PREPARATION OF MULTIPHASE MATERIALS WITH SPARK PLASMA SINTERING

Radek MUŠÁLEK, Zdeněk DLABÁČEK, Monika VILÉMOVÁ, Zdenek PALA, Jiří MATĚJÍČEK, Tomáš CHRÁSKA

Institute of Plasma Physics AS CR, v.v.i., Za Slovankou 1782/3, 182 00 Prague, Czech Republic, EU,
musalek@ipp.cas.cz

Abstract

Spark plasma sintering (SPS), also called Field Assisted Sintering Technique (FAST), represents a novel method of preparation of sintered materials from powders. The main advantage of the SPS method is a high achievable heat rate (>200 °C/min) and high sintering temperatures (up to 2200 °C in our laboratory). Combination of high heating rate, rather high pressures (up to 80 MPa) and electric field fluctuations leads to an effective sintering and significant reduction of sintering time for both coarse-grained and nanocrystalline powders. Composite materials may be easily obtained by mixing or layering of different powders. The paper will introduce several examples of multiphase materials sintered by SPS at our institute and the establishment of procedures for routine testing of sub-sized specimens.

Keywords: spark plasma sintering, powder metallurgy, composites, multiphase materials, FeAl matrix

1. INTRODUCTION

In many applications, conventional materials have already reached their limits. One of the possibilities how to withstand extreme service conditions is to prepare multiphase materials in which properties of two (or more) materials are combined. Such an example may be the reinforcement of ductile primary phase (matrix) with a hard secondary phase, which can increase the material's hardness or wear resistance. Usually, the properties of both phases are quite different and finding optimum sintering conditions may be challenging. One of the possibilities of effective preparation of multiphase materials is the SPS method where multiphase materials may be prepared by simple mechanical mixing and/or subsequent layering of the input materials (powders). Layering may be used in cases when both the internal cohesion of individual layers as well as mutual bonding of the layers can be achieved. By gradual change of the volumetric ratio of powder mixing for each layer, even functionally graded materials may be effectively introduced. On the other hand, for the mechanical mixtures, only sintering of the dominant phase is necessary and matrix reinforced by a second phase may be easily produced in this way.

The SPS method enables effective preparation of multiphase materials in laboratory conditions as very small amounts of materials are needed (in our laboratory typically about 5 grams per one sintered sample). The principle of SPS is quite simple – powder or powders are placed between two graphite punches and constrained by a graphite die. The material is compressed and internally heated by Joule's heat generated by pulsed direct current passing directly through the punches, die and the powder. No external heating elements are therefore needed which significantly decreases the overall thermal capacity of the heated volume and enables extremely high heating rates and short sintering times and effectively reduces grain growth. Vacuum or protective atmosphere in the sintering chamber helps to out-gas the heated powders and improves overall purity of the sintered compacts. On the other hand, many issues connected with SPS are still not solved, e.g. detailed models of sintering mechanisms, plasma formation in the sintered materials, optimum way of avoiding carbon contamination from the dies, formation of carbides, temperature reading in the process zone, etc. More details about SPS technology and its possibilities are provided e.g. in [1,2].

In this study, our first experiments with the formation of multiphase materials by sintering of mechanical mixtures are introduced. Iron aluminide (FeAl) was selected as a primary phase (matrix), as it was already successfully sintered achieving negligible porosity [3,4]. Moreover, low sintering temperature of FeAl (1100 °C in this case) and short sintering times (5 minutes) promised a high throughput of the sintering process. FeAl is also a promising material for SPS sintering because of its excellent corrosion resistance, low density and high strength, since traditional methods of preparation of FeAl (casting, rolling, etc.) are quite challenging [5,6].

As a secondary phase, two ceramics (alumina and yttria stabilized zirconia) and one metallic powder (stainless steel 316L) were selected. Powder mixtures were obtained by mechanical mixing of rather coarse powders which are also used in our laboratory for plasma spraying by a Water Stabilized Plasma (WSP) system. The aim of the study was to prove the concept of preparation of multiphase materials by SPS, to find optimum sintering conditions and set up routine testing of basic properties of the sintered bodies.

