



USE OF COLD GAS DYNAMIC SPRAYING OF BI-METALLIC POWDER MIXTURES AS ALTERNATIVE TO CLASSIC POWDER METALLURGY ROUTE FOR PRODUCING INTERMETALLIC MATERIALS

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Resume

The paper presents cold gas dynamic spraying (or Cold Spray) as a novel surface treatment technology capable not only of surface modifications but also being used as bulk creating technology. This is demonstrated on numerous samples where bi-metallic powder feedstock is deposited into bulk, self-standing pieces of material that does not need the support of substrate. Mixtures from the group of Fe, Al, Ti, Ni, Cu were used for the initial bi-metallic mixtures. The deposited samples were then subjected to annealing at temperatures ranging from 300 to 1100°C in protective atmosphere and resulting morphologies and microstructures were analysed. Generally materials with high proportion of intermetallic phase content were obtained. These are discussed as potential scaffolds for metal or polymer matrix composites or as hi temperature resistive supports for catalysts with filter functions.

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1. Introduction

Due to the similarities, the innovative low-temperature cold gas dynamic spray process (cold spray, CGDS, CS) [1] is regarded as one of the thermal spray techniques (Fig. 1). It is a novel surface treatment technology whereby protective or function performing coatings are readily applied onto prepared substrates. The coating is not formed by means of thermal input but high kinetic energy impingement and corresponding severe plastic deformation. The resulting material exhibits practically zero oxidation, extremely low porosity and excellent machinability among other interesting features. As such the cold spray process is also suitable for producing self-supporting (bulk) material

by depositing thick coatings onto disposable substrate.

In thermal spray processes finely divided metal or non-metal material is deposited in a molten or semi-molten state onto a prepared substrate to form a spray deposit ("coating") [2]. The material is inserted in various forms, heated in gaseous medium and propelled towards the substrate surface [3]. Depending on the technology, the high velocities of acting gases cause acceleration of the small particles of the material up to 1400 m.s⁻¹ [1]. Eventual heating can cause further increase in the particles kinetic energy and likely cause partial or full-scale melting of the particles [4]. The immense kinetic energies stored in particles account for the large

amount of both elastic and plastic deformation of the molten or semi-molten particles during the process of its solidification at the surface. The solidified particles are called 'splats' and due to common concurrence of acting temperature and velocity, their resulting shape is far from ideal spheres, with their shape best described as lamella [4]. A synchronous relative movement of the thermal spray source against the substrate enables covering the substrate in individually deposited layers, each consisting of millions of the solidified splats. The final coating thickness is influenced by a number of spray gun passes, relative speed of the gun towards the surface, the efficiency of the deposition process and material deposition rate (indicated in $\text{kg}\cdot\text{s}^{-1}$ and proportional to the number of particles entering the jet) and could generally vary from 5 μm (a single layer coating) up to several mm (usually a coating with graded or sandwich layer structure). However, vast amounts of oxidation is typically present in the thermally sprayed deposit, which is the effect of inevitable presence of oxygen either from the fuel or from surrounding atmosphere, which takes part in the stream of semi-molten particles transported to the substrate. This means that it is quite difficult to create metallurgically clean deposit consisting only of metallic phases. The coatings exhibit inimitable, messy structure consisting of the solidified splats, unmolten or partly molten particles, both amorphous and recrystallized phases, voids, micro-cracks, and various impurities such as oxide inclusions [7]. As such, the properties of the final coatings may vary significantly from those of the feedstock material, often resulting in deterioration in the targeted performance.

1.1 Cold gas dynamic spray process

The newest of all the thermal spray processes, cold spray is the next progressive step in the development of high kinetic energy coating processes, following the trend of increasing particle spray velocity and reducing particle temperature (Fig. 1). In the process,

a compressed gas such as helium, nitrogen or air is divided into pressure gas (pressures up to 5 MPa, flow rates up to 90 $\text{m}^3\cdot\text{hr}^{-1}$) and a feeder gas. The pressure gas is moderately heated and exits the spray gun via a conical convergent-divergent Laval nozzle [5] accelerated to supersonic velocities. The feedstock powder is injected axially into the feeder gas flow at the gun nozzle intake and accelerated to velocities of 300-1500 $\text{m}\cdot\text{s}^{-1}$ [5] (Fig. 2). Contrary to its high-temperature counterparts, cold sprayed coating is not built up by means of melting and solidifying of impinging particles. Instead, bonding in cold spray is associated with a solid-state plastic deformation, namely adiabatic shear instabilities caused by high strain deformation rate during impingement, thereby producing dense coatings without the feed-stock material being significantly heated [1].

Cold spray has some unique features as compared to other thermal deposition techniques. Bonding of particles occurs solely when the impact velocities of particles exceed a critical value, v_{critical} [6] This critical velocity depends on the type of spray material, the powder quality, particle size and the particle impact temperature. Particles cold sprayed below the threshold value merely act as abrasives, a process similar to grit-blasting. The nozzle exhaust gas velocity propelling the particles is given as:

$$v = \sqrt{\frac{TR}{m_a(\text{gas})} \cdot \frac{2k}{k-1} \cdot \left[1 - \left(\frac{P_e}{P} \right)^{\frac{k-1}{k}} \right]} \geq v_{\text{critical}} \quad (1)$$

where $k = \frac{c_p}{c_v}$ is the isotropic expansion factor, c_p and c_v are the specific heats of the gas at constant pressure or volume, respectively, T is the absolute temperature of the inlet gas, R is the ideal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), $m_a(\text{gas})$ is the molecular weight of the used pressure gas and P_e and P are the absolute pressures of the exhaust gas at the nozzle exit and the inlet gas, respectively. Arising from equation 1, the ideal solution for fabricating cold sprayed coatings is the usage of helium as the propellant

gas, due to its inert character, viscosity, and the velocities attained by the particles in the jet. Due to the He production costs, helium recuperation

systems were recently introduced. However, majority of the nowadays CGDS production uses N_2 or N_2/He mixtures.

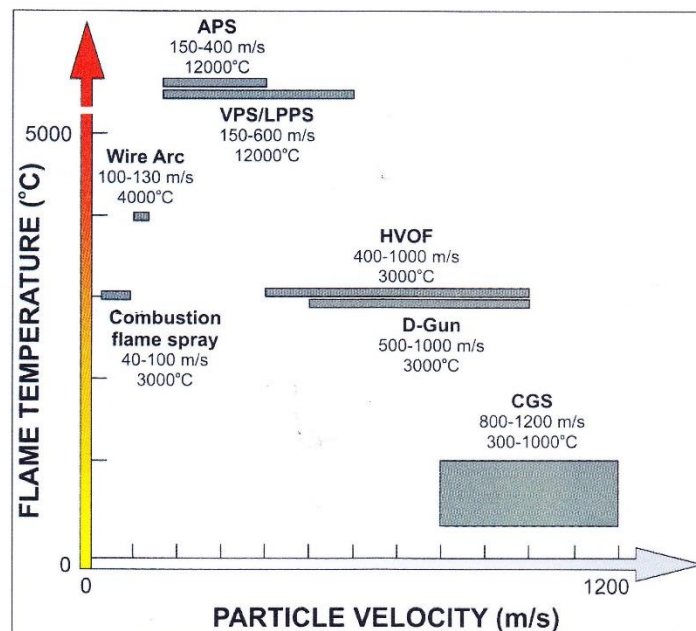


Fig. 1. In flight temperatures and velocities of the feedstock material in various thermal spray processes. (full colour version available online)

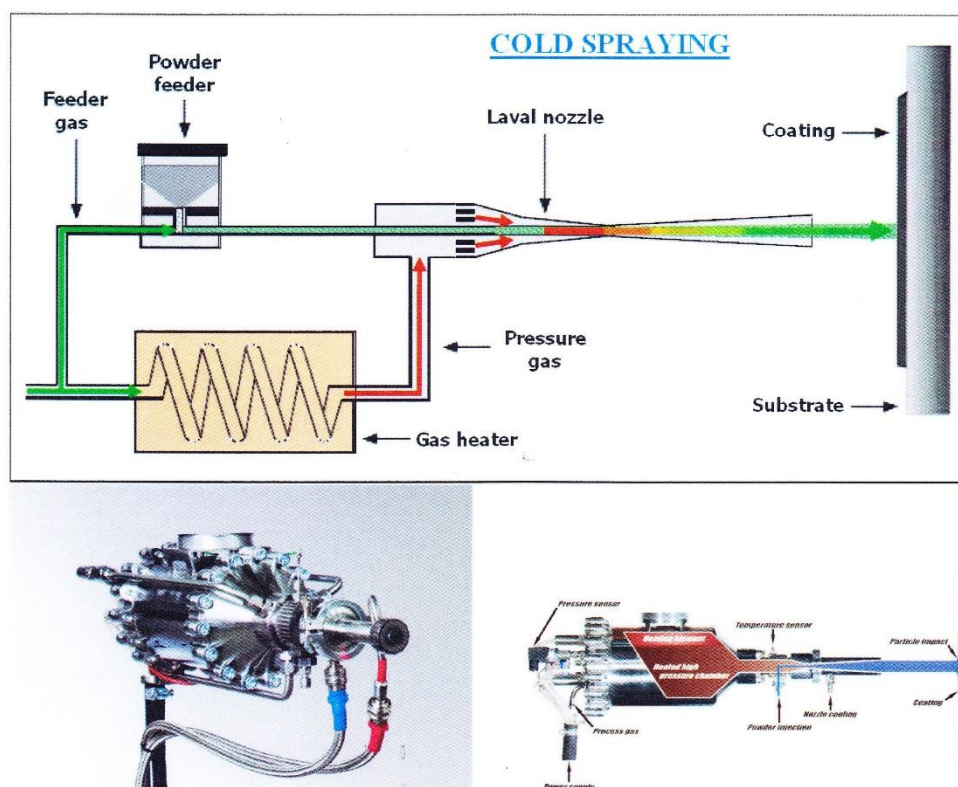


Fig. 2. Schematics of cold spray process and commercial high-pressure gun (image courtesy of Impact Innovation GmbH). (full colour version available online)

1.2 Properties of coatings prepared by CGDS

Due to its ambient-temperature character (Fig. 1), cold spraying eliminates the detrimental effects of high temperatures experienced with other thermal spray techniques. Phase and composition changes of the original feedstock are negligible and the substantial reduction of material oxidation in cold-sprayed coatings results in dramatic increase of thermal and electrical conductivities of metallic coatings. Further, the absence of oxides improves the intrinsic bonding strength, resulting in superior adhesion strengths among the thermal spray processes. Also the contact between individual particles is direct metallic without any oxide separation. Coating hardness is also improved. It was shown that cold spray coatings exhibit strict isotropy of their intrinsic mechanical properties in the elastic range [8] that could eventually open up a whole new range of possibilities. Other advantages of cold spray technique include extended components lifetime [9, 10], reduced material loss by vaporization, low gas entrapment (in voids) and insignificant grain growth and recrystallization. High spray rates (up to $10 \text{ kg}\cdot\text{hr}^{-1}$) and deposition efficiency (up to 99 %) allow fast coating build-ups of about $250 \text{ }\mu\text{m}$ per pass. The inherent residual stresses induced by cold spray are of compressive nature, allowing production of thicker coatings, even production of bulk materials which is later shown in this study.

1.3 CGDS coatings applications

Typical applications of cold spray technology include coatings with increased thermal conductivity, wear and fatigue resistant coatings on biomedical implants [11], deposition of electrical conductors in electronics industry [12], corrosion protection coatings with enhanced performance due to low oxide content and deposition onto glass or aluminium and other comparatively low-temperature melting substrate materials to locally increase hardness or wear resistance. CS coatings are frequently used as oxidation or corrosion protection [13].

Furthermore, cold spray allows spraying materials with low decomposition temperatures, e.g. polymers. Combining the advantages, CS can produce composite coatings of highly dissimilar materials, such as metal-matrix composites [14] or small-grain intermetallic alloys [15].

The thermal load on the substrate and preceding layers from consecutive nozzle passes is minimal as opposed to high-temperature spray processes. Therefore, the resulting stresses are of compressive nature [16] and the coating delamination and decohesion is restrained. Thereby, the overall coating adhesion is significantly improved, reaching up to 300 MPa, higher than the coatings produced by other (thermal) spray techniques. Also, the moduli of the coatings are approaching those of the respectively polycrystalline bulks [8]. These factors allow for production of thick coatings and cold spray is capable of being implemented in additive manufacturing (freeform fabrication, [17, 18]). This allowed for manufacturing of reactive bulk deposits for intermetallic materials production.

1.4 CGDS as compaction process for in situ intermetallics production

The intermetallic materials present an interesting group with some outstanding qualities. Intermetallics usually have high strength and lower ductility – characteristics that are connected to their crystal lattice type. Applications of intermetallic materials are very diverse, starting from electronic industry (GaAs, InAs, InSb); use of intermetallic precipitates (NiAl) for strengthening of superalloys; to bulk materials used as casting alloys (TiAl, NiAl).

Iron aluminides - FeAl and Fe₃Al phases are attractive for their high temperature properties and also because the raw materials are relatively cheap. Iron aluminides have low specific weight and high resistance against oxidation and carburization. They exhibit reasonable resistance in the presence of sulphur as well. So besides the high temperature

applications, which are common to all aluminides, use in chemical industry is also applicable for iron aluminides [20, 21].

Usually these materials are manufactured using casting technologies such as precision casting under protective atmosphere or vacuum and consecutive limited machining. Powder metallurgy also represents one of the very promising and sometimes the currently only realistic manufacturing route for some intermetallics. As such, powder metallurgy inherently brings limitations to possible size of the final product or its shape variability, should the machining and the amount of inevitable scrap material be reduced as much as possible. As it was mentioned earlier here, the cold spray process allows creating bulk deposits that need not to rely on substrate considering overall shape and component strength. It is possible to deposit big amounts of material in times allowing for real technical use.

To test the possibility of using cold spray in place of compacting steps such as cold pressing, extrusion or HIP, cold spray has been used to form massive deposits with arbitrary shapes from heterogeneous bi-metallic mixtures [22, 23].

2. Experimental

Cold spray technology produces coatings with little or no phase and structure changes as compared to the original feedstock, post-spray heat treatments to restore initial phase composition are therefore unnecessary. In combination with high coatings machinability this allows for refurbishment of worn metallic components, such as e.g. damaged shafts, gears, of steels, aluminium or magnesium alloys [19]. Similar approach was used in the presented experiments, where metallic powders were deposited on relatively thin aluminium sheet, which was subsequently peeled off from the much thicker and bulkier deposit material.

Always bi-metallic powders were used for deposition. Deposits were produced by low-pressure cold spray technique using nitrogen was used as working gas with temperature $T = 400\text{ }^{\circ}\text{C}$ and pressure about 50 bar. Gas flow was about 250 slm. The samples were deposited by 8 to 20 passes. (Fig. 3) Thickness of the deposits varied between 6 and 12 mm. Cu, Fe, Al, Ti and Ni Powders were purchased from GTV and HC Starck.



Fig. 3. As deposited bulk samples (NiFe, CuFe FeAl, from left to right).
(full colour version available online)

The deposits were subjected to extensive annealing experiments in protective atmosphere of Ar. The annealing temperatures ranged from 300 to 1100 $^{\circ}\text{C}$. The samples were heated fast to the desired temperature; 2 hours were used for the isothermal annealing. After two hours, the samples were moved out from the hot zone, but still left in the protective Ar atmosphere until cooled to 100 $^{\circ}\text{C}$. Only then were the samples left to cool on air.

The samples showed microstructures altered by diffusion controlled reactions with new intermetallic phases or solid solutions precipitates. Typically, porosity was formed along with intermetallic materials. This observation was also reported by other authors on particular FeAl based materials elsewhere [24]. Microstructure was evaluated using metallography and analytical SEM (Fig. 4).

Fracture behaviour was assessed by breaking the samples at room temperature.

3. Results description

3.1 As-deposited materials

The microstructure of the as-deposited material consisted of metallic matrix and nickel, aluminium or iron individual grains which corresponded to original individual powder particles. The deposited materials showed a shift in the chemical composition favouring aluminium, titanium, copper, nickel or iron in different systems [16, 24, 25]. This phenomenon corresponds to different deposition efficiency of the different metals deposited together (Table 1). The as-deposited microstructure of the samples typically exhibited a porosity of less than 1%. On fracture surface, typically the metallic matrix, although severely deformed still exhibited ductile fracture, while the minority phase particles delaminated from matrix.

Table 1

Chemical composition of as-deposited (CGDS) materials, (wt%).

weight		weight	
Ti-Al		Ni- Fe	
Al	23	Ni	95.3
Ti	77	Fe	4.7
Ni-Al		Fe- Cu	
Al	55	Cu	90.2
Ni	45	Fe	9.8
Fe-Al			
Al	49		
Fe	51		

3.2 Deposits after annealing

Fe-Al system

Al_5Fe_2 phases were identified in the material already after annealing starting at 500 °C. Minor part of the iron particles reacted after two hours of annealing leaving

heterogeneous structure. Annealing at 600 °C created FeAl and FeAl_2 microstructure with substantial porosity. The material changed its character into open interconnected porosity structure. The outer shape of the sample was maintained, although the macroscopic dimensions of the sample increased. Some remnants of un-reacted iron could be seen in the microstructure in Figs. 5 and 6.

Ti-Al system

First intermetallic phases were identified after 300 °C annealing. Layer of $\text{Al} + \text{TiAl}_3$ and layer of $\text{TiAl} + \text{TiAl}_2$ mixtures formed at the Al - Ti particles interface. Gradual formation of the TiAl_3 intermetallic phase started after 450 °C annealing. 550 °C showed distinctive intermetallic areas at Al-Ti contacts and at boundaries between originally individual titanium particles. Some newly formed porosity can be seen at 550 °C and interconnected porosity has evolved after annealing at 600 °C/2h when also local melting could be identified. Even at 600 °C areas of pure unaffected titanium could be identified, while no pure aluminium areas were found in the microstructure in Fig. 7.

Ni-Al system

The deposits exhibited first intermetallic formation of Ni_3Al phase after 450 °C. At 500 °C concentric layers of intermetallic phases Ni_2Al_3 , NiAl and NiAl_3 with gradually changing chemical proportions of nickel and aluminium formed on the nickel particles. Sample annealed at 550 °C showed distinctive areas of the Ni_2Al_3 and NiAl_3 intermetallic phases with interconnected porosity (Fig. 8). The pores are comparable in size with the original powder particles. Unreacted nickel particles remains were still visible after 550 °C.

Fe-Cu system

The system shows practically zero solubility in solid state at room temperature, therefore no intermetallic was observed.

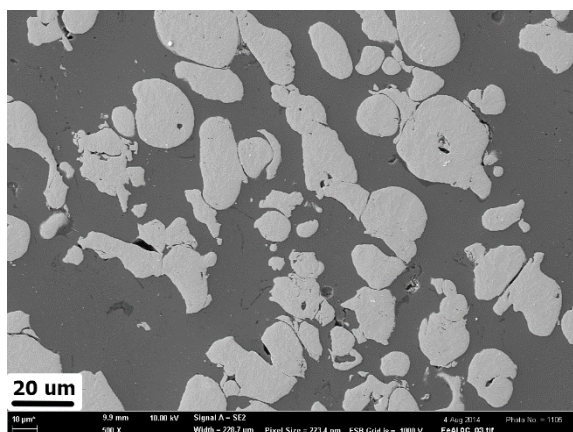


Fig. 4. Typical microstructure of well deposited material by cold spray (FeAl in BSE mode, dark aluminium, light iron).

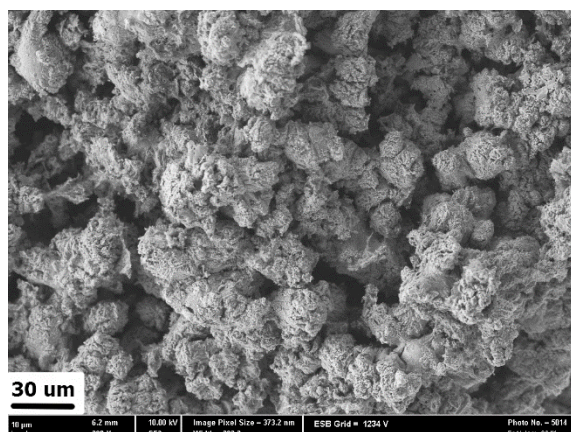


Fig. 5. Typical morphology of porous reacted deposit (FeAl 600°C, reacted intermetallic particles with open porosity in SE mode).

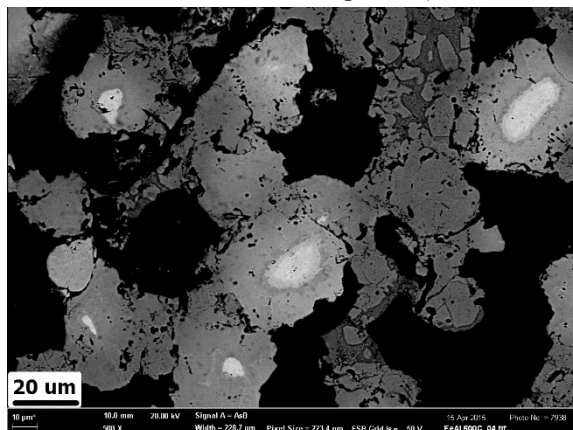


Fig. 6. Typical microstructure of mostly reacted material after annealing with massive porosity (FeAl 600°C, bright areas unreacted iron, grey areas Fe-Al intermetallic phases, black areas are pores).

