PHASE AND THERMAL ANALYSIS OF MICROSTRUCTURE EVOLUTION OF BI – METALLIC MATERIALS DURING HEAT TREATEMENT

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Abstract

Properties of materials made from elemental metallic powders deposited by cold gas dynamic spraying were studied – Fe-Al, Fe-Cu and Fe-Ni. The samples were annealed in protective atmosphere and macroscopic features like porosity were evaluated before sectioning. All samples were subjected to microstructure and thermal properties study. The mixtures were deposited on an aluminium substrate, so that the resulting material was free-form consolidated from the powder mixtures by high impact energy without melting or oxidation of the individual powder particles. The samples have been subjected to microstructure and phases analysis by scanning electron microscopy (SEM) and X – ray diffraction (XRD) analysis. The results from microstructure study and further observations are evaluated with the aim of possible feasibility to use the ColdSpray/annealing route as manufacturing technique for materials with useful properties.

Keywords: intermetallics, cold spray, diffusion annealing, reaction diffusion, microstructure analysis

1. INTRODUCTION

Intermetallic materials are interesting due to their excellent properties which are given by chemical composition and also by their by their crystallographic arrangement (crystal lattice type). Intermetallics usually usually have high strength, high hardness and low ductility and often good oxidation resistance at elevated temperatures.

Iron aluminides are attractive for their low specific weight, good wear resistance, high resistance against oxidation and carburization. Their raw materials are even relatively cheap. They can be useful in high temperature applications and in chemical industry. It is expected that FeAl-based alloys will substitute stainless steels or Ni-based superalloys. Potential uses of these intermetallics can be found in heating elements, sintered porous gas-metal filters, coating metallic alloys and catalytic converter substrates. [1][2] Unfortunately, iron aluminides have still some problems in fabrication. [3] It is given by their low ductility, large difference in the melting temperatures of Fe and Al and for sure their exothermic nature of formation of iron aluminides. The most frequently applied phases of iron aluminides are FeAl and Fe_3Al. [3]

Second examined system of deposited materials was the iron copper mixture. This system is unique because it has negligible miscibility in the solid state in equilibrium at temperatures below 700 ˚C. Total miscibility is considered to be only about 3 %. The reason for that behaviour is in thermodynamic; the enthalpy of mixing iron and copper (ΔH_{mix}) is approximately (+) 13 kJ/mol. [3] Copper alloys are generally known for their plasticity, toughness and high thermal conductivity. Their weaknesses are poor wear resistance and oxidation resistance. Alloys with larger amount of copper are suitable for applications where are required high strength or high electrical conductivity. Against that Fe-rich alloys are used as age-hardened ones. The system Fe–Cu can be produced by mechanical alloying, plasma spraying and laser cladding.[5][6][7]

The third bi–metallic material was a mixture of iron and nickel. This system contains some often used magnetically soft materials. The best known alloys of nickel and iron is the Invar alloy having low coefficient of expansion. [7] Nickel based alloys generally are regarded as high temperature resistant having high creep

strength. Nickel based materials are also widely recognized as catalysts for the fixed-bed methanation reaction of CO to CH4. Fe is being added to tune the catalytic behaviour. Usually the metallic catalyst is dispersed with ceramic support. In this study, only the metallic part was prepared as bulk material. Based on previous experiments, a porous structure was expected to evolve. Low iron content material has been deposited by cold spray in order to evaluate the feasibility of intermetallic material formation by heat treatment [8][9].

Cold spray technique uses accelerated solid powder particles to develop coating on substrate. This method makes use of expansion of working gas in Laval-type jet to super-sonic speeds. Temperature of working gas is lower than melting temperature of each component. Powder particles are carried by working gas and accelerated. Because these particles aren't melted during impact and flight, there is for example minimum oxidation and minimum residual stresses. [10][3]

2. EXPERIMENTAL SETUP

Cold spray technique was used to deposit the analysed materials. Nitrogen was used as working gas with temperature T = 400 ˚C and pressure about 50 bar. Gas flow was about 250 slm. FeAl samples were deposited by 20 passes, FeNi samples by 10 passes and FeCu samples by 8 passes. Deposited materials are in the fig. 1. Thickness of each deposit is on fig.2.

