyrometer.

The metallurgical specimens prepared by standard procedures were analyzed by the optical and the scanning electron microscopy. LECO LM 247 AT microhardness tester was used to analyze the hardness HV0.5 changes (a hardness profile) from the surface to the volume in the quenching trace axis. For the microstructural characterization, the scanning electron microscope (SEM) ULTRA PLUS, Carl Zeiss GmbH, Germany, equipped with dispersive X-ray spectrometer (EDS) X-MAX, Oxford Instruments, England, was used. For the surface analysis, the detector of the secondary electrons (SE) type Everhar-Thornley and the four-quadrant silicon detector of back scattered electrons (BSE) were used.

3. Results

Traces having width of 10 mm were processed by a surface quenching on the 42CrMo4 high grade steel. Basic experiments were optimized from the point of view of the used electron beam current \( I_{\text{EB}} \). The optimal energy density conditions were estimated only based on the observation of the occurrence of melted areas on a specimen surface. The melted areas were brighter than the quenched ones. A slightly molten surface could not be identified by observing the microstructure because it was also a fine martensitic structure. The maximum hardness of the quenched and the molten
material was the same and therefore it could not be used to determine the optimal EB current for hardening.

The length of the field deflection was determined by a pyrometric measurement of the temperature profile within the irradiated area. Too long SWY caused a significant drop in a temperature, while too short one did not exploit all the potential of the technology. An optimized parameter SWY for an individual tested movement rate are given in the Table 1.

**Table 1: Optimal length SWY of the field resulted from temperature profile.**

<table>
<thead>
<tr>
<th>Movement rate mm·s⁻¹</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field length mm</td>
<td>5</td>
<td>8</td>
<td>12</td>
<td>18</td>
<td>25</td>
</tr>
</tbody>
</table>

From the macroscopic point of view, a constant width of traces was observed in the beam movement direction. A continuous quenching depth decrease to the trace edge was observed in the direction perpendicular to the beam movement (Fig. 2). The microstructure in the surface quenched area of all the traces consisted of a fine martensite (Fig. 3). The finest martensite was obtained at the one point deflection and the coarsest at the field one. A continuous change of the fine martensitic structure to the basic material created by a tempered martensitic structure with complex carbides was observed in the transition area (Fig. 4).

**Fig. 2 The macrostructure of the surface hardened area in a perpendicular direction - field deflection.**

**Fig. 3 The microstructure (SE) of (a) basic material, and hardened layers, (b) one point, (c) six points, (d) line, and (e) field deflection regimes respectively.**

**Fig. 4 The microstructure of the transition area of field deflection sample, (a) SEM – SE mode, (b) SEM – BSE mode**

The comparison of the profiles of hardened layers made by different deflection modes shows that the lower number of deflected points forms a wider track - Fig. 5 (except one point regime). The track made by the field deflection is the deepest and the one made by the one-point deflection the shallowest one. They both have a significant curvature in the comparison to the 6 points or the line deflections that are rather parallel to the surface. Different movement rates have a negligible influence on the profile of the trace. The Offset has a significant effect on the shape of the track. As the value rises, the trace is wider and, on the contrary, too low values lead to an easier melting as well as a significant deformation of the profile of the trace - Fig. 6.

**Fig. 5 Comparison of the profiles of hardened layers**

**Fig. 6 The influence of Offset on the profiles of the hardened layers – 6 points deflection**

The movement rate has only a little effect on the depth of the hardened layer (Fig. 7) once applying one-point deflection and the field deflection. For the field deflection, it is the result of optimizing the field length SWY. The depth depends significantly on the movement rate for the 6 points and the line deflection. The depth gradually increases with the decreasing speed and the greatest difference can be seen between 5 and 10 mm·s⁻¹.
The increasing Offset leads to an increase of the hardened layer depth (Fig. 8). It is interesting that at higher values of the Offset there is no significant difference between deflections. The one point and the field deflection differ from the other ones with a lighter response to an Offset change.

Maximal hardness values (up to 740 HV0.5) were reached by the one point deflection because the heating and especially the cooling processes are very fast. The experiments with the other deflection’s modes give the hardness between 600 and 700 HV0.5. The measured values decreased from the surface to the volume. The continuous decrease of the microhardness was observed on the interface between the quenched area and the basic material. No decrease of the microhardness of the basic material was observed near the hardened traces (Fig. 9). Hardness profiles were the same in the middle of the track as closer to the edges (except the different hardening depth).