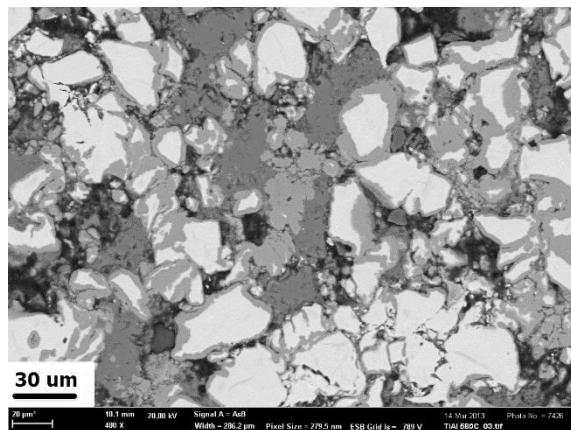


Fig. 7. Gradual evolution of intermetallic phases in TiAl deposit after annealing at 500°C. (bright unreacted titanium particles surrounded with TiAl intermetallic bands – light grey, TiAl₃ dark grey areas, black pores).

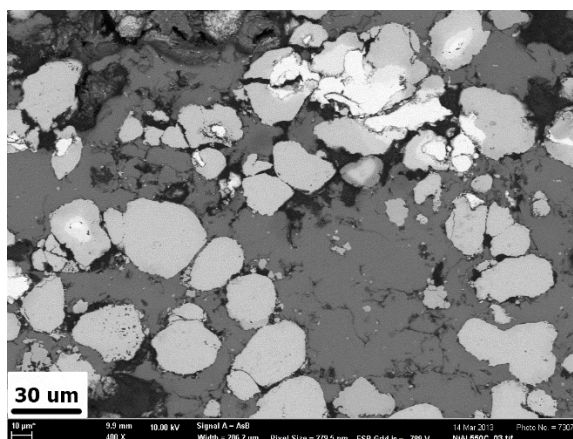


Fig. 8. Microstructure of NiAl deposit after 550°C annealing – intermetallic particles NiAl medium grey in unreacted dark grey Al matrix, some bright Ni unreacted particles still visible.

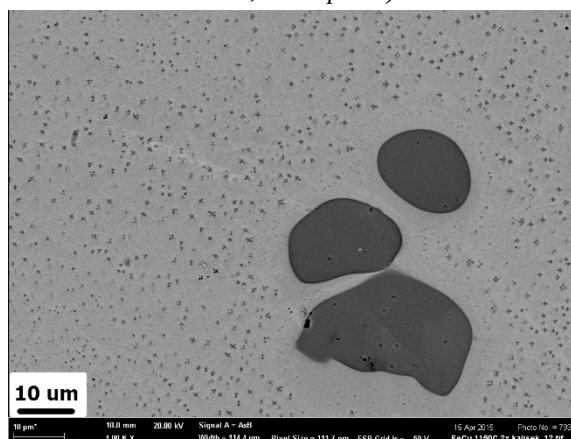


Fig. 9. Fine Fe rich precipitates in Cu phase arising from immiscibility in FeCu system, three big original Fe particles. After 1150°C annealing.

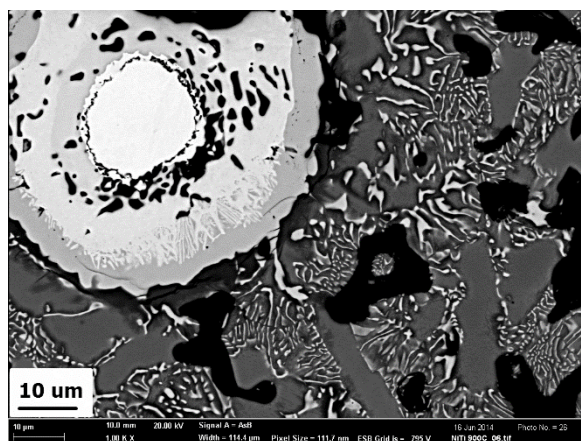


Fig. 10. Kirkendall porosity around gradually dissolving Ni particle and porosity from Ti deposited particles in NiTi sample after 900 °C annealing (brightest unreacted Ni core surrounded by NiTi and Ti₂Ni intermetallic rings and matrix of eutectoid mixture α Ti-Ti₂Ni with black pores).

However evolution of precipitation microstructures with both precipitated in iron and in copper based grains was identified (Fig. 9). The iron based particles contained 3 at. % Cu and 3 at. % Fe were found in copper particles. Iron precipitates had size about 1–2 μ m. Strengthening was measured in both iron and copper particles caused by precipitation of the other counterpart element form the system.

Fe-Ni system

Solid solution of about 90 at.% Fe and 10 at.% Ni was partially formed after 500 °C annealing, which was followed by extensive homogenization at higher temperatures. Due to low iron content, the iron could be dissolved in nickel matrix without any microstructural effects.

Ni-Ti system

The NiTi samples annealed at temperatures of 600 and 700 °C exhibit already minor new phases formation. At 800 °C new phases were formed rapidly around the nickel particles by mutual diffusion. Both Ti₂Ni and TiNi₃ were identified. This mixture is likely to be the result

of decomposition of NiTi under 620 °C. Also eutectoid mixture can be found occasionally, which indicates the presence of beta titanium solid solution. Homogeneous microstructure of eutectoid accompanied by Ti₂Ni intermetallic and titanium solid solution was generated after high temperature annealing of 900 °C.

4. Conclusions

Cold spray technology produces coatings with little or no phase and structure changes as compared to the original feedstock and has been found as efficient tool for preparation of surface coating and bulk (composite) materials.

Intermetallic phases formed in the studied cold spray deposits once sufficient temperature was reached. Since these reactions predominantly happen at solid state, the formation of new phases is controlled by mutual diffusion of the two reactants. This in all of the samples eventually results in formation of porosity in material. As the two constituents diffuse mutually intermetallic phase is formed and Kirkendall type (in the solid state) of porosity arises creating concentric circles around individual particles in some cases.

At higher temperatures even liquid-solid reaction of (aluminium rich) melt and the still solid second constituent particles could be identified the best in the Ni Al system. The semi- melted state during intermetallics formation leads to increased open porosity caused by flow of the melted component on the still solid scaffold from already reacted intermetallics and second unreacted component. When aiming for bulk material, which usually is the ultimate goal of similar studies, porosity is regarded as negative feature. However, when this open porosity is uniform in size and can be reproduced, the annealed deposit represents a new material quality.

As such the reacted intermetallic sponge can be used as high temperature creep resistant support for catalysts, filtering applications or for manufacturing of metal matrix composites by infiltration of the sponge by appropriate liquid metal. Also the use in biomedical applications as reconstructive bone scaffolding can be considered.

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References

- [1] A. Papyrin, V. Kosarev, S. Klinkov, A. Alkimov, V. Fomin: Cold Spray Technology, Elsevier, Netherlands, 2007.
- [2] P. Changnon, P. Fauchais: Ceram. Int. 10(4) (1984) 119-131.
- [3] S. Sampath, X.Y. Jiang, J. Matejcek, L. Prchlik, A. Kulkarni, A. Vaidya: Mat Sci Eng A 364 (1-2) (2004) 216-231.
- [4] V. Pálka, E. Postrková, H.K. Koerten: Biomaterials 19(19) (1998) 1763-1772.
- [5] M. Raessi, J. Mostaghimi, M. Bussmann: Thin Solid Films 506-507 (2006) 133-135.
- [6] X. Ning, J. Jang, H. Kim: Appl. Surf. Sci. 253(18) (2007) 7449-7455.
- [7] P. Fauchais, M. Vardelle: Pure & Appl. Chem. 66(6) (1994) 1247-1258.
- [8] H. Seiner, J. Cizek, P. Sedlak, R. Huang, J. Cupera, I. Dlouhy, M. Landa: Surf. Coat. Technol. 291 (2016) 342-347.
- [9] J. Cizek et al: J. Therm. Spray. Technol. 24(5) (2015) 758-768.
- [10] J. Cizek, O. Kovarik, J. Siegl, K.A. Khor, I. Dlouhy: Surf. Coat. Technol. 217 (2013) 23-33.
- [11] B. At-Mangour, R. Mongrain, E. Irissou, S. Yue: Surf. Coat. Technol. 216(1) (2013) 297-307.
- [12] B. Wielage, T. Grund, C. Rupprecht, S. Kuemmel: Surf. Coat. Technol. 205(4) (2010) 1115-1118.
- [13] J. Cizek, O. Man, P. Roupova, K. Loke, I. Dlouhy: Surf. Coat. Technol. 268 (2015) 85-89.
- [14] S. Grigoriev, A. Okunkova, A. Sova, P. Bertrand, I. Smurov: Surf. Coat. Technol. 268(12) (2015) 77-84.
- [15] V. Jan, J. Cupera, J. Cizek: Surf. Coat. Technol. 268 (2015) 216-223.
- [16] K. Spencer, V. Llzín, N. Matthews, M.X. Zhang: Surf. Coat. Technol. 206(19-20) (2012) 4249-4255.
- [17] J. Pattison, S. Celotto, R. Morgatr, M. Bray, W. O'Neill: Int. J. Machine Tools Manuf. 47(3-4) (2007) 627-634.
- [18] A. Sova, T. Gorigiev, A. Okunkova, I. Smurov: Int. J. Adv. Manuf. Technol. 69(9) (2013) 2269-2278.
- [19] V.K. Champagne, P.F. Leyman, D.J. Helfrich: Magnesium Repair by Cold Spray. Army Research Laboratory, 2008, USA.
- [20] F. Gärtner, T. Stoltenhoff, T. Schmidt, H. Kreye: J. Therm. Spray. Technol. 15(2) (2016) 223-232.
- [21] S. Marx, P. A. Köhler, G. Hüttel: J. Therm. Spray. Technol. 15(2) (2006) 177-183.
- [22] Lee JC, Kang HJ, Chu WS, Ahn SH.: CIRP Annals - Manufacturing Technology. 56(1) (2007) 577-580.

[23] M. Dyčka, et al: In Metal 2015. Ostrava: Tanger, 2015, pp. 147-154.

Tanger, 2015, pp. 157-166.

[24] I. Páleníková, et al: In Metal 2015. Ostrava:

[25] T. Novoselova, P. Fox, R. Morgan, W. O'Neill: Surf. Coat. Technol. 200(8) (2006) 2775–2783.



OPTIMIZATION OF WELDING PARAMETERS OF Ti6Al4V ALLOY USING ELECTRON BEAM

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Resume

Titanium alloys and their weld joints find wide application, in particular in the aircraft, automotive and chemical industries, because of their outstanding specific strength and corrosion resistance. The high reactivity of these alloys and the strong degradation effect of elements contained in the atmosphere (H, N and O) make it necessary for these alloys to be welded in protective atmospheres or in vacuum. From this viewpoint, Electron Beam Welding is an advantageous welding technology, especially in large series production. In the literature, there is sufficient information about the effect of the basic welding parameters, namely accelerating voltage, current and welding speed, on the properties of welded joints. In the paper, the effects of the spot diameter and beam focusing on the penetration depth and the weld shape in the Ti6Al4V alloy are studied. The results obtained are complemented by an analysis of the microstructure and microhardness measurements across the welds.

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1. Introduction

Titanium and its alloys are one of the best engineering materials for use in industrial applications [1, 2]. This is due to their properties such as excellent strength-to-density ratio, high fatigue strength, toughness, and good corrosion resistance. These properties make titanium alloys attractive for aerospace applications [3] and also for many chemical, marine, military and sports applications, even though the price of these alloys is relatively high.

Ti6Al4V alloy is the most widely used titanium alloy, accounting for more than 60 % of the world production of this alloy and serves as the world standard in aerospace applications [4]. At room temperature, this alloy contains the HCP α phase and the BCC β -phase. The mechanical and physical properties of this alloy are controlled by microstructural

development during thermo-mechanical processing [5, 6].

At temperatures above 350 °C, particularly in molten state, titanium is very reactive with atmospheric oxygen, nitrogen, hydrogen, and carbon. These interstitial elements reduce ductility and toughness and increase strength and hardness [6]. Contamination by these elements during welding can be caused by poor preparation and cleaning of the joint and filler materials, poor shielding of the weld zone or impurities in the gas.

Titanium may be joined by a variety of conventional fusion welding processes, but its chemical reactivity requires precaution in order to avoid contamination of the fusion and heat-affected zones. Fusion welding of titanium alloy is possible in inert gas shielded arc and high-energy beam welding processes such as Electron

Beam Welding (EBW) and plasma welding [7]. The EBW process is considered superior to others because of the deep and narrow weld zone, reduced heat-affected zone (HAZ) and high reliability. EBW is used relatively often for the welding of Ti alloys, since welding is carried out inside a chamber in which a vacuum is maintained to protect the weld from contamination. Great joint depth, which can be achieved with a high beam power density (1.5×10^4 to $1.5 \times 10^5 \text{ W} \cdot \text{mm}^{-2}$), and keyhole-mode welding increase the productivity and reduce heat input in comparison to arc-welding processes [8].

The effect of accelerating voltage (U), beam current (I) and welding speed (v) on the depth of penetration and the whole geometry of the weld were studied in [9] for Ti6Al4V alloy via a series

of weld trials. The objective of the present study was to optimize the welding parameters of commercial Ti6Al4V alloy by EBW, namely the influence of the spot diameter and the distance of the EB focus from the surface, the size and shape of the weld (weld penetration, the width of the weld metal and HAZ), the microstructure and hardness of individual areas.

2. Experimental material and procedures

The Ti6Al4V alloy was produced by the VSMPO-AVISMA Corporation, Russia. Data on the chemical composition, given in Table I, and results of tensile tests of the alloy in as-supplied condition, that is, annealed at 780°C/1 h/air, have been taken from a copy of the “Inspection Certificate” (see Table 2).

Table 1

Chemical composition (in wt. %) of alloy Ti6Al4V.

Al	V	Fe	O	C	N	H	Ti
6.46	4.11	0.21	0.166	0.007	0.004	0.0055	balance

Table 2

Mechanical properties.

Orientation	Yield strength $R_{p0.2}$ (MPa)	Tensile strength R_{mT} (MPa)	Elongation A (%)
longitudinal	970-980	1000-1011	14.4-16.0
transverse	985-1010	1020-1040	14.6-15.0

Table 3

Varying parameters of EBW.

Specimen	Beam current I (mA)	Spot diameter (mm)	SURF (mA)
0-1	15 - 20	0.1	- 3
0-2	12 - 17	0.1	- 3
0-3	15 - 20	0.2	- 3
0-4	12 - 17	0.2	- 3
0-5	18	0.3	- 3
0-6	18	0.6	- 3
0-7	18	0.9	- 3
0-8	18	1.2	- 3
0-9	18	0.2	0
0-10	18	0.2	5
0-11	18	0.2	10
0-12	18	0.2	15
0-13	18	0.2	- 5
0-14	18	0.2	- 10
0-15	18	0.2	- 15
0-16	18	0.2	- 20

Material for individual tests was cut from an $8 \times 250 \times 1000$ mm sheet metal plate. Electron beam welding was carried out using an AG&COKGaA device with a K26 industrial welding chamber (a product of the German Probeam company). The parameters of the welds are given in Table 3, together with the designations of individual samples. With all the samples, the welding speed was identical ($20 \text{ mm} \cdot \text{s}^{-1}$) and so were the accelerating voltage used (120 kV) and the working distance (750 mm). The term spot diameter used in Table 3 corresponds to the diameter of electron beam circular scanning patterns, and the term SURF gives in the given case the values in mA corresponding roughly to the electron beam focusing above (+) and below (–) the surface of individual samples, in mm.

Specimens for the metallographic analysis were ground, polished and etched in Kroll's reagent (2 ml HF, 8 ml HNO_3 , 92 ml distilled H_2O). The study of microstructures was carried out using a Zeiss Axio optical microscope and a Zeiss Ultra Plus scanning electron microscope equipped with EDS Oxford analyser.

HV0.1 microhardness tests were conducted using a LECO LM 274AT device.

3. Results and discussion

The microstructure of the Ti6Al4V in as-supplied state (i.e. annealed state) is formed by polygonal grains of the α -phase and, on a much smaller scale, by irregular configurations of the β -phase, which mainly occurs on the α -phase boundaries, as evident in Fig. 1. Part of the α -phase is arranged in lines, with the β -phase occurring inside these grains. The α -phase is assumed to be the result of the transformation of the β -phase, which occurred at an annealing temperature of 780°C . Via the EDS method it was established that the content of vanadium in the β -phase ranged between 18 and

22 wt. %, which testified to the high value of the coefficient of interphase distribution of vanadium between the two coexisting phases. For the sake of completeness, it should be added that the aluminium content measured in the β -phase is within a narrow range of 2.5 - 4.8 wt. %. In the case of the chemical composition of the α -phase it is quite the contrary (8.6 - 9.6 wt. % Al and 2.8 - 3.3 wt. % V). The state described above is probably a non-equilibrium state.

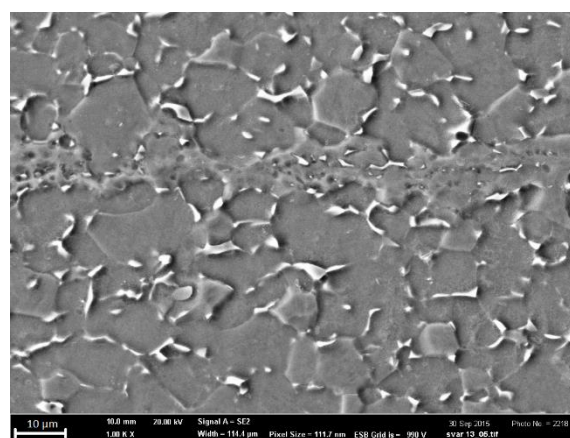


Fig. 1. Microstructure of base material, etch. Kroll, SEM.

One of the pictures of the structure of the welds is given in Fig. 2. Evaluating the structures of all the weld variants given in Table 3 revealed that in the welds there were no discontinuities of the crack and bubble types. The obtained set of pictures of weld structures made it possible to determine the weld depth and the shape and size of the weld metal (WM) and heat-affected zone (HAZ). The shapes and dimensions of the welds are given in Figs. 3 and 4 for individual sizes of the spot diameter, with the beam current, accelerating voltage and welding speed remaining constant. It is obvious from Figs. 3 and 4 that with increasing values of the spot diameter the weld depth decreases markedly while the width of WM (molten pool) increases. The shape and dimensions of the weld, that is, the values of WM and HAZ, also change analogously, with the HAZ width barely changing with the spot diameter value.

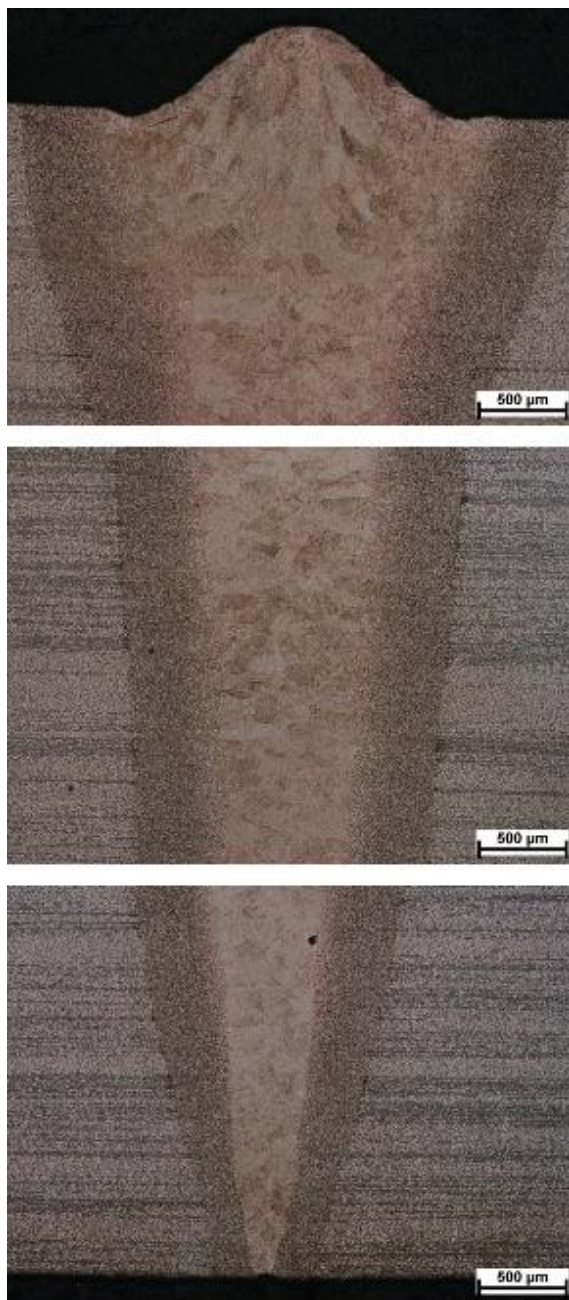


Fig. 2. Macrophotography of EB weld joint.
(full colour version available online)

A simple relation holds for the beam diameter, $d = s I/U$, where I is the beam current, U is the accelerating voltage, and s is a constant given by the electron gun optics. Thus in our case the beam diameter was constant. If the beam diameter or the size of spot diameter increases, it can be expected that for a given beam energy given by the $U \cdot I$ product the energy will accumulate in a larger volume of material and, consequently, the weld depth will decrease.