Fig. 1 Deposits of system FeNi, FeCu and FeAl (from left side)

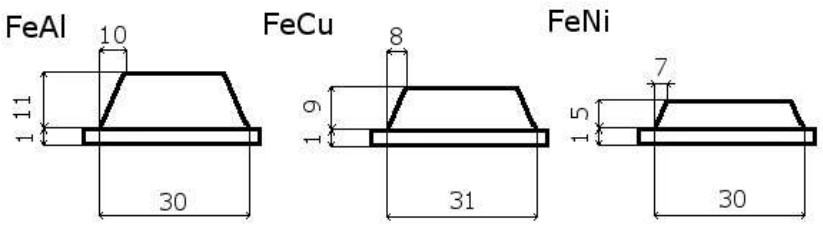

Fig. 2 Scheme of mechanical dimensions of the deposits

Each sample was cut from the relevant deposit by low speed saw and then annealed . Samples of FeAl were annealed at 550 ˚C, 650 ˚C and 750 ˚C. Pieces of FeCu were annealed at 900 ˚C and 1100 ˚C. FeNi samples were annealed at 500 ˚C and 700 ˚C. Each sample was annealed for 2 hours. The annealing was done in tube furnace under flowing argon protective atmosphere (1.0 l/min, 4.8 purity). The substrate material which was a commercial purity aluminium sheet was always removed before annealing.

After annealing the samples were fractured in two pieces. One piece of the material was used to prepare a metallographic sample by grinding and polishing techniques. Fracture surfaces were evaluated by electron

microscopy. Metallographic samples were analysed with light and electron microscopes. The Zeiss Axiovert Z1m and Zeiss UltraPlus FEG-SEM were used for light an electron microscopy respectively. OXFORD EDS mounted on the UltraPlus ws used for the chemical analyses.

Vicker's micro-hardness measurements were realized on each sample to provide mechanical property even though they were small and had large porosity. Indenting forces F1 = 0,09807 N or F2 = 0,1961 N were applied for 10 seconds.

3. EXPERIMENTAL RESULTS

3.1. FE-AL

Powders of Fe and Al were originally mixed in ratio Fe:Al 60:40 at.% (fig. 3). However, the as-sprayed material consisted from 68 wt.% Al and 32 wt.% Fe. The reason for this behaviour is that the chosen parameters during spraying weren't ideal.

The fracture surface of the as-sprayed material shows that aluminium particles were joined together very well (fig. 4). Aluminium still exhibits ductility fracture on some places, while iron particles were delaminated from the aluminium particles without braking.

