PROPERTIES AND STRUCTURAL DEVELOPMENTS OF HIGH PURITY Al PROCESSED BY ECAP

TIBOR KVAČKAJ, RÓBERT KOČIŠKO, JANA BIDULSKA, ROBERT BIDULSKÝ, JAN DUTKIEWICZ

a Department of Metals Forming, Faculty of Metallurgy, Technical University of Košice, 042 00, Košice, Slovakia,
b Politecnico di Torino, Sede di Alessandria, 15 100, Alessandria, Italy, “Institute of Metallurgy and Materials Science, c Polish Academy of Sciences, 30 059 Kraków, Poland

Keywords: aluminium, ECAP, TEM, strength, ductility

1. Introduction

The traditional process is to obtain the improvement in the mechanical properties of aluminium alloys through the precipitation of a finely dispersed second phase in the matrix. This is accomplished by a solution treatment of the material at a high temperature, followed by quenching. The second phase is then precipitated at room or elevated temperatures. For aluminium alloys this procedure is usually referred to as age hardening and it is also known as precipitation hardening. Conventional forming methods are ineffective in the achieving of favourable properties area of produced parts, adequate to structural properties; moreover through them only limited levels of structural and strength-plastic characteristics can be obtained. The solution may be non-conventional forming methods as well as Severe Plastic Deformation (SPD), such as more preferable are equal channel angular pressing – ECAP and equal channel angular rolling – ECAR technologies, to obtain results structured at the nm level. A combination of high strength and ductility of ultrafine polycrystalline metals, prepared by SPD, is unique and it indeed represents interesting cases from the point of view of mechanical properties. In the past decade, the research focused on to strengthen Al alloys without any ageing treatment, via SPD.

The present paper focused on the effect of ECAP on the properties and structural developments of high purity aluminium processed by twelve ECAP passes in room temperature.

2. Experimental material and conditions

Experimental material high purity aluminium (99.999 % Al) was prepared by zonal refining. Structure after producing was heterogeneous with average grain size \( d_g \approx 650 \mu m \). Mechanical properties before ECAP processing are given in Tab. I.

The ECAP process was carried out at room temperature by route C (sample rotation around axis about 180° after each pass) in an ECAP die with channels angle \( \Phi = 90^\circ \). The scheme of ECAP method is shown in Fig. 1. The round-shaped samples \( d_0 = 10 \text{ mm}, l_0 = 80 \text{ mm} \) were extruded twelve ECAP passages at rate of \( 1 \text{ mm s}^{-1} \). The static tensile test on the short specimens \( d_0 \times l_0 = 5 \times 10 \text{ mm} \) was performed. Tensile test was done after every second ECAP pass by EN 10002-1. Subsequently, characteristics of the strength (yield strength: YS; ultimate tensile strength: UTS) and elongation (El.) were determined. The microhardness test was done on polished surface in longitudinal direction of sample after every second ECAP pass. Transmission electron microscopy (TEM) analysis with electron diffraction in longitudinal direction of sample was done on thin foils. The thin foils were prepared using a solution of 5 % HF at a temperature \(-25^\circ C\) and the time 30 s.

3. Results and discussion

The mechanical properties are in Fig. 2. Ultimate tensile strength (UTS) is slightly sensitive on ECAP passes and substructure formation. Yield strength (0.2 % YS) is decreasing up to 6th pass where achieved local minimum. From 6th up to 12th pass is growing. Elongation to failure (El.) is inversing to 0.2 % YS. Microhardness dependence is given in Fig. 3 from which resulting microhardness growth with an increase of ECAP passes.

TEM analysis was performed on samples after 8th and 12th ECAP passes and micrographs are shown in Figs. 4–6. Initial structure is creating with large polyedric grains \( d_g \approx 650 \mu m \) and low dislocation density. Dislocations generated with severe plastic deformation are arranged to dislocation walls, which later transform to subgrains with low or

Table I

<table>
<thead>
<tr>
<th>0.2%YS [MPa]</th>
<th>UTS [MPa]</th>
<th>El [%]</th>
<th>HV10[-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>52</td>
<td>27</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Fig. 1. ECAP equipment with detail information about angles
high angles as it is seeing in Fig. 5. Subgrains are equiaxial with average size $d_{sg} \sim 2.2 \mu m$.