For a weld depth b , the authors of [9] give the Equation (1)

$$b = C \frac{P}{TD} \sqrt{\frac{K}{vd}} \quad (1)$$

where C is a constant, P is the beam power, T is the melting point, D is the thermal diffusivity, k is the thermal conductivity and v is welding speed. T , D and k are physical constants so Equation (1) can be rewritten in the form (2)

$$b = CPC_1 \sqrt{\frac{1}{vd}} \quad (2)$$

where $C_1 = \sqrt{K}/TD$ is the material constant. In the given case, the beam diameter in Equation (2) can be replaced by the spot diameter size; then with increasing spot diameter size the weld depth decreases and the weld shape is also changed, as can be seen from Figs. 3 and 4. From the weld shape it can be concluded that for a spot diameter larger than 0.3 mm the mechanism of beam penetration operating in this case is predominantly conduction-mode welding.

The growing value of positive focusing results in an increased diameter of the beam incident on the surface, which, in agreement with Equation (2), leads to decreasing weld depth with increasing distance of focusing of the EB on the surface of the metal sheet (quantified as the “SURF” value); by contrast, the width of WM and HAZ increased on the surface of metal sheet, with the overall shape of the weld remaining almost without change (Fig. 5).

The growing size of negative focusing up to -10 mA led to increasing weld depth; increasing the negative focusing still further had the opposite effect and the weld shapes then corresponded to the removal (predominantly by conduction) of the introduced heat (see Figs. 5 and 6).

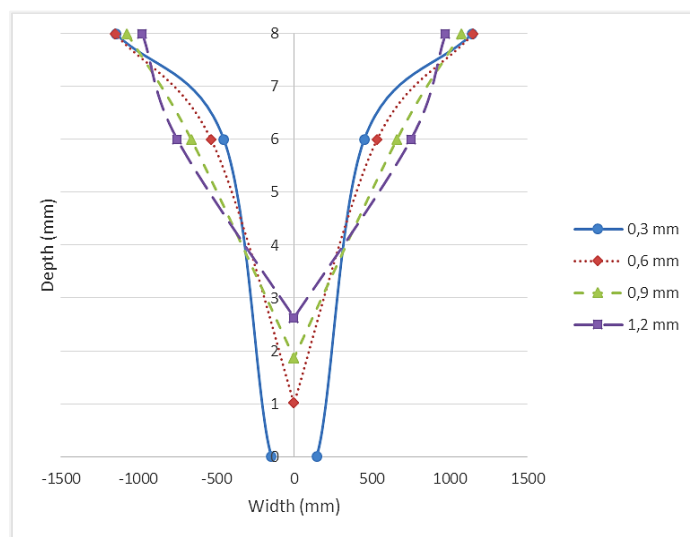


Fig. 3. Influence of the "Spot" on the WM size and shape.
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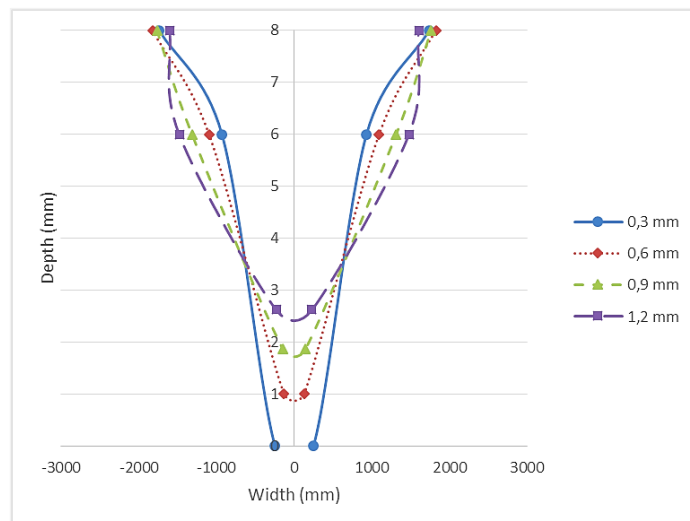


Fig. 4. Influence of the "Spot" on the weld size and shape.
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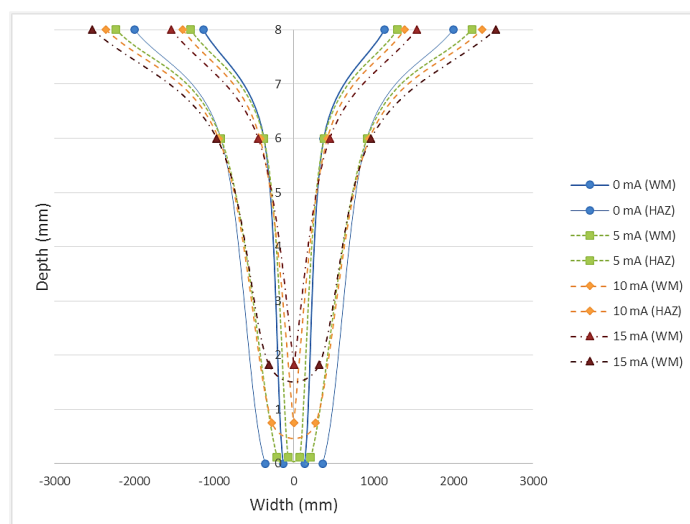


Fig. 5. Shape and dimensions of the welds depending on the size of positive focusing.
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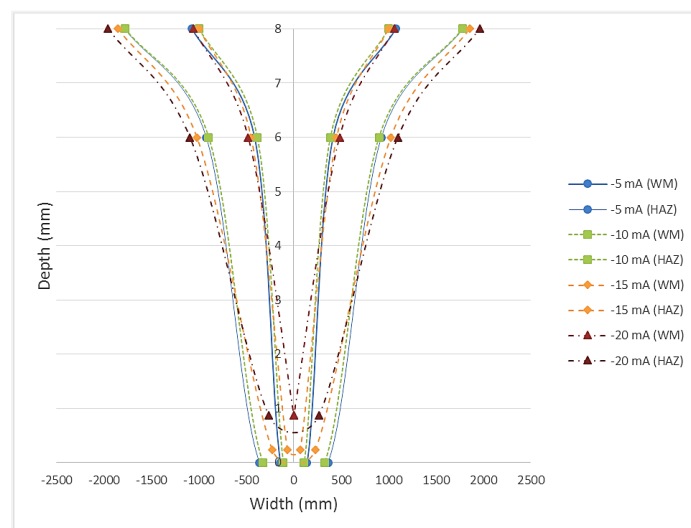


Fig. 6. Shape and dimensions of the welds depending on the size of negative focusing.
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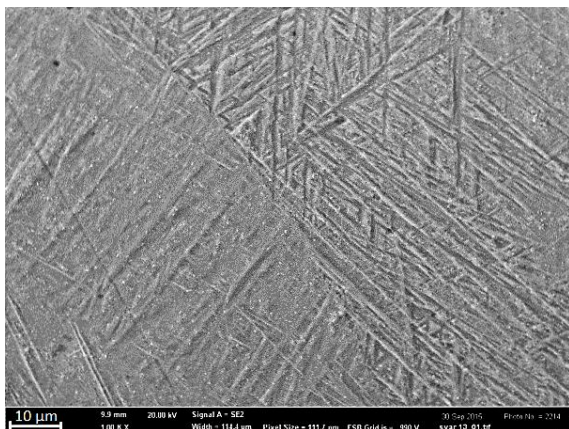


Fig. 7. Microstructure of WM, etch. Kroll, SEM.

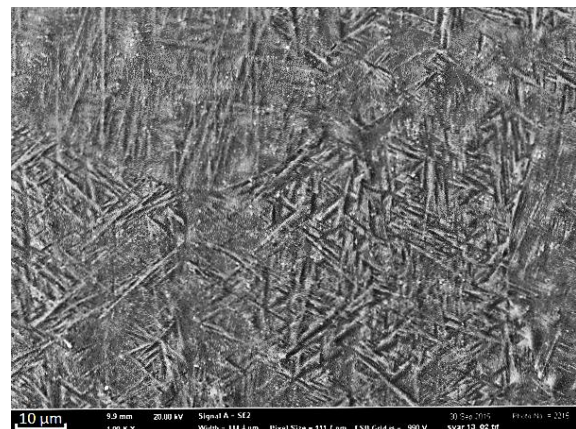


Fig. 8. Microstructure of HAZ
(with HAZ followed by WM), etch. Kroll, SEM.

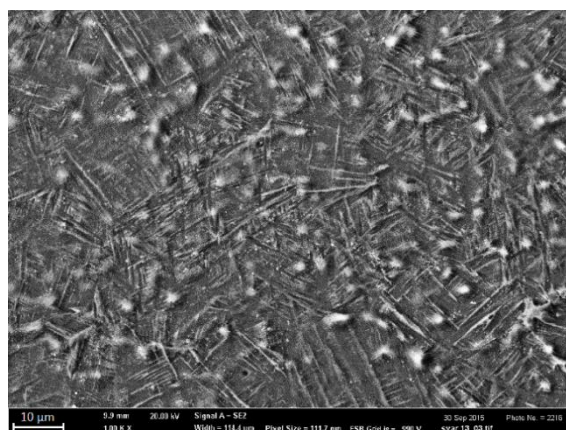


Fig. 9. Microstructure of HAZ (with HAZ followed by BM), etch. Kroll, SEM.

The microstructure of the weld metal is formed by α' martensite and, to a lesser degree, probably also by the β -phase (Fig. 7). The structure of HAZ changes continuously from a predominantly martensitic structure with a major proportion of non-transformed β -phase (Fig. 8) to a structure close to the basic material (Fig. 9). The latter is formed by a mixture of α -phase of acicular and polygonal morphology with the β -phase, whose content is higher when compared with unaffected basic material.

The microstructure analysis was complemented by the measurement of the content of titanium, aluminum and vanadium across the weld interface, using the EDS method, on a line segment 800 μm in length (700 points).

The results of this analysis are given in graphical form in Fig. 10. It is evident from this figure that in the course of welding in a vacuum (pressure 3 to 8×10^{-5} mbar) there was no selective evaporation of any of the elements under analysis, which is also attested by the mean concentration values of Ti, Al and V, as calculated for WM and BM (Table 4). It is evident from the standard deviation values, also given in Table 4, that for vanadium they are higher in the case of the BM than in the case of with the WM. This finding is associated with the larger dimensions of the β -phase in the BM and, as mentioned earlier, with the fact that the concentration of vanadium in this phase attains values of up to 22 wt. %.

Table 4

Concentrations in wt. % of Ti, Al and V in weld zones.			
Area	Ti	Al	V
WM	90.0 $\pm$ 1.0	5.7 $\pm$ 0.5	4.3 $\pm$ 0.9
BM	90.1 $\pm$ 1.5	5.7 $\pm$ 0.6	4.2 $\pm$ 1.5

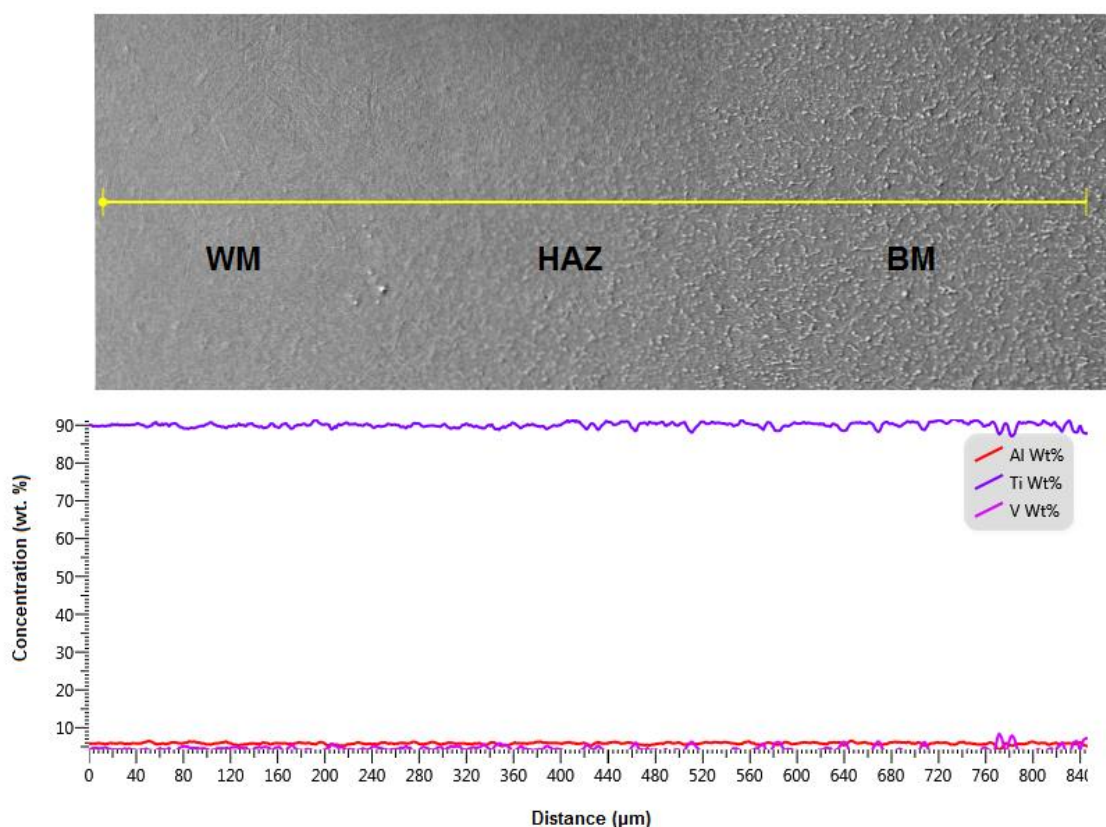


Fig. 10. Concentration distribution of Ti, Al and V across the weld.
(full colour version available online)

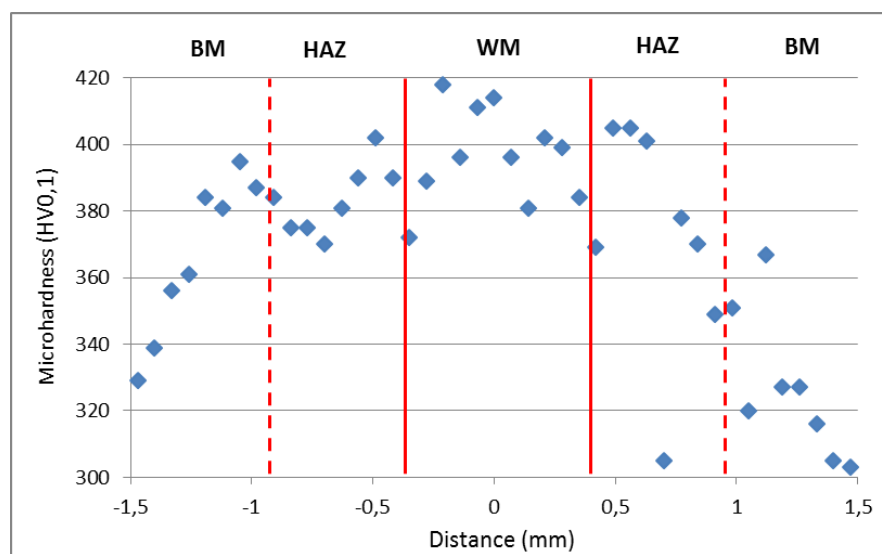


Fig. 11. Microhardness HV0.1 across the weld, spec. 14.
(full colour version available online)

An example of the development of HV0.1 microhardness values across the weld of sample 14 can be seen in Fig. 11. The values of 380 - 420 HV0.1 correspond to the martensitic structure of WM in the whole set of samples; the same values were measured by the authors of [9]. Laboratory heat treatment - quenching at 1035 °C/10 min/water - led to the value of 390 HV1 with predominantly martensitic structure while the heat treatment mode 1035 °C/10 min/water with predominantly acicular and less frequently Widmannstätten morphology of the α -phase led to the value of 320 HV1, with a BM hardness of 330 HV0.1. The HV values under different loading are not fully comparable but it can be said that substantial differences in the microstructure correspond with pronounced changes in hardness values. In the welds examined, the differences in values between WM and BM amounted to as much as 70 HV0.1. The same differences were observed by the authors of [10], who additionally compared the results of tensile tests and impact bending tests on samples taken from BM and EBW. In the case of EBW the fracture surfaces were in the WM. It follows from the above comparison that the yield point values (960 MPa) and tensile strength values

(1000 MPa) do not change but in WM there were drops in the values of elongation (12.7 → 7.7 %), contraction (34.3 → 21.0 %) and impact energy (16 → 10 J). The weld joint is thus considerably more brittle and must therefore be annealed.

4. Conclusions

The effects of spot diameter in the range of 0.3 - 1.2 mm and focusing in the interval of -20 to +15 mA, on the penetration depth and weld shape in Ti6Al4V alloy were studied under constant values of the beam current I (18 mA), accelerating voltage U (120 kV) and welding speed v (20 mm·s⁻¹). The study yielded the following knowledge:

- Increasing the size of the spot diameter has the same effect on the weld depth as the beam diameter, that is, with increasing spot diameter the depth of the weld decreases and the weld width increases, particularly in the weld face area.
- Positive focusing of the electron beam has an analogous effect on the weld depth to increases in the spot diameter value.
- Increasing the negative focusing to -10 mA led to increased weld depth; increasing the negative focusing still further had the opposite effect.

- The conditions in which the welds were produced probably did not lead to selective evaporation of the alloy elements (verified for a spot diameter of 0.2 mm and focusing of -10 mA).
- The marked differences in the hardness values of WM (400 HV0.1) and BM (335 HV0.1) indicate the necessity of post-weld heat treatment of real welds.
- For the 8 mm thick metal sheet and the I, U and v values used, the spot diameter should range between 0.3 and 0.6 mm with focusing at -3 mA, while focusing should acquire values of +5 mA (too wide a weld) and -5 mA (to be preferred).

Acknowledgements

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References

- [1] R.R. Boyer, G. Welsch, E.W. Collings, eds.: Materials properties handbook: Titanium and titanium alloys, ASM International, Materials Park, OH 1994.
- [2] M.J. Donachie: Titanium: A Technical Guide, 2nd edition, ASM International, Materials Park, OH 2000.
- [3] R.R. Boyer: Mater. Sci. and Eng. A213 (1996) 103-114.
- [4] J.L. Barreda, F. Santamaria, X. Azpiroz, A. M. Irisarri and J. M.. Varona: Vacuum 62(2-3) (2001) 143-150.
- [5] S. Banerjee, P. Mukhopadhyay: Phase Transformation, Examples from Titanium and Zirkonium Alloys, Elsevier 2007.
- [6] G. Lütjering: Mater. Sci. Eng. A243 (1998) 32-45.
- [7] Li, Leijun et al. eds.: ASM Handbook: Welding Fundamentals and Processes, Vol. 6A. ASM International, Materials Park, OH 2011.
- [8] H. Schultz: In: Electron Beam Welding, Woodhead Publishing Ltd. 1994.
- [9] T.S. Balasubramanian, M. Balakrishnan, V. Balasubramanian, M.A. Muthu Manickam: STWJ 16(8) (2011) 702-708.
- [10] G. Thomas, V. Ramachandra, K. V. Nagarajan, B. Pant, B. K. Sarkar and R. Vasudevan: In: Welding Research Supplement, 1989, pp. 336-341.



EFFECT OF MILLING AGENT (METHANOL) ON PHASE COMPOSITION AND STRUCTURE OF AlCoCrFeNiTi_{0.5} HIGH ENTROPY ALLOY POWDERS

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Resume

In the last decade, high-entropy alloys (multi-principal element alloys) were developed as a new family of materials with high application potential. The effects of anti-agglomeration milling agent on the phase composition, structure, and size of non-equiatomic AlCoCrFeNiTi_{0.5} mechanically milled powders were investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) with an energy dispersive spectroscopy (EDS) detector were utilized for microstructural analyses. During mechanical alloying (MA), a supersaturated Cr-based solid solution with BCC structure with significantly reduced grain size was formed after 10 hours of milling. During the annealing of milled powders, this solid solution decomposed into a mixture of four different phases. It was found that the use of milling agent had an extensive influence on the milled powders' properties. Significant differences in phase composition, microstructure, and powder particle size were observed, with more favourable results in the case of milling in the presence of the milling agent.