It was not confirmed that the movement rate affects the hardness. Too high defocusing causes a total reduction in the hardness in the entire layer. The Offset value 400 mA resulted in the average hardness of 570 HV0.5 of the hardened track and it represents a 20% decrease in comparison with a sharper beam (Fig. 9).

4. Conclusion

The work was focused on effect evaluation of the type of a deflection (one point, 6-points, line, field) of the electron beam on the hardened layers. The results showed that the deflection mode can affect a number of track parameters. The martensitic structure is the finest by the one point deflection and the coarsest one is formed by the field deflection. This mode affects a little the maximum hardness. The highest hardness 740 HV0.5 has been observed by the one point deflection. For the other regime types, the maximum values are near 700 HV0.5.

The geometric profiles of the tracks in cross-sections are different for each of the applied deflection types. The 6-points and the line one are parallel to the surface and the one point together with the field one are significantly curved. The widths of the tracks were similar except of the one point regime. The depths of hardened layers were in the range 0,1-1,5 mm. The lowest depth of tracks was made by the one point deflection and the deepest one by the one point.

The movement rate affects only the depth of the hardened layer. The depth slightly increases with the speed decrease. The defocusing affects the depth more significantly. Moreover, the increasing Offset leads to wider tracks. Too low Offset can severely distort the profile of the hardened layer. Too high values again lead to an overall reduction in the hardness of the layer. The lower Offset can considerably distort the profile of the hardened layer. Too high values lead to a total hardness reduction of the layer.

Acknowledgments

The works have been supported by the project NETME centre plus (Lo1202), project of Ministry of Education, Youth and Sports under the “national sustainability programme”. Support of Czech Science Foundation project Nr. 13-35905S is further acknowledged.

References


Abstract: the paper presents a cutting tool complex cooling system (CCS) based on the use of the first-order phase transitions for cutting process thermal stabilization by prolongation of the fusible material melting (e.g., Rose’s metal) with the help of the heat pipes. Combined cutting tools and mills with indexable inserts are designed and manufactured. The time of temperature stabilization, depending on the amount of consumable substance is calculated. It is shown that the size of the container with fusible substance can provide a melting time equal to or multiple of the execution time of technological operations.

KEYWORDS: HEAT PIPE, COMBINED CUTTING TOOL, PHASE TRANSITION, FUSIBLE MATERIAL

1. Introduction

One of the trends of modern engineering is a growing interest in the "dry" cutting. In the dry processing we can receive a number of advantages, which include improving working conditions and increasing its efficiency by reducing costs due to the lubricant-cooling agents and their recycling. It is obvious that "dry" cutting is the most appropriate technology in the interrupted cutting especially in the milling process. In this case, the temperature in the cutting zone continuously varies within a wide range and can reach 1000°C. In this case there is a sharp change of temperature at the moments of entry and exit of the cutting edge from cutting zone. The cutting edge is thus subjected to thermal shock and cyclic stresses that can contribute to thermal cracking [1].

Scope of "dry" cutting applications is constantly expanding due to the fact that the treatment of a number of structural materials, particularly in machining of titanium alloys the use of coolants may affect their technological heredity.

2. Results and discussion

One of the ways of temperature stabilization (inhibition of the temperature increasing) is the heat absorption with the help of changing the physical state of matter (evaporative cooling of open and closed types, the use of low-melting substances).

The application experience of the cooling with the help of phase-changed processes in other technical fields allows to make a conclusion about the validity of the same approach in the case of modular cutting tools. The results of the comprehensive study of the evaporate cooling system for combined cutting tools in the dry cutting were published [2]. The complex cooling system (CCS) was analyzed. CCS is based on the heat sink due to the absorption of latent heat of fusion of the working substance (Rose metal) with a melting point 96 °C located in the container inside the holder and implanted heat pipe (HP). HP using allows to delay the melting process. The design of a modular cutting tool based on the standard cutter as well as the design of the combined mill are presented (Fig.1,2).
3. Conclusions

1. An alternative method of temperature stabilization under dry cutting is the absorption of heat by changing the state of aggregation of a substance, based on the use of phase transitions of the first kind.

2. Determination of the container with fusible substance parameters gives the opportunity to stabilize the optimal temperature of the cutting process and thus reduce the rate of wear of the tool cutting edge.