Substructure after 12th ECAP pass is equiaxial with low misorientation and average subgrain size $d_{sg} \sim 1 \mu m$ (Fig. 6). The significant substructure refinement was observed after 6th ECAP pass. Yield strength starts to grow also after 6th pass, what coincide with strengthening from grain size refinement after the Hall-Petch equation.

5. Conclusions

The investigation of high purity aluminium material processed by ECAP method refers on slight sensitivity ultimate tensile strength in dependence on ECAP passes. Stronger influence from ECAP passes on yield strength, elongation, microhardness and subgrain diameter was recognized.

The values were changed in following intervals:

- $Y_S = 26–39$ MPa,
- $UTS = 49–52$ MPa,
- $A = 27–56\%$,
- $d_{sg} = 650–1 \mu m$.

From the literature analysis is resulting non-uniform opinion on softening mechanisms of high purity Al during or after SPD in ECAP unit. The opinions are recognizing from recovery in dynamic and static regime up to recrystallization in dynamic, metadynamic and static regime. Tensile test results show that, in the stress-strain curves, the stress increased with increasing strain conditions due to severe plastic deformation via ECAP. However, it was observed also that the ECAP exhibited decrease in ductility.

SPD via ECAP may be a very useful process on increasing mechanical properties with only partial decrease and acceptable of ductility. Strengthening of material is caused by grains refinement and strain hardening of solid solution.

This work is supported by Slovak Agency APVV-20-027205. J. Bidulská thanks the bilateral project SK-PL-0011-09.

REFERENCES

Figure 6. TEM microstructure after 12\textsuperscript{th} ECAP pass ($d_{sg} \approx 0.98 \mu m$)

The high purity aluminium (99.999 % Al) was processed by SPD in ECAP unit at ambient temperature with route C. Influence of plastic deformations defined by number of ECAP passes on microstructure and mechanical properties was observed. The diameter of grain size was reduced from initial state before ECAP to $d_{sg} \approx 0.98 \mu m$ obtained after 12\textsuperscript{th} ECAP pass. Microhardness was increased with ECAP passes. Mechanical properties were slight sensitive, while elongation is depended on ECAP passes.
DIFFICULTIES WE MET WITH AT PRODUCTION OF Fe-B-V MODEL ALLOYS AND SAMPLE PREPARATION

ANNA VÝROSTKOVÁ, LUCIA ČIRIPOVÁ, VIERA HOMOLOVÁ

Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic lciripova@imr.saske.sk

Keywords: chemical homogeneity, weight losses, brittleness

1. Introduction

Boron is the element added into complex alloys and steels. It is known to increase the hardenability and creep strength of alloys \(^1\)-\(^3\). It is also of a big concern in the advanced steels for energy industry because of increasing the creep strength due to segregation at the grain boundaries (GB). Boron segregated at M\(_2\)C\(_6\)/GB interfaces prevents from the carbide particles growth. The precipitation of fine BN particles leading to creep strength increase has been one of the tasks solved in the frame of few EU projects. Vanadium is also a well known alloying element increasing the steel strength.

Calphad method used for phase diagrams modeling is based on the experimental verification of thermodynamic calculation of the diagrams. Concerning the Fe-B-V system there is only very little knowledge up to now. The only information found in literature is in the form of experimental results obtained by Kuzma and Starodub at 1073 K from 1973 year\(^4\).

In the system studied there were included the alloys with high content of B and V resulting in the alloys with high melting temperatures. Vanadium is known to form stable borides with melting temperatures from 2000 to more than 3000 K. The borides are brittle with high hardness, what caused some problems during sample preparation.

2. Material and methods used

The experimental alloys were prepared from elements of relatively high purity: Fe (99.98 %), B (99.9 %), and V (99.8 %). The alloys were produced in argon arc furnace with a water-cooled copper pan using non-consumable tungsten electrode and Zr getter. As can be seen in Fig. 1, the alloys cover roughly all possible areas of three-phase existence.