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1. Introduction

High-entropy alloys (HEAs), proposed by Yeh et al. [1], are multicomponent alloys with simple solid solution phases. They consist of more than four elements in equimolar or near-equimolar ratio, in contrast to traditional alloys, which are based on only one element with a structure composed of a mixture of solid solution and ordered intermediate phases. The stability of any phase in the structure can be calculated by the equation (1):

$$\Delta G = \Delta H - T \Delta S \quad (1)$$

where ΔG is the Gibbs free energy, T is temperature, ΔH is the mixing or formation enthalpy, and finally ΔS refers to entropy.

The more negative the Gibbs free energy becomes, the more stable the particular phase is. A means of stabilizing solid solution phase is by increasing the entropy (sometimes referred to as the level of disorder). If we consider only the configurational entropy of the solid solution consisting of different elements, it can be calculated by the equation (2):

$$\Delta S_{conf} \cong -R \sum_{i=1}^n c_i \ln c_i \quad (2)$$

where R refers to the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). From this expression, we can assume that the entropy will be higher when an increasing amount of constituent elements have equiatomic concentrations [2]. When the entropy is high enough, it suppresses the formation of ordered

phases, and a stable high-entropy state (simple solid solution) is achieved. These alloys should benefit from solid solution strengthening of many elements with different atomic radii present in the lattice, causing severe lattice strain, while retaining reasonable ductility due to inherent BCC and FCC solid solution plasticity [3]. Consequently, many interesting properties arise from this unique structure, such as a good combination of strength and ductility [4], outstanding low-temperature ductility and fracture resistance [5], high-temperature creep resistance and strength [6, 7], high hot wear resistance [8], good electrochemical properties [9], and so on.

Mechanical alloying (MA) is a solid-state powder-processing technique involving repeated cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill [10]. In combination with the proper densification method, it is a simple yet efficient method for preparation of many advanced materials including high-entropy alloys [11, 12, 13]. In the MA process, for efficient milling of metal powders, the use of milling agent is needed to prevent excessive cold welding, which results in coarsening of powder particles, sticking of the powders to the milling vessel and balls, and decreased milling yield [14]. In general, surface-active liquid like ethanol or stearic acid is used. The most significant disadvantage of the introduction of organic milling agents is without doubt the resulting contamination of the powders by elements contained in the milling agent, most notably C, O, and sometimes N. These usually form very stable ceramic compounds and decrease the final mechanical properties of the materials [10]; they can also influence the overall phase composition and alloying behaviour [15]. Another concept could be to use this phenomenon for the production of in situ reinforced metal-ceramic composites [16].

Although HEA powders have been produced by MA in the past, a systematic research on the effect of milling agent use

on the phase composition, size, morphology, and structure of powders has not yet been reported.

2. Experimental setup

AlCoCrFeNiTi_{0.5} (in atomic proportions) HEA powders were prepared by MA of the elemental powders. Elemental powders of Fe, Ni, Cr, Al, Co, and Ti with commercial purity and mean particle size of 45 μm (325 mesh) were put into a steel milling bowl with 15-mm diameter balls and sealed with argon gas. A ball-to-powder ratio of 10:1 was used. The sealed bowl was then moved to a high-energy planetary ball milling machine (Pulverisette 6). Powders were milled at a speed of 400 rounds per minute. The milling process was carried out either in the presence of methanol as a milling medium or without it. After milling, both powders were subjected to annealing in a tube furnace with high purity argon gas for 1 h at 1050 °C with subsequent furnace cooling. The microstructures of the produced materials were evaluated using a Carl Zeiss scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS) detector. The X-ray diffraction (XRD) technique was used to observe the structural changes of powders during milling and annealing. A Philips X'Pert diffractometer (40 kV) with Co K α radiation ($\lambda = 1.790307 \text{ \AA}$) was used for measurements. The XRD patterns were recorded in the 2θ range of 30-120° and analysed with X'Pert High Score Plus software. Rietveld method using has been utilized for crystallite size determination. Hardness measurement was carried out on Vickers microhardness meter Leco LM 247AT with load of 25g.

3. Results and discussion

In Fig. 1a,b, the powder XRD patterns are presented. It can be clearly seen that after mechanical milling, one supersaturated BCC solid solution with a lattice parameter of 2.87 $\text{\AA}$

was formed in both cases, regardless of the use of the milling agent (methanol). Extensive peak broadening is a sign of grain refinement induced by drastic cold deformation during the milling process. There is a considerable difference in the calculated crystallite size, which was 50.1 Å for powder milled with methanol and 69.1 Å without this agent. This phenomenon indicates the beneficial effect of the use of milling agent. The phase composition after annealing is however completely different (Fig. 2a, b). Powders milled with methanol are composed of ordered B2 NiAl like phase (visible superlattice (100) peak), face-centred cubic (FCC) phase, a minor tetragonal sigma phase, and titanium carbide phases. The presence of tetragonal sigma phase has been reported in HEA systems in the past [17] and is most likely attributed to slow cooling after the annealing temperature. Titanium carbide is the result of the titanium reaction with methanol during annealing. Methanol

is an organic compound consisting of carbon and oxygen. During milling, it disintegrated and dissolved into the powder particles' lattices. Titanium has a high affinity for carbon and therefore formed titanium carbide upon heating. This process is sometimes referred to as mechanically activated synthesis [18]. Compared to this, the powder milled without methanol consists of only two major phases, namely ordered B2 and sigma phase with traces of FCC peaks. The slight shift in the peak of the B2 phase seen in Fig. 3 suggests a small difference in the phase lattice parameter and therefore a different chemical composition from the previous case. This is most probably the result of the presence of titanium in the B2 lattice, unlike in the case of powder milled with methanol, where titanium was trapped in titanium carbide. Both of these ordered phases, especially the sigma phase, are considered extremely brittle, and therefore bulk materials prepared from this powder would also most probably be brittle.

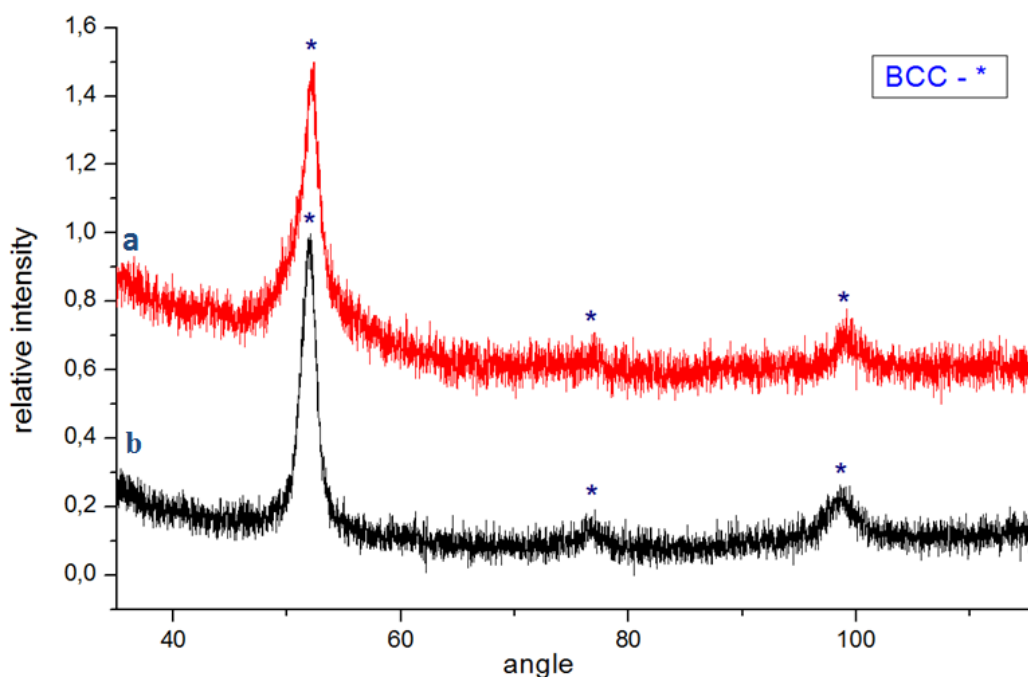


Fig. 1. XRD patterns of powders after mechanical alloying for 10h with 400RPM milling speed of: a) powder with use of milling agent b) powder without use of milling agent.
(full colour version available online)

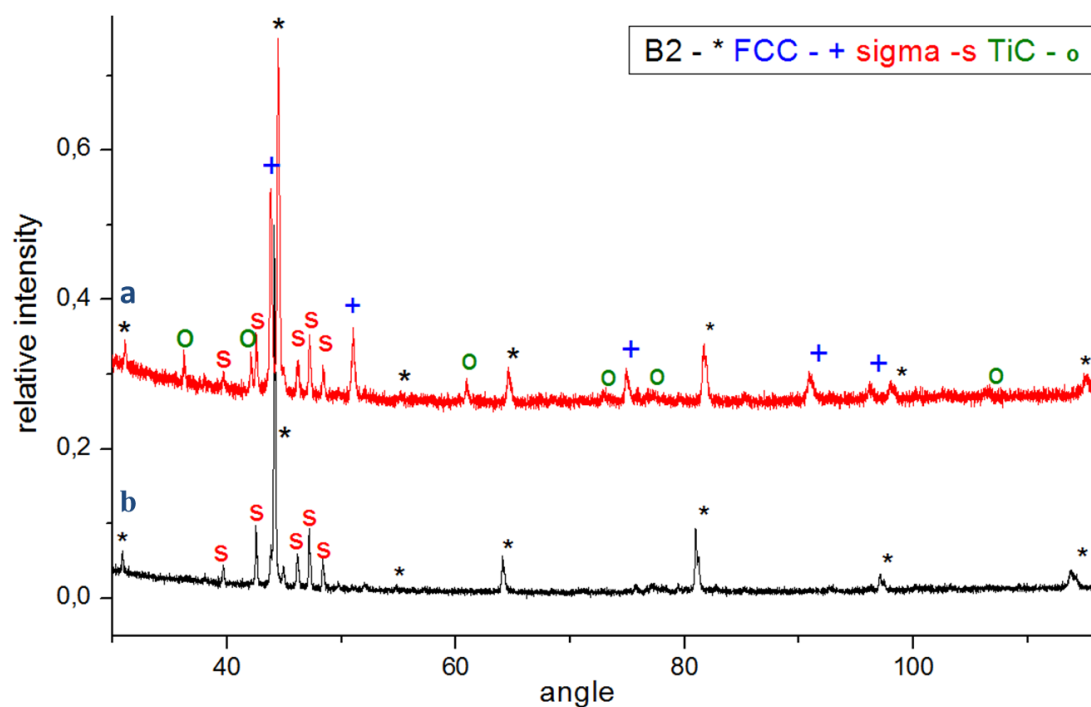


Fig. 2. XRD patterns of powders after mechanical alloying and annealing of: a) powder with use of milling agent b) powder without use of milling agent.
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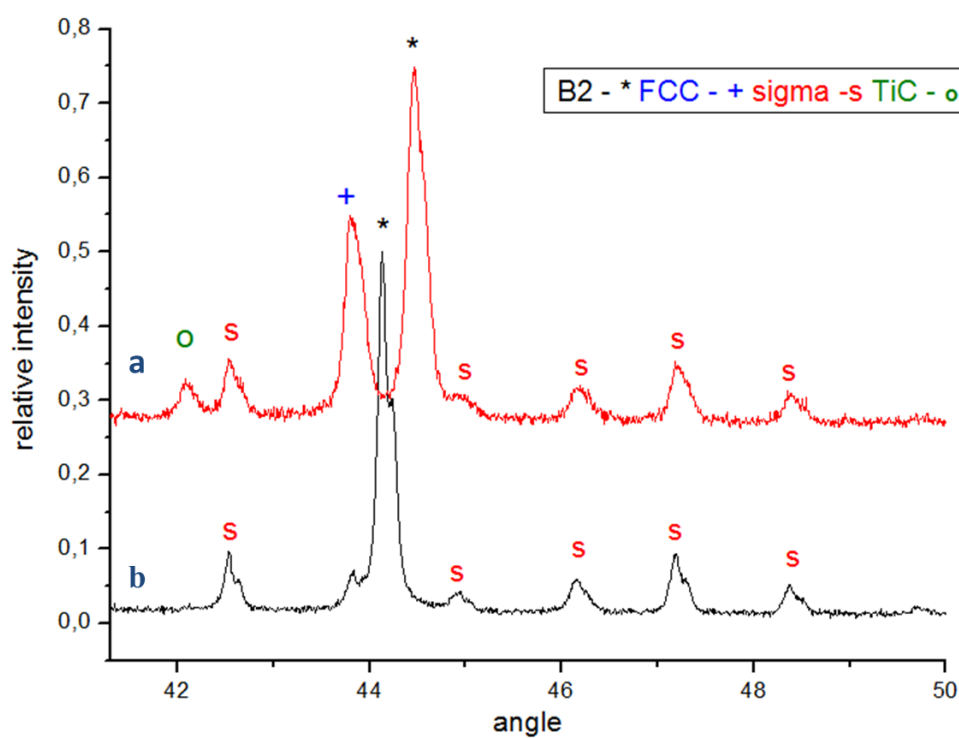


Fig. 3. XRD patterns of powders after mechanical alloying and annealing close up: a) powder with use of milling agent b) powder without use of milling agent.
(full colour version available online)

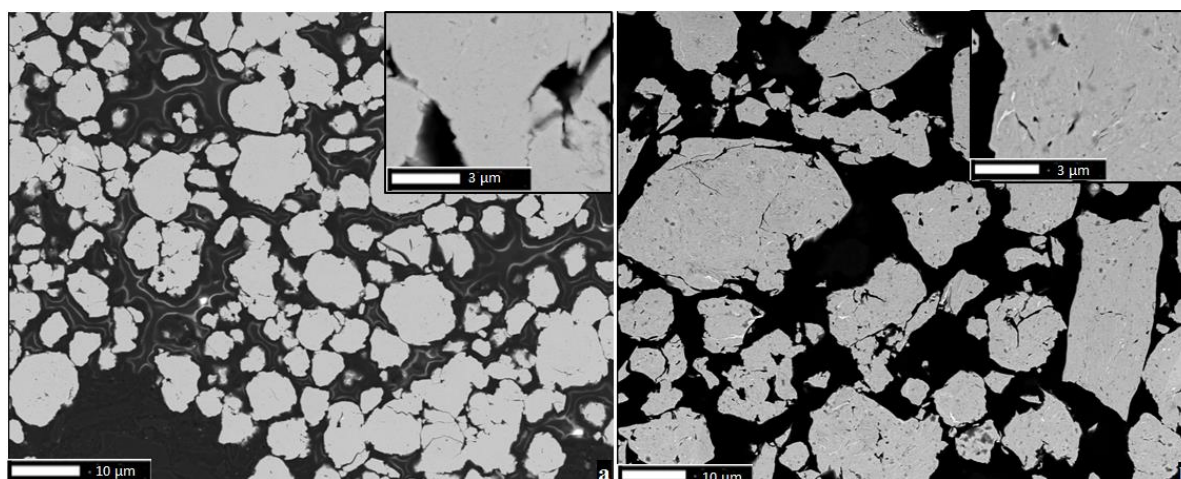


Fig. 4. SEM images of microstructure in backscattered mode after mechanical alloying of a) powder with use of milling agent b) powder without use of milling agent.

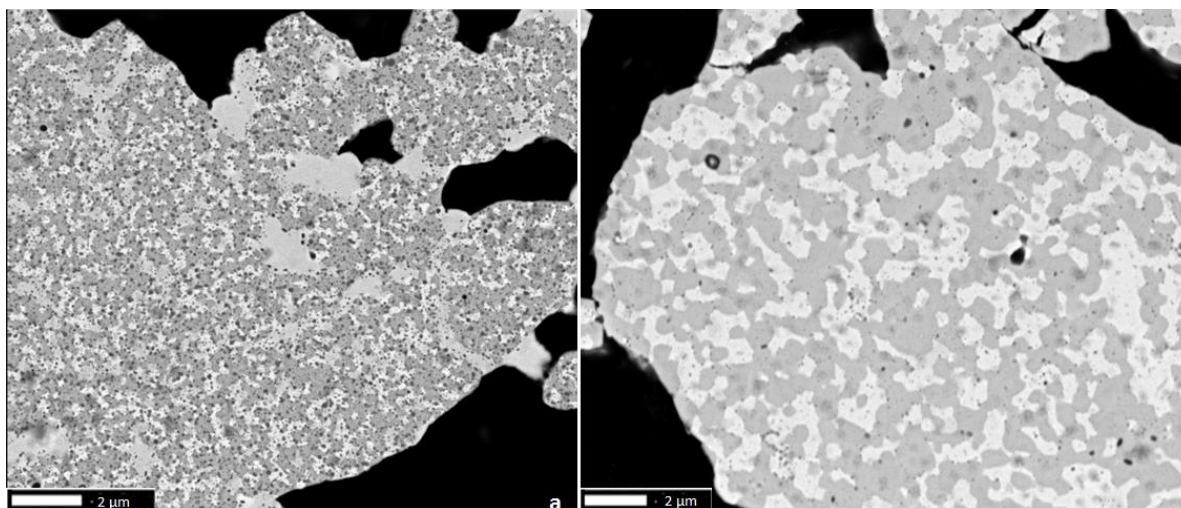


Fig. 5. SEM images of microstructure in backscattered mode after mechanical alloying and annealing of: a) powder with use of milling agent b) powder without use of milling agent.

Table 1
Elemental composition of the microstructural features of annealed powders milled with milling agent.

Element (at. %)	Al	Ti	Cr	Fe	Co	Ni
Grey phase (B2+TiC)	23.5	12.4	11.7	14.01	17.1	21.0
White phase (FCC+sigma)	4.95	1.79	25.6	33.4	20.6	13.5

Table 2
Elemental composition of the microstructural features of annealed powders milled without milling agent.

Element (at. %)	Al	Ti	Cr	Fe	Co	Ni
Grey phase (B2)	27.67	14.31	5.42	10.25	20.32	22.00
White phase (sigma)	6.23	2.28	39.10	33.10	13.00	15.90

Comparing the SEM images in Fig. 4, a coarser particle size is evident for the powder milled without methanol, in which structural inhomogeneities were present in the form of layers seen in the close up view in Fig. 4b. These layers with different shades of grey in BSE mode (different chemical compositions) are the remains of the original deformed powder particles. These were not sufficiently fractured during mechanical milling. On the other hand, the powders milled in the presence of methanol show almost perfect chemical homogeneity. Therefore, it can be concluded that methanol, a surface-active agent, is adsorbed on the particle surfaces and promotes powder fracturing and subsequently the quality of the mechano-chemical alloying process. The differences in structures are even more visible in the case of annealed powders (Fig. 5). For powders milled in the presence of methanol, an extremely fine microstructure is obtained. Bearing in mind the results of the XRD phase analysis and EDS point chemical analysis (Table 1 and 2), we can assume that white phase is FCC Cr-Fe enriched phase or a mixture of FCC and sigma phases. Grey phase appears to be an Al- and Ni-enriched ordered B2 phase with fine dispersion of titanium carbide present as black dots. These particles are probably the key cause of the very fine grain size of the whole structure, as they trap grain boundaries during heating, thus preventing grain growth. Unfortunately the size of most grains was well under the resolution limit of EDS point analysis, and therefore it was impossible to measure every phase separately. However, powders milled without the presence of methanol have comparably coarser grains of white Cr-Fe-enriched sigma phase and grey Al-Ni-based B2 phase.

The size of few powder particles was sufficient to perform microhardness test presented in Table 3. Both powders showed very high hardness levels, namely 789HV for powders after milling with methanol and 753HV for powders without methanol.

Due to small difference in average hardness values, we can assume that milling agent has only negligible effect on hardness after milling. Relatively high hardness is most probably result of extensive work hardening during milling process. However after annealing process, the difference in hardness becomes more apparent, attributing to differences in phase composition. Annealed powders milled with methanol exhibit hardness of 881HV in contrast to 630HV for powders milled without it. This is most probably due to simultaneous contribution of finer grain structure, and dispersion strengthening of extremely hard carbide phases. Another phenomenon occurred, when softer powders milled without methanol were surprisingly seemingly more prone to cracking during indentations. This could be the consequence of inherently more brittle structure composed of B2 and sigma ordered phases as suggested before.

Table 3
Microhardness test results with 25g load.

Milling agent	Milled hardness	Annealed hardness
Methanol	789	881
None	753	630

Based on the previous results it can be summarized that the effect of the milling agent on mechanically milled powders is questionable. It improves the process of alloying during milling and also reduces the powder particle size and crystallite size. It also promotes the formation of the extremely fine stable titanium carbide dispersions preventing the grain coarsening during high temperature annealing thus increasing hardness of the structure. On the other hand dispersion of titanium carbide could decrease fracture toughness of bulk alloy produced from the powders. Therefore its application to the alloying process should be considered, depending on desired properties of the resulting powder compacts.