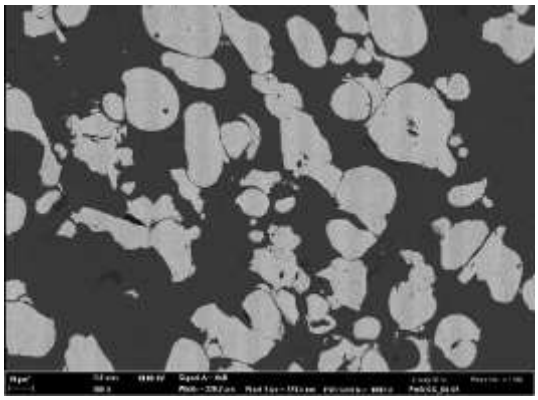

Fig. 3 *Microstructure of as deposited material*

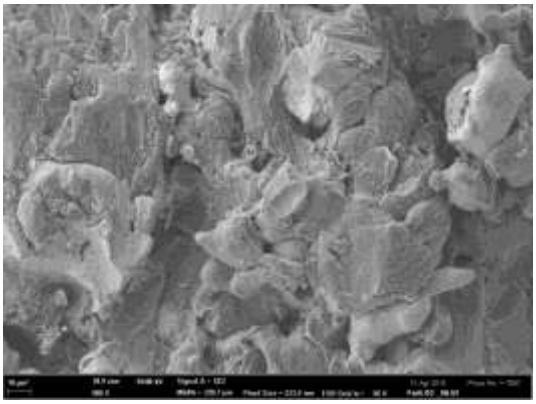

Fig. 4 *Fracture of the as deposited material*

First intermetallic phases were formed at 550 ˚C by mutual diffusion (fig. 5). Intermetallics occurred around iron particles on the interferences aluminium and iron particles. Porosity of the sample was higher than in as-sprayed material. These intermetallic phases were identified to be were $Al_{70}Fe_{30}$ according to analysis (fig. 6). This composition probably corresponds to non-equilibrium stage that eventually evolves in Al_3Fe. Micro-hardness of this sample was for aluminium particles 33 HV0,01, for iron particles 316 HV0,01 and for intermetallics about 1193 HV0,01.The sample fractured by cleavage in the intermetallic particles. Together Fe delamination and Sal ductile fracture is still visible (fig. 7).

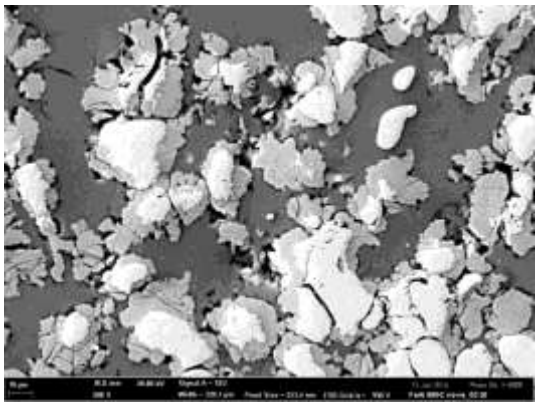

Fig. 5 *Microstructure of sample annealed at 550 ˚C*

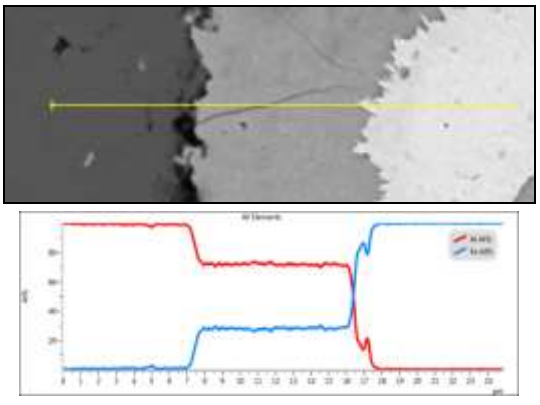

Fig. 6 *Linescan analysis, red line – aluminium, blue line – iron*

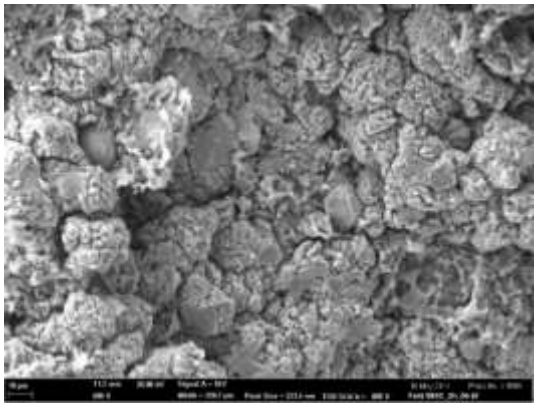

***Fig. 7**: Fracture surface of sample annealed at 550 ˚C*

Microstructure changed with rising temperature. In the sample annealed at 600 ˚C microstructure areas of fine lamellar mixtures, some isolated small remnants of iron and some solid solutions was revealed (fig. 8). The lamellar mixture was attributed to phases FeAl + $FeAl_2$. Solid solutions around remnants of iron changed their chemistry gradually into intermetallic phases. Microstructure of sample annealed at 650 ˚C was formed with the same phases as previous sample annealed at 600 ˚C. There were lamellar mixtures, isolated small remnants of iron and some solid solutions. Main difference was in the ratio of the phase areas (fig. 9). The chemical composition of solid solution at lower temperature was 60 at.% Fe and 40 at.% Al (fig.10). At this higher temperature homogeneous phase areas were generally bigger. The lamellar mixture had in this sample bigger inter-lamellar distance. Gradual change of chemical composition of the solid solution reaches Fe:Al ratio to be 50:50 at.%. (fig. 11). The changes of chemical composition are much more smoother at higher temperature. Porosity reached its maximum at 600 ˚C. Micro-hardness of the sample annealed at 600 ˚C was 1040 HV0,025. Sample annealed at 650 C had 1056 HV0,01 and for lamellar mixture 988 HV0,01.