Prepared samples should have weight around 15 g, however mass loss after the production achieved values from 0 to 2 mass\%, extremely 7 %. That is why verification of the alloy chemical compositions was carried out by atom absorption spectrometry method. The alloys were cut to slices by electric spark method and annealed at 1353 and 903 K after being sealed in silica glass. Phase analyses of the states after the melting and annealing have been done by EDX and X-ray diffraction methods.

3. Results and their discussion

An advantage of the model alloys production in argon arc furnace is the protective atmosphere ensuring the protection against the oxidation of the bath. However the big disadvantage is the microstructure heterogeneity resulting from the use of water cooled copper pan. The melt in contact with the plate solidifies very quickly compared to the cap part of the loaf-shaped cast. The upper part then consists of large columnar crystals and bottom part of very fine equiaxed ones often with different chemical composition, Fig. 2a, b.

Also the imperfect stirring of the alloys containing vanadium borides with high melting temperature (because of insufficient heat input) was another source of the heterogeneity. In these cases only a part of the alloy under the arc was in liquid state, the rest remained in solid state heated to under-liquid temperature. The resulting shape then was irregular instead of the loaf-shape, Fig. 2c.

To avoid this we have tried to prepare the alloys in induction furnace, however we met with problems of a suitable
The kind of porosity does not influence the alloy purity and hence bubbles of different size were created. Fortunately this liquid state. Argon, entrapped in the alloys could not flow out from similar reasons.

Porosity of prepared melts was another phenomenon observed mainly in the alloys with higher melting temperatures, Fig. 2, when only a part of batch under the arc was in liquid state. Argon, entrapped in the alloys could not flow out and bubbles of different size were created. Fortunately this kind of porosity does not influence the alloy purity and hence the phase equilibria. It however, makes difficulties at grinding and polishing during a sample preparation. Moreover, most of prepared alloys is very brittle and porosity deteriorates this material property, as well. Therefore the handling with alloys at cutting and other processes of sample preparation and analysis had to be very careful.

Another form of free surfaces in the alloys was relatively dense net of cracks, Fig. 4. The cracks created in hard boride phases most probably already during fast cooling after the melting of alloys. Water cooling after isothermal annealing supported the tendency to cracking.

Chemical composition-microstructure homogeneity of alloys in our investigation is of crucial importance. Therefore most of melts was few times re-melted. Nunes et al. and Lima et al. used 3 and 5 melting steps respectively for the preparation of their V–B alloys. In our case this number was sufficient only for iron-rich alloys, e.g. 67Fe−18B−15V, 68Fe−27B−5V. For most of other alloys 11 to 14 remelts were needed as well as the reduction of the batch weight to 9–10 g. In spite of this few of the alloys still show the signs of heterogeneity, Fig. 2b.

Above mentioned mass losses of individual elements during melting and re-melting resulted from the elements lower latent heat of liquefaction compared to the melting temperature of the respective alloy.

According to our measurements the hardness increases in the order VB, V₆B₅V₂B₁ and VB₂ from 1500 do 3500 HV0.05. Values for FeB lay between 1700 and 2100, for Fe₂B they achieve values of 1600-2000 HV0.05. The ferritic matrix (Fe-V solid solution) is soft, with only 600 HV0.05 and pure Fe should have value only 140 according to Gončarov et al. Zhou et al. refer the value above 1700 for Fe₂B. Moreover β-rhombohedral boron in the alloys with amount of boron above 50 at.% is the second hardest elementary crystal after diamond.

The mentioned extremely high hardness led to the sample cracking and crumbling (see Fig. 4) during the preparation and resulting roughness of samples reduced the analyses quality. In some cases the slices broke into few pieces during cutting and grinding procedures. Thin slices had to be treated manually without using any holder and the process of grinding took quite a long time because of the alloy hardness. We have found that handling should be gentle during grinding and the grinding itself should be as short as possible to avoid mentioned cracking and crumbling. Almost no polishing was needed after the grinding with finest papers no. 2400 (Stuers). One of possible ways to get a flat sample surface could be the use of ion millling, in some cases also electrolytic polishing could be helpful.

