

PRODUCTION OF HYDROXYAPATITE-TITANIUM COMPOSITE POWDERS BY HIGH-ENERGY BALL MILLING SUITABLE FOR SPARK PLASMA SINTERING PROCESSES

Michaela Matějková^{1,*}, Ivo Dlouhý¹

¹ Institute of Materials Science and Engineering, NETME centre, Brno University of Technology, Technická 2896/2, 616 69 Brno, Czech Republic

*corresponding author: e-mail: matejkova@fme.vutbr.cz

Resume

Hydroxyapatite-titanium (HA-Ti) composite powders were prepared by high-energy ball milling for subsequent production of samples by spark plasma sintering (SPS). Different milling times for the preparation of HA-Ti composite powders were used. The microstructural properties and phase composition of the composite powders were studied by scanning electron microscopy and X-ray analysis. The results showed no formations of new phases in the structure during high-energy ball milling and a gradual reduction of the particles size with increasing milling time. Sintered samples from HA-Ti composite powder were prepared. A cross section analyzed by SEM and phase composition obtained by X-ray diffraction was studied. The results showed changes of phase compositions in the structure.

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1. Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA) is a bioceramic material widely used in dentistry and orthopedics applications due to its favorable osteoconductive and bioactive properties. HA has similar chemical composition and crystal structure to apatite in the human skeletal system and is therefore suitable for bone implants. However, poor mechanical properties like low fracture toughness limit the use of HA in load-bearing orthopedic applications. One of the possibilities of overcoming these mechanical limitations is to use ceramic-metal composites to achieve the necessary mechanical strength and bioactive properties [1 - 6].

For this purpose one of the suitable metals appears to be titanium. Titanium and titanium alloys have been widely used for medical applications due to their high specific strength, high corrosion resistance, low density, and good biocompatibility.

HA-Ti composites represent a biomaterial with good mechanical and biological properties [1, 3]. Therefore, the preparation of these composite materials has attracted considerable attention in recent years. Studies have shown that the adhesive and cohesive strengths can be increased significantly by combining HA and Ti as reinforcing additives [1, 7-9]. However, due to the higher sintering temperature, phase changes could occur in the composites.

The objective of this study was to produce HA-Ti composite powders by high-energy ball milling for subsequent spark plasma sintering (SPS). High-energy ball milling is a process in which a mixture of powders (metallic, non-metallic or a combination of both) is actively deformed in a controlled atmosphere, under a high energetic ball charge [10-12]. As such, the high-energy ball milling is a potential method for the preparation of various interesting solid-state materials and

has the advantage of the weakening surface-bonded species by pressure to enhance thermodynamic and kinetic reactions between solids [11 - 15]. The constituent powder particles are repeatedly fractured and welded, and so powder particles with a very fine structure can be obtained after milling [9 - 14].

Compared to conventional sintering, SPS allows sintering at lower temperatures and shorter duration by charging the intervals between powder particles with electrical energy, and efficiently applying a high-temperature spark plasma [16]. For this reason, the compacted powder is sintered under uniform heating to a high density and shorter duration, suppressing grain growth, which eventually allows the production of nanostructured ceramics [16, 17].

In this study, HA-Ti composite powders with 60 vol. % HA were produced by high-energy milling under different milling conditions. The most suitable composite powder obtained was then used for spark plasma sintering processes, whose properties were then analyzed.

2. Experimental

Hydroxyapatite powder (Medicoat) of a particle size $<63\ \mu\text{m}$ and titanium powder (GfE Metalle und Materialien GmbH) of a particles size $<45\ \mu\text{m}$ were used as the initial feedstock materials (Fig. 1).

Blends of 60 vol. % HA were prepared in stainless steel vials for high-energy ball milling. The powders were milled in inert atmosphere (argon) by using 500 g stainless steel balls with a diameter of 10 mm under 360 rpm. Every hour, 0.5 g of ethanol was added to vials to prevent the powder from sticking to the walls of the vials. Parts of the powders were sampled after 4, 6, 8 and 10 hours of milling. Particle morphology and cross sections of the ball-milled composite powders were analyzed by scanning electron microscopy (SEM), whereas quantitative chemical analyses were performed using energy dispersive spectroscopy (EDS). To observe their cross sections, the composite powders were embedded in low-viscosity epoxy resin (EpoFix Resin, EpoFix Hardener, Struers) and ground and polished using standard metallographic procedures. The phases present in the composite powders after the milling were determined by X-ray diffraction (XRD 3003 TT, Cu K_{α} , 40kV, step 0.05° , 3s per step, $20\text{-}165^{\circ}$).

After 10 hours of milling, the obtained HA-Ti composite powder was sintered to disc of 20 mm in diameter and 5 mm in thickness by a spark plasma sintering machine (SPS 10-4, Thermal Technology LLC, California, USA). A sintering temperature of $1000\ ^{\circ}\text{C}$ and a dwell time of 5 min were used. A heating rate of $100\ ^{\circ}\text{C}/\text{min}$ was applied. The composite powder was uniaxially compressed throughout the sintering process at a pressure of 60 MPa.

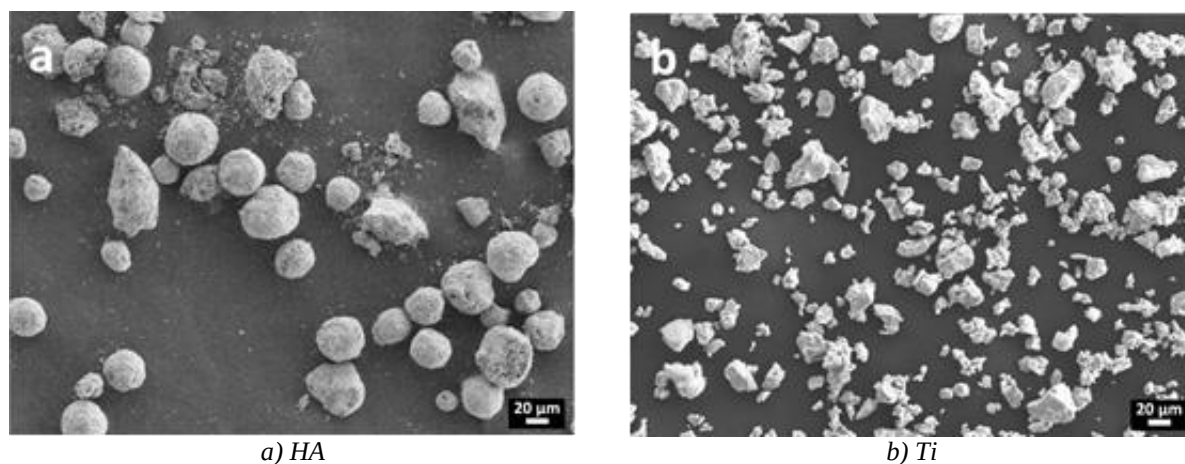


Fig. 1. Morphology of powders.

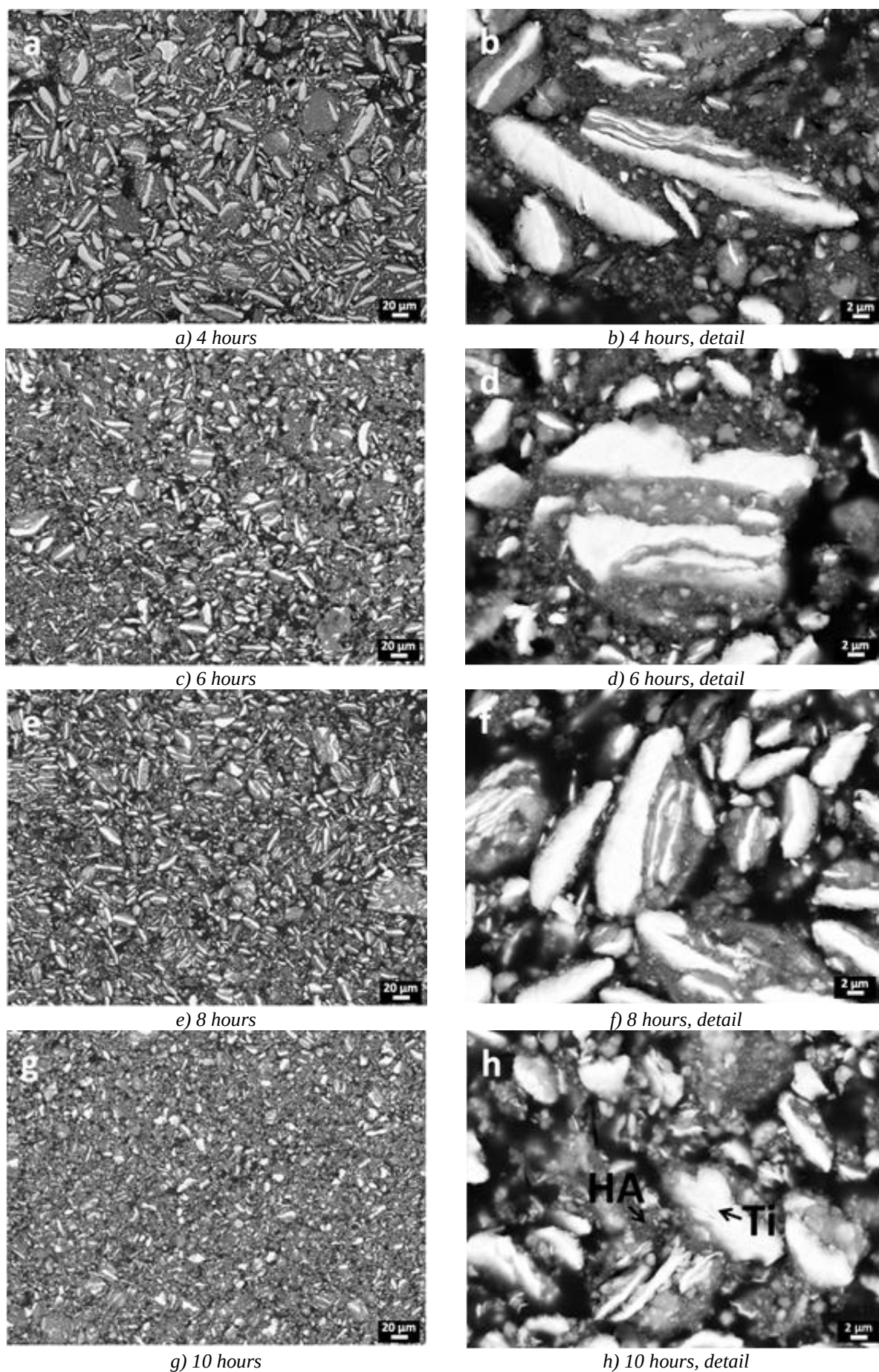


Fig. 2. SEM images of cross-section of HA-Ti composite with 60 vol. % HA after specific hours of milling.

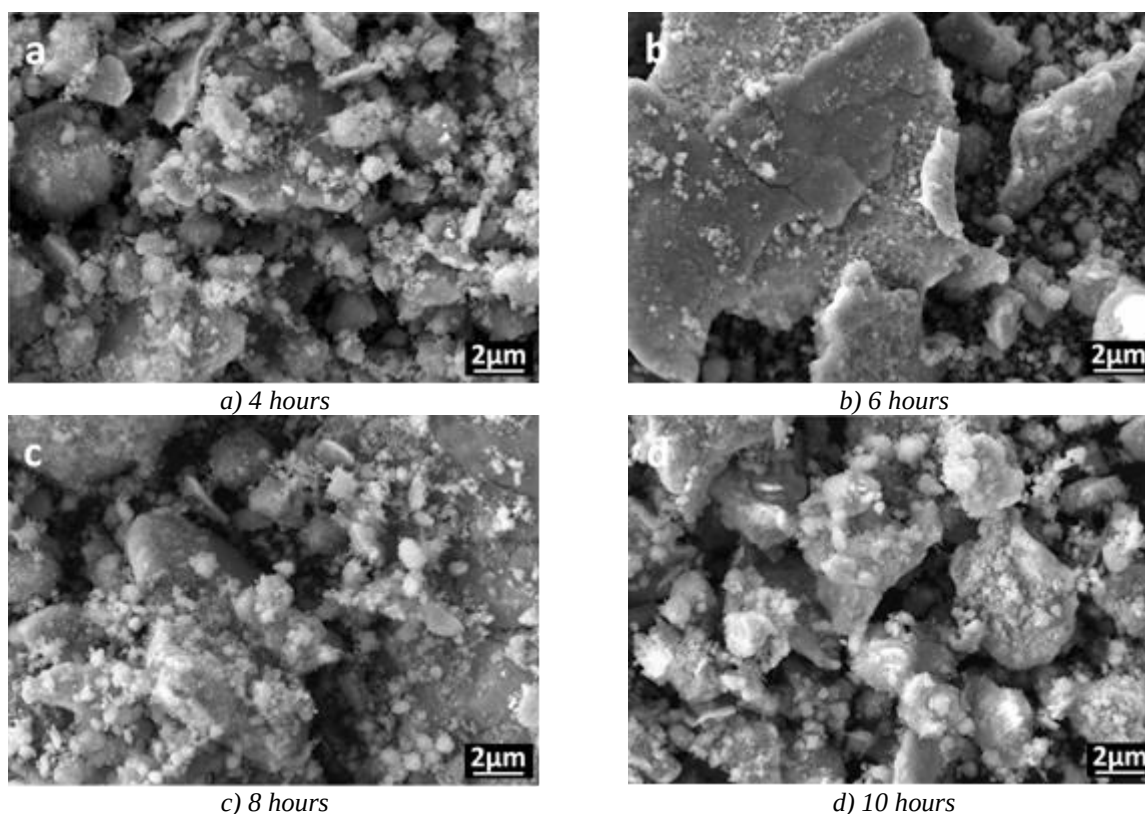


Fig. 3. SEM images of morphology of HA-Ti composite powders with 60 vol. % HA after specific hours of milling.

X-ray diffraction and SEM analyses of the SPS sample were performed. The cross section of SPS sample was analyzed via SEM and the phases present were determined via X-ray diffraction.

3. Results and discussion

First the influence of high-energy ball milling on the morphology of particles and agglomeration was studied. Cross sections of particles of HA-Ti composite powders with 60 vol. % HA for all milling times are shown in Fig. 2. No separate HA and Ti particles in the composite powders could be observed for all milling times. SEM images show that Ti particles were coated with HA. The gradual reduction of particles size and the change in the shape of Ti particles with increasing time were evident. The plate-shaped Ti particles observed after 4 hours of milling (Fig. 2a, b) gradually changed their morphology to a near spherical-shape, as observed in Fig. 2g, h. It is obvious that with increased milling time,

the particle size decreased and HA-Ti composite particles were formed.

Fig. 3 shows the morphology of HA/Ti composite powders after 4, 6, 8 and 10 hours of milling. SEM analyses of the morphology of HA-Ti powders showed that the particle size increased in the initial period (Fig. 3b); however, after longer milling times, the materials deplete their plasticity and frequent particle breakups led to a decrease in the average size (Fig.3d).

The changes during milling such as change in particle shape, decrease in particle size, and formation of composite particles correspond with the results of high-energy milling [18]. First brittle HA particles are broken up by ball milling, while Ti particles are plastically deformed, eventually attaining plate-like shape. With increasing time, Ti plate-like particles could not withstand repeated mechanical deformation and broke up into smaller particles. Due to their high surface energy, HA particles tend to adhere to larger Ti

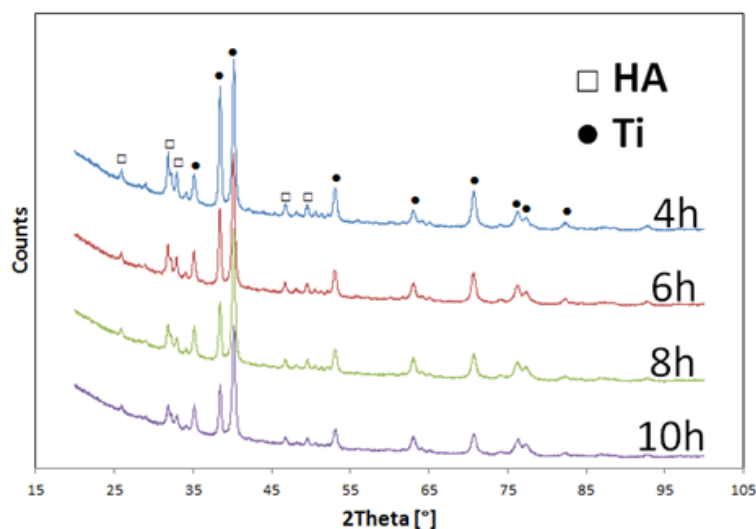
particles, which lead to the formation of composite particles. The impact of milling balls causes the following break-up of the composite particles, which leads to a decrease in particle size and produces particles with higher specific surface area and thus enhances the adhesion between Ti and HA [19].

Fig. 4 shows the XRD patterns of HA-Ti composite powders for all applied milling times. The XRD analyses showed that the HA-Ti composite powders were composed of HA and Ti phases and therefore no formations of new phases in the structure were found. For these reasons, high-energy milling is a suitable technology for the production of HA-Ti

composite powders.

Cross-section morphologies of the sintered samples are shown in Fig. 5. Fig. 5a, b shows that the structure is well densified in the center of the sample. Towards the edge of the samples, a porous structure is evident (Fig. 5c, d), which can be favorable for bio-applications. Surface porosity leads to improved long-term stable fixation of bone implants [20].

Fig. 6 shows the XRD patterns of an SPS sample prepared from HA-Ti composite powder after 10 hours of milling. It reveals that the sample contained TiO_2 (38 %), CaTiO_3 (28 %), CaO (3 %) and TiO (31 %) phases, indicating major changes in the HA structure during sintering.



4. XRD patterns of the HA-Ti composite powders after 4, 6, 8 and 10 hours. (full colour version available online)

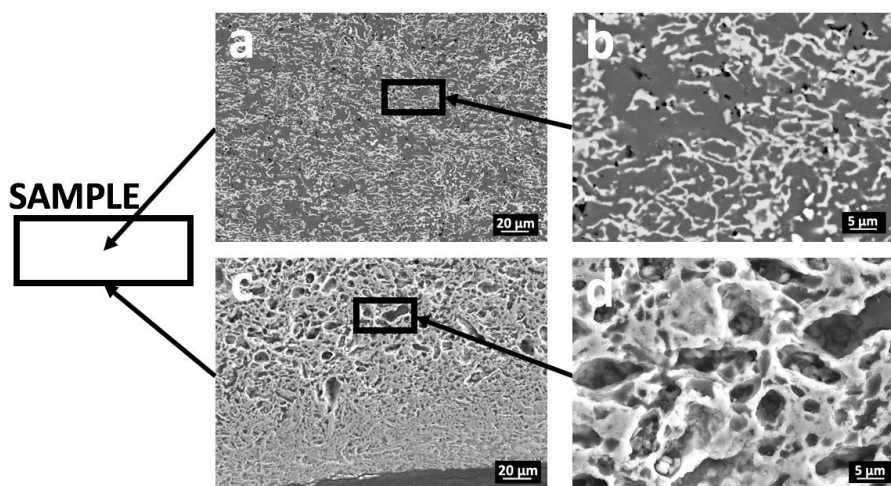


Fig. 5. Cross-section morphologies of the sintered samples by spark plasma sintering process.

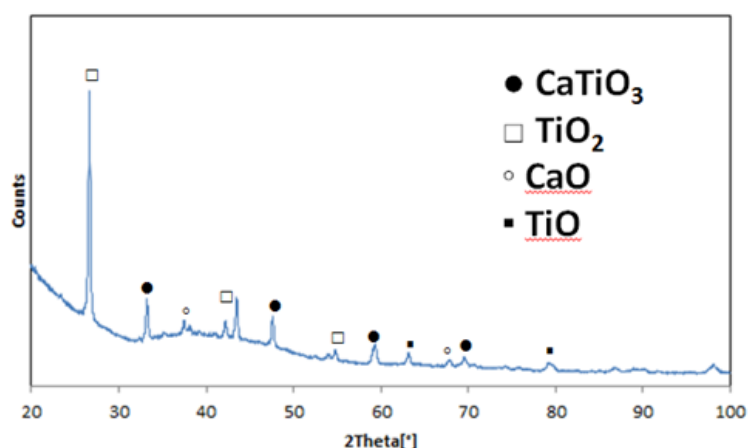


Fig. 6. XRD patterns of the SPS sample.
(full colour version available online)

4. Conclusions

The effect of processing parameters on high-energy ball milling of HA/Ti composite powders was examined. HA and Ti powders with 60 vol. % HA were milled for 4, 6, 8 and 10 hours. From the results of observing the obtained HA-Ti composite powders it could be concluded that:

- no formations of new phases in the structure during high-energy ball milling were observed, which could be caused by sufficient cooling pauses during milling;
- milled powder gradually changed morphology to a near spherical-shape and reduction in particle size were confirmed;
- sintered samples from HA-Ti composite powder can be prepared by applying spark plasma sintering method;
- porous structure observed on sintered sample is favorable for bio-applications either in form of the bulk material or biocompatible coating.

The results have shown that high-energy ball milling is a suitable method for the preparation of HA-Ti composite powders for SPS processes.

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FRACTURE TOUGHNESS TRANSITION OF FERRITIC-PEARLITIC STEEL AT STATIC AND DYNAMIC LOADING EVALUATED BY MASTER CURVE CONCEPT

Libor Válka^{1,*}, Ivo Dlouhý¹

¹ Institute of Materials Science and Engineering, NETME centre, Brno University of Technology, Technická 2896/2, 616 69 Brno, Czech Republic

*corresponding author: e-mail: valka@fme.vutbr.cz, tel.: +420 541143172

Resume

The paper focuses on assessing the usability of fatigue pre-cracked Charpy type specimens when evaluating the resistance of steel with ferritic-pearlitic structure to the initiation of unstable fractures. The suitability of using the specimens is evaluated on the basis of comparing experimentally established values of fracture toughness on pre-cracked Charpy type specimens and the values of this characteristics determined using Compact Tension (CT) specimens. For the evaluation and comparison of the fracture toughness temperature dependences determined on individual specimen types the master curve concept quantifying fracture toughness transition was applied. In the case of the steel employed, very good agreement was found to exist between the characteristics determined on individual types of specimen. It was shown that fracture toughness determined on pre-cracked Charpy type specimens can be regarded as a representative measure of resistance of the material employed to the brittle fracture occurrence.

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1. Introduction

In technical practice, the most vulnerable to exhibit unstable failures are components and structures in which the initiation or existence of crack failures can be expected. The probability of the occurrence of brittle fracture failure in a structure depends not only on internal factors such as the microstructure of material, but also on external effects, including temperature and loading rate in particular. For steels with ferritic base microstructure, the risk of brittle fracture occurrence increases sharply in steel structures operating (permanently or temporarily) in the transition region of the steel used or in structures exposed to dynamic mode of loading. Evaluation of the material resistance to the initiation of unstable fractures is in such cases based on parameters and characteristic

introduced by fracture mechanics. These include fracture toughness, defined as a resistance of material (structure) to the initiation of unstable fracture under the presence of a priori defects of the type of cracks.