4. Conclusions

High entropy alloy powders were successfully synthesized by mechanical milling with and without the addition of methanol as milling agent. Significant influence of milling agent on phase composition, powder particles size and milling performance has been observed, namely:

- the milling agent promotes mechanical alloying process during milling and prevents powder agglomeration, therefore decreasing particle size and slightly crystallite size as well;
- by introduction of methanol to process, dispersion of fine titanium carbide is formed upon heating, significantly changing hardness and phase composition of the alloy powders;
- titanium carbide dispersion inhibits grain coarsening of the structure during annealing, its effect on fracture resistance needs further investigation.

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References

- [1] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.-H. Tsau, S.-Y. Chang: Adv. Eng. Mater. 6(5) (2004) 299–303.
- [2] K. Zhang, Z. Fu: Intermetallics. 22 (2012) 24-32.
- [3] Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z.P. Lu: Prog. Mater. Sci. 61 (2014) 1-93.
- [4] Y. Wang, S. Ma, X. Chen, J. Shi, Y. Zhang, J. Qiao: Acta Metall. Sin. English Lett. 26(3) (2013) 277-284.
- [5] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie: Sci. 345 (2014) 1153-1158.
- [6] W.-R. Wang, W.-L. Wang, J.-W. Yeh: J. Alloys Compd. 589 (2014) 143-152.
- [7] Y.-J. Chang, A.-C. Yeh: J. Alloys Compd. 653 (2015) 379-385.
- [8] M.-H. Chuang, M.-H. Tsai, W.-R. Wang, S.-J. Lin, J.-W. Yeh: Acta Mater. 59(16) (2011) 6308-6317.
- [9] Y.Y. Chen, U.T. Hong, H.C. Shih, J.W. Yeh, T. Duval: Corros. Sci. 47(11) (2005) 2679-2699.
- [10] C. Suryanarayana: Prog. Mater. Sci. 46(1-2) (2001) 1-184.
- [11] J. Joardar, S.K. Pabi, B.S. Murty: J. Alloys Compd. 429(1-2) (2007) 204-210.
- [12] Z. Fu, W. Chen, H. Xiao, L. Zhou, D. Zhu, S. Yang: Mater. Des. 44 (2013) 535-539.
- [13] S. Fang, W. Chen, Z. Fu: Mater. Des. 54 (2014) 973-979.
- [14] A. Nouri, C. Wen: Solid State Mater. Sci. 39(2) (2014) 81-108.
- [15] J. Keskinen, A. Pogany, J. Rubin, P. Ruuskanen: Mater. Sci. Eng. A. 196(1-2) (1995) 205-211.
- [16] J.J. Le Claire, E.A. Laitila, D.E. Mikkola: Scr. Mater. 50(1) (2004) 95-98.
- [17] I. Moravcik, J. Cizek, P. Gavendova, S. Sheikh, G. Sheng, I. Dlouhy: Mat. Letters - submitted to the journal.
- [18] M.-H. Tsai, K.-Y. Tsai, C.-W. Tsai, C. Lee, C.-C. Juan, J.-W. Yeh: Mater. Res. Lett. 1(4) (2013) 207-212.
- [19] M. Razavi, M.R. Rahimipour, R. Kaboli: J. Alloys Compd. 460(1-2) (2008) 694-698.



INFLUENCE OF PROCESSING ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF MAGNESIUM ALLOY AZ91

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Resume

This paper deals with differences of mechanical characteristics and fracture surface morphology of AZ91 magnesium alloy in extruded state and after subsequent equal channel angular pressing (ECAP). According to the results, the tensile properties were not controlled by grain size only as values of the tensile strength and 0.2 proof stress were similar for both alloys despite having average grain size 15.9 μm for the extruded alloy and 1.2 μm for the ECAPed alloy. In contrast, microhardness seemed to be dependent solely on the grain size. Fractographic analysis has shown changes in the damage mode from quasi-cleavage fracture in extruded state to rather ductile fracture with dimple morphology in exECAPed state during tensile loading.

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1. Introduction

As one of the lightest metallic structural materials, magnesium and its alloys are promising materials in various applications in industries where weight reduction is demanded. Application of magnesium alloys is still limited because of problems connected with its limited ductility and relatively low strength [1]. Mechanical properties of magnesium alloys in the as-cast state are often insufficient for many applications, while other processing methods have limitations due to HCP (hexagonal close packed) crystal lattice of the magnesium alloy matrix. Primarily, a processing method such as cold working is problematic and there is a risk of crack formation (caused by a lack of independent active slip systems at room temperature). Due to this fact, processing at elevated temperature is used to avoid possible cracking [2].

It is well known that the grain size is a very important microstructural factor affecting mechanical behavior [3]. Wrought magnesium alloys are in the focus of designers thanks to better mechanical behavior than cast Mg alloys. Grain refinement via working leads to significant mechanical properties improvement of the alloys, but for some specific application further enhancement of properties usually connected with more pronounced grain refinement is required [4].

An effective way to mechanical properties enhancement is to use one of the severe plastic deformation (SPD) methods, especially equal channel angular pressing (ECAP) due to its good potential for control of microstructural evolution [5, 6]. Processing of magnesium alloys via SPD methods is usually conducted at or above 150 °C [7 - 9].

As a consequence of different methods of the semi-product preparation following into the different resulting microstructure, the fracture mechanism of magnesium alloys vary from brittle to partly ductile (quasi-cleavage) strongly depending on the state of material and on the correlation between tensile and extrusion axis [10 - 15].

In this paper, the microstructure and its influence on tensile properties, microhardness and fracture mode of AZ91 magnesium alloy in the as-extruded state and after ECAP were analyzed.

2. Material and experimental methods

AZ91E magnesium alloy in extruded initial state with chemical composition given in Table 1 was used in this work. This alloy was subjected to ECAP process (exECAP) in the laboratory of Politecnico di Milano, Italy, using four passes through ECAP die (the angle between channels Φ was 110°) at temperature 200°C using route B_C; ECAP direction was identical to the extrusion direction. Samples for metallographic analysis were prepared by conventional mechanical grinding and polishing procedures. Microstructural analyses were performed using light optical microscope Zeiss Axio Observer Z1.m. For more detailed microstructural study of the sample in ex-ECAP state and fractographic analysis of fracture surface of broken tensile test samples after tensile test scanning electron microscope Zeiss Ultra Plus 50 was used. The samples for tensile tests were machined from billets so that their longitudinal axis was identical with the extrusion and ECAP direction. Dimensions of the gauge length of the tensile test samples differed due to differences in available volume of the billets and were $\phi 8 \text{ mm} \times 40 \text{ mm}$ for extruded alloy and $\phi 5 \text{ mm} \times 25 \text{ mm}$

for exECAPed alloy. Tensile tests were performed using Zwick Z250 testing machine at room temperature with a loading speed 2 mm/min . Microhardness HV 0.1 was measured using Leco LM 247AT microhardness tester.

3. Results

The microstructure of extruded alloy was inhomogeneous, consisting of rather equiaxial grains with the average grain size of $15.9 \mu\text{m}$, and a large amount of $\text{Mg}_{17}\text{Al}_{12}$ particles (determined by EDS analysis) in a form of clusters aligned parallel to the extrusion direction were present in the microstructure (Fig. 1a, extrusion direction marked by arrow). After the ECAP processing the microstructure of the sample exhibited significant grain refinement and the final microstructure was almost unimodal with the average grain size of $1.2 \mu\text{m}$ with only few large grains ($\sim 10 \mu\text{m}$) remaining in the material volume (Fig. 1b). An increase of $\text{Mg}_{17}\text{Al}_{12}$ particles amount and its refinement and redistribution was observed after the ECAP process (Fig. 1c - white particles), whereas this process of $\text{Mg}_{17}\text{Al}_{12}$ particles precipitation during ECAP is typical for analyzed alloy [16, 17].

According to the tensile tests results (Fig. 2, Table 2), $\sigma_{0.2}$ proof stress and ultimate tensile strength achieved for material in extruded state was 260 MPa and 366 MPa , respectively, elongation at the break was 15.7% . All these values were slightly lower for material in the exECAPed state ($\sigma_{0.2}$ proof stress - 251 MPa , ultimate tensile strength - 359 MPa , elongation at the break - 11.9%) even though the average grain size was smaller. The microhardness of the material exhibited opposite tendency with values of $73 \text{ HV } 0.1$ for extruded material and $106 \text{ HV } 0.1$ for exECAPed material (see Table 2).

Table1

Chemical composition of studied AZ91E alloy.

Elements	Mg	Al	Cu	Fe	Mn	Si	Zn	Others total
Composition, wt. %	Balance	8.70	0.001	0.003	0.20	0.04	0.67	<0.03

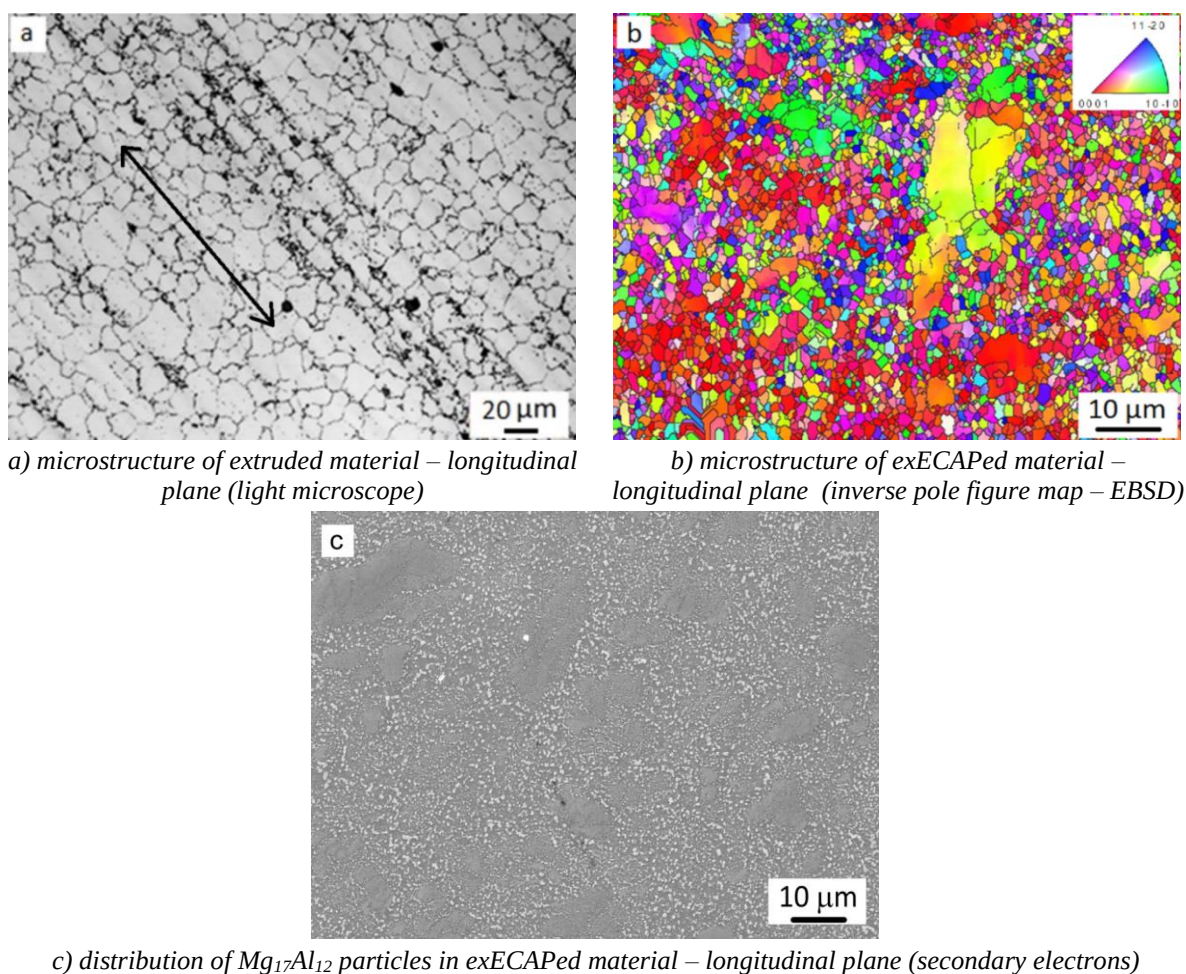


Fig. 1. Microstructure of experimental material.
(full colour version available online)

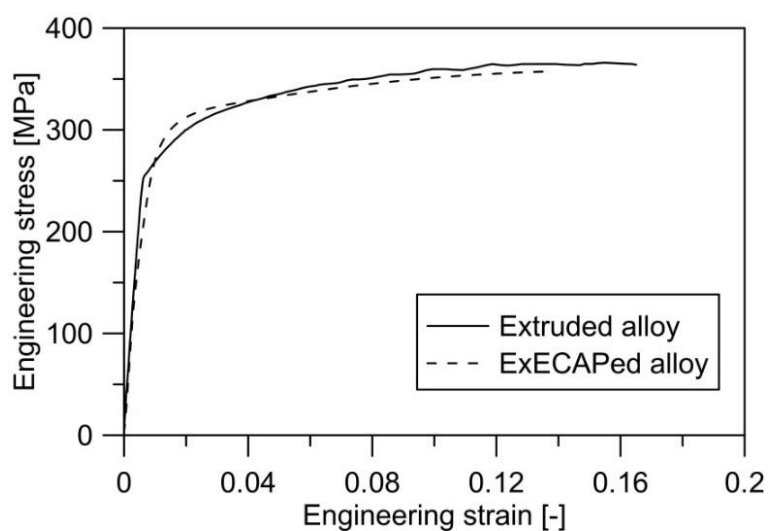


Fig. 2. Engineering stress-strain curves at room temperature.

Table 2

Material characteristics for analysed states.

State of material	Average grain size (μm)	0.2% proof stress (MPa)	Ultimate tensile strength (MPa)	Elongation (%)	Microhardness (HV 0.1)
Extruded	15.9	260	366	15.7	73
exECAP	1.2	251	359	11.9	106

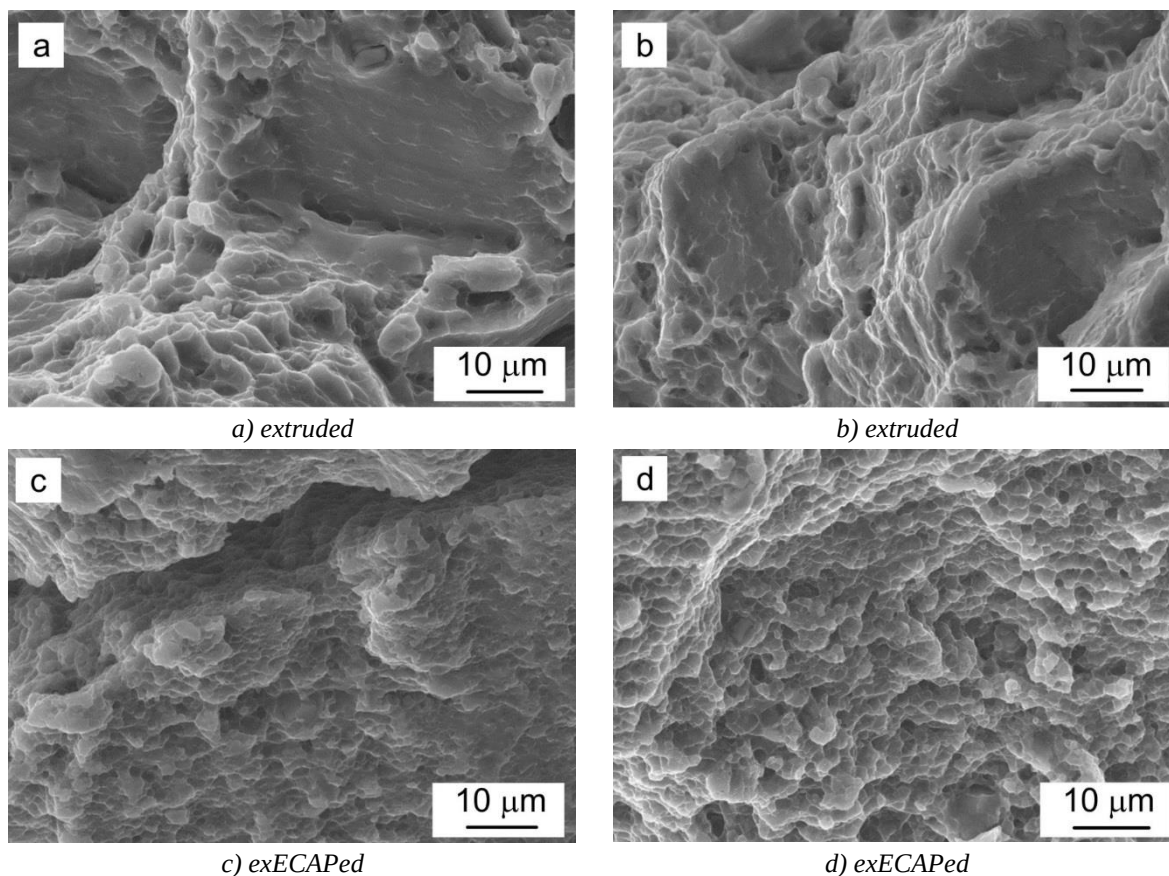


Fig. 3. Fracture surface of the specimens failed in tensile test.

Fracture surfaces of the samples broken during tensile test were analyzed by means of SEM. In the case of the extruded samples, the fracture surface consisted of transgranular, quasi-cleavage fracture in which cleavage planes and tearing edges appeared (Fig. 3a, b). After 4 passes through ECAP die (exECAP state) the fracture surface of the tensile test sample slightly changed, the presence of semi-cleavage planes was rather poor and the amount of dimples was substantially higher in comparison with the extruded state. Moreover the dimples were tiny and shallow (Fig. 3c, d).

4. Discussion

According to the obtained results, the tensile properties are not solely dependent on the average grain size of the material while improving proof stress and ultimate tensile strength via ECAP is rather insignificant even if grain refinement is considerable. This phenomenon is not unusual for ECAPed alloys and according to literature data is caused by various microstructural features especially by texture weakening [15,18,19].

The decrease of elongation at the break together with a slight decrease of tensile strength

also sometimes occurred during ECAP after particular number of passes [18]. In this case this behaviour could be attributed to a significant increase of amount and redistribution of $Mg_{17}Al_{12}$ particles in the microstructure during ECAP, these particles, located both on grain boundaries and inside grains, act as obstacles for dislocations movement and influence resulting deformation behaviour of the material. Possible cause of changes in character of strengthening during plastic deformation, which results in partly different shape of stress-strain curves during tensile tests (Fig. 2), could be also the mentioned increase of $Mg_{17}Al_{12}$ particles amount during ECAP process.

Contrary to the tensile properties the measured microhardness correlates strongly with the average grain size. These results are in agreement with literature data [15]. Moreover microstructural changes due to ECAP process led to fracture micromechanism change [20], nevertheless level of this change was not sufficient enough to increase the elongation at the break if compared with the extruded state [21].

5. Conclusions

Initial microstructure in extruded state was rather inhomogeneous with average grain size of $15.9 \mu m$. A homogeneous microstructure of refined grains with average size of $1.2 \mu m$ was obtained after 4 ECAP passes.

The higher values of $\sigma_{0.2}$ proof stress, ultimate tensile strength and elongation were achieved by extruded alloy when compared to exECAPed state.

Alloy in exECAPed state exhibited slightly lower tensile characteristics than extruded alloy despite having smaller average grain size which was caused probably by texture modification and also possibly by $Mg_{17}Al_{12}$ particles precipitation during ECAP.

Slight changes in fracture micromechanism from quasi-cleavage (extruded state) to rather

ductile character (exECAPed state) were observed. These changes did not lead to increase of elongation at the break during tensile test.

Microhardness increased with decreasing average grain size reaching value of 106 HV 0.1 for alloy in exECAPed state.

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References

- [1] B. L. Mordike, T. Elbert: Mater. Sci. Eng. A 302(1) (2001) 37-45.
- [2] S. Agnew, Ö. Duygulu: Int. J. Plast. 21(6) (2005) 1161-1193.
- [3] R.W. Armstrong: Acta Mechanica 225(4-5) (2014) 1013-1028.
- [4] H. T. Kang, T. Ostrom: Mater. Sci. Eng. A 490 (1-2) (2008) 52-56.
- [5] L. S. Toth, C. Gu: Mater. Charact. 92 (2014) 1-14.
- [6] B. Chen, D. L. Lin, L. Jin, X. Q. Zeng, C. Lu: Mater. Sci. Eng. A 483-484 (2008) 113-116.
- [7] E. Mostaed, M. Hashempour, A. Fabrizi, D. Dellasega, M. Bestetti, F. Bonollo, M. Vedani: J. Mech. Behav. Biomed. 37 (2014) 307-322.
- [8] H.J. Yang, X.H. Shao, S.X. Li, S.D. Wu, Z.F. Zhang: Mater. Sci. Forum 667-669 (2011) 839-844.
- [9] P. Molnár, A. Jäger, P. Lejček: J. Mater. Sci. 47(7) (2012) 3265-3271.