The fracture surfaces of these two samples were very similar (fig. 12 and 13). Higher presence of brittle fracture was observed.

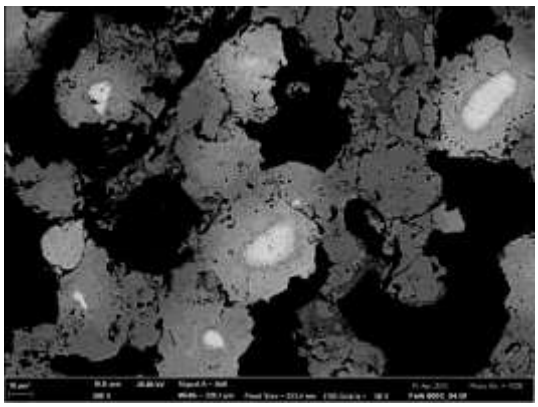

***Fig. 8** Microstructure of sample annealed at 600 ˚C*

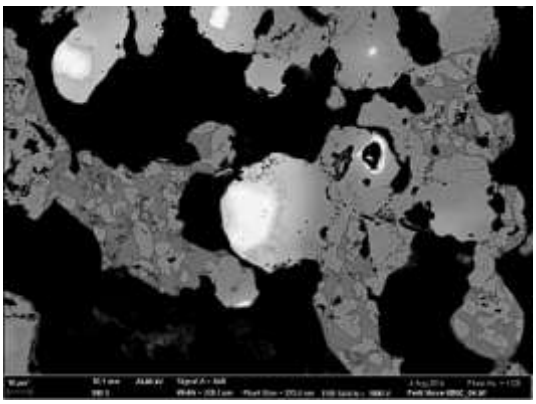

***Fig. 9** Microstructure of sample annealed at 650 ˚C*

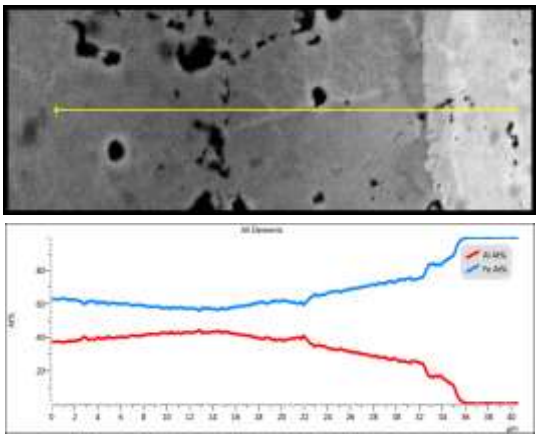

Fig. 10 *Linescan analyze made on sample annealed at 600 ˚C*

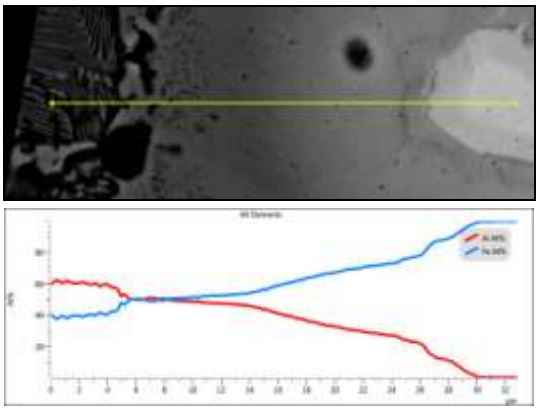

Fig. 11 *Linescan analyze made on sample annealed at 650 ˚C*

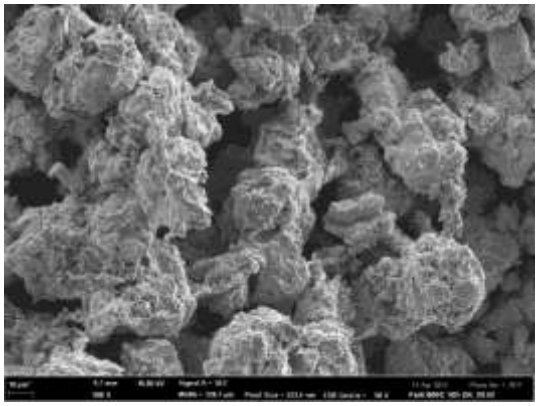

Fig. 12*: Fracture surface of sample annealed at 600 ˚C*

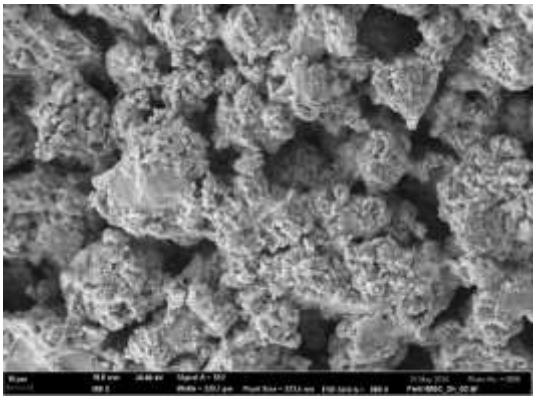

Fig. 13*: Fracture surface of sample annealed at 650 ˚C*

4. FE-CU

Microstructure of the as-sprayed sample is formed by copper and iron particles (fig. 14). Copper particles showed strong plastic deformation. Very small amount of porosity was obsedrved. There were no microcracks or cracks in deposited material. Although the elemental powders were mixed in ratio Cu:Fe 50:50 at.%, the final composition was about 90,2 wt.% Cu and 9,8 wt.% Fe. The micro-hardness values for iron particles was about 837 HV0,01 and for copper particles 276 HV0,01.

The fracture surface shows that copper particle break by ductile mechanisms with some delamination. Iron particles were delaminated from copper particles (fig. 15).