Structures operating in a comparatively broad interval of temperatures and under conditions of static and dynamic loading include components of railway bogies, axles, wheels or wheelsets. Circumferential parts (rims) of railway wheels belong to the most stressed parts of these components where cracks can appear due to local overheating of the material during braking or as a result of fatigue loading at wheel/rail contact locations. Such defects once having critical dimensions can lead to brittle, unstable fractures being initiated along the whole profile of the wheel. According to the UIC 812-3 standard [1], the fracture

behaviour evaluation of railway wheel rims requires measuring the fracture toughness on specimens having 30 mm in thickness under conditions complying with the ASTM E 399 standard [2]. This is explained arguing that using specimens of greater thickness is less prone to the presence of microstructure gradients occurring, in particular, near the wheel rim surface. The microstructure heterogeneity is associated with the heat treatment technology used in the manufacture of the wheel, when during the spraying of the wheel rim a pronounced temperature gradient appears in the circumferential parts of the wheel. Thus there may exist microstructure regions (volumes) that satisfy the resistance criteria when 30 mm thick specimens are used but, simultaneously, with locally lower resistance to brittle failure. To record the local values of fracture toughness in the wheel rim it seems to be of greater advantage to use the PCVN type specimens (Pre-cracked Charpy V-Notch) loaded statically or dynamically by 3-point bending [3, 4]. One of the reasons for this modified approach is the possibility of localizing the specimen closer to the wheel tread. However, another reason is seen in refraining from the mechanical averaging of the actual material response and obtaining exact conditions for establishing the actual resistance to the brittle failure [5].

In the case of static and/or quasi static loading of steels with ferritic basic microstructure and the yield strength ranging from 275 to 825 MPa, the so-called fracture toughness master curve concept [6, 7] can be used to describe the temperature dependence of fracture toughness in the transition region. If the applicability of this approach was also proved for the case of dynamic loading,

it would be possible to predict not only the level of fracture toughness but also determine the failure probability in dependence on the two dominant external factors, temperature and loading rate [8].

2. Experimental material and testing methodology

The R7T ferritic-pearlitic steel was used as experimental material (Fig. 1), employed in the manufacture of railway wheelsets. Its chemical composition is given in Table 1.

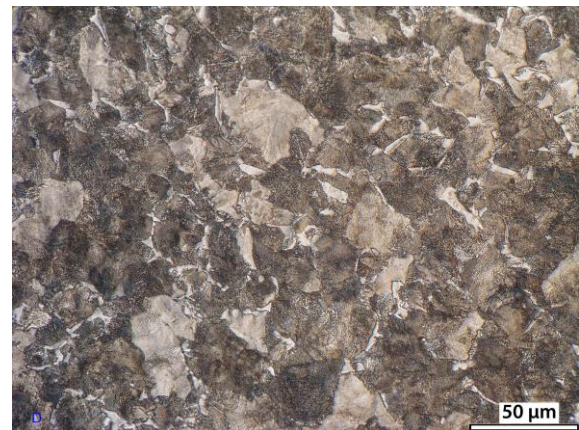


Fig. 1. Ferritic-pearlitic microstructure of R7T steel. (full colour version available online)

The fracture behaviour of pre-cracked specimens was examined exploiting Compact Tension (CT) specimens having 30 mm in thickness, corresponding to the UIC 812-13 standard [1] and referred to in the following as CT(30) specimens. In addition, pre-cracked Charpy V-notch (PCVN) specimens have been also employed. The locations of specimen extraction are shown schematically in Fig. 2. The PCVN specimens were taken from two locations, one closer to (location “I”) and one farther from (location “II”) the wheel tread.

Table 1

Chemical composition of steel R7T (in wt. %).

C	Mn	Si	Cr	Ni	Al	Cu	Mo	P	S	V	N
0.47	0.69	0.29	0.19	0.02	0.035	0.09	0.003	0.018	0.009	0.004	0.006

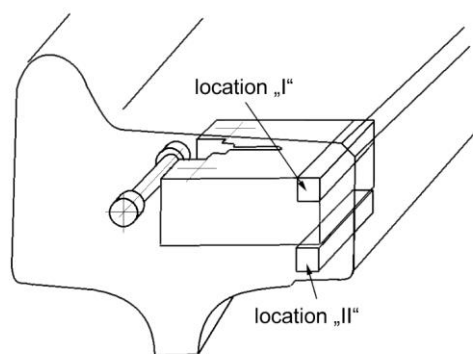


Fig. 2. Specimen localisation scheme in the wheel rim.

According to UIC 812-3, the fracture toughness is established based on the K_Q parameter for the instant of attaining force F_5 ; the F_5 is a force corresponding to the intersection point of the load F – displacement q trace and a straight line with the slope 5 % lower than the slope of the linear part of the $F - q$ record, even in case when the record continues after attaining this value (thus showing that elastic-plastic behaviour occurred). The fracture toughness established in this way represents a valid value K_{Ic} in some cases, in others only a provisional value K_Q . The measurement of static fracture toughness of CT(30) and PCVN specimens was conducted on a Zwick Z250 universal test machine at a loading rate of 1 mm/min while dynamic fracture toughness of PCVN specimens was measured on an instrumented impact tester at an impact rate of $1.5 \text{ m} \cdot \text{s}^{-1}$ of the hammer tup. Unlike with PCVN specimens where fracture toughness was measured within a certain temperature interval, the static fracture toughness of CT(30) specimens was only determined at room temperature. The fracture toughness evaluation proceeded in keeping with standard procedures [9].

3. Results and discussion

3.1 CT(30) specimens, static loading

In the case of CT(30) specimens loaded statically at room temperature, two types

of the deformation and fracture mechanical response of material could be identified being quantified by the following parameters:

- linear elastic fracture toughness K_{Ic} (or K_Q according to UIC 812-3) with values lying in the interval from 60 to $90 \text{ MPa} \cdot \text{m}^{1/2}$. In this case, no pronounced differences in the microstructure and hardness over the specimen thickness could be observed;
- elastic-plastic fracture toughness K_{Jc} (or K_Q according to UIC 812-3) after a larger elastic-plastic deformation in front of the crack tip and K_{Jc} values lying in the interval of 70 to $105 \text{ MPa} \cdot \text{m}^{1/2}$. For specimens included in this group, greater differences in the microstructure and hardness over the specimen thickness could be observed than in the preceding case.

Irrespective of the nature of the failure, the mean value of fracture toughness K_Q determined on the CT(30) specimens was higher than the $80 \text{ MPa} \cdot \text{m}^{1/2}$ value prescribed in the UIC 812-3 standard (see Fig. 3).

3.2 PCVN specimens, static and dynamic loading

The temperature dependence of static and dynamic fracture toughness of PCVN specimens, together with the values established on CT(30) specimens can be found in Fig. 3. In the transition region, three types of fracture behaviour could be established in keeping with the general description of the fracture toughness temperature dependence which is given, for example, in [10]:

- K_{Ic} – fracture toughness fulfilling the conditions of linear-elastic fracture mechanics;
- K_{Jc} – fracture toughness at the initiation of unstable fracture after preceding elastic-plastic deformation;
- K_{Ju} – fracture toughness corresponding to the initiation of unstable fracture after a certain length of ductile tear.

The mean value of fracture toughness in dependence on temperature in the transition

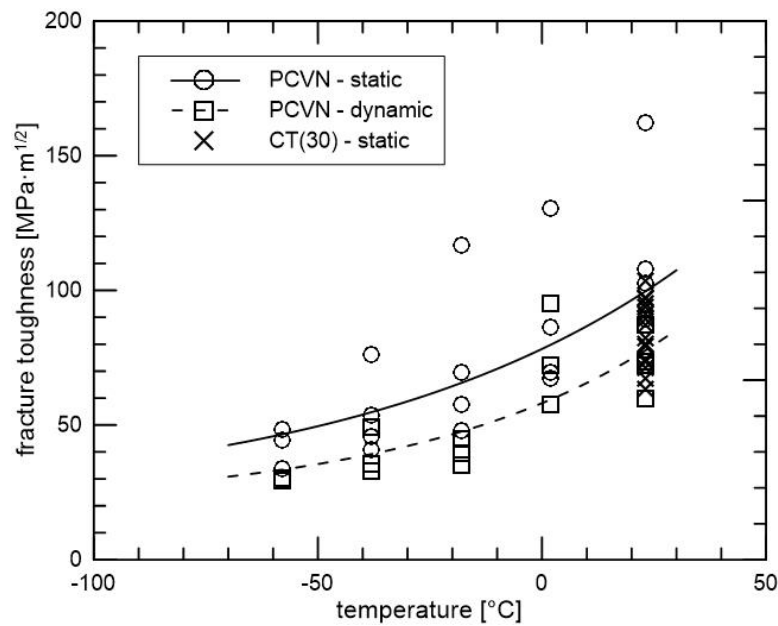


Fig. 3. Temperature dependence of static and dynamic fracture toughness of PCVN and CT(30) specimens.

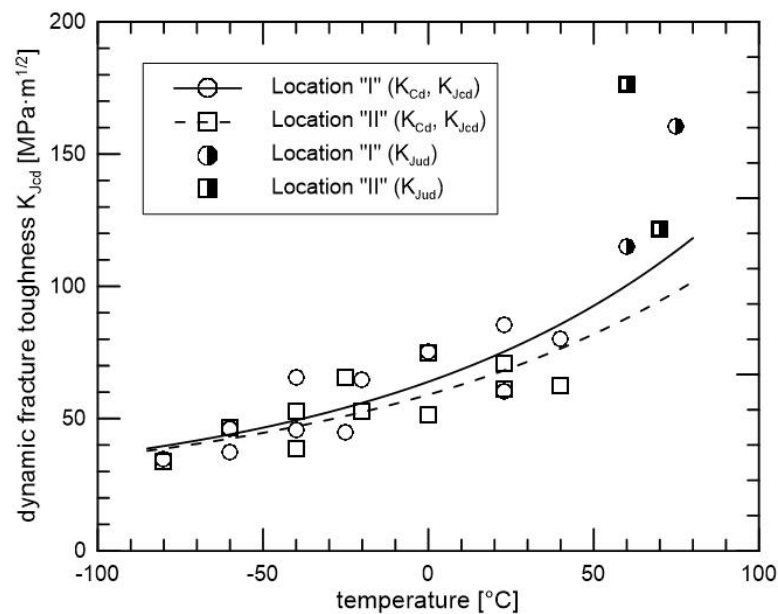


Fig. 4. Comparison of dynamic fracture toughness of PCVN specimens taken on sites "I" and "II".

region can be described by an exponential function in the form of $(K_C, K_{Jc})_{\text{mean}} = K_{\min} + A \exp(BT)$. The value $K_{\min}$ given in the equation is the minimum fracture toughness value corresponding to the physical and technological principles, T is an absolute temperature. Choosing $K_{\min} = 20 \text{ MPa}\cdot\text{m}^{1/2}$, the temperature dependence of the mean fracture toughness value obtained for quasi-static loading can be expressed in the form

$$(K_C, K_{Jc})_{\text{mean}} = 20 + 1.435 \exp(0.01356 T) \quad (1)$$

and for the case of dynamic loading in the form

$$(K_{Cd}, K_{Jcd})_{\text{mean}} = 20 + 0.280 \exp(0.01799 T) \quad (2)$$

Included in the calculation were in both cases only the values of fracture toughness satisfying the condition of limit value (validity

range) of fracture toughness K_{Jc} in the transition region given by relation [11]

$$(Eb_0R_{p0.2} / K_{Jc}^2) \geq 30 \quad (3)$$

where E is Young's modulus of elasticity, b_0 is the ligament, i.e. the length of the unbroken cross section in front of the fatigue crack ($W - a_0$), and $R_{p0.2}$ is the yield strength of material at a given temperature.

Fig. 4 gives a comparison of the temperature dependence of dynamic fracture toughness of PCVN specimens as obtained in locations "I" and "II". Experimental data was again fitted with exponential dependence in the form of $(K_c, K_{Jc})_{\text{mean}} = K_{\min} + A \exp(BT)$. The graph reveals a modest decrease in the values of fracture toughness in the region of higher temperatures for specimens taken on the site farther from the wheel rim.

3.3 Fracture toughness correlation obtained using CT(30) and PCVN specimens

The quantification and prediction of the fracture toughness temperature dependence based on the fracture toughness master curve concept consists in the knowledge of the mean values shape of the fracture toughness temperature dependence established for specimens having thickness $B = 25 \text{ mm}$ (1T). This dependence can be described by the equation

$$K_{Jc(\text{med})} = 30 + 70 \exp[0.019 (T - T_0)] \quad (4)$$

where T_0 is the so-called reference temperature at which the fracture toughness median attains the value $K_{Jc(\text{med})} = 100 \text{ MPa}\cdot\text{m}^{1/2}$; units of T and T_0 are in $^{\circ}\text{C}$. It has been proved [12, 13] that in steels with yield strength between 275 and 825 MPa the fracture toughness measured on 1T specimens and plotted in $(T - T_0)$ coordinates exhibits an identical temperature dependence as regards not only the transition curve shape but also the size of the scatter band. According

to the fracture toughness Master curve concept, the only parameter determining the transition behaviour is the position of reference temperature T_0 on the temperature axis.

It follows from the above that for the master curve concept to be applied, the fracture toughness values obtained via specimens of different sizes (thicknesses) must be adjusted to a thickness of 1T. To adjust the values of fracture toughness in the transition region, the following equation can be used [10, 14]

$$K_{Jc(B1)} = K_{\min} + (K_{Jc(B)} - K_{\min})(B/B_1)^{0.25} \quad (5)$$

where $K_{Jc(B1)}$ is the predicted value of fracture toughness for specimen having thickness B_1 , and $K_{Jc(B)}$ is the experimentally determined fracture toughness using a specimen of thickness B .

To estimate the size and shape of the scatter band of fracture toughness in the transition region, description via the Weibull three-parameter distribution can be used in the form

$$P_f = 1 - \exp\{ -[(K_{Jc} - K_{\min})/(K_0 - K_{\min})]^m \} \quad (6)$$

where K_0 is the scale parameter and m the shape parameter (Weibull exponent). If $K_{\min} = 20 \text{ MPa}\cdot\text{m}^{1/2}$ is chosen, then for the above-mentioned group of steels with ferritic basic microstructure the value m is approximately equal to 4. Equation (6) gives the probability of the failure (fracture initiation) for a random specimen from the set tested; the distribution function of the cumulative failure probability is independent of the specimen size and temperature.

The graph in Fig. 5 gives the temperature dependence of fracture toughness for CT(30) specimens. Since fracture toughness was only measured on CT specimens at room temperature, the temperature dependence after the correction of fracture toughness values

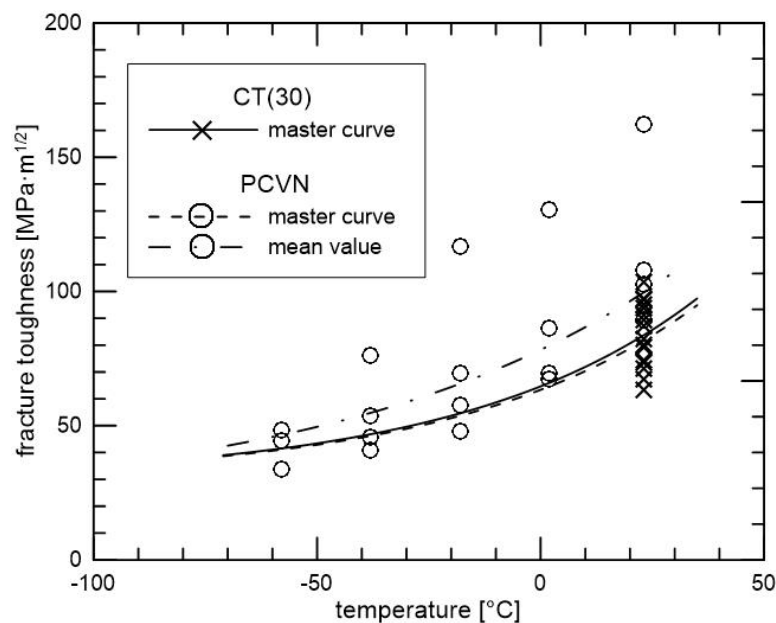


Fig. 5. Fracture toughness master curve for CT and PCVN specimens.

to the specimen thickness 1T (Eq. (5)) was calculated using the Master curve concept, see Eq. (4). The reference temperature of CT specimens of 25 mm in thickness (1T) was established as $T_{0(CT)} = 37\text{ °C}$ and the equation for temperature dependence can be given in the form

$$K_{Jc(\text{med}),CT(1T)} = 30 + 70 \exp[0.019 (T - 37)] \quad (7)$$

The same procedure was also applied to statically loaded PCVN specimens. After correction to the 1T thickness, the exponential function was fitted to the experimental data, and the reference temperature $T_{0(PCVN)} = 39\text{ °C}$ was established as the temperature corresponding to the median value of fracture toughness $K_{Jc(\text{med})} = 100\text{ MPa}\cdot\text{m}^{1/2}$. For PCVN specimens, the equation of the fracture toughness master curve can be written in the form

$$K_{Jc(\text{med}),PCVN(1T)} = 30 + 70 \exp[0.019 (T - 39)] \quad (8)$$

The above temperature dependence is also shown in graphic form in Fig. 5. In all the cases, only those fracture toughness values were included in the calculations that fulfilled the validity condition given by Eq. (3).

It is evident that the temperature dependence of fracture toughness expressed in the form of Master curves for CT and PCVN specimens is very similar. Also, the levels of the reference temperatures of the two types of specimen are almost identical, $T_{0(CT)} = 37\text{ °C}$ and $T_{0(PCVN)} = 39\text{ °C}$.

Experimental results obtained for the R7T steel, which is used in the railway wheelsets manufacture, indicate good agreement between quasi-static fracture toughness determined on CT(30) specimens and quasi-static and dynamic fracture toughness values established on pre-cracked Charpy type specimens. It can thus be concluded that PCVN specimens are suitable for the evaluation of resistance to unstable fractures, and that the characteristics obtained by means of these specimens represent both a local manifestation of fracture behaviour and the overall resistance of a given steel to brittle fracture initiation. Successful correlation, however, is conditioned by the fulfilment of certain conditions that result from the relation between the microstructure of the material and its fracture behaviour. They are, above all, the condition limiting the validity of fracture toughness values K_{Jc} (Eq. (3)), the condition of the applicability of the weakest link model and of the Weibull distribution

for the probability of fracture initiation, and finally the validity of the Master curve concept for the temperature dependence of the fracture toughness values in transition region.

4. Conclusion

a) The fracture toughness of R7T steel was determined under conditions of quasi-static and dynamic loading of pre-cracked Charpy V-notch type specimens taken from the surface of railway wheel rim. Due to impact loading, the mean values of dynamic fracture toughness at room temperature were by approximately $15 \text{ MPa}\cdot\text{m}^{1/2}$ lower compared to quasi-static fracture toughness.

b) The application of the fracture toughness Master curve concept was demonstrated for the fracture toughness determination related to specimens of standard thickness (1T) from data obtained on PCVN specimens, i.e. Charpy type specimens. Very good agreement was found between the reference temperatures T_0 for CT(30) (37 °C) and PCVN (39 °C) specimens.

c) The fracture toughness values determined on PCVN specimens can be regarded as a representative measure of the resistance of a given microstructure to unstable fracture initiation. As follows from a comparison with the fracture behaviour of CT(30) specimens this fracture toughness can be used not only for the evaluation of the local resistance of material to brittle failure but also for an overall evaluation of the resistance of material to this type of the fracture.

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MECHANICAL PROPERTIES OF AlSi10Mg ALLOY PROCESSED BY SLM

Libor Pantělejev^{1,*}, Roman Štěpánek¹, Daniel Koutný², David Paloušek²

¹ Institute of Materials Science and Engineering, NETME centre, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

² Institute of Machine and Industrial Design, NETME centre, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

*corresponding author: e-mail: pantelejev@fme.vutbr.cz, tel.: +420 541143188

Resume

The paper deals with mechanical properties of AlSi10Mg aluminium alloy processed by the selective laser melting (SLM) technique. The influence of surface quality and building orientation of the samples on mechanical properties was evaluated. It was found that orientation of the samples had no effect on tensile properties (UTS, 0.2% proof stress) whereas surface quality had a significant effect. An 11% increase in ultimate tensile strength was found in the case of samples of lower surface roughness, and an increase of almost factor two in elongation at break was found for machined samples in comparison to as-built samples.

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1. Introduction

Today, when demands for fast production of parts of complex shapes tend to increase, the additive manufacturing technologies (AM) are in the centre of interest [1]. One of the most widely used technologies is Selective Laser Melting (SLM); during this process the final shape of component is manufactured by selective melting of powder material layer by layer [2, 3]. Aluminium alloys are used in automotive and aircraft industries mostly for their high specific strength, thus the manufacturing of components by SLM technology and its optimization are really demanded. The processing parameters (laser power (L_p), laser speed (L_s), hatch distance (H_d) or layer thickness (L_t)) play a significant role in the final properties of SLM processed materials. Inappropriate combination of parameters could result in a major decrease of mechanical properties compared with

conventionally fabricated materials, caused by the occurrence of a high amount of defects in the microstructure. The complex analysis of the influence of individual parameters on the final microstructure results in the so-called processing window, which is optimal for specific materials [4, 5]. The most common defect in materials processed by AM is porosity. The origin of pores could be defined by a proper identification of its type [3, 6]. Porosity in the form of spherical cavities (gas-induced porosity) is caused by gas induced into molten metal or transferred into the material already with the powder created during the gas atomization process [7, 8]. In case that the level of introduced energy is not sufficient (lack of fusion) and the metal powder is melted improperly, irregularly shaped pores of different sizes could be found in the microstructure and non-molten powder particles could be located inside of these pores [4, 5, 9]. On the other

hand, if the level of introduced energy is too high, porosity in the form of keyholes takes place in the material [7]. Another type of porosity is shrinkage porosity, originating due to incomplete metal flow to the required melt region [10, 11]. A significant problem in aluminium alloys processed by laser technology is also their susceptibility to cracking [12 – 14].

Besides the processing parameters, the final properties of material are also influenced by the orientation of processed component in the building chamber (regarding the building direction), scanning strategy [15 – 17] and loading conditions [18]. The aim of the paper is to evaluate the influence of sample orientation (compared to the building platform) in combination with different surface qualities on the mechanical properties of AlSi10Mg alloy.

2. Material and experimental methods

AlSi10Mg alloy processed by the SLM method was used in this work. Material in the form of powder was provided by LPW Technology Ltd. The powder exhibited inhomogeneity in particle size and morphology (Fig. 1), declared range of size was 20 - 63 μm . The morphology of particles was evaluated using a Zeiss Ultra Plus scanning electron microscope (SEM). Chemical composition of the powder is given in Table 1. The SLM 280HL (SLM Solutions Group AG) machine equipped with 400 W ytterbium fibre laser with Gaussian profile was used for sample processing. Inert nitrogen atmosphere was used during powder processing in the building chamber.