2. EXPERIMENTAL

Spark plasma sintering was carried out in the SPS 10-4 (Thermal Technology LLC, USA) instrument. The sintering temperature was 1100 °C, dwell at maximum temperature 5 minutes and compressive pressure 60 MPa [3,4]. Die and punches (20 mm diameter) were manufactured from high-strength graphite. Graphite foil was used to prevent direct contact of the sintered material with the die and punches and prolong their life-time. During the sintering, temperature was controlled by a thermocouple inserted into a channel drilled into the bottom graphite punch so that the thickness of the graphite wall was 4 mm. For higher temperatures, calibrated pyrometer can be used. However, in both cases, the temperature has to be considered as a technological parameter of the sintering process rather than reading of the exact temperature in the center of the sintered body. During sintering, changes of the punch position are monitored as it changes as the material sinters (and thus decreases its volume) while the pressure is kept constant. Example of the process monitoring, enabling a very good repeatability of the process, is in **Fig. 1**.

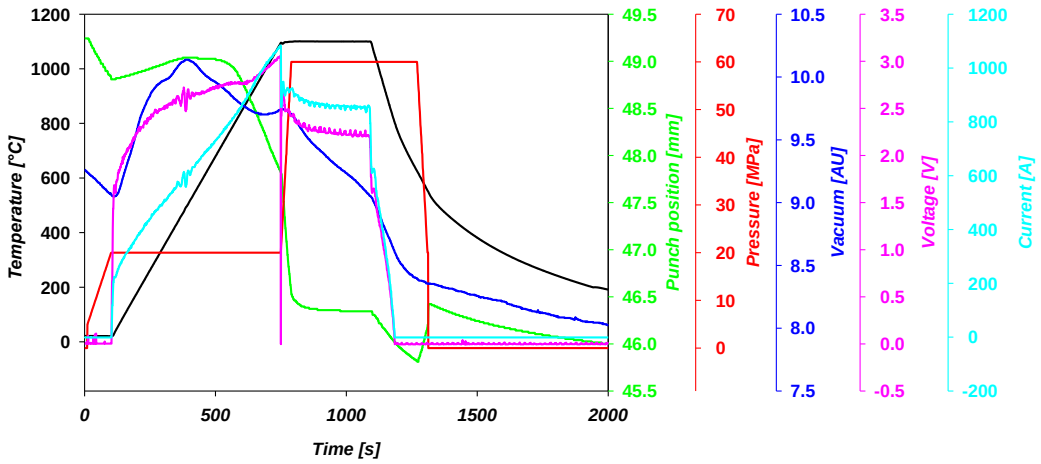


Fig. 1 Record of sintering of FeAl + Al_2O_3 sample

Powders used in this study are listed in **Tab. 1**. Based on known bulk density of each material, powders were mixed so that the volumetric ratio of the matrix to secondary powder was 3:1. Weighted amounts of powders were mechanically mixed for several minutes and the blend was used as input powder for the sintering. For comparison, a compact of 316L steel only was prepared with the same sintering conditions. For illustration, results obtained for Wall Colmonoy 88PTA powder sintered at 925 °C for 5 minutes and 60 MPa pressure are also included. This material has multiphase microstructure even without introducing a secondary phase due to precipitation of fine sub-micron metallic borides and carbides from the Ni-Cr-B matrix. Some coarser (tens of microns) angular precipitates were also observed in the powder.