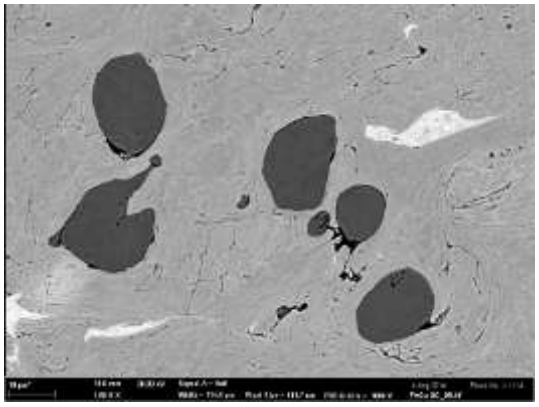

Fig. 14*: Microstructure of the as deposit material*

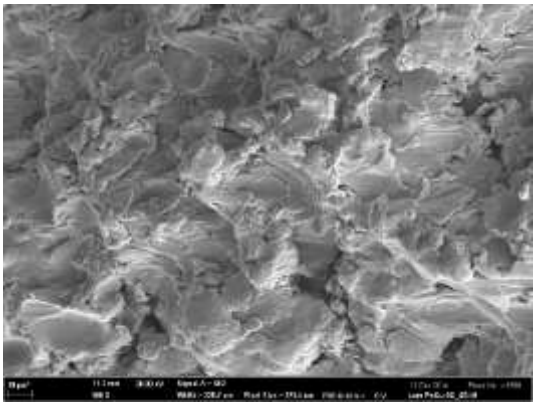

Fig. 15*: Fracture of the as deposit material*

After annealing at 900 and 1100~C, recrystallization twins can be found in both microstructures, in copper particles. No visible reaction between the metallic particles and evolution of strong porosity is striking. (fig. 16 and 17). The highest porosity was in the sample annealed at 900 ˚C. These pores are situated mainly on interfaces between copper and iron particles and between individual Cu splats. Linescan analysis of the sample annealed at 900 ˚C showed that microstructure around iron particle was formed with 3 at.% Cu in iron particle and with 3 at.% Fe in copper particles(fig. 18). The highest temperature had more pronounced changes in chemical composition (fig. 19). Solid solution of about 90 at.% Fe and 10 at.% Cu was found in the originally iron particles. Fluctuations of chemical composition in copper particles were observed; likely caused by iron rich precipitates. These iron precipitates had size about 1–2 μm. Measured micro-hardness of the sample annealed at 900 ˚C for iron particles was 320 HV0,01 and for copper particles was 86 HV0,01. Micro-hardness of the sample annealed at 1100 ˚C for iron particles was about 412 HV0,01 and for copper particles about 104 HV0,01.