4. Concluding remarks

The goal of the work was to prepare homogeneous and clean model Fe-V-B alloys.

1. Most difficulties in achieving required homogeneity resulted from high melting temperatures and hardness of the alloys.
2. To reduce chemical heterogeneity and avoid porosity, the equipment with higher heat input than that of argon arc should be used.
3. The minimising the weight of alloys is also useful. It means to avoid any alloy re-melting.
4. Only high quality materials should be used for sample grinding and polishing to avoid its contamination and shortening the duration of the sample preparation process.

The authors acknowledge the financial support of the project VEGA 2/0042/09 and the project MVTS SAV solved in the frame of the COST Action 536.

REFERENCES


Fig. 3. Contamination of alloys with Si; a – EDX-spectrum of the strange phase with Si; b – FeSiB₂ phase (light background in the figure)

Fig. 4. Pores and cracks in brittle borides; a – 67Fe-18B-15V alloy; b – 13Fe-25B-62V alloy
A. Výrostková, L. Čiripová, V. Homolová (Institute of Materials Research SAS, Košice, SR): Difficulties We Met with at the Production of Fe-B-V Model Alloys and Sample Preparation

The work describes problems to be solved during the preparation of Fe-B-V alloys and samples for phase analysis. Main request on the material used in the research focused on modeling of phase diagrams by Calphad method is its purity and homogeneity. The problems to be solved were the compaction of the powders of different mesh, high melting temperature of some alloys with high boron content and weight losses. Extremely hard and brittle alloys led to further difficulties with material cutting and sample preparation. In the paper some of the ways used to prepare the samples of required quality are mentioned.
CONTACT STRENGTH AND CRACK FORMATION IN LAMINAR CERAMICS

LUCIA HEGEDÜSOVÁ, LADISLAV CENIGA, JÁN DUSZA

Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic lhegedusova@imr.saske.sk

Keywords: contact test, microstructure, cone cracks

1. Introduction

Conventional tests for determination of strength of ceramics describe failure behaviour related to a simple stress state which is mostly uniaxial with insignificant gradients. Considering practical applications, mechanical loading leads to an inhomogeneous multi-axial stress state which can be simulated, regarding laboratory measurements, by contact line or point loading. The contact line/point is induced by two opposite rollers and spheres. Weibull analysis is commonly used for describing the values of the bending strength results which are characterized by the characteristic strength $\sigma_0$ and the Weibull parameter $m$ which is the measure of the scatter in strength values. The Fett’s theory which defines relationships between parameters of the Weibull analysis for the four-point bending test ($\sigma_{0,bend}$, $m_{bend}$) and single-cycle contact test using rollers ($\sigma_{0,cont}, m_{cont}$) is derived as

$$m_{bend} \approx 2 m_{cont, r}, \quad \sigma_{0,bend} \approx \sigma_{0,cont, r} \quad (1)$$

The characteristic strength $\sigma_{0,cont}$ and $\sigma_{0,bend}$ results from experimental values of $\sigma_{0,cont}$ and $\sigma_{0,bend}$, respectively, defined as

$$\sigma_{bend} = \frac{3P(S_1 - S_2)}{2W^2}, \quad \sigma_{cont, r} = \frac{1.96P}{tW} \quad (2)$$

$S_1$ and $S_2$ represent outer and inner spans, respectively. $W$ and $t$ are dimensions of a sample along directions parallel and perpendicular to a direction of the applied force $P$ at failure, respectively.

Finally, the stress $\sigma_{cont, x}$ along with the Young’s modulus $E$ have the forms

$$\sigma_{cont, x} = \frac{1 - 2v_m}{3\pi} \left[ \frac{6PE^2}{R^2} \right] \frac{1}{E} \left[ \frac{1 - v^2}{E_s} + \frac{1 - v^2}{E_m} \right]^{1/3} \quad (2)$$

where $E_s$, $v_s$, and $E_m$, $v_m$ are the Young’s modulus, the Poisson’s ratio for the spheres and a ceramic material, respectively.