3. The temperature stabilization method for dry cutting can be applied in other types of the technological systems (deep hole boring, reaming, etc.).

4. Bibliography

**MATHEMATICAL MODELLING OF HOT PLASTIC DEFORMATION OF MICRAALLOYED STEELS**

Ph.D. Opiela M.
Institute of Engineering Materials and Biomaterials – Silesian University of Technology, Gliwice, Poland
E-mail: marek.opiela@polsl.pl

**Abstract:** The article concerns the possibility to optimize the parameters of forging process with the method of thermo-mechanical treatment of microalloyed steels by means of mathematical modelling of yield stress obtained from conducted plastometric hot compression tests. To describe the yield stress, rheological model proposed by C.M. Sellars was used. Based on this model, the course of experimental and theoretical stress-strain curves has been verified using a minimum of goal function, for the most accurate matching of analyzed curves of investigated steels. Numerical calculations with the method of finite element method (FEM) were performed taking into consideration test results of compression of specimens in Gleeble 3800 simulator, in a temperature range of 900–1100°C and at the strain rate of 1, 10 and 50 s⁻¹. Obtained results allow to conclude that assumed rheological model along with coefficients, determined with the method of inverse analysis, describe satisfactorily the values of yield stress steels of studied steels.

**Keywords:** RHEOLOGICAL MODEL, INVERSE ANALYSIS, MICROALLOYED STEELS

1. **Introduction**

Initially, the modelling was limited to a theoretical solution to the problem of force parameters of the process, i.e. determination of forces and moments, taking into account the phenomenon of material strengthening, as well as frequently adopting simplifying assumptions, lowering the accuracy of calculations [1,2]. The FEM method used nowadays allows modelling of mechanical, thermal and structural phenomena. The most important advantage of this method is the possibility to analyze local values of various parameters of these phenomena, taking into consideration heat exchange and the effect of strain rate in calculation of plastic flow of the material. Nevertheless, the effective use of this method for modelling of industrial processes of plastic working is mainly determined by the knowledge of yield stress, which depends mainly on the microstructural condition of hot deformed austenite. The necessity to include the impact of austenite microstructure on the value of yield stress in the thermomechanical model has led gradually to integration of these models, and additionally to the development of physical modelling with the use of torsion and compression plastometric tests [3-5]. However, it should be noted that in specimens subjected to torsion or hot compression, there is non uniformity of strain, strain rate, stress and temperature [1, 2, 6-10], caused by phenomena such as friction at the sample-tool interface, subsequently - heat generated as a result of strain and friction and also heat discharged to the tool and to the environment. In addition, the temperature of specimen changes during plastometric test, and its distribution is difficult to determine (e.g. with the use of thermomechanical simulators with working automatic control system and implemented resistance heating of samples). As a consequence, interpretation of direct test results is equivocal and requires further processing of obtained results. Application of the inverse analysis allows, in these cases, to effectively eliminate disturbances and determine adjusted values of yield stress, which may be the representative characteristic of investigated material, independent of the type of plastometric test, the shape of sample used, friction conditions, as well as heat exchange in a sample-tool system [11-15]. The essence of this method consists in numerical simulation of σ-ε flow curves obtained during performed laboratory tests, and successively in optimizing model parameters in such a way as to minimize the difference of the expected and measured parameters related to assumed rheological model [16,17].

The paper presents possibilities for the mathematical modelling of hot plastic deformation concerning some selected products obtained by forging structural steels with microadditions in the range of technological parameters simulating such processes in the plastometric compression test. Special attention was paid to the verification of the rheological model developed by Sellars et al. [3,18,19] describing the flow stress as a function of the deformation and temperature, as well as strain rate and the effect of dynamic recrystallization, which dominates in the hot deformation for the investigated structural steels with microadditions of Ti, Nb and V.

2. **Experimental procedure**

The test were carried out on laboratory melts of structural steels with microadditions, the chemical compositions of which is shown in Table 1. Plastometric tests were carried out using the thermomechanical test simulator Gleeble 3800, in the Institute of Iron Metallurgy in Gliwice, Poland. Axisymmetrical samples 10 mm in diameter and 12 mm in length were used in this research study. Continuous compression tests of samples up to true strain ε=1 were conducted in order to obtain σ-ε curves and activation energy of plastic deformation. Specimens were resistance-heated in a vacuum at a rate of 3 °C/s to a temperature of 1150 °C. The samples were held at 1150 °C for 30 s and cooled to a deformation temperature of 1100, 1050, 1000, 950, and 900 °C.