- [10] R. B. Figueiredo, T. G. Langdon: J. Mater. Sci. 45(17) (2010) 4827-4836.
- [11] N. Subrahmanya Prasad, N. Naveen Kumar, R. Narasimhan, S. Suwas: Acta Materialia 293 (2015) 281-293.
- [12] D. Ando, J. Koike, Y. Sutou: Mater. Sci. Eng. A 600 (2014) 145-152.
- [13] Y. Z. Lü, Q. D. Wang, W. J. Ding, X. Q. Zeng, Y. P. Zhu: Materials Letters 44(5) (2000) 265-268.
- [14] X. Li, X. Feng, S. Wang, W. Qi: Rare Metal Mat. Eng. 43(12) (2014) 2927-2930.
- [15] F. Akbaripناه, F. Fereshteh-Saniee, R. Mahmudi, H. K. Kim: Mater. Des. 43(1) (2013) 31-39.
- [16] S. Fintová, L. Pantělejev, L. Kunz: Mater.Sci. Forum 782 (2014) 384-389.
- [17] J. Gubicza, K. Máthis, Z. Hegedűs, G. Ribárik, A.L. Tóth: J. Alloys Comp. 492(1) (2010) 166-172.
- [18] S. M. Masoudpanah, R. Mahmudi: Mater. Des. 31(7) 2010 3512-3517.
- [19] M. Janeček, S. Yi, R. Král, J. Vrátná, K.U. Kainer: J. Mater. Sci. 45(17) (2010) 4665-4671.
- [20] M. L. Hu, Z. S. Ji, X.Y. Chen: Transaction of Nonferrous Metals Society of China 20(6) (2010). 987-991.
- [21] J. Lin, Q. Wang, L. Peng, H. J. Roven: J. Alloys Comp. 476(1-2) (2009) 441-445.



FRACTURE BEHAVIOUR OF WELD JOINTS MADE OF PEARLITIC AND BAINITIC STEEL

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Resume

The paper is concerned with microstructure evaluations and the hardness and fracture behaviour of welded joints made from cast bainitic Lo8CrNiMo steel and pearlitic rail steel of the type UIC 900A. The materials mentioned are predetermined for frogs of switches. The study is based mainly on microstructural observations and hardness measurements of the base materials, weld, and heat affected zone (HAZ). Dynamic fracture toughness was evaluated based on data from pre-cracked Charpy type specimens. The pearlitic UIC 900A steel and its HAZ had the lowest dynamic fracture toughness values and therefore the highest risk of brittle fracture. At application temperature range, this steel is on the lower shelf of the ductile-to-brittle transition, and the tempering in the HAZ did not affect the toughness substantially. The cast bainitic steel in the weld joint is characterized by higher toughness values compared to the pearlitic one, and a further increase in toughness may be expected in the HAZ. The weld zone itself is characterized by high scatter of toughness data; nevertheless, all the values are above the scatter band characterizing the pearlitic steel.

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1. Introduction

The current stage of advances in rail transport can be characterized by increasing speed, growth of axle load and transported volume, and the requirement to extend the rails' operating lifetime. In consequence of this trend, the demands regarding the quality of rail materials and the search for new designs and material solutions are increasing significantly [1–3]. One of the most important and most stressed part of the track superstructure is the frog. According to the structural solutions of crossings, frogs can be categorized as: (i) built-up, where the parts are manufactured from flat-bottom rails or special frog profiles, respectively; (ii) mounted-monolithic, consisting of certain compact units (weldments); and (iii) a monoblock, where a frog and connecting rails are designed as a compact block; that is, four rails are welded to the cast frog. Welding is done mostly by flash welding technology [4].

Austenitic manganese steel UIC 866 is a well-known material that is still used for the manufacture of cast frogs. This steel can be strengthened by cold forming and retains excellent toughness at very low temperatures. The disadvantage of this steel is its production cost and difficult machining, especially its problematic surfacing and welding with conventional rail materials. Compared with austenitic steel, the low-carbon bainitic alloy steel Lo8CrNiMo presents an advantageous combination of material and process parameters [5, 6]. This steel has been extensively studied and it has been shown that the key parameters surpass those of manganese austenitic steel UIC 866 in many cases. One of these key features is the dynamic fracture toughness, which represents the resistance of the material to fracture under dynamic loading conditions [6].

Therefore, within the complex study of cast bainitic crossings, the fracture behaviour of weld

with pearlitic rail steel was evaluated. The weld hides a number of pitfalls from the microstructural point of view, including negative impacts on the fracture behaviour. On the other hand, however, it could open the way for use in monoblock crossings. The study also includes in-service bending tests [7] and the evaluation of fractures in welds of pearlite and bainitic rails, but it cannot be done without an analysis of the impact of potentially negative structures on the dynamic fracture toughness.

The aim of this study was to determine the risks associated with welding of bainitic and pearlite steels and whether the weld joint reduces the overall resistance to brittle fracture under dynamic loading.

2. Materials, test specimens, and experimental procedures

Bainitic cast (Lo8CrNiMo [1]) and standard pearlitic rail UIC grade 900A steels with the chemical composition shown in Table 1 were used as the test materials.

Type UIC 60 rails with a length of approximately 0.75 m were cast from the bainitic Lo8CrNiMo steel and were subsequently annealed by slow heating to the austenitizing temperature of 900 - 920 °C, cooled by compressed air, and tempered at 260 - 280 °C. The dwell time (four hours) at austenitizing temperature guarantees the desired austenite homogeneity. Cooling by compressed air follows the achievement of such a cooling rate, which provides the higher hardness and strength required for rail profile materials, mainly for crossing frogs. A tempering temperature of 260 - 280 °C ensures the reduction of internal stresses. This method of heat treatment resulted in the mainly bainitic structure of Lo8CrNiMo steel.

Lo8CrNiMo steel castings were welded by flash welding technology ("butt") with standard rail steel type UIC 60 of grade UIC 900A, which also had a length of ca. 750 mm. The welding was carried out on a computer-

controlled Schlatter GAA 100/580 resistance welding machine in DT Výhybkárna a mostárna, s.r.o. Prostějov. The total loss of both materials after flash welding and squeezing was on average 29.3 mm, and the length loss of the Lo8CrNiMo steel was about 13 mm. The results presented in this paper represent data obtained from four weldments.

To determine the exact positions of the specimens relative to the position of the weld axis, a detailed analysis of a part length of 120 mm (120×172×12 mm) cut out from one of the weldments was made. Besides etching on the macrostructure, measurements of hardness were taken over the entire surface. A detailed metallographic analysis and hardness HV10 measurements were then carried out on strips cut off from the head and base of the plate.

Based on the results obtained from the plate, the exact positions of the test specimens taken from other weldments were determined. The fracture behaviour of both base materials (i.e. bainitic cast iron and pearlitic rail steel) was monitored, as well as the fracture behaviour in the heat affected zone (HAZ) in the location of the highest brittleness of these materials and in the axis of the weld. The most brittle place was considered to be the part of the HAZ at which the highest hardness was measured. To determine the dynamic fracture toughness, the Charpy-type test specimens with fatigue cracking [referred to as "pre-cracked Charpy" (PC)] were manufactured from the abovementioned parts of the rails. The fatigue crack was oriented perpendicular to the rail head surface and the fracture spread inwards in the rail. Dynamic loading was carried out on an instrumented impact tester according to the ESIS standard [8]. Tests were conducted at temperatures from -60 to +80 °C, and the impact velocity was within the range of 1.0 - 1.4 m.s⁻¹ (i.e. low blow testing). Procedures of fracture toughness determination based on the relevant standards are described in [7, 9].

Table 1

Chemical composition of Lo8CrNiMo bainitic steel and UIC 900A pearlitic rail steel (in wt. %).

	C	Si	Mn	P	S	N
Lo8CrNiMo	0.11-0.15	max 0.5	0.5-0.8	max 0.015	max 0.012	max 0.012
900A	0.6-0.8	0.1-0.5	0.8-1.3	max 0.04	max 0.04	-
	Cr	Ni	Mo	Al	Ti	V
Lo8CrNiMo	1.6-2.0	2.6-3.0	0.4-0.5	max 0.045	0.05	max 0.13
900A	-	-	-	-	-	-

3. Experimental results and discussion

3.1 Hardness and microstructural analysis

To get an idea about the size and shape of the HAZ and to determine the location and course of the weld axis, etching of the macrostructure of the plate cut out in the longitudinal direction in the axial plane of the rail was performed. Oberhoffer and Whiteley etchants were used for etching, respectively. The shape of the HAZ fits the rail profile; that is, the HAZ width of the head and foot of the rail is wider than the HAZ width of the web, whereas the HAZ of the bainitic steel is wider than the HAZ of the pearlitic steel (43 mm compared with 29 mm). The axial plane of the weld is clearly visible in Fig. 1a. An apparent difference between the rolled pearlitic structure with the fibres deformed near the weld axis as a result of squeezing and the dendritic structure of Lo8CrNiMo steel is clearly visible. It is apparent from Fig. 1a that the weld is not an ideal plane because of the larger plastic deformation of the bottom half of the UIC 900A rail at the moment of weld creation.

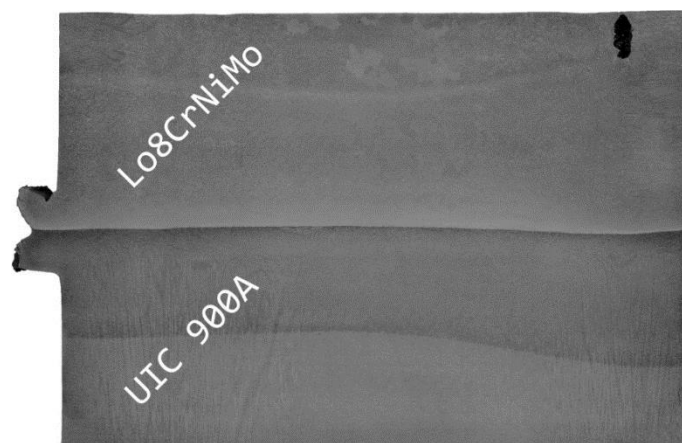
For the mapping of properties in the weld area, HAZ, and base material, hardness measurements were performed on the surface of the plate. The hardness HRC was measured in the direction perpendicular to the plane of the weld with a puncture distance of 10 mm. The distance between rows of stitches was 10 mm in the head and foot parts of the plate and 20 mm in the web. The progress of hardness in the head, web, and base parts of the rail is shown in Fig. 1b, c, d.

For verification and possible refinements of hardness behaviour in relation to microstructure, the Vickers hardness was evaluated in the same

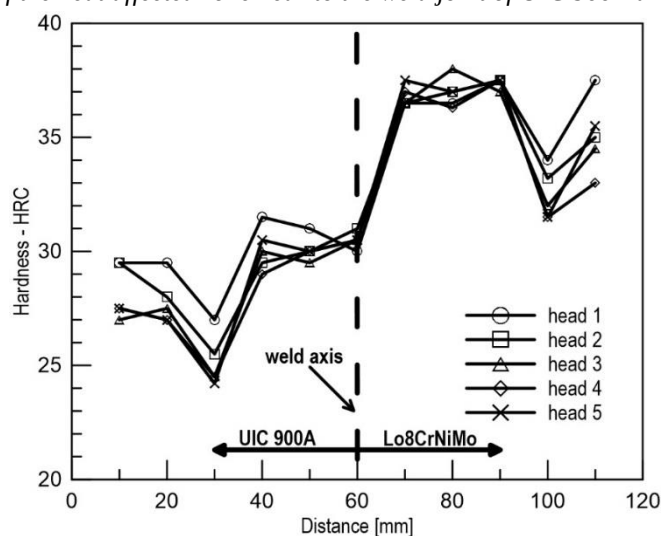
direction. Hardness HV10 was measured on strips 25 mm in width cut off from the head and base of the plate with a step of 5 mm from the plate edge (see Fig. 2a, b). Two rows of stitches were measured in the strip of the head part, one of them closer to the top of rail, the second closer to the centre of the head rail. The positions of the maximum hardness values were established based on the hardness behaviour and served as the starting points for the positioning of the PC test specimens.

In the area of local overheating in the vicinity of the weld axis on the side of the UIC 900A rail, the metallographic analysis (Fig. 3a) showed a coarsening of the ferrite-pearlite structure, with ferrite excluded on the pearlitic grains boundaries. A Widmanstätten morphology was observed in some cases. A lamellar pearlitic structure of grain size 3 - 4 according to the ČSN 42 0462 standard [10] was apparent in the pearlite. In the direction of the UIC 900A base material, the structure became a fine-grained pearlitic structure with a smaller portion of ferrite. The pearlitic structure with occasional occurrence of structurally separated ferrite also occurred in the area of maximum hardness (about 17 mm from the weld axis; see Fig. 3b). The structure away from that point towards the base material is almost purely pearlitic.

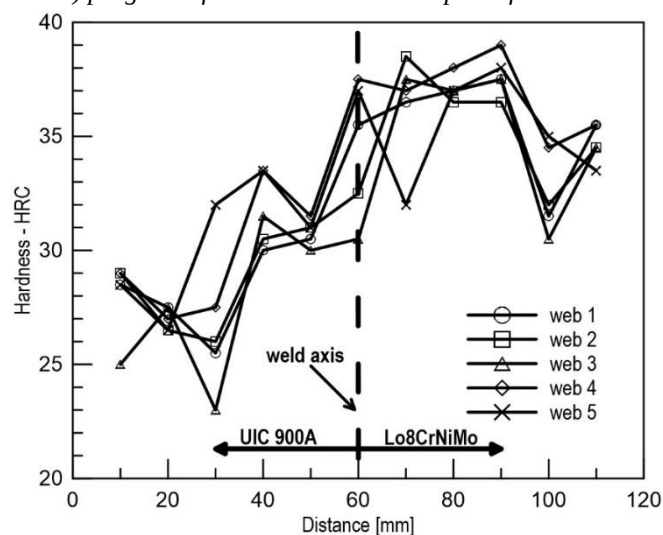
In the area of local overheating of the Lo8CrNiMo steel, a bainitic structure with coarse bainitic ferrite laths was apparent. Similarly, in the HAZ, the structure of Lo8CrNiMo steel consisted of morphologically rough bainitic ferrite with carbides. The same conclusion applies to sites with the maximum hardness (about 24 mm from the weld axis; see



a) macrostructure of the heat affected zone near to the weld joint of UIC 900A and Lo8CrNiMo steels

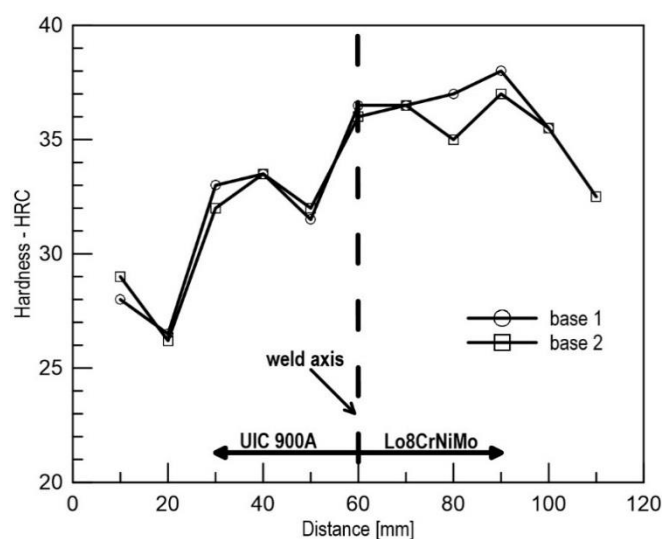


b) progress of hardness in the head part of the weld



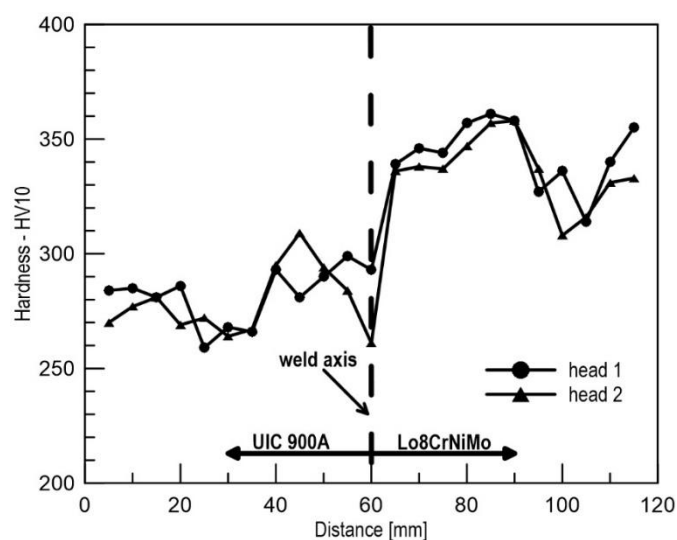
c) progress of hardness in the web part of the weld

Fig. 1. Macrostructure of the heat affected zone near to the weld joint of UIC 900A and Lo8CrNiMo steels and the progress of hardness.

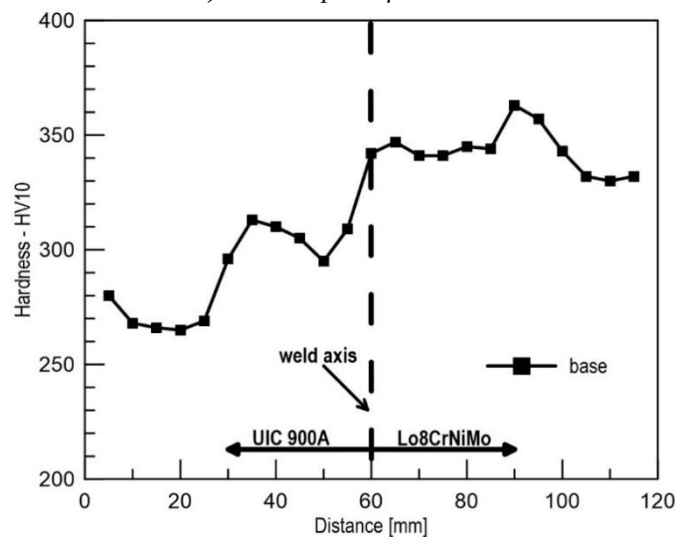


d) progress of hardness in the base part of the weld

Continuing of Fig. 1. Macrostructure of the heat affected zone near to the weld joint of UIC 900A and Lo8CrNiMo steels and the progress of hardness.



a) the head part of the weld



b) the base part of the weld

Fig. 2. Hardness behaviour, HV10.

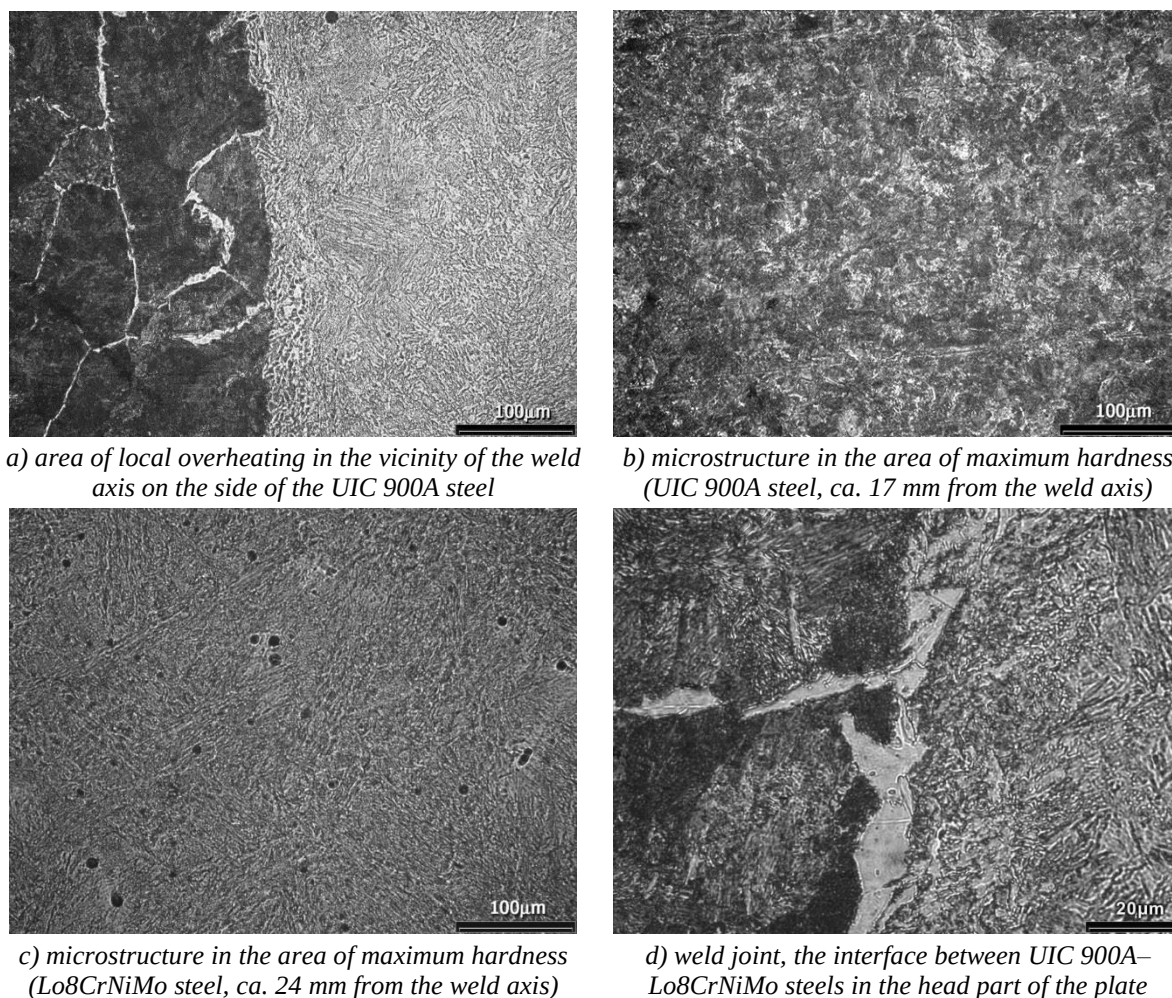


Fig. 3. Microstructures observed in the location of the UIC 900A–Lo8CrNiMo steels weld joint (Nital).