Two sets of cylindrical samples were

processed for the evaluation of mechanical properties. The samples were SLM processed using the following parameters: laser power (L_p) 350 W, laser (scanning) speed (L_s) 933 $\text{mm}\cdot\text{s}^{-1}$, hatch distance (H_d) 170 μm , layer thickness (L_t) 50 μm , chessboard strategy, building platform heating: 120 $^{\circ}\text{C}$, both sets of samples were built with an angle of 0 and 90 $^{\circ}$ (in relation to the building platform plane - Fig. 2), samples were not heat treated after processing. The gauge length of set A of samples was in as-built state with dimensions of $\varnothing$ 5 mm $\times$ 25 mm (in horizontal position on Fig. 2), the gauge length of set B of samples was additionally machined to dimensions of $\varnothing$ 6 mm $\times$ 30 mm (in vertical position on Fig. 2). Microhardness HV 0.1 was measured on the cross sections of clamping heads of samples from both sets after their polishing, using a Leco LM 247AT microhardness tester. Tensile tests were performed using the Zwick Z250 testing machine at room temperature at a loading speed of 2 $\text{mm}\cdot\text{min}^{-1}$.

A fractographic analysis of samples broken during tensile tests was performed using a Zeiss Ultra Plus scanning electron microscope.

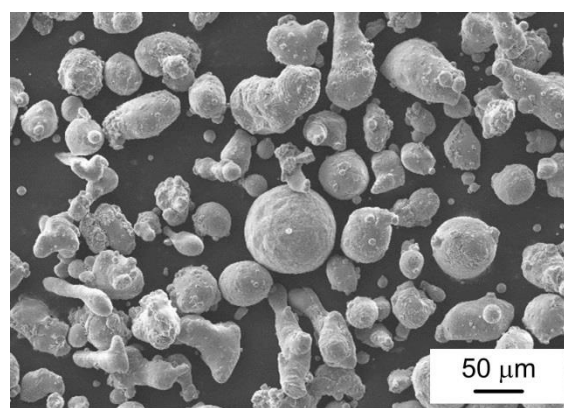


Fig. 1. Morphology and size of powder particles (SEM).

Table 1

Chemical composition of AlSi10Mg powder.

Elements	Al	Si	Mg	Fe	Zn	Cu	Ni	other
Composition, wt. %	balance	10.0	0.4	0.11	<0.1	<0.05	<0.01	<0.37

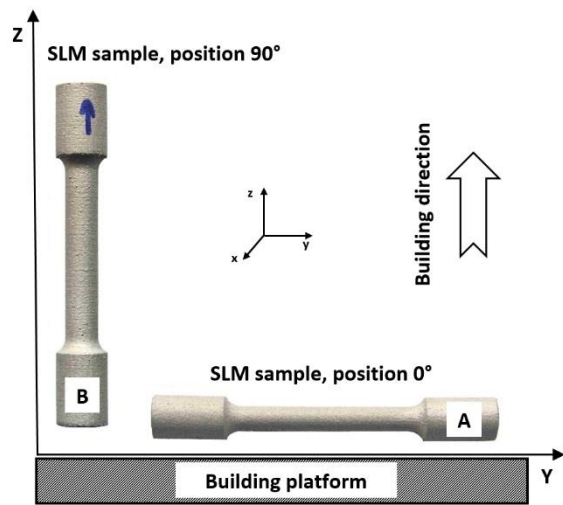


Fig. 2. Built position of samples on building platform.

A metallographic analysis for microstructural evaluation was performed on samples prepared from the clamping head sections of samples from both A and B sets after tensile tests. The plane observed was parallel (samples with a building angle of 0°) and

perpendicular (samples with a building angle of 90°) to the building direction. The samples were conventionally prepared using wet grinding, and polished using diamond paste. After etching, the samples were analysed using an Olympus GX 50 light microscope (LM).

3. Results

According to the results of tensile tests (Table 2, Fig. 3) the orientation of samples affects only elongation of both as-built and machined samples. The building direction and surface quality has no influence on 0.2% proof stress but ultimate tensile strength is affected by the surface quality. The average ultimate tensile strength (UTS) of as-built samples is about 45 MPa lower compared with UTS of machined samples. The average microhardness is comparable for both sample orientations, with values of 122 HV 0.1 for 0° orientation and 116 HV 0.1 for 90° orientation (Table 2).

Table 2

Mechanical characteristic for evaluated states.					
Sample	Orientation	0.2% proof stress [MPa]	UTS [MPa]	Elongation [%]	Microhardness HV 0.1
as-built	0°	231	377	3.6	116
as-built	90°	242	376	2.7	114
machined	0°	244	423	6.8	128
machined	90°	242	421	4.2	118

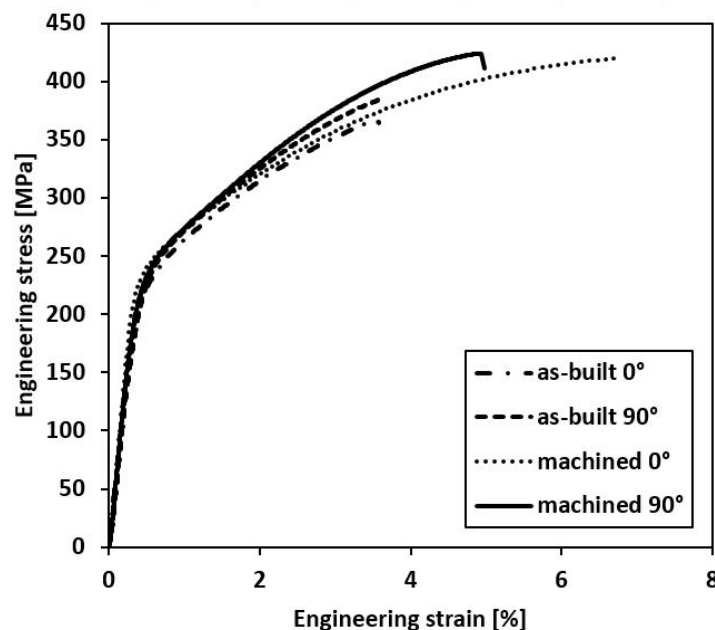


Fig. 3. Engineering stress-strain curve (room temperature testing).

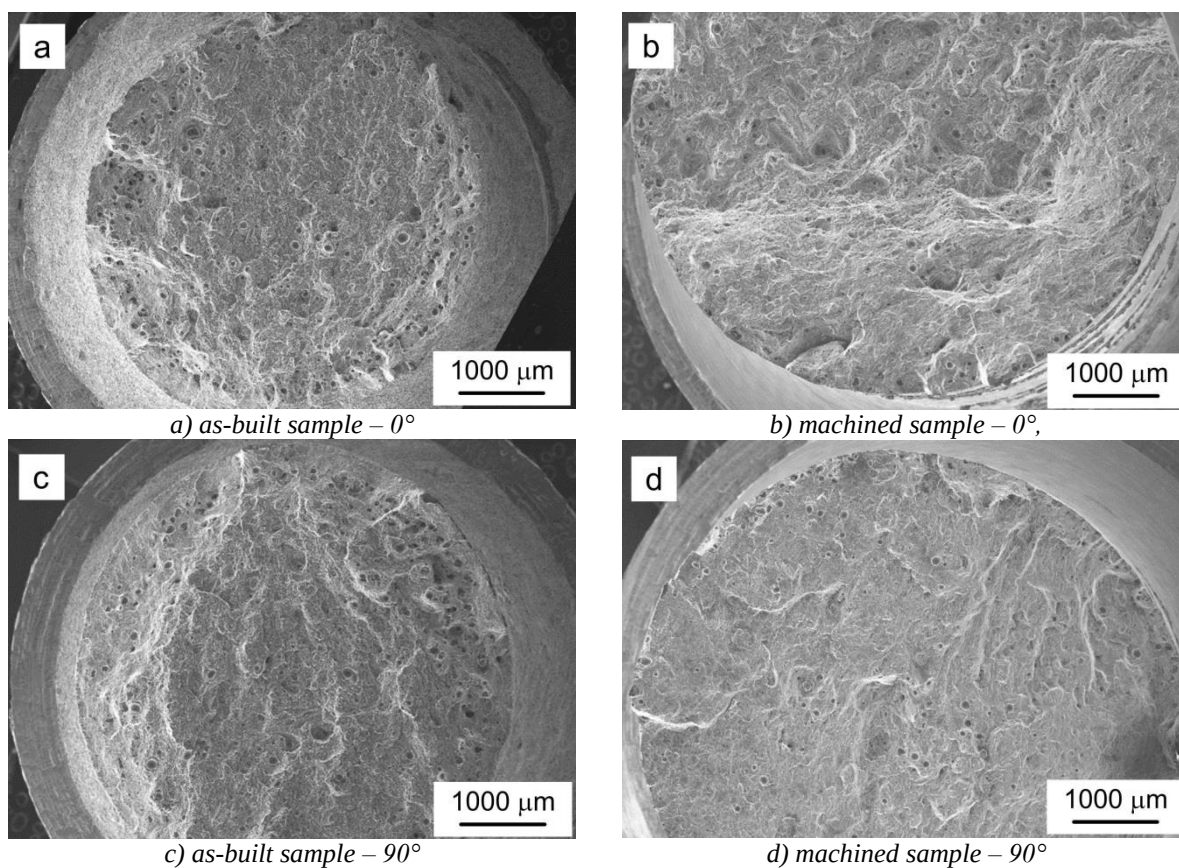


Fig. 4. Fracture surface of specimens broken in tensile test – overview (SEM).

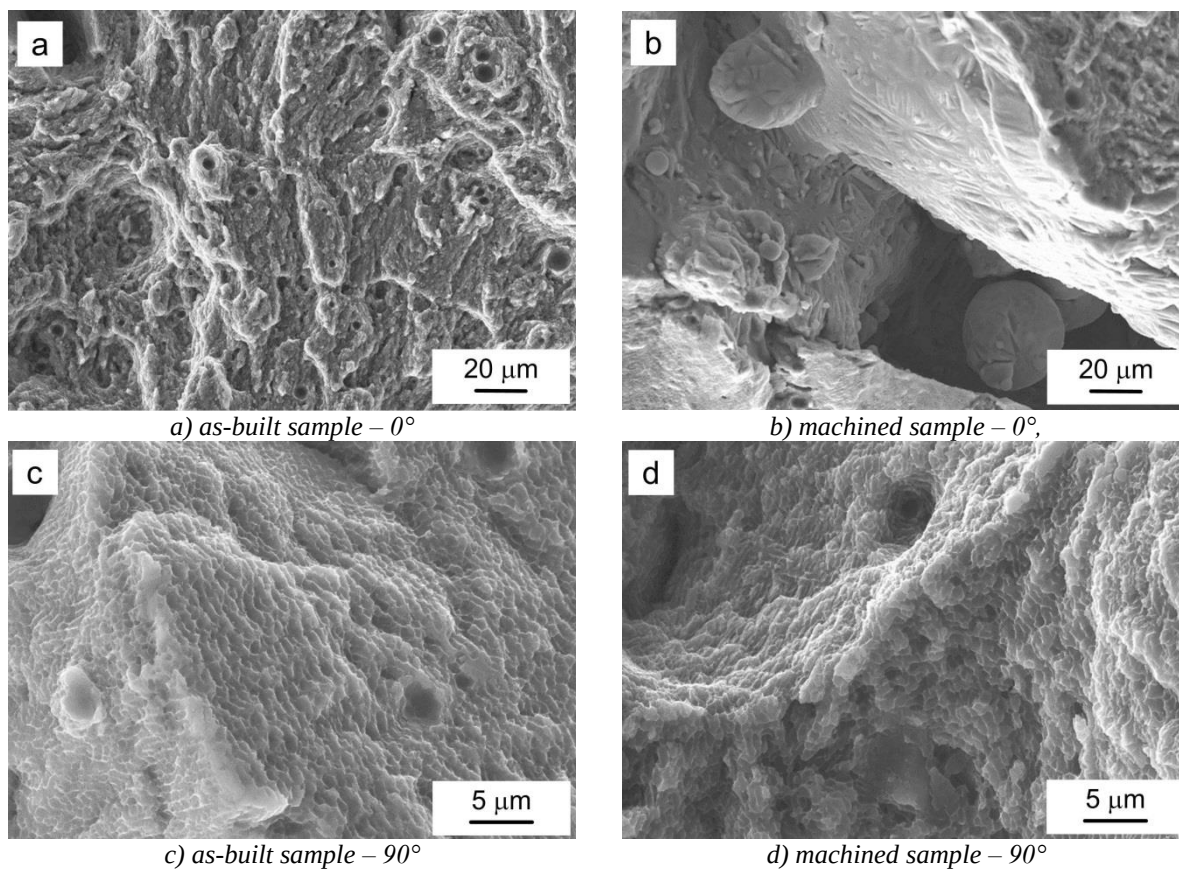
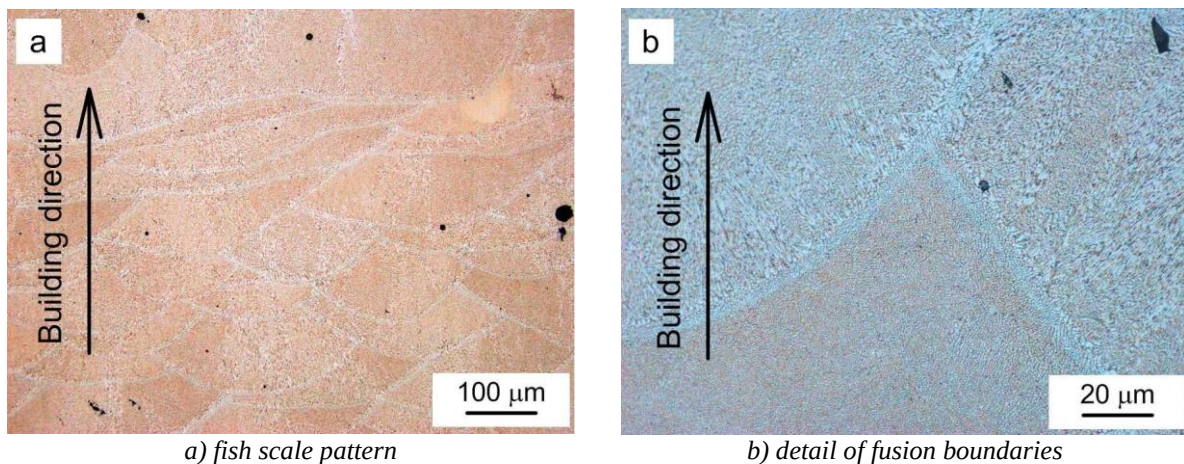
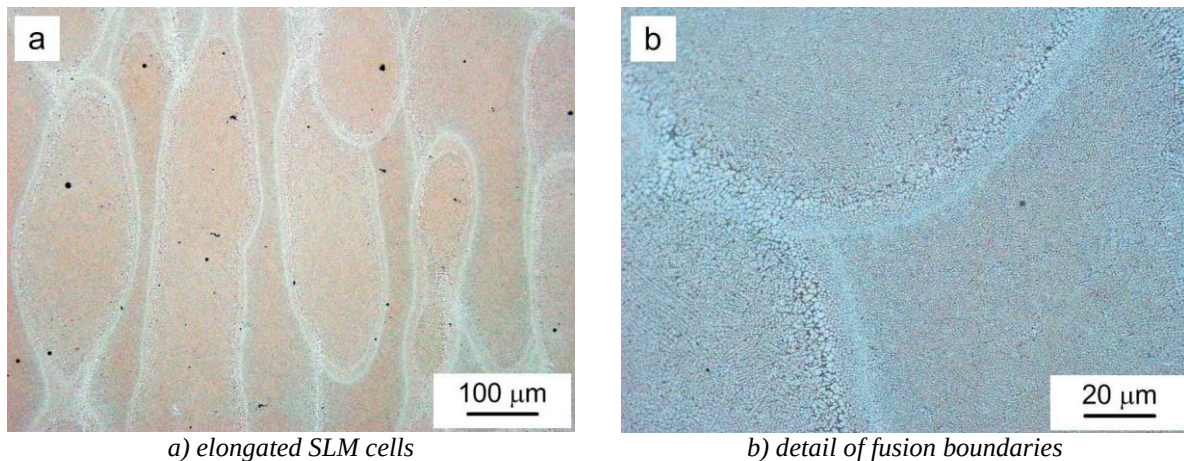


Fig. 5. Fracture surface of specimens broken in tensile test – detail (SEM).



a) fish scale pattern
Fig. 6. Microstructure of SLM material at different magnification, longitudinal (X-Z) plane (LM).
(full colour version available online)



a) elongated SLM cells
Fig. 7. Microstructure of SLM material at different magnification, transverse (X-Y) plane (LM).
(full colour version available online)

A fractographic analysis of the samples broken during tensile tests was performed (Figs. 4 and 5). The fracture surface of all samples was rugged, with numerous gas porosity type inhomogeneities (Figs. 4 and 5a). Cavities with non-molten powder particles were also locally observed (lack of fusion porosity, Fig. 5b). The distribution of spherical pores was rather random over the whole cross-section of machined samples, compared with concentric circles of pores mostly in the subsurface layer of as-built samples (both building orientations), Fig. 4. In the central area of the cross-sections of as-built samples, pores were distributed rather randomly and in a lower amount (Figs. 4a, c). The fracture mechanism was of ductile character in all cases with small-dimple morphology, which indicates low energetic

fracture (Figs. 5c, d).

Figs. 6 and 7 show the microstructure of SLM processed samples at various magnifications. Pores of different types are visible in the microstructure (gas pores and pores originating due to lack of fusion). The microstructure consists of single welds (SLM cells) separated by fusion boundaries; these cells and fusion boundaries are formed from solid solution α and fine particles of eutectic Si, respectively (Figs. 6 and 7). In the direction parallel to the building direction, a typical pattern of fish scale can be seen (Fig. 6), with the average interlayer melt pool depth (Fig. 6) being 90 μm . In the perpendicular section to the building direction, overlapping of laser track is clearly visible, with well-defined scan contours of SLM

cells (Fig. 7). This specific microstructure of elongated cells with dimensions exceeding hundreds of microns is given by the scanning strategy used.

4. Discussion

According to the results of the complex analyses performed, both 0.2% proof stress and UTS are independent of the building orientation [15], which affects only the elongation of analysed material. The elongation of machined samples built at a building angle of 0° was 38 % higher compared with samples built at a building angle of 90°. As-built samples exhibited smaller differences, with just 25 % higher elongation of samples with 0° building angle compared with samples with 90° building angle. An increase in elongation of AlSi10Mg alloy, dependent on the building angle, was also observed in [15] and [17]. The processing parameters used in [15] were different, compared with the present work: lower laser power ($L_p = 200$ W) and higher scan speed ($L_s = 1400$ mm/s) while in [17] the processing parameters were comparable with the present work, with the exception of heating the building platform to a higher temperature (200 °C) and an almost 2.5× higher hatch distance ($H_d = 420$ µm). The slight differences in mechanical properties obtained by the authors therefore should be linked to the differences mentioned above.

The surface quality of SLM processed samples had no significant influence on 0.2% proof stress in contrast to UTS and elongation. UTS increased by 11 % in machined samples (both building directions), and elongation increased by 47 % (0° orientation) and 36 % (90° orientation), respectively. According to the fractographic analysis (Figs. 4 and 5) the level of porosity was different in as-built and machined samples, especially in the subsurface layer. It can be assumed that the higher mechanical properties of machined samples (both orientations) are reached owing to the lower amount of microstructural defects

(subsurface porosity is removed during machining) and so the matrix of material is not weakened by pore occurrence as in the case of as-built samples [19]. All observed mechanical properties of both as-built and machined samples prepared by SLM are higher compared with conventionally cast material (UTS 2.5× higher, elongation 2× higher) [20].

In contrast to the SLM processing parameters it seems that orientation of sample has no significant influence on yield strength and UTS (in agreement with [15, 17] as well) contrary to [21] where yield strength of samples with 0° orientation was markedly higher than for 90° orientation. This divergence is probably caused by different total volume of SLM processed material from which tensile test samples were made of.

5. Conclusion

AlSi10Mg alloy processed by SLM technology exhibits an inhomogeneous cellular microstructure with inhomogeneities of the type of gas-induced and lack-of-fusion porosity.

0.2% proof stress and UTS are not significantly affected by the building orientation unlike elongation, which is significantly higher in the case of 0° orientation.

Surface quality and subsurface porosity significantly affect tensile strength and elongation, when the material with higher surface quality achieved approx. 420 MPa UTS compared with 376 MPa UTS, and about half the elongation of the material with lower surface quality (as-built state).

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COLD GAS DYNAMIC SPRAY DEPOSITION AS ADDITIVE MANUFACTURING OF ARCHITECTURED MATERIALS

Lukáš Řehořek^{1,*}, Ivo Dlouhý¹, Vít Jan¹

¹ Institute of Materials Science and Engineering, NETME centre, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

*corresponding author: e-mail: rehorek@fme.vutbr.cz

Resume

The paper is focused on the cold gas dynamic spray process as a useful tool for additive manufacturing of free-standing parts and in particular the production of architected materials. The idea is demonstrated on samples of dual metal composition. The computed trajectory of channels was produced via a CNC milling machine and subsequently filled with another metal by the cold spray process. The microstructure of the deposited material and the interface with the substrate were studied. These types of produced architected materials are discussed as potentially new structural materials.

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1. Introduction

Cold gas dynamic spray (CGDS) is also known as cold spray (CS), kinetic spray, supersonic particle deposition, dynamic metallization, high velocity particle or powder consolidation or kinetic metallisation. The most commonly used are CGDS and CS. CGDS is a member of the thermal spray process family (Fig. 1). In comparison with other methods of thermal spraying, CGDS is distinguished by its low temperature and supersonic particle speed. The temperature of the process gas (N, He) remains below 1100 °C, ensuring the absence of particle melting, and the supersonic speed gives the necessary energy to the particles for extensive plastic deformation and thereby metallic bonding and mechanical interlocking with a substrate and subsequently with the deposited coating material [1].

CGDS equipment usually consists of a source of process gas from which it is distributed into two branches, one for gas

preheating (300–1100°C) and the other for powder mixing. The two branches are joined in a gun, and the gas and particle mixture is accelerated through a convergent-divergent nozzle to supersonic velocity (up to 1200 m·s⁻¹).

Due to the low gas temperature, CGDS offers unique advantages compared to other thermal spray technologies, including very high (almost theoretical) density of coating, production of compressive stresses, ultra-thick layers, small spray trace and precision deposition control, no or limited oxidation, deposition of thermally sensitive materials such as polymers and bioactive materials, no grain growth, and no phase transformation.