Table 1 Specification of input powders

Material	Manufacturer & designation	Nominal particle size [μm]	Particle shape
FeAl (29 wt%Al)	LERMPS-UTBM, custom-made	50 - 90	spherical
Al_2O_3 (white alumina)	Korund Benátky, s.r.o., F240	28 - 70	angular
YSZ (yttria stabilized zirconia)	H.C. Starck, AMPERIT 825.1	22.5 - 45	angular
AISI 316L	GTV GmbH, 31.46.10	105 - 150	irregular
Wall Colmonoy 88PTA	Wall Colmonoy, F6604A	53 - 150	spherical

After sintering, compacts were ground in order to remove the protective graphite foil. Each compact was sectioned by 3 parallel through-thickness cuts made with a precision saw with diamond blade into 4 beams. One beam was used for materialographic analysis and hardness testing, one for evaluation of 3-point bending strength and one for XRD analysis. The last beam is usually used for porosimetry analysis, but this was omitted in this study, due to a very low porosity of the compacts (see further).

Materialographic samples were prepared with Tegramin-25 (Struers, DK) polisher using standard grinding and polishing ending with a 1 μm diamond suspension and OP-S. Vickers hardness was evaluated on polished cross-sections by Nexus 4504 (Innovatest, NL) hardness tester with 5 kg load so that the indents were bigger than typical grain size. 11 indents were applied for each sample. The microstructures and damage introduced by indentation were observed in low vacuum mode in scanning electron microscope EVO® MA 15 (Carl Zeiss SMT, D) equipped with EDS system XFLASH 5010 (Bruker, D).

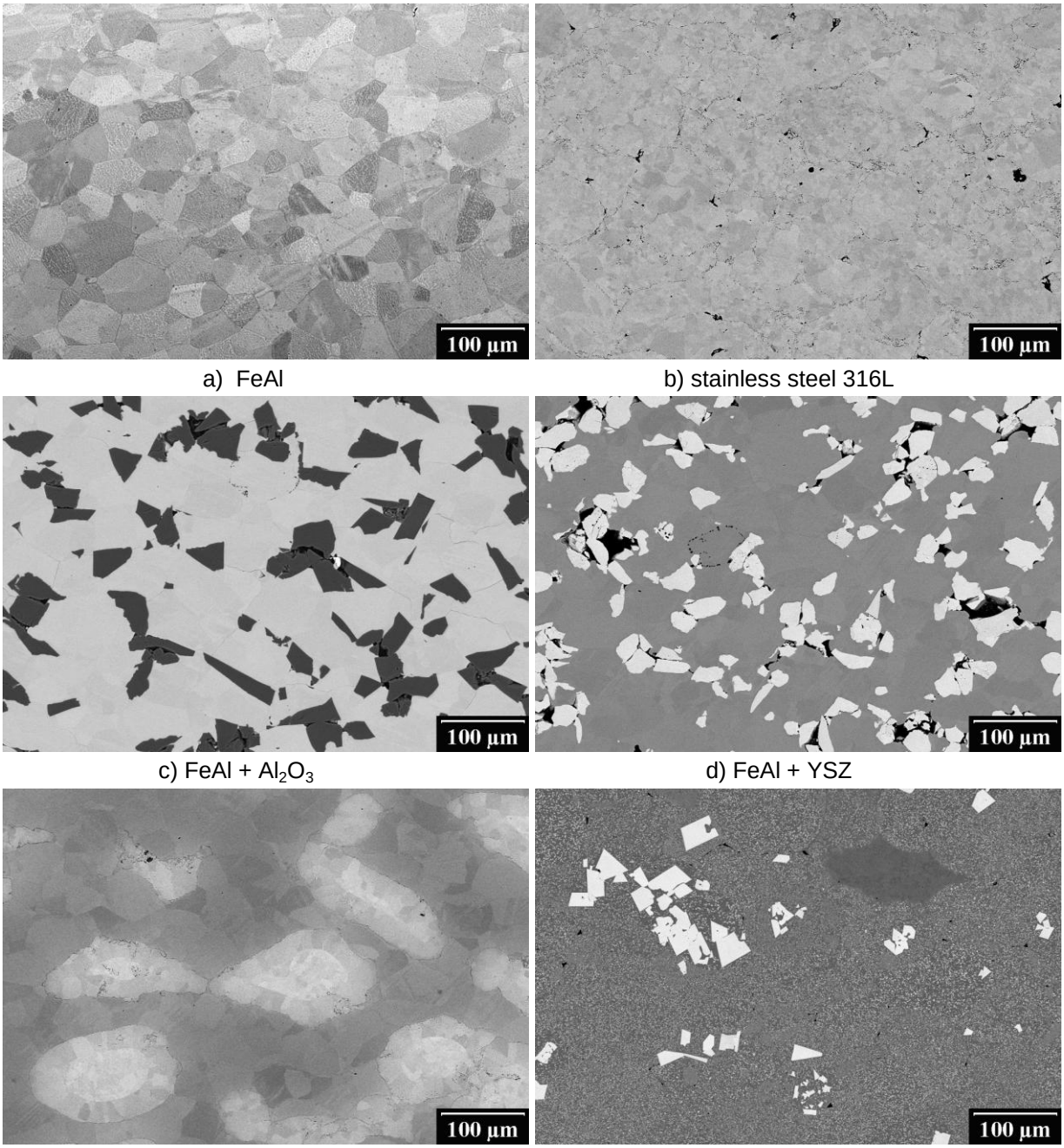
Strength was evaluated by 3-point bending test of beams with typical dimensions 4 x 4 x 19 mm using universal testing machine Instron 1362 (Instron, UK) upgraded with 8800 series electronics. Testing was carried out according to ASTM C1161-02, slightly modified with respect to the character of available samples and equipment. All surfaces of the samples were ground by P220 SiC paper in order to remove any possible materials damage caused by the cutting process. The four long edges of each specimen were uniformly chamfered at 45° on grinding paper. The bearing cylinders of the 3-point bending fixture were made of hardened steel (5 mm in diameter) and the the support span was 14 mm. Loading with constant cross-head speed of 0.2 mm/min was applied until a sudden fracture of the specimen. From the known specimen dimensions, support span and maximum load, 3-point bending (flexural) strength was evaluated. Fractographic analysis of broken specimens was carried out in SEM. Please note that only one sample was available for each compacted body so the strengths evaluated in this way are rather informatory. On the other hand, fractures with well-defined and comparable loading conditions were provided in this way.