Compression of specimens was done at a strain rate of 1, 10 and 50 s⁻¹. Tantalum foils were used to prevent sticking, and graphite foils were used as a lubricant to minimize the effect of friction on the flow curves. Additionally, both surfaces were covered with a nickel-based substance. Activation energy of the process of plastic deformation was calculated with the use of Energy 4.0 program [20, 21], basing on the following relationship:

\[ \dot{\varepsilon} = A(\sinh(\alpha \varepsilon)) \exp(-Q/RT), \]

where: \( \dot{\varepsilon} \) – strain rate, \( \sigma \) – value of stress corresponding with the maximum value of flow stress, T – deformation temperature, R – the universal gas constant, A, \( \alpha \), n – constants.

In constitutive equations, actually applied for the purpose of modelling the processes of hot working, the effect of dynamic recovery and dynamic recrystallization are not always conveyed explicitly. The equation in wich both components are distinctly separated, elaborated at the University of Sheffield by Sellars et al. [3,18,19], takes the following form:

\[ \sigma_p = \sigma_0 + \left( \frac{(\varepsilon_{\text{opt}} - \varepsilon_{\text{o}})}{1 - \exp\left\{ -\frac{\varepsilon}{\varepsilon_{\text{c}}} \right\}} \right)^{1/2} \]

\[ - R, \]

where the respective variables are defined as follows:

\[ R = 0 \] for \( \varepsilon \leq \varepsilon_{\text{c}} \),

\[ R = \left\{ \sigma_{\text{ss}}(\varepsilon) - \sigma_{\text{ss}} \right\} \left[ 1 - \exp\left\{ -\left( \frac{\varepsilon - \varepsilon_{\text{c}}}{\varepsilon_{\text{y}} - \varepsilon_{\text{c}}} \right)^2 \right\} \] \]

\[ \text{for } \varepsilon > \varepsilon_{\text{c}} \]

200
The variable in equation (2) are as follows:

\[ \sigma_p \] - flow stress, \( \sigma_0 \) – the maximum stress when the plastic strain \( \varepsilon = 0 \), \( \sigma_{ss(e)} \) – the onset of steady-state conditions in the extrapolated curve, \( \sigma_{ss} \) – the onset of steady-state conditions in the experimental flow stress curve, \( \sigma_0 \) – plastic deformation, \( \varepsilon_c \) – strain for the onset of dynamic recrystallization, \( \varepsilon_0 \) – the “transient strain constant” and effectively defines the curvature of the flow-stress curve between \( \varepsilon_c \) and \( \varepsilon_{ss} \).

The model of direct task, simulating the experiment is most often a model with three basic elements: experiment, model of the experiment and computer program based on FEM was used for the purpose of compression of axisymmetrical samples.

Calculations with the use of FEM method were the basis for the inverse solution, which aims to define such rheological model of material which, when introduced into the model of direct task, will provide stress values that are closest to those obtained with the experiment. This boils to searching for a minimum, in respect to the parameters of rheological model, i.e. determination of the goal function. The next step of mathematical modelling was searching for a function, and in fact verifying assumed dependence according to C.M. Sellars, to describe in detail the changes of yield stress in a wide range of plastometric external variables present in tests, namely temperature and strain rate. Example of calculation results obtained basing on FEM in the form of dependence of yield stress versus deformation for investigated steels has been shown graphically in Fig. 1 and 2.

The numerically determined values of the coefficients assumed in the model, taking into account the Simplex algorithm concerning the analyzed stress-strain curves are shown in Table 2, which also contains the values of the energy of activation of the process of deformation and the final values of the goal function \( \Phi \), representing the accuracy of the modelling solution. Due to measurement errors and limitations with the model, different values were obtained for the goal function (equation 3) concerning of investigated steels.