Typical materials applicable in CGDS are: a) metals, e.g. magnesium, aluminium, titanium, nickel, copper, tantalum, niobium, silver, gold; b) alloys, e.g. nickel-chromium, bronze, aluminium alloys, brass, titanium alloys, MCrAlY; and c) mixed materials (metal matrix combined with hard phases), e.g. metal

and ceramics, composites [3 – 5].

Thanks to the above behaviour, CGDS can be used in many areas, for example surface functionalisation, structural and dimensional restoration, art/decoration, and additive manufacturing (AM) (bulk manufacturing) [6 – 9].

1.1 Surface functionalisation

The first industrial application of CGDS was in surface engineering for the functionalisation of surfaces. CGDS coatings can offer protection against corrosion and high-temperature oxidation, and can improve the wear properties of engineering components. CGDS is also successfully employed in medical applications, where it is used to improve the biocompatibility of implants.

CS deposition offers the possibility of prolonging the lifetime of expensive parts in the aerospace industry. For example, the Boeing Company studied the improvement of H-47 Chinook Rotor Blade durability in conditions of sand and dust. For the successful protection of blades, a combination of niobium on a titanium substrate was chosen [10]. Solution for cost-effective protection against corrosion using the CS can be found. Bala et al.

[11] presented NiCrTiCRe powder deposition on SA 516 boiler steel of Power Plant Boilers.

This deposition technology is also an ideal process for products requiring electrical conductivity [12]; Goris et al. [13] presented the use of CGDS as a tool for the production of an improved back-contact module of MWT solar cells.

1.2 Dimensional restoration

CGDS is also utilised in the restoration of objects; the ability to save on substrate material is highly appreciated by restorers. This process is applied both to antique technical objects, such as cars (body or engine defects) or aeroplanes, and to antique art objects, such as sculptures. In some cases, CGDS is the only applicable method of restoration [14].

The CGDS process also seems to be appropriate for repairing metal components and structures of aircraft. Matthews et al. [15] explored the possibilities of extending the limit of validity of aircraft structural components and restoring the structural integrity of corroded panels. They showed that CGDS is suitable for repairing corrosion damage and that the repaired structures have a dramatically increased fatigue life.

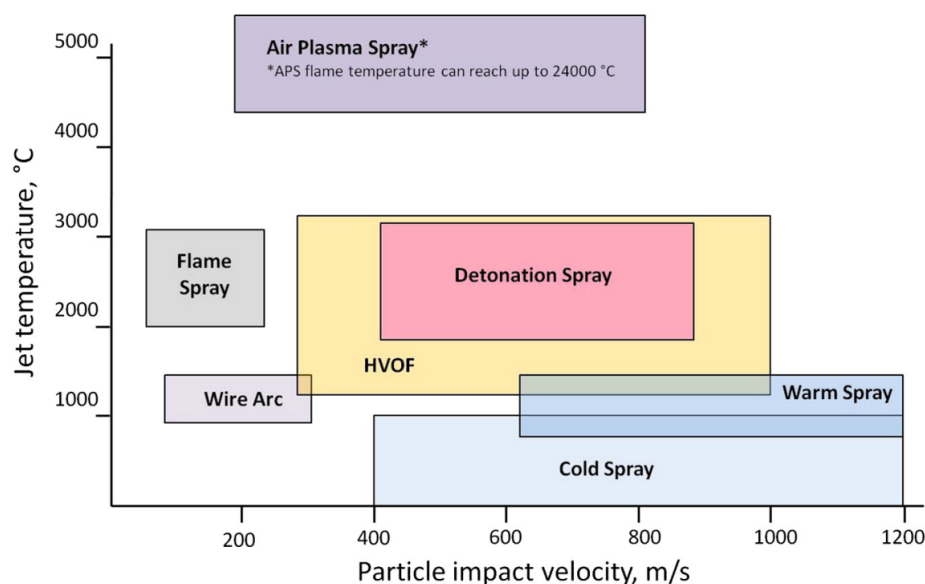


Fig. 1. Thermal spray family chart [2].
(full colour version available online)

1.3 Art and decoration

For its specific benefits, CGDS can also be used for combining disparate materials such as metal and glass. This feature is used in art and decoration and creation of artistic works. Examples of “painting” with metal on a glass substrate can be found in [16].

2. Additive manufacturing (AM) by CGDS

An exciting possibility of the CGDS method is its utilisation in AM processing. In common AM techniques, the structure is produced layer by layer from powder, by laser or electron beam sintering. The resulting structure is actually formed in 2D+ regime by cladding one 2D layer upon another. The same principle is used in fused deposition modelling (FDM), stereolithography, or selective (laser, electron, arc) sintering based 3D printers.

A component or structure produced by CGDS has no tensile residual stresses, in contrast to those produced by selective laser melting (SLM) 3D printing. During CGDS deposition, compressive residual stresses are incorporated into the structure and increase the mechanical properties and fatigue resistance by cladding layers at a high velocity without melting. Bagherifard et al. [17] analysed free-standing samples of Inconel produced by CGDS and SLM. After heat treatment (HT), the mechanical properties of the CGDS samples

were enhanced, and superior to those produced by SLM. Tensile test curves for the CGDS and SLM samples are depicted in Fig 2, with a comparison of states before and after HT. Note also that elastic properties of pure metals have been shown to be fully isotropic [18].

CGDS offers many advantages in the field of AM. Unlike common 3D additive printers, the powder particles stay in the initial state which opens the possibility for the AM of very specific materials (ODS alloys, etc.). The CGDS gun can be fitted on a robot arm with 6 or 7 controlled axes, which may extend the ingrained production habits of AM. In this configuration, the direction of powder deposition can be controlled, and thus real 3D structures can be produced [19].

It is possible to control the structure build-up process by layering the powder from many directions and by modifying the powder feed rate and transverse rate. If the feed rate is low and the motion of gun is quick, flat tracks are produced. On the other hand, when the feed rate is high and the transverse rate is low, the tracks are rounded; it is also possible for sharp triangular tracks to be developed in this way.

By combining the parameters, the deposition process can be finely controlled. Structures can be produced by layering thin coatings or by tessellating the triangular track profile as shown in Fig. 3.

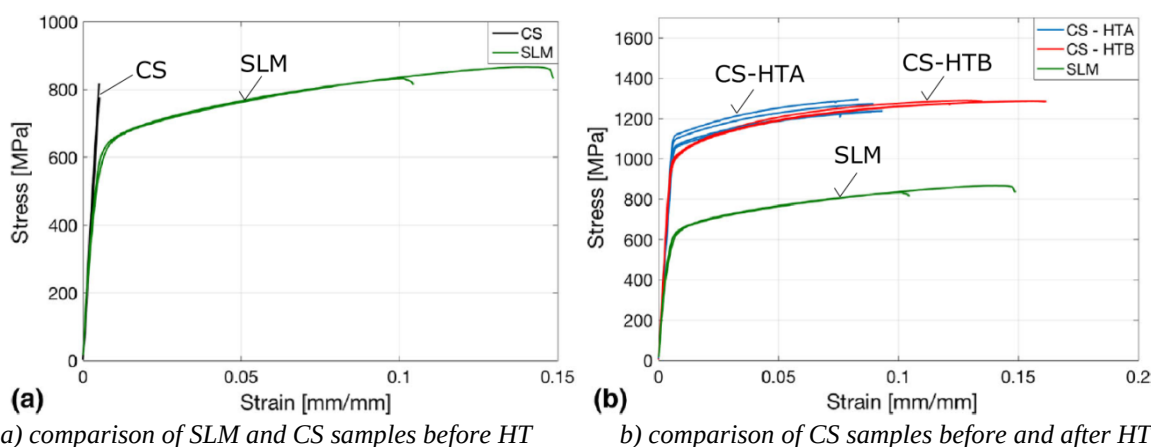
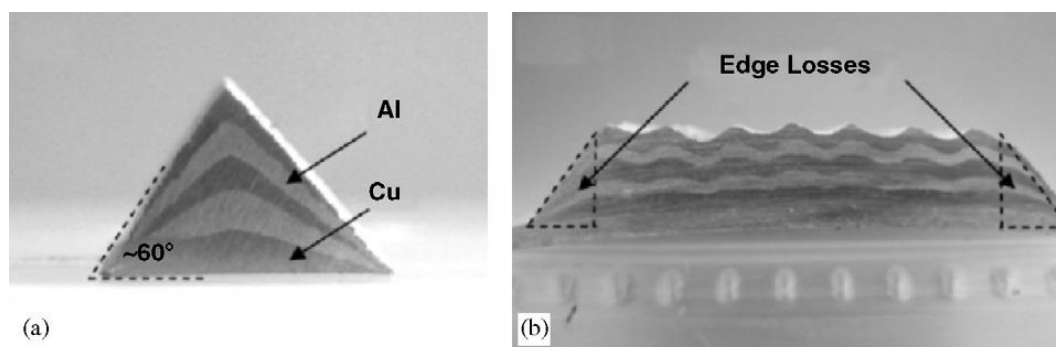


Fig. 2. Tensile test data.
(full colour version available online)



(a)

(b)

a) track growth

b) layer building and edge losses

Fig. 3. Photographs showing (a) track growth, and (b) layer building and edge losses [20].
(full colour version available online)

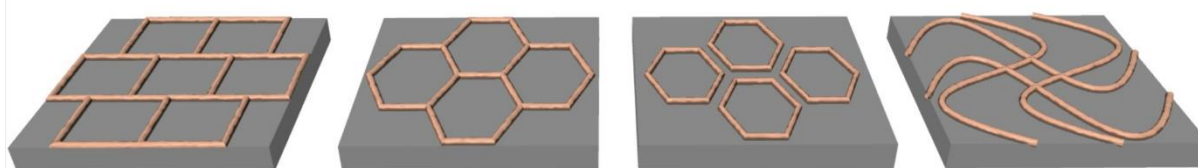


Fig. 4. Examples of one-layer internal reinforcing structural patterns.
(full colour version available online)

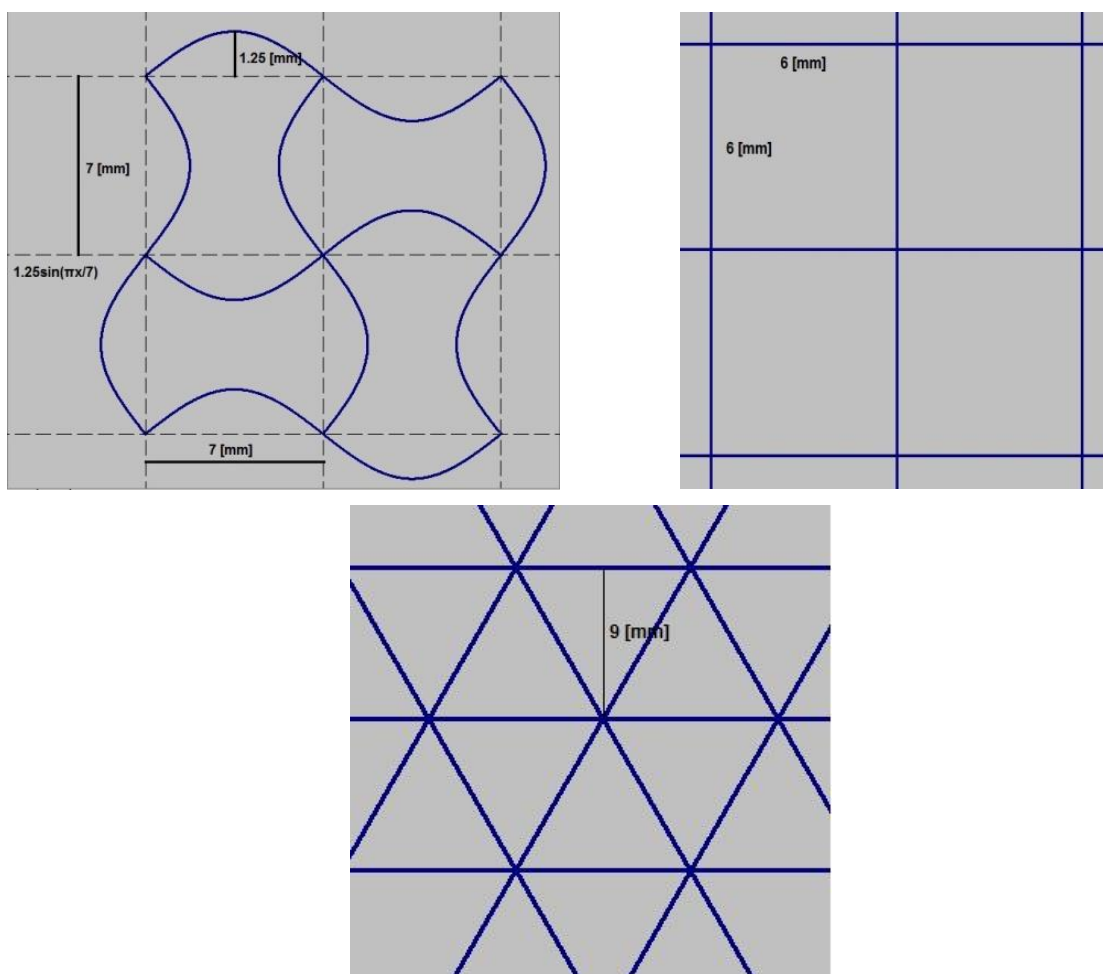


Fig. 5. Basic geometrical patterns applied for reinforcing the aluminium matrix by iron architecture.
(full colour version available online)

Furthermore, CGDS provides the possibility of combining metals to form an internal architecture within a component. Different powders can be deposited, either combined or separately, to produce a shape from two or more metals. In this way, multimaterial structures or components can be created. For example, engineering parts could be reinforced with stronger material only in places exposed to stress, thus allowing material and/or weight savings. This idea can be further extended, and via a combination of appropriate metal materials and geometrical patterns, internally architected structures can be produced.

Schematic examples of such structures are depicted in Fig. 4. For example, a matrix made of a soft metal like aluminium could be reinforced by incorporating structural patterns of a hard metal. By creating these internal reinforcements layer by layer, new properties can be achieved, which could surpass the properties of the individual starting components.

3. Experimental

The aim of the experiment was to verify the use of CGDS technology as an AM process for forming reinforcing metal structures

in the matrix of another metal. For this verification, aluminium alloy EN AW5754-H22 was chosen as the matrix, and pure Fe (99.9 %) was deposited by CGDS in reinforcing beams. The aluminium alloy was chosen as representative of common alloys and the pure Fe as representative of a powder with good spray effectiveness and higher mechanical properties (Young's modulus, hardness). The CGDS method was used to prepare three kinds of sample, which differed in the geometry of the reinforcing beams. Two of the beams were linear, forming either squares or triangles, and the third was in the shape of a sinusoid in the x and y axes. The three beam geometries are shown in Fig. 5.

The production process consisted of two phases, depicted in Figs. 6 (a, b). First, grooves of 1 mm in width and depth were formed in the aluminium plate by means of a shank mill. The grooves were then filled using CGDS. Figs. 6 (c, d) indicate further steps of composite formation, however these were not used in this work. The device used was the Impact Spray System 5/11 from Impact Innovations, GmbH. The powder parameters and the parameters for spraying are listed in Table 1. Total spray thickness was 3 mm on average.

Table 1

<i>Parameters of CGDS process.</i>		
Sample No.:		3.1.1-3.
Settings	Unit	
Parameters CS		
Impact Gun		5/11
Nozzle type/material		Out1/SiC
Inlet pipe standoff	mm	35
Process gas		N ₂
Gas pressure	bar	50
Gas flow rate	m ³ ·h ⁻¹	93
Gas temperature	°C	900
General Parameters		
Standoff distance	mm	30
Gun travel speed	mm·s ⁻¹	500
Powder		
Description		Fe
Supplier/Lot		Nanoval AO/068/GM
Particle distribution	µm	10–32

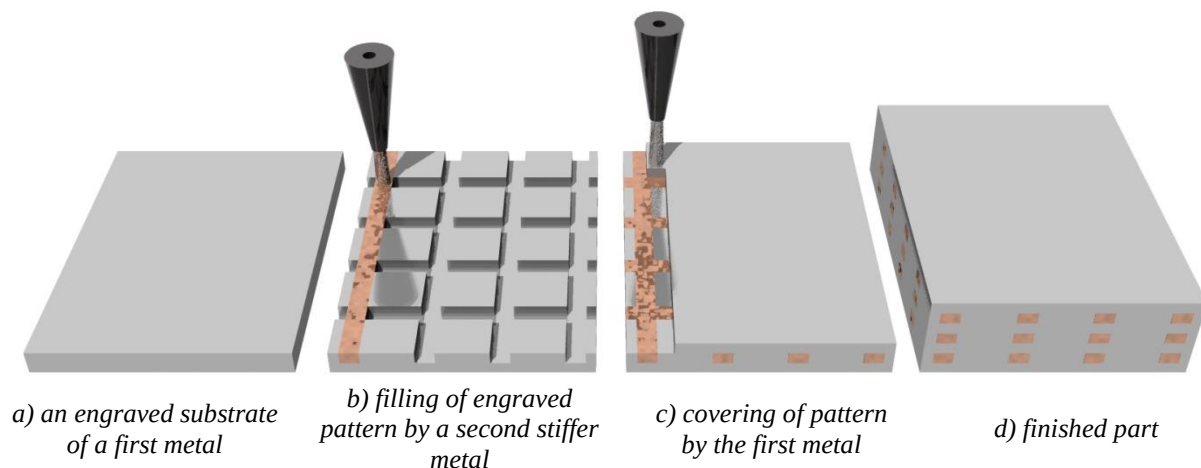


Fig. 6. AM stages of a multimaterial architected composite using CGDS.
(full colour version available online)

4. Description of results

Samples created with this method are shown in geometrical form in Fig. 7 as squares, sinusoids and triangles when viewing in order from the left to right. The samples were 100 mm $\times$ 170 mm in dimension. During CGDS deposition of the coating, material is simultaneously deposited both in and around the grooves in the substrate. Thus, the newly deposited layer retains the original geometry of the grooves. This occurs even with a considerable thickness of deposited material; at a coating thickness of 1 mm, the groove width was 1 mm. This effect could be used, for example, to form of a cooler layer on the surface of a thermally stressed component, similar to Dupuis et al. [7].

During the CGDS process, the milled groove was filled well. The groove bottom has a very good interface structure, while the vertical walls contain more defects. The defect types present in the microstructure of the deposited material can be sorted into three groups: a) large cavities, b) longitudinal cracks, and c) micropores.

On the walls parallel to the particle stream, coating deposition is difficult, and large cavities form. This is documented in Fig. 8. Impaired adhesion on the vertical walls continues even after the transition from the substrate

to the coating layer. While the spray fills the grooves, material is simultaneously deposited on the surface of the substrate around the grooves, effectively increasing the groove's height above the substrate. Thus, even after the deposited material has filled the matrix, the 'new' groove must be filled. Furthermore, the groove's vertical walls, where adhesion of particles is difficult, are still being formed. This process continues throughout the spraying process and thus preserves the relief. The entire cross section of the sample relief and a detail of the spray interface are shown in Fig. 9.

Hardness HV1 of the substrate and the deposited layer were measured in several locations. The values do not differ depending on the location. HV1 of the aluminium substrate is 57 ($s = 1.3$) and HV1 of the Fe coating is 234 ($s = 8.9$) (measured in the groove, between the substrate and the longitudinal crack, and above the crack). From the hardness values of each component, one can deduce the other mechanical properties in general. The Fe coating is thus stiffer than aluminium and acts as a strengthening phase.

Another phenomenon observed in the CS structure were the longitudinal cracks passing through the deposited material at a constant distance (about 300 μm) from the surface of the substrate (Fig. 10).



Fig. 7. Milled patterns and parts of samples filled by CGDS of Fe. (full colour version available online)

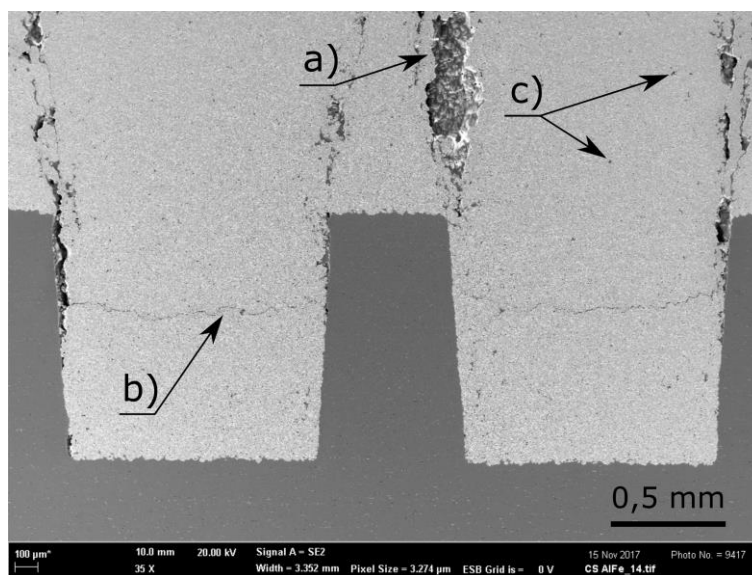


Fig. 8. Detail of milled grooves filled by CGDS of Fe.

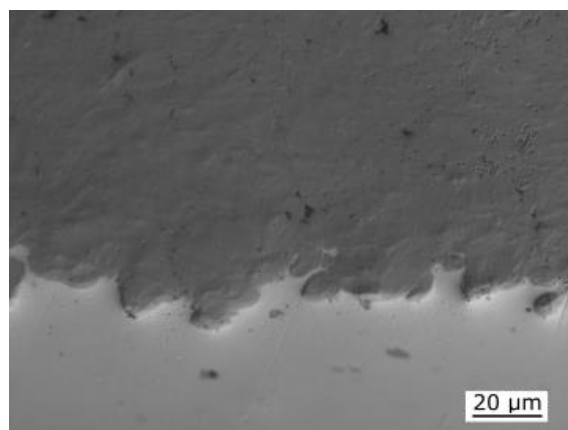


Fig. 9. Entire cross section of milled groove and coating of Fe (left), interface of substrate and Fe coating (right).

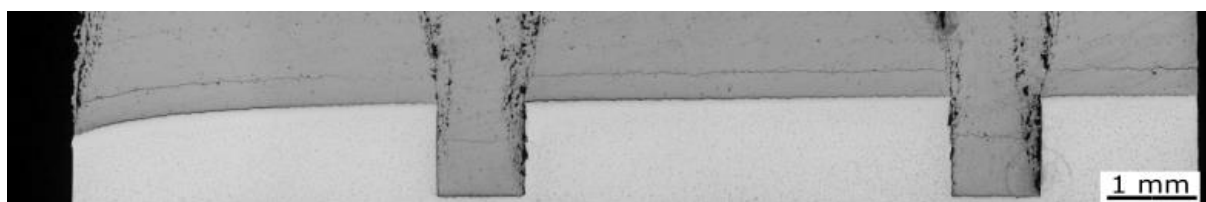


Fig. 10. Longitudinal cracks passing through sprayed deposit (detail of two grooves).