The paper deals with the determination of contact strength of laminar composite ceramics by opposite rollers and spheres. Results of the single-cycle contact tests are compared with those of the standard bending test, and an analysis concerning the Fett’s theory is presented. Additionally, the contact test by the spheres is also performed in a multi-cycle mode.

2. Experimental material and tests

An experimental material is represented by $\text{Al}_2\text{O}_3$-ZTA laminar composite ceramics which is made by tape casting followed by binder burn-out and sintering, where $ZTA = 60$ vol.% $\text{Al}_2\text{O}_3 + 40$ vol.% $\text{ZrO}_2$. This 9-layered material of five layers of $\text{Al}_2\text{O}_3$ and four layers of $\text{ZrO}_2$ was prepared at the Institute of Science and Technology for Ceramics, Faenza, Italy.

The bending test was applied at $S_1 = 40$, $S_2 = 20$ (mm). The single-contact mode by rollers of a standard hardened steel was performed in such way that the load $P$ increased to a value of failure of specimens, where $D = 3$ mm is a diameter of the rollers, $L = 10–15$ mm is length of specimens, and $W = 3$ mm, $t = 4$ mm.

The contact modes by standard hardened steel spheres with the radius $R = 2.5$ mm were applied to specimens with the dimensions $W = 3$ mm, $t = 4$ mm, $L = 25$ mm, at a loading range of 0–5 kN. Additionally, the multi-cycle contact mode was performed at the frequency $f = 10$ Hz and the number $n = 10^2$, $10^3$, $10^4$, $10^5$ of cycle.

Specimens loaded without their failure were cut through a centre of a contact surface and polished due to optical and electron microscopy used for the determination of the cone crack length $c$, and the angle $\alpha$ which is measured between a contact surface and the cone crack.

Each of the tests was performed at room temperature. With regard to Eq.(2), material parameters of $\text{Al}_2\text{O}_3$-ZTA and standard hardened steel (SHS) of spheres are presented in Tab. I (ref.3).

3. Results and discussion

Microstructure of the materials was studied by scanning electron microscopy of polished and etched samples. Microstructure of the ZTA layer (see Fig. 1a) consists of relatively fine layers of $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_m$ [GPa]</th>
<th>$v_m$</th>
<th>$E_s$ [GPa]</th>
<th>$v_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$-ZTA</td>
<td>377</td>
<td>0.16</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SHS</td>
<td>–</td>
<td>–</td>
<td>200</td>
<td>0.2</td>
</tr>
</tbody>
</table>
large Al₂O₃ grains and small ZrO₂ grains as dark and bright phases with size of 1 µm and 0.3 µm, respectively, where both phases exhibiting equiaxed shapes are uniformly dispersed throughout the ZTA layer with thickness of 529 µm.

The Al₂O₃ grains with size of 3 µm (see Fig. 1b) in the Al₂O₃ layer with thickness of 193 µm exhibit well-faceted boundaries and sharp triple points. Finally, the two layers, i.e. Al₂O₃ and ZTA, are well defined by straight interfaces with no significant residual porosity at the interfaces (see Fig. 1c).

The Weibull characteristics for the investigated material are as follows: \( \sigma_{0,\text{bend}} = 650 \text{ MPa}, \ m_{\text{bend}} = 19.8; \ \sigma_{0,\text{cont}}, \ m_{\text{cont}} = 715 \text{ MPa}, \ \sigma_{0,\text{cont}} = 3453.3 \text{ MPa}, \ m_{\text{cont}} = 21.6; \ \sigma_{0,\text{cont}} / \sigma_{0,\text{bend}} = 1.1, \ m_{\text{bend}} / m_{\text{cont}} = 2.5.

As presented in Fig. 1b, the Al₂O₃ layer exhibits grains with a diameter of 25–30 µm which is much greater than diameters of <1 µm and 3–5 µm of the Al₂O₃ and ZrO₂ grains of the ZTA layer (see Fig. 1a), respectively.