3. RESULTS

Microstructures of the sintered compacts as observed in SEM are illustrated in **Fig. 2**. For the FeAl, sintering led to a very good densification as no pores were observed and grains showed polygonal shape. For the 316L steel, the same sintering conditions resulted in some porosity (2.4% as obtained from image analysis) but good sintering and annihilation of most grain boundaries was observed. For the FeAl mixed with Al_2O_3 and YSZ, a satisfactory contact between the FeAl grains and secondary phase was observed as well as satisfactory homogeneous mixing of the ceramic phase in the FeAl matrix. For FeAl + Al_2O_3, some cracking along the grain interfaces was noted which was not observed for FeAl + YSZ. Porosity of both FeAl + Al_2O_3 and FeAl + YSZ samples was negligible, which corresponds well with the plateau apparent from **Fig. 1** for punch position evidencing a finished compaction of the material. Most of the pores observed on the micrographs resulted from pull-outs of ceramic phase from the matrix and were therefore a polishing artifact.

However, if the ceramic particles were too closely packed together, it could locally prevent matrix from filling the gaps (see **Fig. 2c,d**).

For the FeAl + 316L sample, negligible porosity was achieved. However, a diffusion reaction between the matrix and the secondary phase was observed. Sintering resulted in a formation of about 20 μm thick layer around each particle. The EDS line scan across this layer proved that Al diffused from the FeAl matrix into the particles whereas Ni from 316L particles was transported towards the matrix-particle interface in the opposite direction. Wall Colmonoy 88PTA showed negligible porosity (about 0.1%) and retained the fine sub-micron as well as coarser precipitates (see **Fig 2f**).