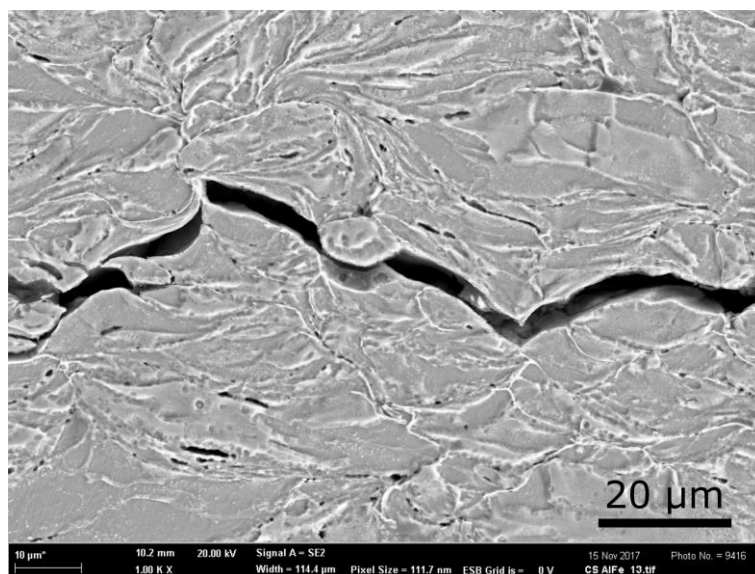


Fig. 11. SEM micrograph of crack presented in CGDS deposit, inter-splat trajectory.

Based on SEM analysis, it was found that this crack passes between the splats created during spray deposition (Fig. 11). The stress in this layer is higher than the mutual cohesion of the particles but not higher than the strength of the spraying material itself. The stress in the layer thus causes crack propagation between the particles and not through them. This implies that the cause of crack formation can be found in the spraying parameters, rather than due to defects within the sprayed Fe powder. Possible causes may be inappropriately chosen spraying parameters, or the relaxation of stress from the substrate (rolled sheet), etc. This will be the subject of further investigation.

The excess material of the deposited layer (approx. 3 mm above the grooves) was used for further analysis. The Fe coating was compared with electrolytic Fe powder by differential scanning calorimetry (DSC). A $10 \text{ K} \cdot \text{min}^{-1}$ heating rate was used in Setaram SetSys apparatus. The resulting DSC signal curves of the analysis are depicted in Fig. 12. For the major transition reactions, both CGDS and electrolytic Fe samples showed the same DSC signal peak at the Curie point temperature (769.27°C and 769.06°C respectively) and almost the same DSC signal peak position for the gamma phase transition (919.14°C and

919.74°C respectively). This indicates that the material used for CGDS deposition and the resulting material of the analysed layer contain a low amount of impurities and oxides.

5. Conclusions

Grooved patterns created by CNC milling of the Aluminium EN AW5754-H22 substrate were covered with pure iron by CGDS deposition. The idea of creating an internal stiffener with a stronger metal (Fe reinforcement) in a less rigid matrix (aluminium alloy) was verified with these samples.

A high quality of coating was observed and the interface between the two metals was investigated on the surfaces perpendicular to the spraying planes. The homogeneity of the deposited material outside the groove area was found to be without any defects and showed very low porosity.

In the vicinity of the groove walls (parallel to the spray direction), a large number of defects were observed due to the inappropriate orientation of these walls to the particle stream. In grooves that had vertical walls better oriented towards the direction of spraying, better substrate-to-spray adhesion was observed (Fig. 9), and

consequently the intersection of the groove was completely filled. Further defects are probably caused by turbulent flow around the grooves during injection.

The DSC analysis shown high purity of the CGDS Fe layer, without significant oxidation.

Acknowledgements

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SURFACE PROPERTY CONTROL BY ELECTRON BEAM DEFLECTION DURING HARDENING

Jiří Matlák^{1,*}, Ivo Dlouhý¹

¹ Institute of Materials Science and Engineering, NETME centre, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

*corresponding author: e-mail: Matlak.Jirka@gmail.com

Resume

The usage of the high-energy electron beam source enables repeated surface quenching of chosen locations of an engineering part surface. Different techniques of electron beam deflection allow creating hardened layers of different shapes, hardness levels and thicknesses. Experiments were carried out with 42CrMo4 (1.7225) steel. The deflection modes tested were one-point, 6-point, line, field, and meander. The influence of process speed and defocusing of the electron beam was also taken into account. The electron beam surface quenching resulted in a very fine martensitic microstructure with a hardness of over 700 HV0.5. The thickness of the hardened layers depends on the deflection mode and is affected directly (except field deflection) by process speed. The maximum hardened depth (NCHD) was 1.49 mm. Electron beam defocusing affects the width of the hardened track and can cause extension of the trace up to 40%. The hardness values continuously decrease from the surface to the material core.

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1. Introduction

Electron beam (EB), together with laser beam, belongs to the advanced technologies that can be used for local surface heat treatment. Both methods have some similar characteristics; however, there are clear differences predetermining which of them will be chosen for a particular application. The fast beam deflection appears to be one of the typical features of EB processing that allows a different distribution of the supplied energy provided adequate programming of the hardening equipment is applied. An EB can be deflected both in a direction perpendicular to the component movement direction and also in a parallel direction [1 - 5].

The properties of the hardened layer can be directly controlled by process parameters. The total supplied power rate is controlled by a combination of the accelerating voltage

“ U_{EB} ” and the electron current “ I_{EB} ”. This energy is distributed to the component surface depending on the selected mode of EB deflection. The scanned area is determined by the dimensions “SWX” and “SWY” and is set together with the scanning frequency in the individual directions “FRQ”, “FRQ2” (Fig. 1). Usually some beam defocusing “Offset” is set up, which can be implemented by shifting 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 “ v_s ” under the hardening beam “EB” [6 - 10].

The aim of the paper is to increase the knowledge of the influence of electron beam deflection modes on surface heat treatment processes, which is not discussed in the literature in comparison with electron

beam welding. The results can be efficiently used when constructing new EB devices and when optimizing and improving electron beam surface hardening processes.

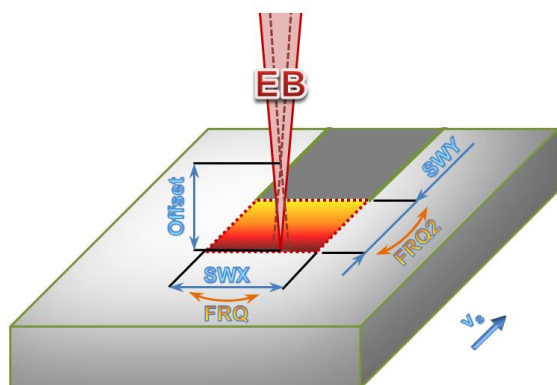


Fig. 1. Figure 1 - The EB surface quenching parameters scheme.
(full colour version available online)

2. Experimental material and methods

Experiments were carried out on the high-grade 42CrMo4 (1.7225 or AISI 4140) steel with the following chemical composition of (in wt. %): C 0.41, Mn 0.69, Si 0.25, Cr 1.04, Mo 0.20, which is a suitable material for surface hardening. It finds application where elevated strength in combination with a defined and high level of toughness are the most important requirements – e. g. shafts or gears. The material to be tested in block shape ($20 \times 40 \times 250$ mm) was in a state after tempering at 600°C for 3 hours with a final fine sorbitic structure and an average hardness of 300 HV0.5.

The surface quenching was performed using 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 widths of the EB hardened traces were set to be $\text{SWX} = 10$ mm except for one-point deflection. The constant accelerating voltage $U_{\text{EB}} = 80$ kV was used for the experiments and the electron beam current I_{EB} was subsequently optimized for each machine configuration. The EB modes tested were: one-point (stable

beam without deflection), 6-point, a line (consisting of 1.000 points distributed perpendicular to the “ v_s ”), a field and a meander. Additional processing parameters such as the defocusing degree and the movement rate in each mode and their effect on the quality of the hardened layer were investigated. The common “Offset” values for each mode were 50, 100, 200 and 300 mA and the current sample-to-beam velocities “ v_s ” were 5, 10, 15, 20 and $25\text{ mm}\cdot\text{s}^{-1}$.

The field deflection mode was programmed to allow the local energy density to increase within a given area. This is used for intense heating on the surface of a treated material during the hardening. The rest of the area, with a lower beam intensity, contributes to the heating of the material deeper into the sample core. The length of the SWY field was determined for each movement rate “ v_s ” based on the change in temperature across the affected area on the sample measured with a pyrometer.

The meander deflection technique differs from the other ones. The meandering pattern is a combination of the controlled component movement and of the electron beam deflection. The resulting EB trajectory on the specimen surface is shown in Fig. 2.

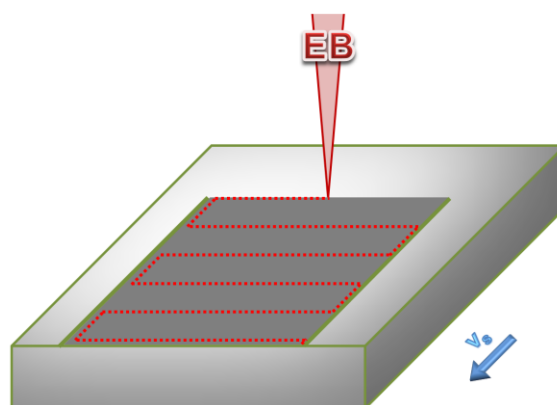


Fig. 2. The EB trajectory (red dotted line) on specimen surface at the meander deflection.
(full colour version available online)

The metallographic specimens prepared by standard procedures were analysed by optical

and scanning electron microscopy. The LECO LM 247 AT microhardness tester was used to analyse the hardness HV0.5 profile from the surface to the sample core in the quenching trace axis. For the microstructural characterization, the scanning electron microscope (SEM) ULTRA PLUS, Carl Zeiss GmbH, Germany was used. For the surface analysis, the detector of secondary electrons (SE), type Everhart-Thornley, and the four-quadrant silicon detector of back scattered electrons (BSE) were used.

3. Results and discussion

Traces having a width of 10 mm were processed by surface quenching on the 42CrMo4 steel. Basic experiments were optimized from the point of view of the used electron beam current I_{EB} . The optimal energy density conditions were specified by the trial and error method based on the observation of the occurrence of molten areas on the specimen surface. The molten areas were brighter than the quenched ones. A slightly molten surface could not be identified by observing the microstructure because it was also formed by a fine martensitic structure similar to hardened layer. The maximum hardness of the hardened and the partially 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 pyrometric measurement of the temperature profile within the irradiated area. When too long, "SWY" caused a significant drop in temperature, while if too short, it did not exploit all the potential of the EB technology. "SWY" parameters optimized for an individual tested movement rate are given in Table 1.

From the macroscopic point of view, a constant width of traces was observed in the beam movement direction. A continuous hardening depth decrease to the trace edge was observed in the direction perpendicular to the beam movement (Fig. 3). The microstructure in the surface-hardened area of all the traces

consisted of fine martensite (Fig. 4). The finest martensite was obtained at the one-point deflection and coarsest martensite at the field mode. The meander-deflected martensite looks fine and very similar to the one-point deflection. No significant microstructure difference was observed when applying the 6-point and the line deflection. A continuous change of the fine martensitic structure to the basic material formed by a tempered martensitic structure with carbides was observed in the transition area (Fig. 5).

A 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. 6 (except the one-point mode). This effect is probably caused by an imperfection of the deflecting system. At the same frequency, the time of stay in a position is shorter at a higher point number and it is not possible to reach the physically programmed position by longer deflecting distances. For that reason, the adequate energy is not delivered to the edges and the hardened track is shorter. The track made by the field deflection is the deepest one; the shallowest ones are made by the one-point and the meander deflections. The material is heated for a longer time by the field mode in comparison to the one point resp. the meander modes. For this reason, the heated depth is higher. The one-point and the field deflections have a significant curvature in comparison to the other deflection modes, which are rather parallel to the surface. Different movement rates have a negligible influence on the trace profile. The "Offset" has a significant effect on the shape of the track. With increasing "Offset" value the trace is becoming wider while, on the contrary, very low "Offset" values lead to easier melting as well as to a significant deformation of the trace profile - Fig. 7. The "Offset" expands the electron affected area and changes points into circles with an indefinite radius. Too low value can cause an insufficient energy coverage of the treated areas and lead to a local decrease in the hardened depth.

Table 1

<i>Optimal length SWY of the field resulted from temperature profile.</i>						
Movement rate	mm·s ⁻¹	5	10	15	20	25
Field length	mm	5	8	12	18	25



Fig. 3. The macrostructure of the surface hardened area in a perpendicular direction - field deflection.
(full colour version available online)

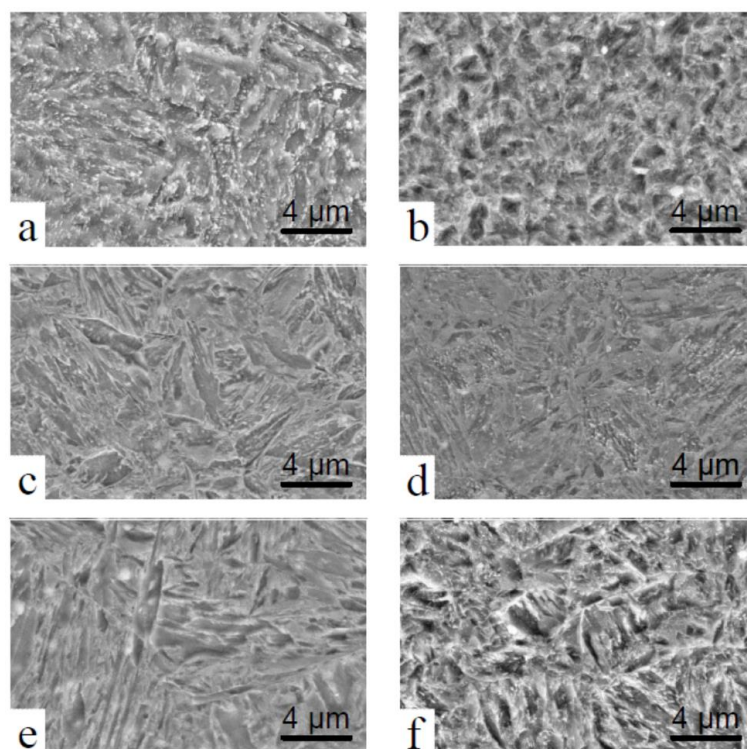
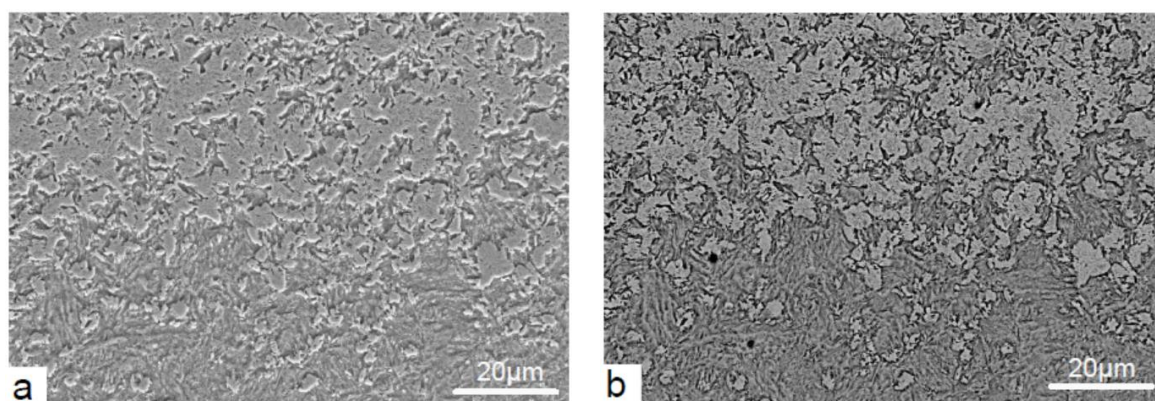


Fig. 4. The microstructure (SE) of (a) basic material, and hardened layers, (b) one-point, (c) 6-point, (d) line, (e) field and (f) meander deflection regimes respectively.



a) SEM – SE mode

b) SEM – BSE mode

Fig. 5. The microstructure of the transition area of field deflection sample.

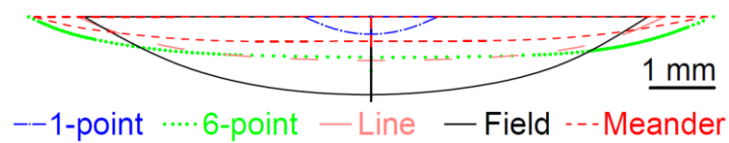


Fig. 6. Figure 6 - Comparison of the profiles of hardened layers.
(full colour version available online)

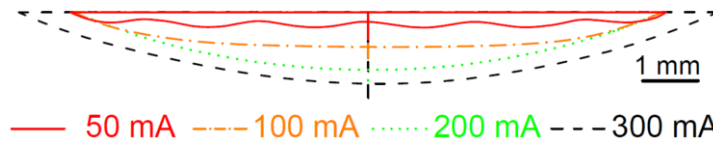


Fig. 7. The influence of Offset on the profiles of the hardened layers (6-point mode; $v_s = 15 \text{ mm} \cdot \text{s}^{-1}$)
(full colour version available online)

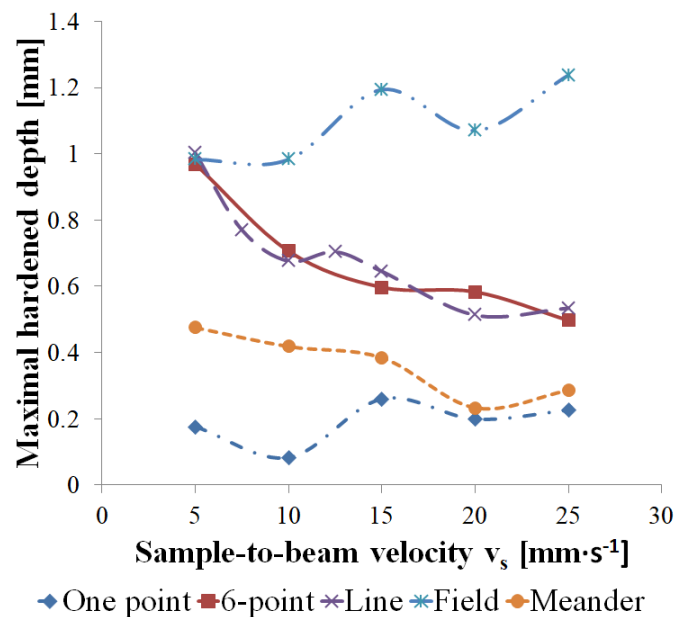


Fig. 8. The influence of sample-to-beam velocity v_s on maximal hardened depth.
(full colour version available online)

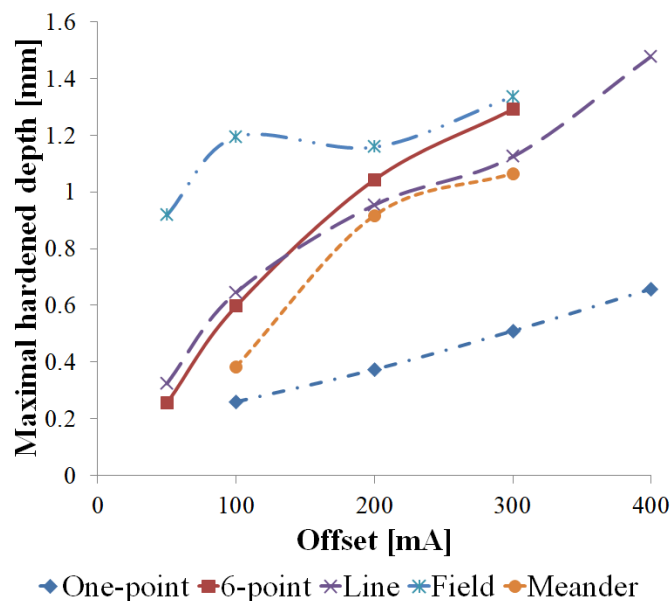


Fig. 9. The dependence of maximal hardened depth on the defocusing Offset.
(full colour version available online)

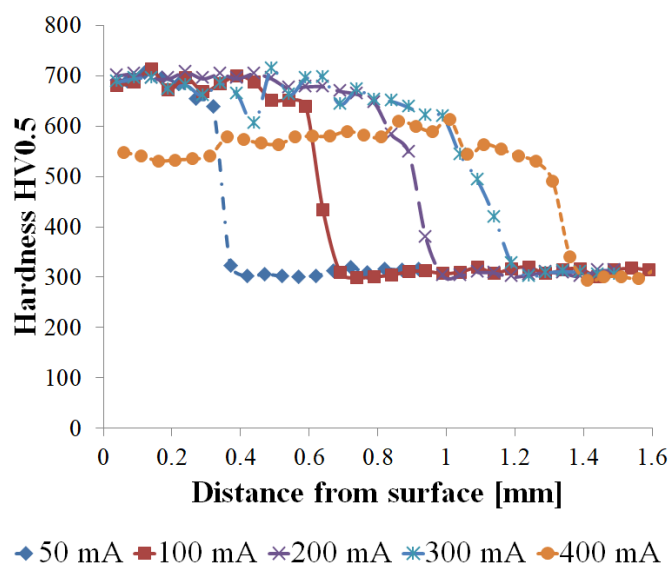


Fig. 10. The influence of the defocusing Offset on the hardness profiles of layers
(full colour version available online)

The movement rate “ v_s ” has only a little effect on the depth of the hardened layer, in particular when applying the one-point, the meander and the field deflection (Fig. 8). 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-point and the line deflection and the dependence is nearly identical. The depth gradually increases with decreasing specimen to the electron beam speed and the greatest change can be seen between 5 and 10 mm·s⁻¹.

An increasing “Offset” leads to an increase in the hardened layer depth (Fig. 9) because this also extends the length of the scanned area, which means a longer heating time. It is interesting that at higher “Offset” values there is no significant difference between different deflection modes. The one-point and the field deflection differ from the other ones by a poorer response to the Offset change.

Maximal hardness values (up to 740 HV0.5) were reached with the one-point deflection because the heating and especially the cooling processes were very fast. Similar values were reached with the meander deflection. The experiments with the other deflection modes give hardness values between 600 and

700 HV0.5. The measured values decreased from the surface to the sample core. A continuous decrease in microhardness was observed on the interface between the quenched area and the basic material. No decrease in the microhardness of the basic material was observed in the vicinity of the hardened traces (Fig. 10). Hardness profiles were the same in the middle of the track as closer to the edges (except the different hardening depths).

It was not confirmed that the movement rate “ v_s ” affected the final surface hardness. Very high EB defocusing causes a total reduction in the hardness in the entire layer. The Offset value 400 mA resulted in an average hardness of 570 HV0.5 of the hardened track and it represents a 20% decrease in comparison with a sharper beam (Fig. 10). This hardness decrease could be caused by sample dimensions and it is not certain whether this is really a technological limit of the electron beam hardening.