Fig. 3c). The structure probably consisted of a mixture of upper and lower bainite.

The weld joint itself is formed by the thin melted layer. Segregated ferrite was observed at the interface between UIC 900A - Lo8CrNiMo steels in the head part of the plate (Fig. 3d). The probable cause was the redistribution of carbon between UIC 900A eutectoid steel and the low-carbon alloy steel Lo8CrNiMo. In the base part of the plate, a similar phenomenon was not observed.

3.2 The fracture behaviour

The following values of dynamic fracture toughness were evaluated:

- K_{Cd} - dynamic linear-elastic fracture toughness for tests terminated by cleavage. Calculated K_{Cd} values fail to fulfil the conditions

given in the ASTM standard [11] although the force–displacement record was mainly linear up to fracture;

- K_{JCd} - the dynamic elastic-plastic fracture toughness converted from the J_{Id} -integral calculated by using the equation (1):

$$(J_I)_{init} = \frac{(K_I)_{init}^2(1-\nu^2)}{E} + \frac{2(A_{pl})_{init}}{B(W-a)} \quad (1)$$

where $(K_I)_{init}$ is the elastic stress intensity factor for the initiation force F_{init} and $(A_{pl})_{init}$ is the plastic area (energy) under the force–displacement record to the force F_{init} . To convert $(J_I)_{init}$ to $(K_I)_{init}$, the relation (2):

$$(K_I)_{init} = \left[\frac{(J_I)_{init} E}{(1-\nu^2)} \right]^{1/2} \quad (2)$$

was used. K_{Jcd} values were calculated for the fracture force F_{FRd} of the tests terminated by cleavage fracture with no prior ductile tearing. The possibility of using Eq. (1) to calculate the J_{Id} -integral was checked, for example, in [9, 12];

- K_{Jud} - post-ductile tearing cleavage dynamic fracture toughness for test terminated by cleavage;
- K_{Jmd} - dynamic fracture toughness values at maximum load F_{max} for stable fracture behaviour and nonlinear test records.

The fracture toughness values obtained in low blow impact tests and the graphical representation of their temperature dependences are presented in Figs. 4 and 5. The curve of the form (3)

$$(K_{Cd}; K_{Jcd})_{mean} = K_{min} + A \exp(BT) \quad (3)$$

was fitted to the experimental data. Having chosen $K_{min} = 20 \text{ MPa} \cdot \text{m}^{1/2}$, the parameters A and B may be calculated by linear regression analysis. After determining the standard deviation, the one-sided tolerance bound calculated with confidence $P = 0.95$ can be established. Both curves are drawn in Figs. 4 and 5. It should be noted that the curves in Figs. 4 and 5 represent only the variation of the dynamic fracture toughness in the transition and lower shelf regions.

A) The fracture behaviour of base materials and their heat-affected versions

The temperature dependence of the dynamic fracture toughness of the standard rail steel UIC 900A is shown in Fig. 4a along with the temperature dependence of the dynamic fracture toughness of the same steel in the HAZ (17 mm from the weld axis). The fracture toughness values K_{Cd} in the HAZ are about the same as or slightly higher than the fracture toughness values of the base material.

A similar temperature dependence for the bainitic cast steel Lo8CrNiMo is presented in Fig. 4b along with the temperature dependence of the dynamic fracture toughness in the HAZ (24 mm from the weld axis). The values obtained correspond to the dynamic fracture toughness level previously observed for this steel [5, 6]. The Lo8CrNiMo steel shows a significant shift of dynamic fracture toughness towards higher values and lower temperatures in comparison with the standard rail steel. The shift of the heat-affected version of Lo8CrNiMo steel towards higher dynamic fracture toughness values in comparison with the base material is more substantial than in the case of UIC 900A steel. The dynamic fracture toughness values measured at $-20 \text{ }^{\circ}\text{C}$ even correspond to the upper shelf value of dynamic fracture toughness.

B) The fracture behaviour of the weld

The temperature dependence of the individual values of dynamic fracture toughness in the weld joint axis area is plotted in Fig. 5a.

Through the experimental data, a curve of the form given by Eq. (3) was fitted along with the one-sided tolerance bound. The figure also contains the waveforms of the fracture toughness of both base metals and their heat-affected versions.

The fracture toughness values exhibit considerable scatter throughout the test temperature range (-60 to $+60 \text{ }^{\circ}\text{C}$). The primary cause of this phenomenon may be the heterogeneity of the weld joint, as a result of which the heads of the cracks can appear in very different structures with vastly different resistances to brittle fracture. An important role is also played by the non-planarity of the melting area, which together with the very small thickness of this area could lead to a different location of fatigue cracks in various test specimens. Although on the surface of the test plate the crack tip was located at the weld axis, in the middle of the plate it could be located in the pearlitic or bainitic part of the weld. The dynamic fracture

toughness values of the weld joint are located in a strip bounded by HAZ values of both base materials. At lower temperatures, the fracture behaviour approaches that of Lo8CrNiMo steel, while at higher temperatures it approaches that of UIC 900A steel. In order to characterize the unique behaviour of the weld, it is necessary to perform additional experiments with respect to the variation of the dynamic fracture toughness.

The experimental data representing the strength properties (hardness HV10) and fracture properties (dynamic fracture

toughness) obtained at room temperature are summarized in Fig. 5b. The fracture behaviour of Lo8CrNiMo steel reaches the upper shelf value at this temperature. A significant finding resulting from this graph is that the lower limit of the toughness scatter band of the weld joint is situated above the scatter band of UIC 900A steel and its HAZ. In terms of resistance to brittle fracture initiation, it can be stated that the UIC 900A–Lo8CrNiMo weld does not reduce the fracture properties of the base materials.

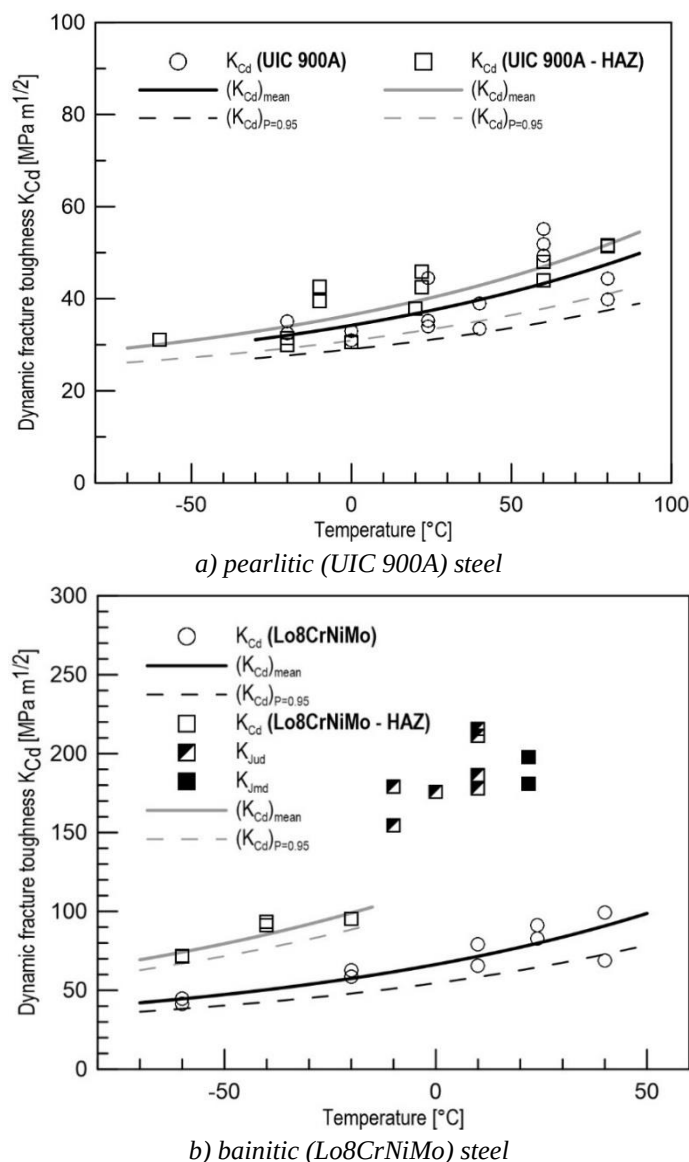
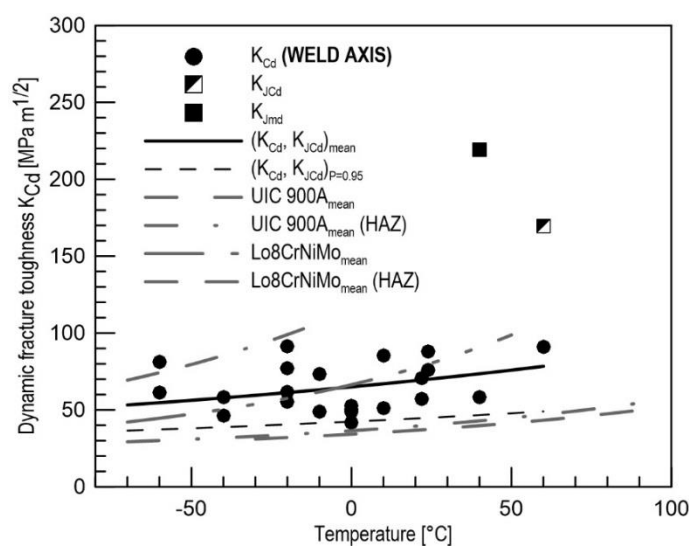
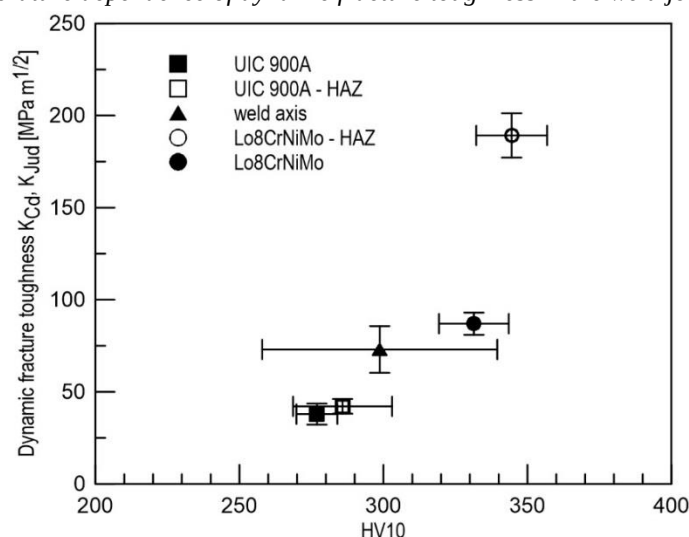


Fig. 4. Dynamic fracture toughness comparison of HAZ and base material.



a) the temperature dependence of dynamic fracture toughness in the weld joint axis area



b) dependence of strength and fracture properties of the weld joint

Fig. 5. The fracture behaviour of the weld.

4. Conclusions

The microstructure and hardness and fracture behaviours of bainitic Lo8CrNiMo and standard rail UIC 900A steels intended for the production of railway frogs have been evaluated in the article.

The maximum hardness values measured in the heat affected zone (HAZ) of UIC 900A steel are between 29 and 33.5 HRC, while those in the HAZ of Lo8CrNiMo steel are between 37 and 39 HRC. The hardness values in the HAZ are not significantly different from those of the base materials. In the head part of the rail, the distance between the weld axis and the point of maximum hardness was about 24 mm

in the case of bainitic steel, while in the case of UIC 900A steel it was ca. 17 mm. The structure of the weld joint on the side of UIC 900A rail steel consists of coarse pearlitic structure with ferrite excluded at the grain boundaries (with Widmanstätten pattern in some cases). Coarse-grained bainitic structure was found on the side of Lo8CrNiMo steel and changed very quickly into the tempered bainitic structure.

In the temperature range from -60 to 80 °C, the fracture toughness of UIC 900A steel is located in the lower shelf region of fracture toughness, where only a weak temperature dependence of fracture toughness

can be found. The temperature dependence of K_{Cd} in the HAZ of UIC 900A steel is basically comparable with the temperature dependence of the K_{Cd} of the base material and is only slightly shifted to lower temperatures and higher fracture toughness values. From this it follows that the resistance to brittle fracture initiation does not deteriorate significantly in this area.

In the temperature range from -60 to 40 °C, the dynamic fracture toughness values of the base material Lo8CrNiMo inhere in the transition region of the temperature dependence of the fracture toughness. The dynamic fracture toughness values of the Lo8CrNiMo steel in the HAZ cover the complete ductile-to-brittle transition in the temperature range of -60 to 22 °C, whereas the fractures were initiated by ductile micromechanism at temperatures above -10 °C. That means that the resistance to brittle fracture increases considerably in the HAZ of the Lo8CrNiMo steel.

Throughout the test temperature range (-60 to +60 °C), the fracture toughness values of the specimens taken from the weld axis exhibit substantial scatter. This effect is probably caused by the heterogeneity and non-planarity of the weld joint, and thus the fatigue crack positions of particular test specimens are in different positions relative to the weld location. The dynamic fracture toughness values of the weld joint are located in a band that is upper bounded by the HAZ values of Lo8CrNiMo steel and lower bounded by the HAZ values of UIC 900A steel.

It can be stated that the weld joint of Lo8CrNiMo and UIC 900A steels does not negatively affect the fracture properties of the base materials.

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References

- [1] E. Karczmarczyk, T. Kufa, P. Matušek: *Hutnické listy* 7-8 (1994) 34-42.
- [2] D. Davis, M. Scholl, H. Sehitoglu: *Railway, Track and Structures* (1997) 14-16.
- [3] U.P. Singh, B. Roy, S. Bhattacharyya, S.K. Jha: *Mater. Sci. Tech.* 17(1) (2001) 33-38.
- [4] E. Schmidová: *Zvyšování užitečných vlastností kolejnicového materiálu (Enhancement of utility properties of the rail material)* (dissertation thesis), BUT 2002. (in Czech)
- [5] J. Zbořil: In: *Vědeckotechnický sborník českých drah 11*, Praha 2001, pp. 63-79.
- [6] M. Holzmann, I. Dlouhý, J. Zbořil: *Hutnické listy* 57 (2003) 8-20.
- [7] B. Zlámal: *Hodnocení svarů bainitické oceli na odlitky (Evaluation of cast bainitic steel welds)* (diploma thesis), BUT 2003. (in Czech)
- [8] ASTM E23.03.03 Proposed standard method of tests for instrumented impact testing of precracked Charpy Specimens of metallic materials, Revised dynamic fracture toughness test methods, Draft 12, September 2000.
- [9] J. Man, M. Holzmann, B. Vlach: *Zváranie* 36 (1987), 291-294 (part I), 323-327 (part II), 355-356 (part III). (in Czech)
- [10] ČSN 42 0462 Zkoušení kovů. Stanovení velikosti zrna ocelí a neželezných kovů (*Metal testing. Methods for estimating the average grain size of steel and non-ferrous metals*) 2014. (in Czech)
- [11] ASTM E 399 Standard test method for plain-strain fracture toughness of metallic materials 2012.
- [12] W.L. Server: *J. Test. Eval.* 6(1) (1978) 29-34.



ZIRCONIA / ALUMINA COMPOSITE FOAMS WITH CALCIUM PHOSPHATE COATING

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Resume

In this study, mechanical properties of calcium phosphate foams were enhanced by zirconia/alumina porous cores prepared by polymer replica technique. This technique was chosen to ensure interconnected pores of optimal size for cell migration and attachment. The porosity of ZA cores (50 – 99%) was controlled by multistep impregnation process, the size of pore windows was 300 – 500 µm. Sintered ZA cores were impregnated by hydroxyapatite or β-tricalcium phosphate slurry to improve bioactivity. The bone like apatite layer was formed on coatings when immersed in a simulated body fluid. Neither of tested materials was cytotoxic. Thus, the composite foam can be potentially used as a permanent substitute of cancellous bone.

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1. Introduction

A lot of research has been done in the field of bone substitutes up today. Ceramic materials seem to be a reasonable choice for reconstruction of non-healing bone defects due to high biocompatibility, high corrosion resistance in body environment and good compressive strength. The highest chemical similarity to the mineral component of mammalian bones was reported for calcium orthophosphates, such as hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) [1]. Hydroxyapatite has excellent bone bonding ability and bone ingrowth properties [2] however it is extremely weak and brittle mainly in porous form and that is why it cannot be used for load bearing components. Porous structure is nevertheless one of the essential criteria in bone tissue engineering because it facilitates cell migration, vascularization and further integration in the body and it provides a mechanical support

to the newly formed bone tissue [3]. It is known that the increasing porosity negatively influence the mechanical resistance of ceramics with exponential dependence [4]. The strongest and the most toughened bioceramics compare to other ceramic materials is undoubtedly tetragonal zirconia (TZP) [5], which is unfortunately nearly bioinert and do not directly bond to bone tissue [6].

It seems reasonable to combine great mechanical properties of zirconia with outstanding biological properties of hydroxyapatite to overcome drawbacks of both materials and prepare composite structure. Various studies [7 - 9] dealt with this approach, however, several problems, such as poor sinterability or decomposition of hydroxyapatite were reported. In the case of zirconia cores coated by hydroxyapatite, the interfacial bonding was problematic.

The purpose of this study was to prepare porous zirconia / alumina composites suitable for bioactive coatings. Alumina can improve the mechanical strength of TZP due to thermal expansion coefficient mismatch between TZP and alumina, resulting in tensile residual stresses in the composite which reduces the critical stress level for tetragonal to monoclinical transformation. Another benefit of alumina is preventing zirconia from unfavourable low temperature degradation in body environment [10] and improving interface bonding between zirconia and bioactive calcium phosphate layer.

Zirconia / alumina foams were prepared by polymer replica technique [11]. This technique was chosen because of its versatility and the possibility to fabricate foam macrostructure that closely resemble the structure of trabecular bone. Slurry technique was chosen for bioactive coatings because it is a simple and inexpensive method resulting in thick ($> 20 \mu\text{m}$) and microporous structure which ensures long-term clinical stability of implant. The relationship between structure and properties of prepared composites was studied in this paper.

2. Materials and methods

2.1 Preparation and sintering of porous ceramic foams

Ceramic foams were prepared via polymer replica technique. Polymer sponge templates (Bulpren S28089 and S28133, Eurofoam, Czech Republic) cut into blocks of $13 \times 13 \times 10 \text{ mm}$ were subsequently immersed into the ceramic slurry. The slurry was prepared from commercial powders Disperal P3 (nanopowder based on boehmite, Condea Chemie, Germany) and HWY-5.5SD (3 mol% yttria stabilized zirconia, Guang Dong Huawang Materials, China). Zirconia powder was bonded by boehmite sol stabilized by 1 M acetic acid. The amount of zirconia powder in the slurry was determined by means of thermal analysis of AlOOH to achieve 2.5, 5 and 10 wt.% of alumina in the structure after sintering. Weight fraction

of solid phase in prepared slurries reached 50, 55 and 60 wt.%. The templates were immersed into the slurry, and slurry surplus was removed by application of compressed air. So-prepared foams were dried at 70°C . The immersion and drying process was repeated until the desired porosity was achieved. The polymeric sponge was subsequently burnt out at 1000°C for 2 h and pressureless sintered in air at $1550^\circ\text{C} / 2 \text{ h}$. Some of the sintered cores were consequently impregnated by calcium phosphate based slurries with the aim to improve bioactivity. Two commercial powders, hydroxyapatite and β -tricalcium phosphate (both Fluka, Switzerland), were added into Butvar B79 (PVB, Solutia Inc., US; 2 wt. % relative to the powder) dissolved in isopropanol. The slurries, containing 40 wt. % of solid phase, were stirred for 2 hrs. Sintered cores were then immersed into the suspension and the excess slurry was removed by compressed air. This step was repeated twice to achieve a homogenous coating. Composite foams were sintered at 1200°C in air atmosphere.