a) FeAl b) stainless steel 316L

c) FeAl + Al_2O_3 d) FeAl + YSZ

e) FeAl + 316L f) Wall Colmonoy 88PTA

Fig. 2 Microstructures of the sintered compacts

Table 2 Results of mechanical testing

Sample	HV5	Flexural strength (MPa)
FeAl	393.1 ± 4.5	998.0
316L	164.2 ± 2.2	770.2
FeAl + Al_2O_3	416.3 ± 22.5	412.2
FeAl + YSZ	383.8 ± 17.7	361.6
FeAl + 316L	333.9 ± 12.7	811.6
Colmonoy 88PTA	841.4 ± 16.4	1138.1

From the comparison of the mechanical testing results (**Tab. 2**), it is obvious that FeAl had significantly higher hardness than 316L sample. Addition of the Al_2O_3 phase to FeAl resulted in slight increase in the hardness but also an order of magnitude higher scatter of the results was observed. Hardness of the FeAl + YSZ composite was comparable to that of FeAl and also an increase in the scatter of the results was observed. FeAl + 316L composite showed hardness according to expectations between pure FeAl and 316L compacts. No cracking was observed during indentation in the FeAl matrix as well as in the newly formed diffusion layer. On the contrary, crushing of the ceramic phase under indenter was quite typical.

Colmonoy 88PTA showed an excellent hardness as well as excellent flexural strength, even higher than FeAl, 316L and FeAl + 316L samples. Addition of the ceramic secondary phase resulted in significant decrease in the flexural strength as the bonding of the FeAl matrix with the ceramic particles was limited. Bonding of FeAl with 316L particles was much more efficient. Fractographs are illustrated in **Fig. 3**.

Please note, that the difference between FeAl + Al_2O_3 and FeAl + YSZ samples may be within the natural statistical error of measurement of the sub-sized samples as only one sample was available. For the 316L sample, non-linearity in the deflection-load curve was observed, which corresponds well to signs of ductile failure observed on the fracture surfaces (ductile dimples and grain elongation in the loading direction).

4. CONCLUSIONS

In this study, sintering conditions previously optimized for FeAl matrix were successfully used for preparation of multiphase materials from mechanical blends of FeAl with two ceramics and one metallic powders. Procedures for evaluation of basic mechanical properties (hardness and flexural strength) on sub-sized specimens were established and tested and provided a mutual comparison of the efficiency of matrix reinforcement and sintering process.

ACKNOWLEDGEMENT

This study was supported by the Grant No. P108/12/P552 (Czech Science Foundation).

REFERENCES

[1] CHANTHAPAN, S., RAPE, A., GEPHART, S., KULKARNI, A., SINGH, J. Industrial Scale Field Assisted Sintering: Is an Emerging Disruptive Manufacturing Technology. Advanced Materials & Processes, 2011, vol. 169, no. 7. pp. 21-26.