4. Conclusion

The work was focused on a evaluation of the deflection mode (one-point, 6-point, line, field, meander) on the surfaces hardened

by the electron beam. The results showed that the deflection mode can affect a number of track parameters. The martensitic structure is the finest when the one-point and the meander deflection modes are applied. The coarsest structure is generated when applying the field deflection mode. The deflection mode affects the maximum hardness to only a little extent. The highest hardness 740 HV0.5 was observed for the one-point deflection mode. For the other regime modes, the maximum values are near 700 HV0.5.

The geometric profiles in the cross-sections of tracks are different for each of the applied deflection modes. The 6-point, the line and the meander deflection modes are parallel to the surface and the one-point mode together with the field-mode are significantly curved. The widths of the tracks were similar except for the one-point regime. The depths of hardened layers were in the range 0.1-1.5 mm. The lowest depth of tracks was produced by the one-point deflection mode and the deepest one by the field mode.

The sample-to-electron beam movement rate affects only the depth of the hardened layer. The depth slightly increases with the speed decreasing. The defocusing affects the depth more significantly. Moreover, an increasing "Offset" leads to wider tracks. If the "Offset" is too low, it can severely distort the profile of the hardened layer. Very high values, in turn, lead to an overall reduction in the hardness of the layer and eliminate the profile differences between the different types of deflection.

Acknowledgements

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MECHANO-CHEMICALLY PREPARED AND SPARK PLASMA SINTERED ALUMINIUM MATRIX COMPOSITE WITH CERAMIC AND INTERMETALLIC REINFORCEMENT

Petra Hanusová¹, Vít Jan¹, Ivo Dlouhý^{1,*}

¹ Institute of Materials Science and Engineering, NETME centre, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

*corresponding author: e-mail: dlouhy@fme.vutbr.cz

Resume

Preparation of aluminium matrix composites reinforced by fine niobium boride particles was investigated while exploiting the advantages of mechano-chemical processing and spark plasma sintering. For this purpose, a mixture of aluminium, niobium and boron (III) oxide powders were subjected to high energy ball milling. Subsequently, spark plasma sintering was applied. The microstructures of the powder mixture before and after sintering were characterized via X-ray diffraction and scanning electron microscopic observation. Nanoindentation was also employed to characterize the composite performance. X-ray diffraction analysis showed formation of niobium boride particles after mechano-chemical processing. The results indicated that the volume fraction of niobium boride particles was significantly increased and intermetallic Al₃Nb particles have been detected after the spark plasma sintering. The instrumented indentation revealed improvement in hardness by 2.9 GPa as well as in the modulus of elasticity by 98 GPa; the final values of 5.7 GPa and 135 GPa respectively being higher than those of comparable aluminium matrix composites.

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1. Introduction

Aluminium-based metal matrix composites (MMCs) are of great interest in the aerospace and automotive industries because of their remarkable mechanical properties. The high specific strength and good corrosion resistance are the key properties contributing to a number of useful applications. Preparation of the aluminium MMCs by powder sintering route is accompanied with a number of obstacles associated, among others, with low wetting performance of the reinforcing phase, as it has been observed for SiC nanoparticles reinforcement [1]. The Aluminium MMCs appear to be still in focus of interest of investigators also because of the possibility to tailor their selected properties towards

specific requirements. The potential possibilities of forming a fine distribution of effectively reinforcing secondary phase particles in aluminium matrix appear to be a strong motivation for further study in this field [1 - 4].

Metal borides are very attractive as a temperature resistant material because of their high melting point, strength and hardness. Good electrical conductivity, low thermal expansion and inertness to most chemicals are also among their notable advantages [5, 6]. Based on these facts, it seems to be reasonable to exploit the metal boride particles for the incorporation into Al matrix. A composite strengthened by these particles can be expected to show high stability at increased temperatures. Further in this respect, the in-situ formation of the strong bond

of boron to metal atoms could enable formation of fine particles inside the fine Al matrix grains which could improve resistance to viscous flow.

Metal borides have various stoichiometric compositions, such as M_2B , MB, MB_2 , MB_4 , MB_6 , MB_{12} and others (M = metal). Formation of a single-phase product generally requires a long reaction time at high temperature [7]. A common way to prepare metal boride powders is by reducing the respective metal oxide with boron oxide and carbon, boron and carbon, boron carbide or an alkali metal and boron oxide [7]. It is well known that the activation during mechano-chemical milling enhances the reactivity of solids, as well as their mixing homogeneity, and lowers the reaction temperature significantly.

From the realistically available borides, the Niobium boride (NbB_2) appears to be a suitable candidate for an aluminium matrix composite formation because it exhibits high values of all melting point, hardness, elastic modulus and mechanical strength. It also has an excellent chemical and oxidation stability [8]. High elastic modulus and strength are the properties enabling effective reinforcement, whereas high melting point and oxidation resistance of the niobium borides are the key parameters for the sintering processes because of the need for stability of the boride particles formed during mechano-chemical reactions. It is thus expected that the niobium borides formed by in situ reactions during milling will be in the form of small size particles with dense distribution throughout the Al matrix with a good interphase bonding enabling effective load transfer.

Results obtained by Jafari et al. [9] indicated that niobium boride particles can be synthesized using an aluminothermic reaction between Al – B_2O_3 – Nb powder particles during mechano-chemical process. Although there is a risk that the final powder will be contaminated from the milling devices due to high reactivity of e.g. Fe of the vial and ball material to boron, this issue can be fixed either

by changing the milling environment or accepting small amount of other than niobium boride particles as the reinforcing phase particles.

Close to theoretical density and low porosity are the key factors required for materials prepared by powder metallurgy route. In addition, the particle volume fraction, particle size, strength of the particle-matrix interface and constraint of the matrix surrounding the particles are the additional factors controlling the composite reinforcement and toughening efficiency. The optimum strengthening and toughening effect is usually generated by fine grained, hard particles randomly and uniformly distributed in the metallic matrix, assuming their interface boundary with the matrix will not be weakened by impurity elements, such as oxygen, trace elements etc. To ensure such conditions, in-situ processing/synthesis appears to be the best choice. The preparation of NbB_2 dispersion by mechano-chemical reaction thus could produce the desired effects [10].

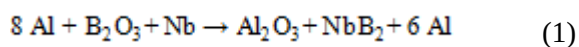
The mechano-chemical synthesis utilizes the mechanical energy introduced by milling to activate chemical reactions and structural changes in the milled powder mixture. The mechanical activation of the chemical reactions by mechanical milling often changes the reaction mechanism. The aluminothermic reduction reactions induced by the high-energy ball milling can stimulate in this way the in situ synthesis of microcrystalline and nanocrystalline metal matrix composites. This approach appears to be a unique opportunity to produce materials that cannot be prepared by any conventional techniques [11].

This contribution aims to present a possibility of the preparation of an aluminium matrix composite containing the NbB_2 particles dispersion as main reinforcement phase. For this purpose, the mechano-chemical reaction and spark plasma sintering processes were employed. The reaction mechanism and the microstructure of the products obtained after

both the mechanical alloying and after spark plasma sintering are also investigated.

2. Materials and Methods

The starting materials utilized in this study included aluminium powder (GTV, particle size 25 – 65 µm), boron (III) oxide (Sigma Aldrich, particle size < 200 µm, purity > 98.5 %) and niobium powder (Sigma Aldrich, particle size < 45 µm, purity 99.8 %). The powders were mixed in ratios corresponding to equation (1). The total weight of initial powder components was 80 grams. The aluminium excess was found to be helpful in converting the reaction course from a combusive to a progressive one. It also appears to foster the retaining of the nanostructure of the product phases, which is the inherent nature of mechano-chemical synthesis [11].



X-ray diffraction pattern of precursors mixture reflected only presence of aluminium, boron trioxide and niobium, respectively, in ratio corresponding to the equation (1) [12].

The mechanical milling was conducted using a high energy ball mill (Fritch Pulverisette 6) in a hardened steel vial and with hardened steel milling balls. The milling conditions are given in Table 1.

To prevent the powder surface oxidation, the vial was filled by high purity argon gas before the milling process. Ethanol was added as a process control agent (PCA) after 20 hours of milling to avoid powder agglomeration. The planetary ball mill was stopped for 30 min after 5 hours of milling in order to minimize

the sticking of the powder to the vial and the balls and also to avoid increasing the local temperature inside the vial. The milling conditions have been fixed during preliminary experiments based on trial and error approach and milling time from 0 to 40 hrs; a detailed study was carried out based on powder morphology and microstructure changes depending on the milling time [12].

The morphology of the powder particles after milling and their internal microstructure were analysed using samples prepared by standard metallographic procedures. The specimens were mounted in epoxy resin, wet ground with up to 4000 grit SiC abrasive papers and then polished with 0.7 µm diamond paste to a mirror finish.

About 70 g of the mechanically alloyed powder was directly loaded into a high strength graphite mould (having 50 mm in diameter) and subsequently consolidated using a FCT Systeme SE – 607 spark plasma sintering device at 1000 °C for 10 minutes under an uniaxial pressure of 95 MPa. A quartz tube with a thickness of 2.5 mm was inserted between the powder/punch arrangement and the sintering mould to suppress sample contamination as recommended by [13]. In order to avoid overheating, the mechanically alloyed powder was heated to 900 °C with a heating rate of 100 °C/min. It was then heated to 1000 °C with a heating rate of 50 °C/min. After SPS, the sintered compact was cooled down to room temperature. Compact sample having a dimension of Ø 50 × (11 – 12) mm was obtained in this way.

The Archimedes method was used to measure the density of the sintered compact. The sample mass was measured both in the air and after submerging it into distilled water.

Table 1

<i>Milling conditions used for this study.</i>					
RPM	Ball/Powder ratio	Ball Diameter (mm)	Milling time (h)	Milling time with ethanol (h)	Total milling time (h)
300	10:1	10	20	15	30

The morphology and microstructure of the mechanically alloyed powder and spark plasma sintered compacts were characterized by X-ray diffraction method (XRD) using a PANalytical X'Pert diffractometer and filtered Cu K α radiation ($\lambda = 0.15406$ nm). The PANalytical X'Pert High Score software was employed to compare the XRD profiles with standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS).

The crystallite size of the samples was obtained by using Williamson – Hall method [14] according to Equation (2):

$$\beta_s \cos \theta = \frac{k\lambda}{d} + 2\eta \sin \theta \quad (2)$$

Where 2θ represents the position of peak maximum, β_s is the peak broadening in radians, λ is the X – ray wavelength, k is the Scherrer constant taken as 0.9, and d is the crystallite dimension. Note that the variable, d , was taken as an approximate upper limit of the lattice distortion.

A scanning electron microscope (FEG-SEM, Zeiss Ultra Plus) that operated at an accelerating voltage of 10 kV was employed for microstructural observations and analyses of the powder after mechanical alloying and of the sintered material. The BSE mode was utilized to reveal contrast between locations with different chemical compositions. Energy dispersive X-Ray spectrometry (EDS), was also employed to investigate the chemical composition in selected locations of the microstructure and elements content in the particles. At least ten particles have been analysed by the microanalysis in order to get corresponding statistical evidence of the approximate element ratio [12]. This enabled to check the presence of the key elements in the microstructure as well as possible trace elements presence in the material.

The indentation tests were carried out using a NHT² Nanoindentation tester (CSM Instruments) with a Berkovich diamond

indenter. All the tests were conducted in the load-controlled mode with peak loads of 10 mN. The indents were performed at a loading rate of 0.05 mN·s⁻¹. A minimum of 15 indents at each load was performed for each specimen, and the average value was obtained in determining the nanohardness and modulus of elasticity.

In addition, in order to obtain overall evaluation of the composite properties the hardness measurement was carried out using a standard hardness tester (Leco LV – 700). The measurements were performed at a 10 kp loading on polished metallographic samples; values presented here represent averages of ten measurements.

3. Results and Discussion

Considering the presence of metallic aluminium, metallic niobium and boron oxide, the thermodynamic balance number of possible interactions should be discussed. In order to follow the fact that the oxide and niobium are in minority while aluminium forms the majority of the reacting mixture, all reactions are considered as being limited by either the boron oxide or the niobium, both of them being set to one mole in the reactions. All other reactants and products masses taking place in the reaction are subject of this constrain. This way it is possible to show, that in the scarcity of one type of atoms situations may occur, that even phases that have exceptionally negative enthalpy of formation will not be formed.

There are three possible reactions where niobium would reduce the boron oxide and directly react with the boron and form a boride.

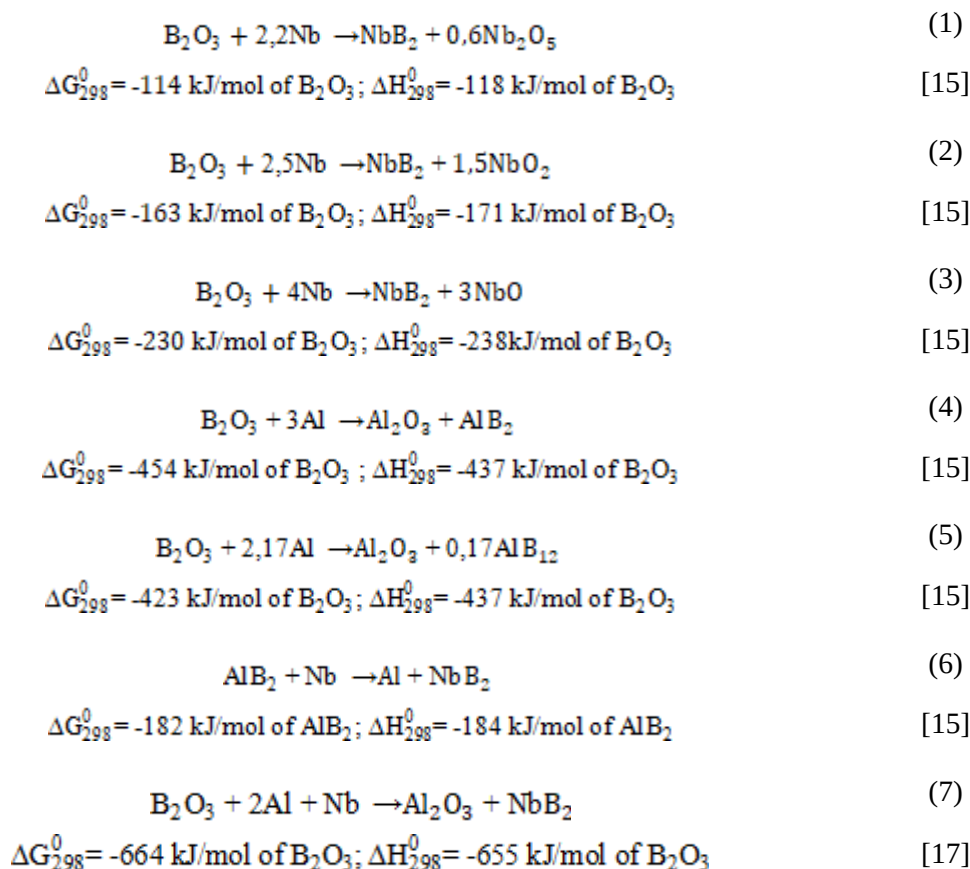
It should be noted that the niobium pentoxide is the most stable substance in the whole system, but when taking into account the limited supply of boron oxide, the energy balancing of the reactions is as stated above. All these reactions are exothermic and therefore thermodynamically possible. It is the kinetic conditions that decide of their likelihood and also the plain fact of niobium

deficiency. The reactions (3) – (5) require up to four-fold excess of niobium over boron oxide molar mass. This much niobium cannot be supplied in the present mixture.

Similarly, aluminium may reduce the boron oxide and directly react with the free boron, there are two types of possible borides in the Al-B system (6) – (7) [16].

The reaction producing aluminium diboride is by far the most exothermic. Considering the excess of aluminium that is present in the mixture it may be assumed that this reaction depicts a viable behaviour. Further on, the niobium may react with the aluminium diboride (8):

While this is a thermodynamically possible set of reactions (reduction by aluminium and then exchange of aluminium and niobium in the boride) and the results of phase composition measurements do testify that it took place in some form, it is possible to consider the case that all three initial components (aluminium, niobium and boron trioxide) are present at the moment of impact of the milling ball when the most heat and mechanical energy is supposed to be present in the reacting mixture as activation energy to whichever changes are about to take place. In such case it may come to the following reaction (9):



All possible reactions of niobium reducing the aluminium trioxide show endothermic character when calculated with the aluminium excess and niobium deficiency. This means no niobium oxide should form. Not all niobium may be available for boride

formation however, since aluminium and niobium form a solid solution. The solubility of niobium in aluminium is neglectable, the solubility of aluminium in niobium is around 8 at % of Al and slowly gets higher with rising temperature. Supersaturated

solutions of up to 12% of Al were reported [18].

It should be noted, that in the Nb-B system, there are several intermediary phases, e.g. borides. There is the one NbB₂ that shows quite large concentration tolerance (approx. 24-37 at. % Nb) and exquisite melting temperature reaching 3000°C. Although the NbB₂ would suggest itself as the prime and most stable phase, it has been shown that also the ratio of available atoms of both elements plays important role. In keys off 1:1 ratio, the NbB boride was formed rather than leaving part of the Nb unreacted and forming NbB₂ [19]. Note the similar outcome has been stated by [9] showing that the reaction running in stoichiometric ratios (not under aluminium content excess) is highly favourable and exothermic. Sharifi et al. reported the two-step reaction mechanism in similar systems [20], [21] where the aluminothermic reaction was included.

The formation mechanism of NbB₂ is here suggested to be divided into two steps in reality. As a first step, formation of aluminium oxide is assumed due to the fact that the Gibbs free energy of Al₂O₃ is comparably lower than that of B₂O₃ and the whole system has excess of aluminium. It is not clear whether the path of the intermediary aluminium boride takes place. It is thermodynamically possible, but should there be niobium present at the place of the initial reduction, the niobium carbide may be formed directly and such reaction is more favourable by mere 28 kJ/mole of boron trioxide. The physical presence of all reactants and the fulfilment kinetic conditions for respective reactions should be the decisive parameters.

Although having negative Gibbs free energy change, the reactions do not necessarily occur at room temperature because of their slow

kinetics. Mechano-chemical activation acts here a solid state powder processing which involves inducing chemical reaction in small volume of a mixture of as received unreacted powders at room or slightly increased temperatures. The reaction taking place during milling is expected to be the result of microstructural refinement, repeated cold deformation and fracture of particles which increases the amount of internal energy of the powder particles making the activation energy level more available [14]. Several distinctive features have been suggested as follows: (a) introducing excess energy into reactants in the form of structural defects, (b) creating high diffusivity paths, (c) providing extensive interface area between reactants during repeated fracturing and cold welding of powder particles and (d) creating a local temperature rise [22, 23].

The heat released locally during the exothermic reaction in micro-volumes (3) provides additional activation energy for reaction between the remaining elements (boron and niobium) present in aluminium matrix. Aluminium oxide does not participate in this reaction because of its low Gibbs free energy.

Fig. 1 shows the XRD patterns of the (a) Al – B₂O₃ – Nb powder mixture mechanically alloyed and (b) spark plasma sintered afterwards.

After 35 hours of mechanical alloying, aluminium, niobium, NbB₂ and NbH were identified in the mixture according to these data. The calculated amount and crystallite size of these phases are shown in Table 2. The content of NbB₂ is not as high as might be expected (4 %) suggesting that the heat resulted from aluminothermic reaction doesn't provide enough activating energy for NbB₂ formation.

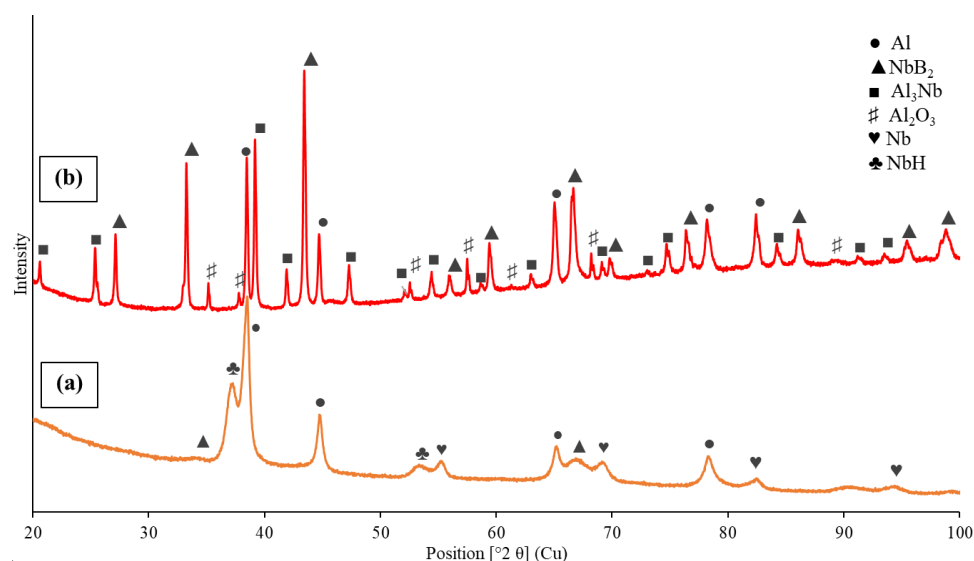


Fig. 1. X – ray diffraction patterns of mechanically alloyed powder (a) before and (b) the bulk after SPS process. (full colour version available online)

Table 2.

Calculated percentage of detected phases and crystallite size – powder after mechanical alloying.

Phase	Al	Nb	NbB ₂	NbH
Ratio (%)	68	13	4	15
Crystallite Size (Å)	188	103	62	126

The obtained XRD results do not correspond fully with the suggested reaction mechanism according to Equations (6) and (8) or the equation (9). Only very limited amount of NbB₂ phase (4 %) was formed during the milling phase and some fraction of Nb (13 %) stayed as separate phase unreacted. In addition, it appears so that the Ethanol, used as a PCA, reacted with the powder mixture during the mechanical alloying and the H atom from the hydroxyl group was relieved. Hydrogen in atom form can easily react with niobium and create the NbH compound [24]. Shang et al. [25] discussed possible reaction mechanisms leading to the formation of niobium hydride. The peaks corresponding to B₂O₃ are not detected in the XRD pattern, this could be related to transformation of its crystal state into the amorphous state, as reported e.g. in [26] or to its very low concentration (below about 4 wt. %) as is often observed for mechanically alloyed alloys and compounds [9].

Typical SEM image of microstructure in particle cross – section after being mechanically milled for 35 hours is shown in Fig. 2. The aluminium matrix formed two different grain types showing two grey levels, so different Nb content in the matrix may be considered. According to EDX area analyses the lighter grains contain traces of niobium (less than 0.3 wt. %), whereas the darker grains appear to be pure aluminium only. Distribution of distinctive minority phase particles can be also identified in the aluminium matrix. The white larger areas represent grains containing mostly niobium. The small particles of polyhedral shape (as similarly identified by [27]), marked with an arrow in Fig. 2., represent NbB₂ particles. They have been identified based on element ratio obtained from EDX microanalysis of at least ten such particles. Presence of these particles has been clearly confirmed by the X-ray diffraction pattern (Fig. 1(b)). The mean particle size of NbB₂ phase was determined to be 200 nm ($\pm$ 80 nm).