The fracture surface of the sample annealed at 900 ˚C showed well developed ductile morphology (fig. 20). Sample annealed at 1100 ˚C was not available for fracture surface analysis.

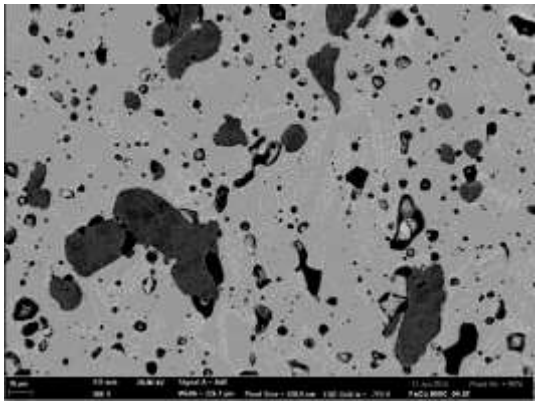

***Fig. 16**: Microstructure of sample annealed at 900 ˚C*

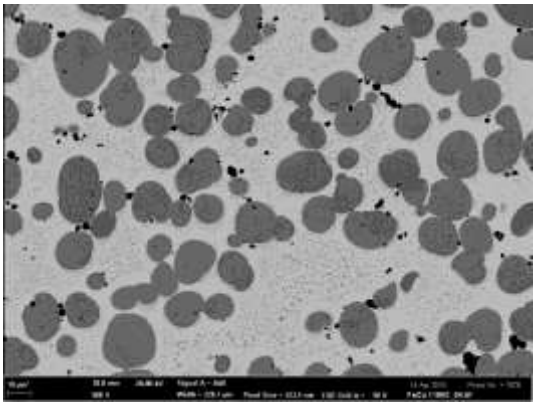

***Fig. 17**: Microstructure of sample annealed at 1100 ˚C*

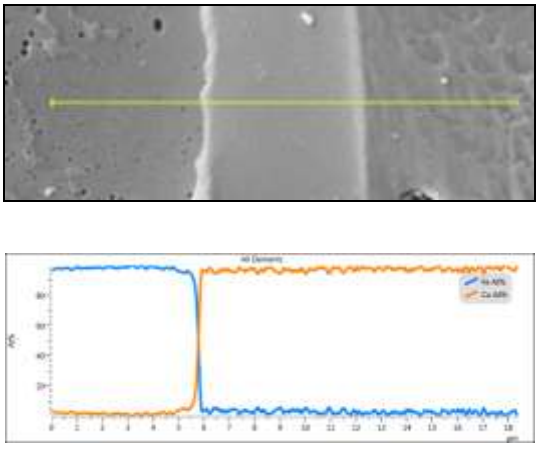

***Fig 18**: Linescan analyze made on sample annealed at 900 ˚C*

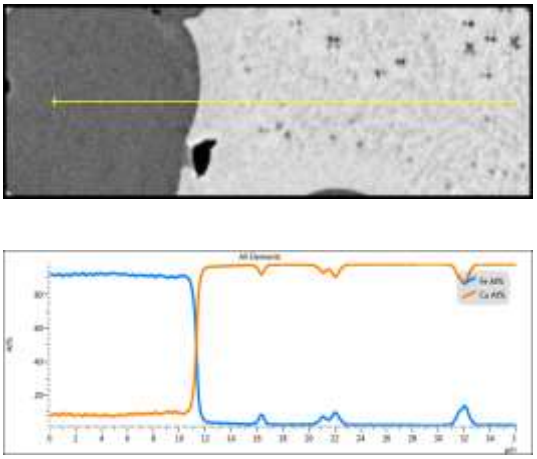

***Fig. 19**: Linescan analyze made on sample annealed at 1100 ˚C*

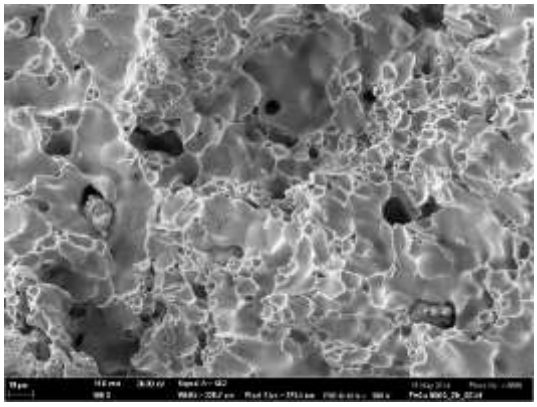

***Fig 20**: Fracture of sample annealed at 900 ˚C*

4.1. FE-NI

This deposit was the thickest one. In the structure of deposit there were many cracks and microcracks and because of it the preparation of samples was difficult. Some of that cracks had size about 200 μm. This was caused by incorrectly chosen spraying parameters. Microstructure of this sample is formed by iron and nickel particles (fig. 21). The amount of porosity is small. Even though the powders of nickel and iron were mixed in ratio Ni:Fe 60:40 at.%, the final composition was 95,3 wt.% Ni and 4,7 wt.% Fe. Micro-hardness for nickel particles avg 349 HV0,01 and for iron particles avg 809 HV0,01.