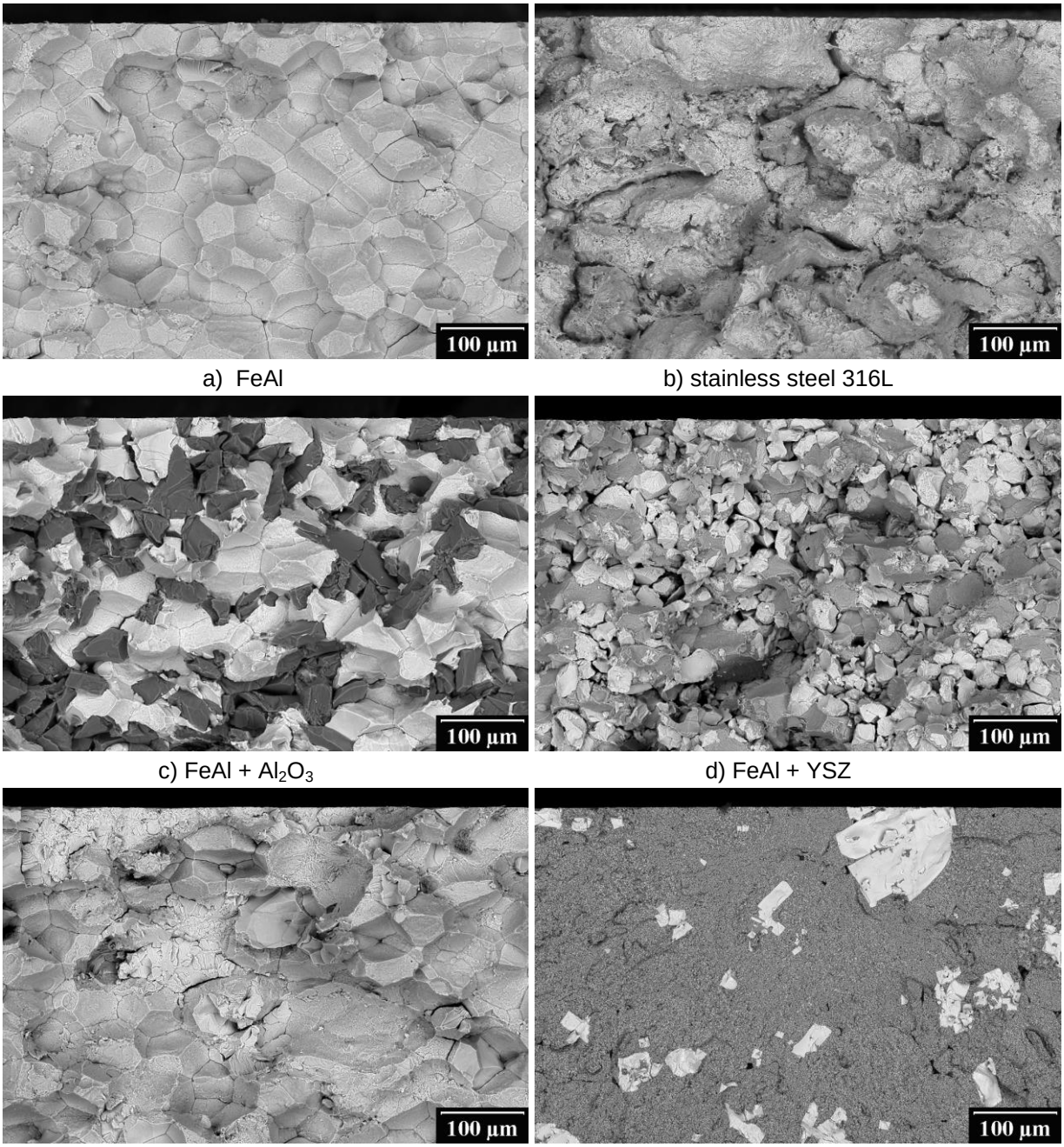
[2] CHANTHAPAN, S., RAPE, A., GEPHART, S., KULKARNI, A., SINGH, J Industrial Scale Field Assisted Sintering an Emerging Disruptive Manufacturing Technology: Applications. Advanced Materials & Processes, 2011, vol. 169, no. 8. pp. 25-28.

[3] SKIBA, T. Characterization of Spark Plasma Sintered and Thermally Sprayed Fe-Al Based Intermetallics (Ph.D. Thesis). Praha: KMAT-FJFI-CVUT, 2010. 160 p.

[4] SKIBA, T., HAUŠILD, P., KARLÍK, M., VANMEENSEL, K., VLEUGELS, J. Mechanical Properties of Spark Plasma Sintered FeAl Intermetallics. Intermetallics, 2010, vol. 18, no. 7. pp. 1410-1414.

[5] DEEVI, S. C. Powder Processing of FeAl Sheets by Roll Compaction. Intermetallics, 2000, vol. 8, no. 5-6. pp. 679-685.

[6] DEEVI, S. C., SIKKA, V. K. Nickel and Iron Aluminides: An Overview on Properties, Processing, and Applications. Intermetallics, 1996, vol. 4, no. 5. pp. 357-375.



a) FeAl b) stainless steel 316L

c) FeAl + Al_2O_3 d) FeAl + YSZ

e) FeAl + 316L f) Wall Colmonoy 88PTA

Fig. 3 Fractographs of samples after 3-point bending test