However, the median square error of the calculation remains within 2-4% limits. This proves that the assumed model fits well with the experimental results. As apparent from the data presented in Table 2, higher accuracy of simulation, represented by lower value of the objective function (\( \Phi = 0.0375 \)), was obtained for steel with Nb microaddition (steel B). The best matching accuracy of model and experimental curves was obtained for steel B, plastically deformed in a temperature range of 900-1100°C at the strain rate of 1 and 10 s⁻¹ (Fig. 2).
Fig. 1. Comparison of modelling and experimental flow curves of the A steel hot compressed at the temperature of 900°C with the rates of: a) 10 s⁻¹, b) 50 s⁻¹

Fig. 2. Comparison of modelling and experimental flow curves of the B steel hot compressed at the temperature of 1000°C with the rates of: a) 1 s⁻¹, b) 10 s⁻¹

Table 2: Optimal coefficients of the rheological model obtained as a results of Simplex optimization concerning the investigated microalloyed steels

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Rheology – σ₀ Coefficients</th>
<th>Activation energy Q, kJ/mol</th>
<th>Goal function Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₀</td>
<td>n₀</td>
<td>α₀</td>
</tr>
<tr>
<td>A</td>
<td>1.30 ∙ 10¹²</td>
<td>0.4897</td>
<td>2451.33</td>
</tr>
<tr>
<td>B</td>
<td>3.54 ∙ 10¹³</td>
<td>0.4532</td>
<td>1787.08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Rheology – strain hardening and dynamic recovery Coefficients</th>
<th>Rheology – strain hardening and dynamic recrystallization Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₀</td>
<td>n₀</td>
</tr>
<tr>
<td>A</td>
<td>1.34 ∙ 10¹⁷</td>
<td>4.9712</td>
</tr>
<tr>
<td>B</td>
<td>6.56 ∙ 10¹⁸</td>
<td>5.9643</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>Rheology – strain hardening and dynamic recrystallization Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₀</td>
</tr>
<tr>
<td>A</td>
<td>2.33 ∙ 10¹⁷</td>
</tr>
<tr>
<td>B</td>
<td>1.12 ∙ 10¹⁷</td>
</tr>
</tbody>
</table>

An analysis of the shape of curves obtained in the compression test allows to state that in the studied range of hot deformation parameters the decrease in strain hardening, both in case of the A and B steel, was caused by the process of continuous dynamic recrystallization. This is also confirmed by the results of evaluating the activation energy of the plastic deformation process of the examined steels. Activation energy of plastic deformation of the A steel, determined with the use of equation (1), is equal to Q = 382 kJ∙mol⁻¹, while activation energy of plastic deformation process of the B steel is equal to Q = 398 kJ∙mol⁻¹, wherein values of constants in this equation for the stress corresponding with εₘ deformations are equal: A = 3.43·10¹³, α = 0.00628, n = 6.93 and A = 7.42·10¹⁵, α = 0.00649, n = 7.17 – for the A and B steel, respectively. Similar values of activation energy of plastic strain process for microalloyed steels have been achieved in the works [24-27]. The obtained values of activation energy for investigated steels is substantially higher than the activation energy of self-diffusion, i.e. when the processes which control the course of plastic deformation are dislocation climbing and form subgrains. This means that the process of plastic deformation of the studied steels is controlled by dynamic recrystallization.

4. Conclusions

Rheological model assumed in the study, proposed by C.M. Sellars, describing the yield stress of investigated steels with microadditions as a function of strain, strain rate and temperature, proved to be the proper and effective tool for appropriate adjustment of the course of experimental and theoretical σ-ε flow curves, determined in plastometric hot compression tests.
Regardless of chemical constitution of steel, assumed \( \sigma_y = f(\epsilon, \dot{\epsilon}, T) \) type function correctly took into account the impact of the process of dynamic recrystallization on yield stress during high-temperature plastic strain.

In the procedure for identification of yield stresses, determined basing on axisymmetrical hot-compression test, the method of inverse analysis appeared to be significantly useful, eliminating practically the majority of disturbances arising from the mechanical test, such as: non-uniformity of deformation, strain rate and temperature of sample, friction phenomenon at the die – deformed metal contact and heat exchange from the sample holder and surrounding, etc. The best matching accuracy of analyzed curves was determined in the work by minimum value of the goal function, which represented simultaneously the best performance of applied inverse solution of finite element method. It has been found that the best matching accuracy of analyzed \( \sigma-\epsilon \) curves was obtained for constructional steel containing 0.28% C and microadditions of Nb, Ti and V (Fig. 2). Minimum value of the goal function \( \Phi = 0.0375 \) was obtained in the entire range of examined conditions of high temperature deformation.

References