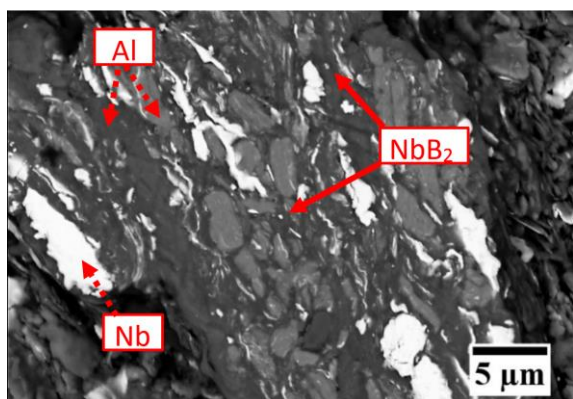


Fig. 2. Cross – sectional SEM image of mechanically alloyed powder mixture.
(full colour version available online)

The mechanical alloying process is characterized by repeated welding and fracturing of the powder particles trapped between the colliding balls during milling. The extent of these individual micro-processes depends on the mechanical behaviour of the powder components [28]. In the composite mixture investigated here, the system is referred to as a brittle/ductile system [27]. As has been shown in works accompanying this study [12], [26], the ductile aluminium particles are flattened and welded to each other during milling, while the brittle B_2O_3 particles are fragmented. The increase of the milling time led to microstructure refinement due to the repeated cold welding and fracturing of the powder particles. Subsequently, the interface area between the phases grew up significantly, which resulted in more pronounced interdiffusion of atoms through high diffusivity paths, such as grain boundaries and dislocations cores created by plastic working. Hence, the reaction kinetics could be increased still at room temperature. The deformation and welding phenomena hardens the material and consequently step by step the tendency to repeated fracture increases. At the end of the milling process, the equilibrium between

welding and fractures has occurred and the steady state was achieved. From that point of view the mechanical alloying for 35 hrs represented optimum milling time for the Al – B_2O_3 – Nb system according to Eq. (6) and (8) or Eq. (9); longer milling time is not effective, for longer milling has shown no substantial changes in microstructural constituents ratio and morphology occurred.

Comparing to the powder state after milling the diffraction pattern of the bulk composite after the SPS process is different as can be seen from Fig. 1 (b). New phases appeared in the aluminium matrix at this stage. The intermetallic compound Al_3Nb and Al_2O_3 oxide were detected. No peak shift was observed for aluminium, indicating that no solid solution was formed during the milling process. No traces of Nb particles were observed in the XRD pattern after the SPS process showing that almost all Nb reacted either into Al_3Nb intermetallic phase or into NbB_2 boride particles. Note also that there was no evidence of niobium hydrides presence as observed in the initial MA powder. In addition, no characteristic peak was observed for other impurities in the XRD pattern that could indicate presence of trace and impurity elements/compounds that could come e.g. from the milling process; this observation has been confirmed by repeated point and/or area microanalyses in SEM.

Table 3 shows the calculated amount and crystallite size of the phases observed after spark plasma sintering. As can be seen, the Bragg peaks became narrower after the spark plasma sintering process. This quantitative change can be assigned to increase of the crystallite size as has been confirmed by results of the calculation.

Table 3.

<i>Calculated percentage and crystallite size of phases identified in the bulk material after SPS.</i>				
Phase	Al	NbB_2	Al_3Nb	Al_2O_3
Ratio (%)	48	22	18	12
Crystallite size (Å)	546	566	660	1796

Fig. 3 shows SEM image of the microstructure in the cross – section of the bulk material after the SPS process. The microstructure is formed by polyhedral grains separated by low density areas.

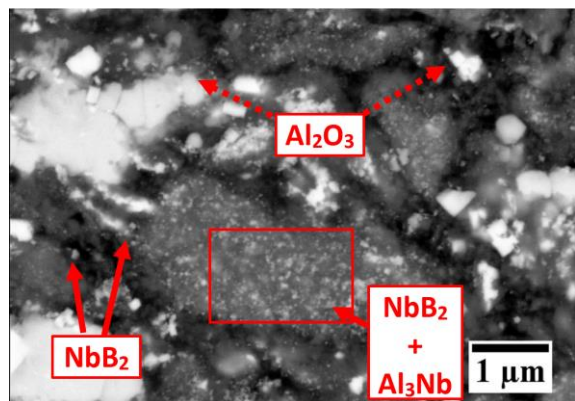


Fig. 3. Cross – sectional SEM image of material after SPS.
(full colour version available online)

This corresponds well to the result of the XRD analysis which shows more pronounced peaks of multiple crystalline phases. Individual NbB_2 particles are present as marked with red arrow in Fig. 3. The size of these marked particles was not higher than 100 nm. The matrix of the material is based on aluminium (grey colour) containing small white dots of NbB_2 particles (having the size between 40 – 100 nm). After mechanical alloying, Nb particles were observed in the powder mixture in a relatively low fraction. During the SPS process (current and pressure applied providing heat and intimate contact between particles for the NbB_2 synthesis), a sufficient amount of energy in the system was achieved to overcome the kinetic energy barrier, thus promoting further the reaction leading to niobium boride particle formation and their volume fraction increase (22 % comparing to 4 %). Note however, that in the same area as NbB_2 particles are distributed the intermetallic Al_3Nb phase particles were also formed under the SPS conditions showing very similar particle size (not higher than 80 nm) and contained in the matrix in similar volume fraction (18 %)

as NbB_2 particles. Larger light particles in Fig. 3 represent alumina particles size of the order of 0.2 μm . The black colour represents voids indicating that the compaction during the SPS process was not quite perfect.

Table 4 shows a comparison of the nanohardness characteristics of the mechanically alloyed and spark plasma sintered material. After the spark plasma sintering process, the enhancement of both the indentation hardness (HIT) and indentation modulus of elasticity (EIT) is evident.

Table 4.
Comparison of the properties from nanohardness tests of composite powder before SPS and bulk material after SPS process.

	HIT (GPa)	EIT (GPa)
Before SPS	2.8 ± 1	37 ± 2
After SPS	5.7 ± 1	135 ± 4

The density of the sintered powder was measured based on the Archimedes law and showing the value of $3.08 \text{ g}\cdot\text{cm}^{-3}$ which is 97.43 % of the theoretical density ($3.17 \text{ g}\cdot\text{cm}^{-3}$). From SEM micrographs it follows that there are evident pores in the microstructures and the SPS sintering condition need to be further optimised from that point of view.

The hardness of the sintered powder was also measured using Vickers method. The average hardness from 10 measurements in different location was determined to be $150 \pm 11 \text{ HV } 10$. This value is comparably higher when considering other reported advanced aluminium matrix composites, e.g. 115 HV as shown in [4].

The observed enhancement of mechanical properties was caused mainly by higher fraction of the hard NbB_2 particles and intermetallic Al_3Nb phase particles, as well as the good ratio of the theoretical density.

4. Conclusions

An aluminium matrix composite containing fine NbB_2 and Al_3Nb particles

as reinforcement was obtained by mechano-chemical reaction of powders followed by spark plasma sintering. The phase analysis proved that the reactions described by Eqs. (6) and (8) alternatively the Eq. (9) were activated by the collision events during the mechanical alloying, in agreement with thermodynamic considerations. Consequently, the reinforcement particles were formed in aluminium matrix and identified as NbB_2 (after mechanical alloying) and $\text{NbB}_2/\text{Al}_3\text{Nb}$ mixture (after spark plasma sintering). Unreacted Nb particles still remained in the powder mixture after mechanical alloying, showing that not all of the reactions during milling took place ideally according to the above equation. However, all niobium was completely reacted during SPS forming the above mentioned fine particles mixture. In addition, the potential for further reinforcement and/or even toughening by additional treatment applications exists.

Based on nanohardness measurement the final mechanical properties appear to be improved. Both the indentation hardness and indentation modulus of elasticity were increased after the SPS process. The mechanical alloying caused the optimization of the powder microstructure by enabling further formation of reinforcing borides during the spark plasma sintering.

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THE EFFECT OF HIGH TEMPERATURE ANNEALING IN DIFFERENT ATMOSPHERES ON PORE FORMATION IN SURFACE REGIONS OF ODS MATERIALS

Vít Jan^{1,*}, Jan Čupera¹

¹ Institute of Materials Science and Engineering, NETME centre, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69, Brno, Czech Republic

*corresponding author: e-mail: jan@fme.vutbr.cz

Resume

Mechanically alloyed oxide dispersion strengthened materials MA 6000 and MA 956 have been annealed at 1100°C for 24 and 240 hours in air, vacuum of 10⁻³ Pa and hydrogen. Mechanical properties after annealing were then tested at room temperature. Mass changes due to oxidation and evaporation were measured. Fracture surfaces, microstructure of the materials and changes in chemical composition were examined.

The results of mechanical tests yielded generally only small changes of mechanical properties after all expositions. On fracture surfaces and polished sections, formation of voids and altered microstructure sub-surface zones in both materials has been studied. Different mechanisms causing void formation are discussed and proposed. Also the mechanisms and reaction sequences of surface oxidation reactions are examined.

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1. Introduction

The use of Oxide Dispersion Strengthened (ODS) materials in high temperature applications is widely considered as very promising step towards achieving higher temperatures and thus higher efficiency values in cases such as gas turbine, in prospective fusion reactors or other most demanding high temperature applications. These alloys combine two important characteristics - good long term stability of microstructure providing creep strength and also high temperature corrosion resistance through surface passivation layers [1, 2, 4, 5].

In the case of the two materials under examination in this contribution - MA956 and MA 6000, iron and nickel form the base of the materials matrix respectively. Strengthening yttrium oxide particles are added

to the microstructure by means of powder metallurgy route in both cases. The oxide layers that formed during high temperature exposition represent a basic and essential mechanism by which a material can protect itself from aggressive environment. In the presented experiments, the materials were annealed in vacuum, air and hydrogen all at the temperature of 1100 °C.

Different mechanisms may be involved in the formation of pores in superalloys during annealing [3, 8 - 11]. These may be related to the reaction of the material with the surrounding environment, the reaction to an external stress applied on the sample under investigation, or the technology of producing a particular material.

The first group of mechanisms explains the creation of cavities by condensation

of vacancies in the metal matrix of the material [3, 6 - 8]. During oxidation, migration of metal ions through the oxide towards the free surface is compensated by the flow of vacancies into the material through the oxide. These vacancies should normally disappear at the oxide-metal interface. When this annihilation does not occur, the vacancies pass into the bulk metal substrate, where again there are possibilities for their extinction at grain boundaries or at interface of the matrix and noncoherent particles. If these mechanisms do not appear to be sufficient, condensation of vacancies must occur. This vacancies condensation is then a mechanism of formation of cavities in areas close to the surface. Another mechanism that may be included in this group lies in dissolving some of the phases in the bulk of the material. Should the formation reactions of oxides on the surface require an element that forms a carbide phase in the material bulk for example. A cavity copying the original shape and size of the dissolved particle is left in the material in such case. The flow of atoms from the disintegrating particle towards the surface is to some extent compensated also by flow of vacancies in the volume of the dissolved particle.

The second group includes mechanisms of formation of cavities involving mechanical stress in the material [3, 6 - 8]. The cavities in the ferritic ODS materials produced by powder metallurgy are attributed to the relaxation of the internal stresses produced by the pressing or extrusion of powder materials. This approach assumes that due to the different properties of the matrix and the oxide reinforcing particles, local stresses builds up in the material, which are then relaxed by diffusion of the matrix atoms and subsequent formation of the cavities (at a sufficient temperature).

The third group of mechanisms relates to the formation of cavities by gas molecules accumulation in the material [3, 6 - 8]. Especially for nickel-based materials,

the formation of cavities filled with CO₂ / CO mixtures is mentioned in the literature. The formation of such cavities is related to the reaction of the carbon dissolved in the metal matrix of the material and the oxygen atoms that diffuse into the material from the external environment. Preferably, at the grain boundaries, new pores can be formed. These are not related to the formation of an oxide layer on the surface of the material.

In connection with materials produced by powder metallurgy, the formation of cavities filled with gas used as a protective atmosphere during powder milling is considered. The molecules of this gas (most commonly argon) are captured in individual powder particles; exposure to high temperatures leads to the release of these molecules and their coupling in the cavity.

Identification of the porosity thus produced may be facilitated by the assumption that the pores should be uniformly present throughout the volume of the material [7, 12, 13].

There is no clear consensus about the mechanism of formation of pores during high temperature exposure ferritic ODS materials. In addition to the mechanism involving the gas molecules trapped in the powder during its production, the possibility is also mentioned that the formation of cavities in the material allows the relaxation of internal stresses introduced into the material during deformation manufacturing (e.g. extrusion). The presented work discusses the viable pore formation mechanisms based on chemical changes and morphology features of the observed pores.

2. Experimental setup

ODS superalloy materials MA 956 and MA 6000 were used in the tests both materials were manufactured by Special Metals Co. purchased through BIBUS Company. Nominal chemical composition of these materials is presented in Table 1.

Table 1

Chemical composition of examined materials.

wt. %	Cr	Ni	Fe	Al	Mo	W	Ta	Ti	Y2O3	Zr	C
MA 6000	14.90	bal	0.78	4.46	1.97	3.93	2.03	2.60	1.09	0.16	0.03
MA 956	19.00	0.10	bal	4.39				0.38	0.52		0.03

Table 2

Mass changes of the samples after annealing experiments.

MA6000	Annealing time /h	AIR 1100°C	VAC 1100°C	HYD 1100°C
g/mm ²	24	-3.94·10 ⁻⁵	-8.24·10 ⁻⁶	1.93·10 ⁻⁶
g/mm ²	240	-5.22·10 ⁻⁵	-5.00·10 ⁻⁵	2.89·10 ⁻⁶
MA956	Annealing time /h	AIR 1100°C	VAC 1100°C	HYD 1100°C
g/mm ²	24	4.49·10 ⁻⁶	-4.40·10 ⁻⁵	1.77·10 ⁻⁶
g/mm ²	240	9.41·10 ⁻⁶	-3.25·10 ⁻⁴	3.95·10 ⁻⁶
g/mm ²	1000	1.84·10 ⁻⁵		

For evaluating the mass changes during annealing, specimens of 10×10×3 mm were cut and polished on SiC paper 2000 grit. These specimens were also used for microstructural examination of the materials.

All specimens were annealed at 1100 °C for 24 and 240 hours in air, vacuum of 10⁻³ Pa and hydrogen of normal pressure. MA 956 samples were annealed also for 1000 hours. Non-annealed specimens were also examined for comparison means. Commercially available hydrogen of 99.99% purity was used in the experiment without any further treatment.

After annealing, the samples were cut to half and metallographic samples were prepared by standard technique. Light and electron microscopy was used to characterize the microstructure and EDS was used for local chemical analysis. In this paper, particularly the results obtained by Philips XL30 SEM coupled with EDAX EDS analyser are shown. The weight changes were measured by analytical Sartorius scale.

3. Results of measurements

3.1 Mass changes

All samples were weighted before and after the annealing. The results are contained in Table 2.

Annealing in air caused weight loss on MA6000 samples and weight gain on MA956 samples. While MA6000 grows oxide layers that fall off the samples, MA956 grows a homogeneous oxide layer that adheres to the surface and adds to the total weight of the sample. After vacuum annealing, both samples showed mass loss. In both cases this is due to evaporation, mainly of chromium from the matrix of both materials. The evaporation of bulk matrix could not be ruled out either. In MA956 it appears so that part of the matrix evaporated, leaving only fine, yttrium, aluminum and titanium containing particles on the surface. Annealing in hydrogen atmosphere produced mass gain on both materials. Both materials developed well adhering oxide layers in this case.

3.2 Microscopic analysis

3.2.1 Air annealing MA6000

When the MA6000 is annealed in the air, a composite layer of aluminum and chromium oxides with embedded nickel matrix particles is formed on the surface (Fig. 1, Fig. 2). The thickness of these layers can be determined only approximately as the oxidation surface attack is uneven and locally falls off. After 24 hours of annealing at an annealing

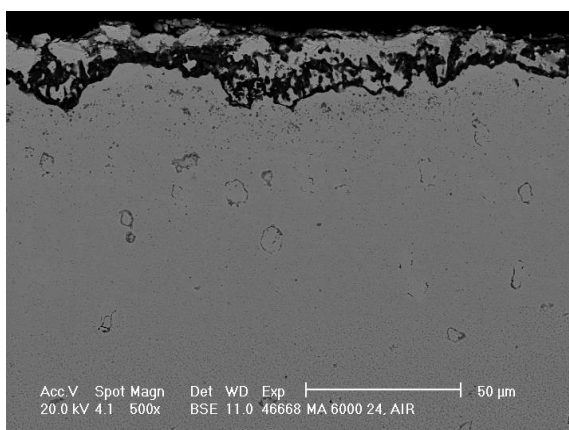


Fig. 1. Microstructure of MA6000 after annealing in air for 24 hours.

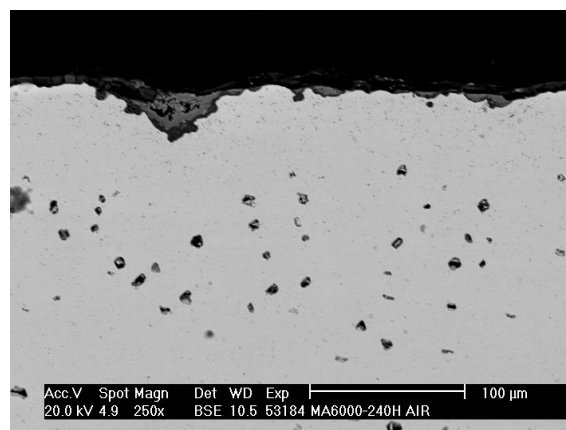


Fig. 2. Microstructure of MA6000 after annealing in air for 240 hours.

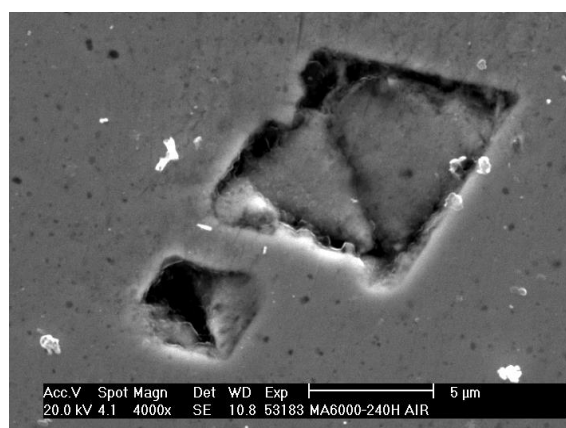


Fig. 3. Pore detail in MA6000 after annealing in air for 240 hours.

temperature of 1100 ° C, the oxide layer has a thickness of 25 µm, after 240 hours there is already a significant loss of oxidation products, the maximum thickness of oxide layer exceeds 50 µm. The uppermost layer of this system consisted of chromium oxide, particles of the original matrix were sealed in the oxide layer. After 240 hours of annealing, the majority of the oxide layer has fell off from the surface of the sample, its composition can only be observed on residues in deeper affected areas. This residual layer is formed by aluminum oxide and the now also oxidized nickel matrix particles.

During annealing in the air, pores gradually formed beneath the surface of the material as far as 100 µm after 24 hours, and 300 µm after 240 hours. After 24 hours (Fig. 1), pores are formed by separating individual particles from the surrounding matrix. After 240 hours (Fig. 2), hollow pores

are already visible. Particles of high titanium, aluminum and yttrium content (Fig. 3) are found on the inner surface of the pores together with residues of the nickel matrix with increased titanium content up to 20 wt. % and low chromium.

Slight decrease in chromium content in matrix of the material has been measured in the vicinity of the surface. Correspondingly to the observed mixed oxide layer with the matrix residues on surface, increase of aluminum and oxygen content was measured on surface.

3.2.2 Air annealing of MA956

With annealing in the air, a compact layer of Al₂O₃ oxide containing small particles with high titanium, aluminum and yttrium content was formed on the MA956 samples. The thickness of this layer is 2 µm after annealing for 24 hours, 6 µm for 240 hours, and 10 µm for 1000 hours

of annealing. The oxide layer adheres well to the surface even after tensile tests (Fig. 4). EDS analysis of the chemical profile of the samples showed oxygen and aluminum in the surface oxide layer; below this layer there was no measurable change in chemical composition compared to the original state.

Newly formed pores inside the material in the structure of MA956 samples were found rather in the core part of the sample than near the surface. These pores have a characteristic oval shape stretched in the rolling direction of the original material. They are also visible on the fracture surfaces, the inner surface of these pores is covered with small particles that have a high content of yttrium, titanium and aluminum (Fig. 5).

3.2.3 Vacuum annealing of MA6000

Vacuum annealing of MA6000 samples

created pores open to the surface. The pore area reaches 20 μm below sample surface after annealing for 24 hours and 250 μm after annealing for 240 hours (Fig. 6). The pores contain small particles with high content of aluminum, titanium and yttrium on the inner walls or residues of the matrix material. In the diffusion affected subsurface area of the sample also particles of mixed tungsten and molybdenum carbides were found. On fracture surface of the annealed sample a recrystallized 8 μm wide area is visible under the surface of 8 μm (Fig. 7). This area corresponds to higher titanium and lower chromium content. Chemical analysis revealed a chromium depletion towards the surface of the material and a slight increase in titanium content. The recrystallized area at the fracture area corresponds to the lowest measured chromium concentration.

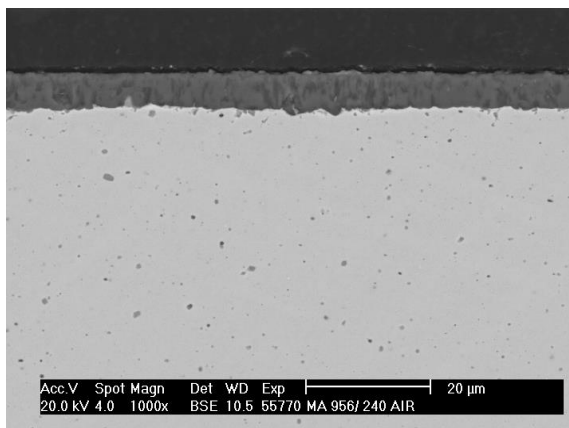


Fig. 4. Surface region with oxide layer on MA956 annealed for 240 hours in air.