Fig. 2 shows a fracture surface of Al₂O₃-ZTA loaded by rollers of the single-cycle contact test along with a large processing flaw in the ZTA layer. Such flaws along with the large grains of Al₂O₃ in the Al₂O₃ layer might be assumed to be a reason of a deviation from the Fett’s theory regarding the ratio \( m_{\text{bend}} / m_{\text{cont}} \) in contrast to the ratio \( \sigma_{0,\text{cont}} / \sigma_{0,\text{bend}} \) which corresponds to the Fett’s theory. Additionally, due to the difference \( \alpha_{\text{Al₂O₃}} < \alpha_{\text{ZTA}} \) in thermal expansion coefficients, the Al₂O₃ and ZTA layers are loaded by compressive and tensile thermal stresses acting in a plane of a layer, respectively. These stresses in each layer exhibit a significant distribution along the plane normal. This distribution might be assumed to be also a reason of the deviation from the Fett’s theory.

Fig. 3 shows SEM micrographs of a cross-section view of Al₂O₃-ZTA with a cone crack which is formed during the single-cycle contact test by spheres. The cone crack as a reason of failure and strength degradation of the material exhibits a perpendicular course below the contact surface, followed by a linear course.

Fig. 4 shows the length \( c = c(n) \) and angle \( \alpha = \alpha(n) \) of the cone crack as functions of the cycle number \( n \), where the cone crack is formed during the multi-cycle contact test by the spheres.
creasing function of $n$. This result is in agreement with that presented in $^5$. In contrast to $c = c(n)$, the function $\alpha = \alpha(n)$ exhibits an increasing-decreasing course with a maximum for $n \approx 10^3$.

Fig. 5 shows SEM micrograph of a cross-section view of Al$_2$O$_3$-ZTA with multiple cone cracks which are formed during the multi-cycle contact test by spheres. The Al$_2$O$_3$ layer is harder than the standard hardened steel of the spheres. The higher hardness of Al$_2$O$_3$ layer is assumed to be a reason of the formation of the multiple cone cracks due to higher deformation of the spheres. The higher deformation is a reason of an increase of the contact surface.

4. Conclusions

Results of this paper concerning the Al$_2$O$_3$-ZTA laminar composite ceramics are as follows. The characteristic strength by the Weibull analysis of the bending test and contact test by rollers are in an agreement with the Fett’s theory. The disagreement of the Weibull moduli of these tests with the Fett’s theory is assumed to be caused by (1) the presence of large processing flaws; (2) much greater grains in the Al$_2$O$_3$ layer than those in the ZTA layer; (3) a significant distribution of thermal stresses, where the distribution is related to a normal of a plane of the Al$_2$O$_3$-ZTA layers.

The contact test by spheres in a single-cycle mode induces a single cone crack in contrast to a a multi-cycle mode which induces multiple cone cracks. The multiple cone cracks are formed due to an increase of a contact surface. The contact surface increase is due to lower hardness of the standard hardened steel of the spheres than hardness of the Al$_2$O$_3$ layer. A dependence of the cone crack length at the multi-cycle mode on the cycle number is in an agreement with results published in $^4, 5$. Finally, a dependence of the cone crack angle on the cycle number exhibits an increasing-decreasing course.

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0034-0; by VEGA 2/0088/08; and by MNT-ERANET HANCOC.

REFERENCES


L. Hegedusova, L. Ceniga, J. Dusza (Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovak Republic): Contact Strength and Crack Formation in Laminar Ceramics

The paper deals with the determination of contact strength of laminar composite ceramics by opposite rollers and spheres. Results of the single-cycle contact tests are compared with those of the standard bending test. Parameters of the Weibull analysis which is considered for the determination of strength of ceramic materials are presented. The contact test by the spheres is also performed in a multi-cycle mode. The multi-cycle mode induces multiple cone cracks in contrast to the single-cycle mode which induces a single cone crack. Parameters of the multiple cone cracks are analysed.

...