2.2 Characterization of slurries and sintered ceramic foams

Thermal analysis of boehmite powder was performed by 6300 Seiko Instruments TG-DTA in a mixture of air and argon in a ratio of 1:1; flow rate $400 \text{ ml} / \text{min}$ and a temperature increase $2^\circ\text{C} / \text{min}$. The zeta potential was evaluated between pH 2 and pH 9 by Zetasizer 3000 HS (Malvern Instruments, UK). Rheological properties of sols and slurries were measured by a rotary rheometer Mars II (Haake, Germany) at shear rate $0.5\text{--}1000 \text{ sec}^{-1}$. The morphology of sintered foams were observed with the use of digital camera AM4115ZTL (DinoLite, Netherlands) and scanning electron microscopy (XL30, Philips, Netherlands and ZEISS Ultra Plus, Germany). The total porosity was calculated from the volume, the mass and the theoretical density as follows [12]: $P = \frac{\rho_t - \rho_b}{\rho_t} \times 100\%$, where ρ_t is the theoretical density and $\rho_b = \frac{m_b}{V_b}$ is the bulk density,

m_b is the mass of the dry test piece and V_b is the total geometrical volume.

The pore sizes and strut thicknesses were determined using image analysis by ImageJ software (National Institutes of Health, US). The samples were embedded in a resin, cut, ground and polished by standard ceramographic methods. The pore size was estimated on cross-sections of ceramic foams.

2.3 Compressive strength

Mechanical properties of prepared ceramic foams were determined by compression test. High-Precision Electric Actuator Systems 8862 (Instron, US) equipped with 5 kN load cell was used for the loading. The crosshead speed was 0.5 mm/min. The compressive strength was determined from the maximal obtained force.

2.4 Biological properties of prepared foams

Bioactivity of cores and coatings was biochemically tested in a simulated body fluid. The solution was prepared according to the corrected Kokubo recipe [13]. Specimens were immersed into SBF solution at 36.5 °C for 1, 2 and 4 weeks. After removal from the solution and rinsing with deionized water, the samples were dried at room temperature for 24 hrs. The presence of the newly formed apatite layer on the surface was observed by SEM.

Cytotoxicity of materials was tested in vitro using direct contact assay according to EN ISO 10993-5 specifications. Ceramic samples were sterilized in autoclave for 20 min at 121 °C. Human osteosarcoma cells of cell line MG63 (from European Collection of Cell Cultures) were cultivated at 37 °C in 5 % CO₂ in Eagle Minimum Essential Medium (EMEM) with high glucose, 1 % L-Glutamine, 1 % non-essential amino acids (NEAA), 10 % fetal bovine serum, 1 % antibiotics and 0.3 % gentamicin. Cell line was then inoculated into a measured amount of cultivation medium and transferred to the surface of sample with the density of 3 500 cells/cm² of a cultivation vessel. After exposition

period (8 or 72 hours) samples were washed by PBS twice and cells were fixated and dried by increasing alcohol series. Dried cell-seeded samples were examined by SEM. Tolerance of cells towards the tested material was evaluated by calculating the percentage of adhered cells.

3. Results

3.1 Characterization of suspensions and sintered foams

Thermal analysis

Thermal analysis was carried out to determine the amount of Al₂O₃ after decomposition of commercial boehmite powder. The TG curve (Fig. 1) indicated a total mass loss of 30.5 %. This value was slightly higher than 28% mass loss reported by the manufacturer, probably due to physically adsorbed water.

Zeta potential

Zeta potential, an indicator of the stability of colloidal dispersions, was measured in aqueous dispersions of boehmite. Results showed that sols behaved stably in acidic range (the ζ -potential between pH 2 and pH 6.5 exceeded 30 mV). The highest value (+60 mV) was measured at pH 4. In alkaline environment, dispersions were not electrically stabilized and tended to coagulate (the ζ -potential was between 20 and -15 mV).

In further experiments, suspensions were prepared from the most stable sols with pH adjusted by acetic acid to pH 4.

Viscosity of suspensions

The viscosity of sols was changed during aging. When the aging time increased, the viscosity decreased from 4 mPa·s to 2.5 mPa·s. The sufficient time of aging was 24 h, when the supposed de-agglomeration of powder was finished and sol was stabilised with almost Newtonian rheological behaviour. The aged sol was filled with zirconia in order to prepare zirconia / alumina (ZA) composite

at weight fraction of solid phase 0.5 to 0.6. Viscosity of slurries increased with increasing content of solid phase from 0.3 to 4 Pa·s (at shear rate 5 s⁻¹) and from 0.06 to 0.4 Pa·s (at shear rate 100 s⁻¹). All prepared slurries exhibited slightly thixotropic behaviour which is beneficial for polymer replica technique.

From a technological point of view, the best results for the 45 ppi sized foams were achieved when impregnated by suspension containing 60 wt. % of solid phase. However, this suspension was too viscous for coating of foams with smaller pores. To avoid blocking

of open cells (“macropores”), the foams with 60 ppi porosity were coated by suspension containing 50 wt. % of solid phase.

Morphology of sintered ceramic foams

Ceramic foams of different total porosity and pore size were prepared by repeating immersion of PU templates into the ceramic suspension. Morphology parameters of sintered foams such as total porosity, strut thickness, cell size and size of windows between adjacent macrocells (pore size) of prepared foams are summarized in Table 1.

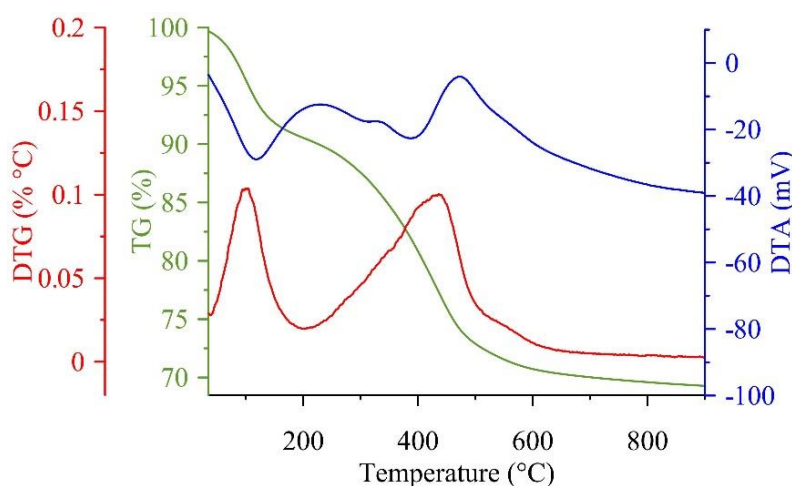


Fig. 1. Thermal analysis of commercial boehmite powder Disperal P3.
(full colour version available online)

Table 1

Porosity, strut thickness, cell size and pore size of ZA foams.

PU porosity	n layers	Porosity (vol. %)	Strut thickness (μm)	Scaffold cell size (μm)	Pore windows size (μm)
45 ppi	1	97 – 99	100 ± 18	1260 ± 420	500 ± 330
45 ppi	2	93 – 94	150 ± 35	1250 ± 390	480 ± 320
45 ppi	3	87 – 90	170 ± 40	1170 ± 380	440 ± 280
45 ppi	4	77 – 81	270 ± 70	990 ± 330	340 ± 240
45 ppi	5	62 – 65	400 ± 130	—	—
45 ppi	6	50 – 55	—	—	—
60 ppi	1	96 – 97	70 ± 17	750 ± 320	380 ± 230
60 ppi	2	91 – 93	100 ± 27	720 ± 240	320 ± 170
60 ppi	3	77 – 83	ca 300 ± 160	—	—
60 ppi	4	59 – 64	ca 340 ± 170	—	—

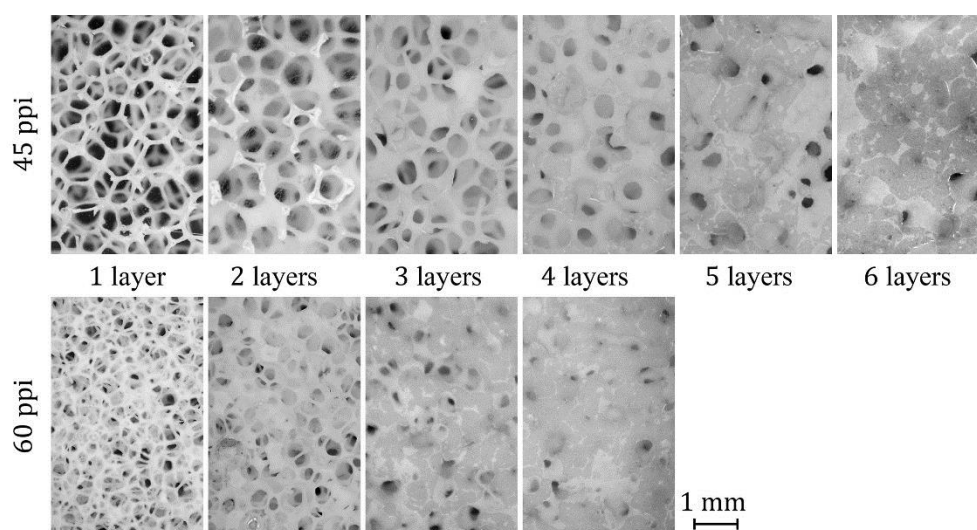


Fig. 2. Thermal analysis of commercial boehmite powder Disperal P3.

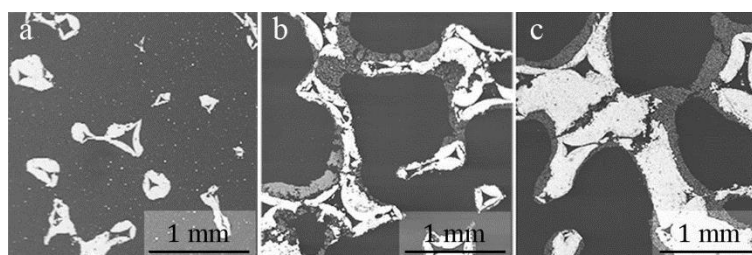


Fig. 3. Cross-sections of bioceramic foams: (a) ZA; (b) ZA coated by HA; (c) ZA coated by β -TCP.

It is evident, that the initial porosity of the polymeric template had a crucial influence on the final foam cell size after sintering. Cell size of ceramic foam corresponded to the cell size of polyurethane foam reduced by shrinkage and by thickness of the strut. With an increasing number of layers, the average thickness of struts grew. The typical reticulated morphology was lost as porosity decreased below 70 % (in the case of larger pores – 45 ppi) and below 80% (for 60 ppi). Overview of macrostructures of prepared foams is shown in the Fig. 2.

Zirconia / alumina substrates with desirable porosity were coated by calcium phosphates in order to improve the biological properties of scaffolds. Foams consisted of 2 layers of ZA (containing 5% Al_2O_3) and CaP coating are shown in Fig. 3. The β -TCP coating firmly adhered to the ZA core. The thickness of both bioactive layers was 20 to 60 μm .

3.2 Mechanical properties

Resistance of some ZA foams to the mechanical loading was characterised by compressive strength. The overview of compressive strength values of ZA foams containing 2.5 to 10 wt. % of alumina is plotted in Fig. 4.

It was experimentally confirmed that strength decreases with increasing porosity. Specimens containing 5 % of alumina exhibited the highest strength, thus this composition was chosen for subsequent biological testing. The measured strength was in accordance with the strength of cancellous bone at comparable porosities. Compressive strength of less porous specimens were not evaluated because all tested samples exhibited strength above the minimum value reported for highly porous cancellous bone [14]. Nevertheless, to ensure sufficient strength to withstand forces generated in the body

it would be convenient to use less porous structures.

3.3 Biological properties

Interaction with SBF

The typical globular morphology of newly formed apatites were locally observable on both HA and TCP coatings after 1 week

of immersion in SBF. The areas containing apatite widespread after 2 weeks. The surface of HA and TCP samples was completely covered by a newly formed apatite layer after 4 weeks. The top view of ZA substrate and Ca-phosphates coatings before and after 4 weeks immersion in SBF is reported in Fig. 5. No change was observed on uncoated ZA substrate.

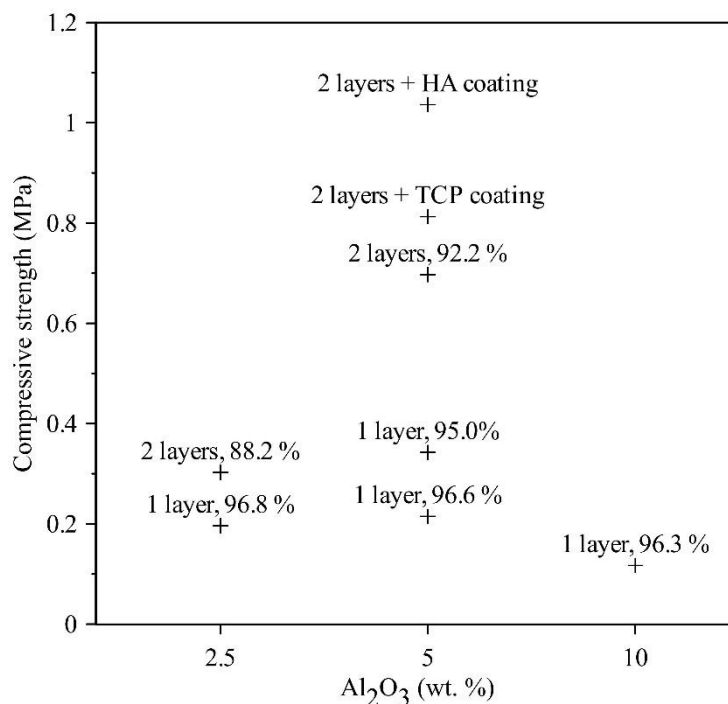


Fig. 4. Compressive strength of porous ZA foams.

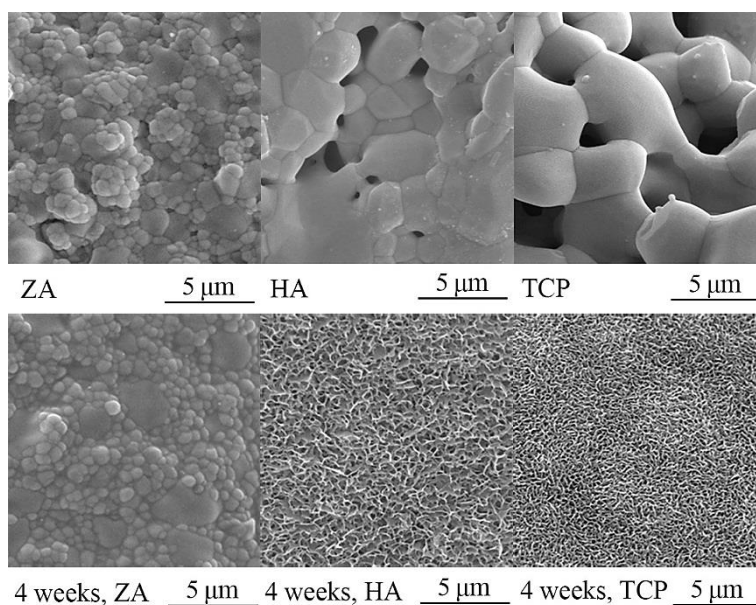


Fig. 5. Microstructure of the ZA substrate and ZA coated by HA a β -TCP before and after immersion in SBF.

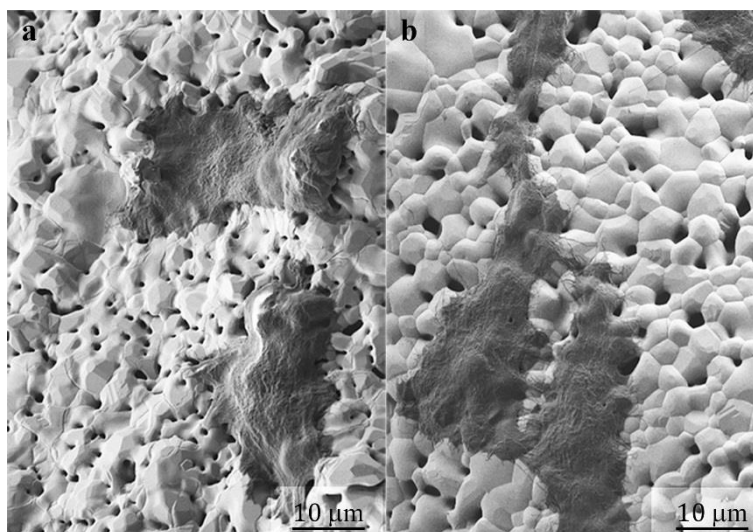


Fig. 6. Cell line MG-63 adhered to the inner struts of: (a) HA; (b) β -TCP.

Cytotoxicity evaluation

Although both zirconia and alumina are considered being bioinert in contact with host tissue, the cytotoxicity of the composite was evaluated by direct contact assay. Direct contact between MG-63 cells and all tested materials did not induce any adverse effect, cells retained characteristic morphology of MG-63 cells (see Fig. 6). The cell density and shape did not differ significantly from that observed for the negative control. Filopodia stretched out from the cells indicated a good adhesion to the bioactive surface of calcium phosphates [15]. The smallest amount of cells (58 %) adhered to the uncoated ZA, 76% of seeded cells adhered to HA layer and the largest number of cells (87%) was observed on the surface of β -TCP coating.

SEM was also used to observe the adhesion and spreading of MG63 cells inside bioactive ceramic foams after 3 days. Micrographs revealed that cells were attached to the walls of struts inside the 3D structure at comparable number as on outer struts. These results suggest that cell migration throughout the 3D structure was possible and that the nutrition and oxygen supply was satisfactory. This result confirmed that all tested materials (ZA, HA, β -TCP) were cytocompatible and could be used in bone tissue engineering applications.

4. Conclusions

Zirconia / alumina based porous foams were fabricated from 3 mol% yttria stabilised zirconia and colloidal boehmite by polymer replica technique. ZA foams of wide range of porosities (50–99 %) were fabricated by multiple impregnation process. Pores were interconnected with dimensions between 300 and 1500 μ m. Based on the results of mechanical testing, 5 wt. % content of alumina was chosen as optimum. The compressive strength of prepared ceramic foams was close to the strength of cancellous bone of the same porosity. The bioactivity of the composite foams was improved by calcium phosphate based surface layer. After 4 weeks in SBF, newly precipitated apatite was observed on both calcium phosphates coatings. Neither of tested materials was cytotoxic. MG-63 cells were able to migrate through the 3D porous structure. The reinforced composite foam behaved bioactive so it can be potentially used in bone tissue engineering applications.

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References

- [1] H. Yoshikawa, A. Myoui: J. Artif. Organs. 8(3) (2005) 131-136.
- [2] S. Samavedi, A.R. Whittington, A.S. Goldstein: Acta Biomaterialia 9(9) (2013) 8037-8045.
- [3] D.W. Hutmacher: Biomaterials 21(24) (2000) 2529-2543.
- [4] S. Meille, M. Lombardi, J. Chevalier, L. Montanaro: J. Eur. Ceram. Soc. 32(15) (2012) 3959-3967.
- [5] J.R. Kelly, I. Denry: Dent. Mat. 24(3) (2008) 289-298.
- [6] M. Hisbergues, S. Vendeville, P. Vendeville: J. Biomed. Mater. Res. B Appl. Biomater. 88B(2) (2009) 519-529.
- [7] H.-W. Kim, H.-E. Kim, J.C. Knowles, Biomed. Mater. Res. B Appl. Biomater. 70B(2) (2004) 270-277.
- [8] H.-W. Kim, S.-Y. Lee, C.-J. Bae, Y.-J. Noh, H.-E. Kim, H.-M. Kim, J.S. Ko: Biomaterials 24(19) (2003) 3277-3284.
- [9] X. Miao, Y. Hu, J. Liu, X. Huang: Mater. Sci. Eng. C 27(2) (2007) 257-261.
- [10] Y. Zhao, L. Jiang, Y. Liao, C. Wang, J. Lu, J. Zhang, W. Li: J. Wuhan Univ. Technol.-Mat. Sci. Edit. 28(4) (2013) 844-848.
- [11] K. Schwartzwalder, H. Somers, A. Somers: Method of making porous ceramic articles: US, 3090094, 1963.
- [12] British Standards Institute Staff. Advanced Technical Ceramics. Monolithic Ceramics. General and Textural Properties. Determination of Density and Porosity, BSI Standards (1993) 1-16.
- [13] T. Kokubo, H. Takadama: Biomaterials 27(15) (2006) 2907-2915.
- [14] T.S. Keller: J. Biomech. 27(9) (1994) 1159-1168.
- [15] H.-J. Jiang, J. Xu, Z.-Y. Qiu, X.-L. Ma, Z.-Q. Zhang, X.-X. Tan, Y. Cui, F.-Z. Cu: Materials 8(5) (2015) 2616-2634.