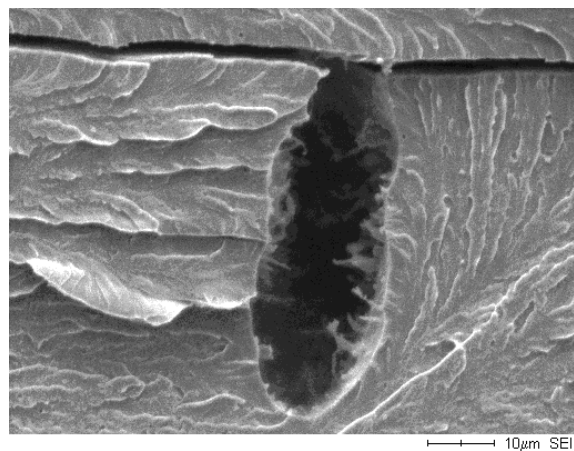


Fig. 5. MA956 annealed for 240 hours in air; detail of pore on fracture surface.

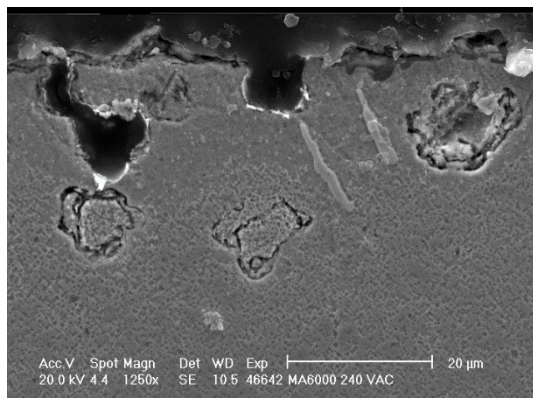


Fig. 6. Surface region microstructure of MA6000 after 240 hours in vacuum.

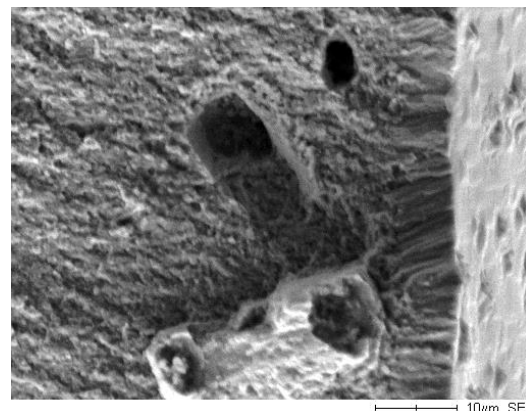


Fig. 7. MA6000 fracture surface after 240 hours in vacuum showing pores.

3.2.4 Vacuum annealing of MA956

During vacuum annealing, the matrix evaporated to certain extent, which resulted in thermally etched surface with a high concentration of (oxide) particles of yttrium, aluminum and titanium (Fig. 8). The chromium and iron content decreased towards surface and due to the accumulation of minor particles on the surface and in its vicinity there is an increase in yttrium and aluminum concentration.

Similarly to air annealing samples, porosity was formed in the material (Fig. 9). The pores are concentrated more in the inner bulk of the sample than in the subsurface areas. The pores have internal surfaces covered with small particles of high content of yttrium, aluminum and titanium

3.2.5 Hydrogen annealing of MA6000

During annealing in hydrogen, a very thin layer of aluminum oxide was formed on the MA6000 surface, through which particles with high titanium and yttrium (Fig. 10, Fig. 11) penetrated. This layer has a thickness of 1 μm after annealing for 24 hours and 2 μm for 240 hours. Chemical analysis showed a decrease in chromium content immediately below the oxide layer formed by Al_2O_3 . The profile also shows an increase in titanium, tungsten and yttrium content in the oxide layer.

3.2.6 Hydrogen annealing of MA956

A continuous aluminum oxide layer was formed on the surface of the samples after annealing in hydrogen, containing fine particles with high content of yttrium and titanium (Fig. 12, Fig. 13). These particles penetrate the entire oxide layer and some of them appear on the surface (Fig. 13). The thickness of the oxide layer is 1 μm after 24 hours and 2.5 μm after 240 hours of annealing. Changes of the chemical composition of the bulk material under the oxide layer could not be detected.

As mentioned before, the pore cavities that may be found in the inner part of the sample bulk contain small oxide particles of yttrium, titanium and aluminium (Fig. 14, Fig. 15).

4. Summary

The effects caused by annealing at 1100 $^{\circ}\text{C}$ in all three environments are predominantly connected to surface reactions of the samples. No distinctive changes have been found in the matrix in the core of both samples with the exception of MA956 pores which is solely result of the high temperature regardless of the environment. Table 3 gives a summary of the chemical changes in at surface regions – e-g oxide containing layers or depleted layers and the microstructurally

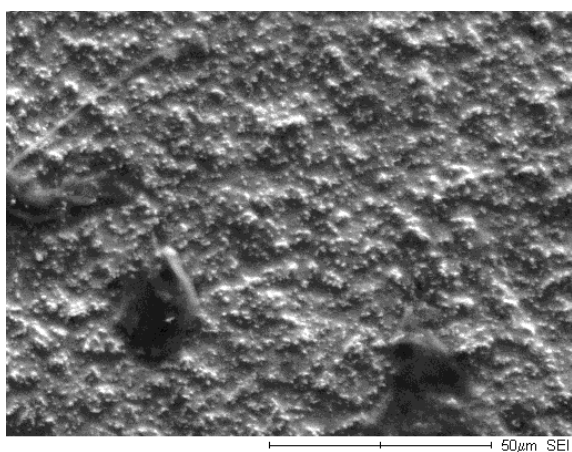


Fig. 8. Surface of MA956 after 240 hours annealing in vacuum.

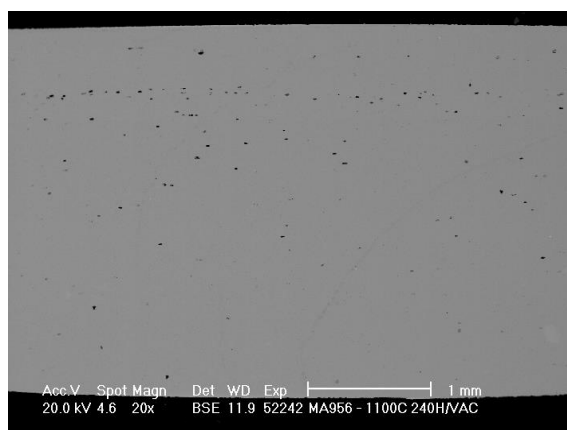


Fig. 9. MA956, 240 hours annealing in vacuum, general overview of the sample showing pores.

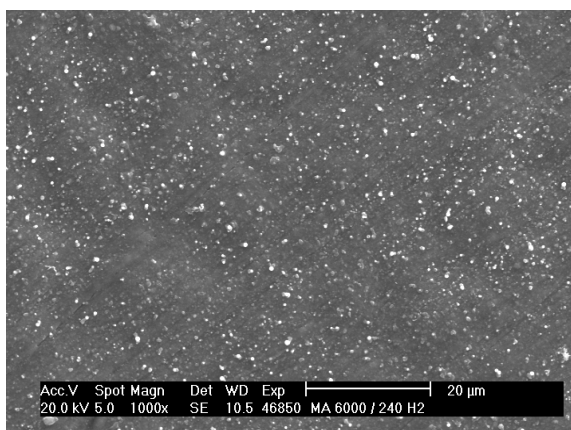


Fig. 10. Surface of MA 6000 after annealing 240 hours in hydrogen.

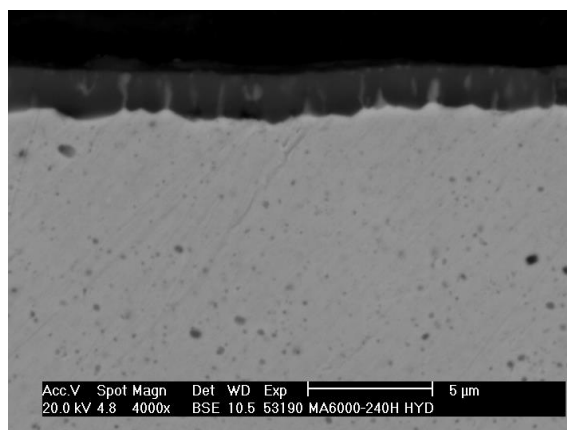


Fig. 11. Detail of oxide layer on MA6000 after 240 hours annealing in hydrogen.

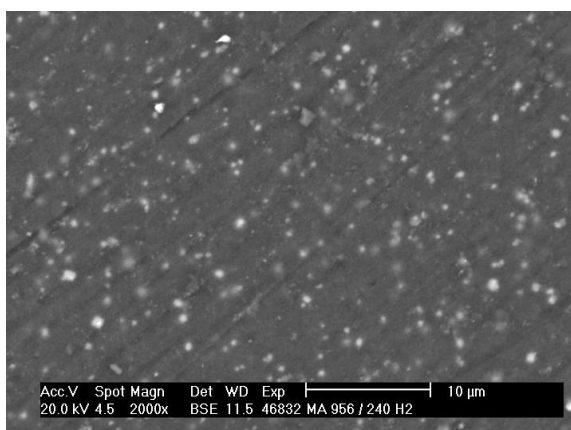


Fig. 12. Surface of MA 956 after annealing 240 hours in hydrogen.

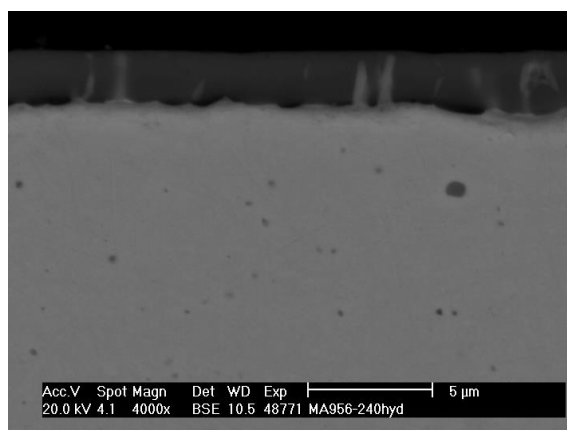


Fig. 13. Detail of oxide layer on MA956 after annealing 240 hours in hydrogen.

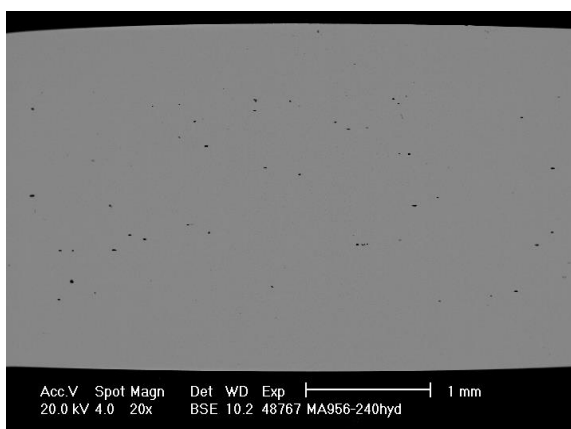


Fig.14. MA956, 240 hours in hydrogen, general overview of the sample showing pores.

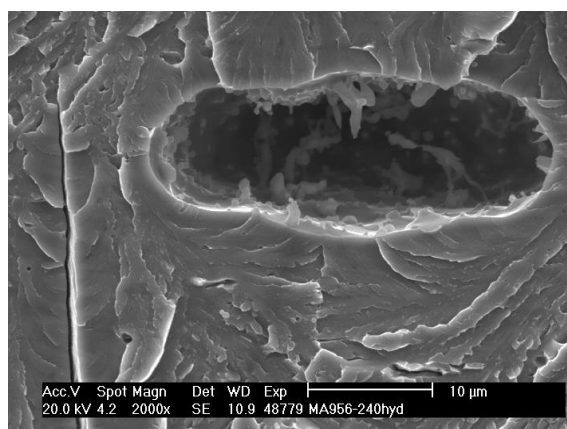


Fig.15. MA956, 240 hours in hydrogen, detail of pore on fracture surface.

Table 3

Chemical composition changes of the samples after annealing experiments.

Wt. % (EDX)		Surface							Sub-surface						
MA 6000		O	Al	Fe	Cr	Ni	Ti	Y	O	Al	Fe	Cr	Ni	Ti	Y
Air 1100°C 240h		16.4	22.0	0	10.8	41.5	2.7	0	1.7	6.7	0.2	16.0	62.6	2.8	0.2
Vac 1100°C 240h		1.3	4.2	0.3	0.6	65.0	3.1	1.2	0.3	1.2	1.0	9.6	84.0	1.8	0.2
Hyd 1100°C 240h		25.0	40.0	0	2.2	10.5	6.1	0	0.8	3.0	0	14.4	77.9	1.3	0.2
MA 956		O	Al	Fe	Cr	Ni	Ti	Y	O	Al	Fe	Cr	Ni	Ti	Y
Air 1100°C 240h		44.0	53.0	0.7	0.2	0.2	0.3	0.2	0.8	5.4	71.0	20.4	0.1	0.5	0.4
Vac 1100°C 240h		1.4	3.2	65.5	11.0	2.0	7.2	4.6	0.6	1.6	70.0	11.5	0.6	1.9	2.2
Hyd 1100°C 240h		37.0	42.0	6.8	2.7	2.0	3.5	0.5	0.9	2.5	74.0	17.3	0.4	0.3	0.3

adjacent subsurface layers. All these values were measured by EDS using signal integration along a 150 µm long line parallel to the surface and only the major constituents with highest changes are shown

4.1 Summary for MA6000

During air annealing experiments MA6000 produces an oxidation layer formed by aluminum oxide and nickel matrix particles, which oxidize eventually too after longer exposition times. The spalling and peeling off of this layer is the main reason for the weight loss of air annealed samples. Under the oxidized surface a pores containing zone is created. The pores have distinguished angular shapes and contain fine particles with higher titanium, aluminum and yttria content. When annealed under vacuum, MA6000 shows decrease in sample weight due to evaporation of chromium from the material. The formation of angular pores with Ti, Al, Y containing particles has been found too. Thin layer of matrix on the surface has been recrystallized. Annealing in hydrogen formed a thin uniform aluminum oxide layer with small other oxides particles.

4.2 Summary for MA956

MA956 exhibits excellent oxidation resistance behaviour with very low weight change. When annealed in air and hydrogen, an aluminum oxide protective layer containing

fine particles, likely yttria and titanium oxides was formed on the surface of the material.

Annealing under vacuum resulted in evaporation of iron and chromium from the matrix material. The material thus exhibited significant weight loss. Large number of fine particles with high content of aluminum, titanium and yttrium remained on the surface of the sample.

All methods of annealing without exception resulted in porosity of the sample material. This porosity is not related to any of the observed surface related phenomena. The resulting pores have an oval shape elongated in the rolling direction of the material and their inner surface is covered with yttrium, aluminum and titanium oxide particles. With longer annealing time, some of the pore cavities were found to be partially filled back by matrix material.

5. Discussion

The types of pores identified in the examined samples differ in several parameters. In view of the position of the pores, it is possible to observe pores open to the surface, below the surface of the metal and within the mass of the material without apparent connection with the subsurface region.

In terms of shape, the pores may be divided according to whether they retain the shape of the particle in place of which they have formed or no parent feature in the microstructure is apparent.

5.1 Pores from vacancy condensation

Annealing of MA6000 gave rise to pores with a characteristic geometric shape in the regions below the formed oxide layer. On fracture surface, small particles with high content of yttrium, titanium and aluminum can be seen in the cavities of the pores, copying sharp-edged particles that are the parent structure of the pores (Fig. 16). Gonzales-Carrasco et al. [14] published a pore formation study in MA6000 during annealing in air and as a cause determined the condensation of vacancies entering the material from the oxidizing surface.



Fig. 16. Angular pores on fracture surface of MA6000 annealed for 240 hours at 1000°C in air.

Pores are formed by evaporation of matrix particles having a higher content of preferably oxidizing elements - titanium and aluminum. The evaporation of these particles begins at their boundary, which is probably already decorated by yttrium oxide particles from the powder manufacturing process. This is consistent with the results [3, 8, 9] where sites with a higher concentration of fine particles of yttrium oxide have been identified as preferred for the formation of cavities during annealing. The increasing depth of the area affected by the formation of cavities in time indicates a diffusion-controlled reaction. The mechanism of cavity formation is related

to the technology of powder production and mixing and compaction.

Another observed fact is the area without visible pores that separates the oxidized surface and the area affected by the formation of cavities. The mechanism of formation of this once again homogeneous layer can be seen in a combination of vacancy transport deeper into the material layers, where larger cavities are formed than close to the surface and in the recrystallization of the surface area of the metal matrix.

It has been reported, that with a sufficiently long annealing time (hundreds of hours in a row), the pores are sequentially closed with matrix material [14]. This phenomenon was not convincingly observed on the MA6000 samples in this study.

5.1.1 Pores from gas molecule condensation

MA956, created cavities unrelated to the surface reactions of the material. The cavities in all samples - i.e. annealed in hydrogen, air and vacuum - had common characteristics. The cavities were always of oval or ellipsoidal shape with the longer axis in the direction of extrusion and rolling of the material. The internal surface of the cavities was always covered with fine particles of high content of yttrium, titanium and aluminum (e.g. Fig. 15). When observing samples annealed for 240 hours, some pores were filled with material with composition identical to that of the matrix. A likely explanation for this phenomenon is that the cavity is filled during longer annealing times. At the fracture areas, filled or partially filled pores may be observed (Fig. 17). Two possible mechanisms were discussed in connection with pores in ferritic ODS materials. The more frequently mentioned mechanism explains the formation of cavities by condensation of the gas molecules used in the milling and mixing of powders, most often argon. The second proposed mechanism aims

at relaxation of stresses introduced into the material during extrusion.

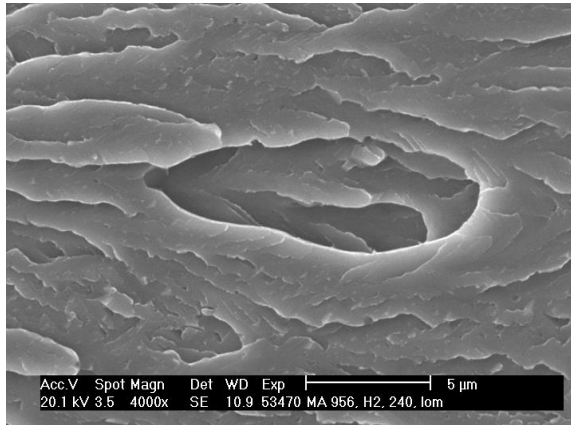


Fig. 17. Detail of filled-in pore in MA956 after 240h annealing in hydrogen.

By combining both approaches - which are probably not mutually exclusive - it would be possible to arrive at the following combined pore formation mechanism in MA956:

During extrusion and rolling of the material, the metal matrix is deformed while the oxide particles in the material do not deform. In the manufactured material, the oxide particles are stressed by pressure while the surrounding matrix by tensile stresses. At the same time, argon atoms originating from the protective atmosphere are dissolved in the metal matrix [6, 8].

By exposing the material to high temperature, the internal stresses in the matrix will be relaxed by metallic atoms diffusion on the oxide-matrix interface. This creates tiny cavities, the free surface of which is an opportunity for argon atoms to leave the metal lattice. Thus both mechanisms can act simultaneously. Cavities are first formed by stress relaxation, because experiments with ferric ODS materials that have not been subjected to the appropriate deformation (about 10-15%) do not show porosity, although powder milling takes place in an argon atmosphere. Neither of the mechanisms directly explains the presence of large number of yttrium-rich,

titanium and aluminum particles on the pore surface.

5.2 Creation of new layers on samples surface.

The creation of new layers on the surface of materials is an essential feature of corrosion-resistant materials that facilitate the passivation in aggressive environments [16, 17]. For the two material under examination here layers of Cr_2O_3 , Al_2O_3 , or their mixtures may be expected to form.

5.2.1 Oxide surface layers during air annealing

On the MA6000 a Cr_2O_3 oxide layer is formed first while layer of metal matrix is retained under this outer layer, and only beneath this mixed layer an aluminum oxide is formed. Considering the chemical composition of MA6000, both oxides -chromium and aluminum- might protect the material [18]. However, long-term exposure times at high temperatures will leave a more stable alumina on the surface of the material. An increased exposure time at high temperatures eventually leads to the loss of the outer layers. This results in weight loss of the material. The ultimate result of long-term oxidation of MA6000 is the alumina protective layer.

MA956 shows a typical property for ferrite ODS reinforced with yttria oxide dispersion - selective formation of only alumina on the surface upon exposure to the oxidation environment [12, 21, 22]. This also caused weight gain during the annealing [13, 19, 20]. The probable cause of only Al_2O_3 production is a complex mechanism that shortly after the first oxide layer is formed, yttrium atoms diffuse into the oxide layer at the metal oxide interface which prevents metal atoms diffusion through the oxide towards the oxidation atmosphere. Thus only transport of oxygen ions through the layer towards the metallic substrate is possible and the oxide molecules are formed at the metal oxide interface. Experiments have

shown that increasing the yttrium concentration in the material (to 1 wt. %) increases the permeability of the oxide layer for oxygen ions meaning faster oxidation. At very low concentrations of yttrium, rippled and broken layers of alumina are formed.

5.2.2 Oxide layers created in hydrogen atmosphere

During annealing in hydrogen, layers of aluminum oxide with a thickness of units of micrometres have been produced on both materials. The formation of these layers was probably caused by an insufficient purity of the hydrogen atmosphere, which contained a small amount of oxygen, or air humidity.

The mechanism that caused also MA6000 that predominantly grows chromium oxides to create a very compact aluminum oxide in this atmosphere may be related to the stability of both oxides. Al_2O_3 is thermodynamically more stable, therefore, even when chromium oxide has formed on the surface of the samples, it is likely to be reduced and the oxygen reacted with aluminum to a more stable alumina. This hypothesis is also supported by the measurements of chemical composition profiles on the samples. These show a decrease in the content of chromium in the substrate material under the thin layer of Al_2O_3 . This suggests a proposed mechanism where either chromium oxide is formed, decomposes and chromium atoms evaporate out of the material while oxygen atoms form aluminum oxide.

Considering that hydrogen of 99.99% purity was used in the experiment, at 100 kPa of the atmospheric pressure, the 0.01 % of impurities gives partial pressure of 10 Pa for impurities. It is very likely that this included also some humidity that caused the oxidation in atmosphere consisting in vast majority of hydrogen

6. Conclusions

Samples of two ODS materials were subjected to annealing at 1100°C in three

different environments – air, vacuum and hydrogen.

In MA6000 the voids after air exposure have been observed in a sub-surface zone, after vacuum exposure two types of voids were identified one in the base material and one reaching the surface. In MA956 after all exposures only voids in the middle of the specimen were observed. The formation of these voids has been studied and possible mechanism is proposed.

Mainly chromium oxides have been identified on MA6000 surface after air annealing, these did not adhere well to the surface of the samples, hence the mass loss. On MA956 aluminium oxides formed a uniform, well adherent layers, hence the mass gain during oxidation. In case of hydrogen exposition, both materials developed aluminium oxide layer with titanium particles embedded in it. This is put into connection with possible minor contamination of the hydrogen atmosphere.

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