The fracture surface showed delamination joining cracks and microcracks from deposition of the material (fig. 22).

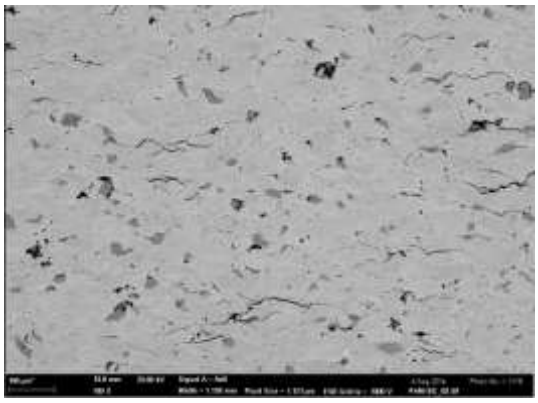

***Fig. 21**: Microstructure of the as deposit material*

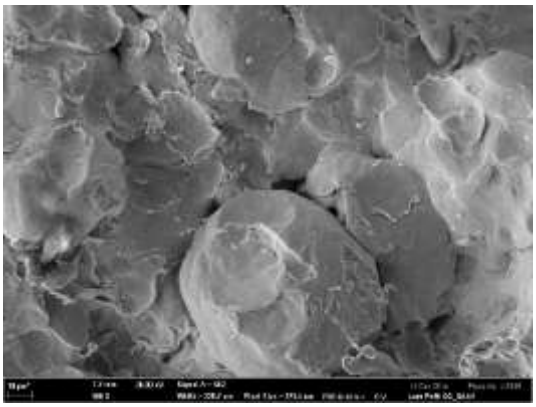

***Fig. 22**: Fracture of the as deposit material*

Microstructure after annealing at 500 and 700°C was formed by nickel and iron particles, pores and some microcracks and cracks (fig. 23 and 24). Microcracks and cracks were gradually recovered at both temperatures and their numbers lowered. The porosity had increasing tendency with higher temperature. Porosity existed on interfaces between splats and between iron and nickel particles. Minor mixing areas of about 8 μm were found after 500°C (fig. 25). With increasing temperature the higher diffusion rate formed solid solution about 90 at.% Fe and 10 at.% Ni. (fig. 26). Micro-hardness of sample with 500 ˚C annealing was for iron particles about 385 HV0,01 and for nickel 153 HV0,01. Measured micro-hardness of sample annealed at 700 ˚C for iron particles were 345 HV0,01 and for nickel particles about 136 HV0,01. Values of micro-hardness are smaller with higher temperature for both particles, which is probably caused by recovering plastic deformation strengthening of both metals.

The fracture surfaces started to change with increasing temperature. Delamination was mainly observed for lower temperature (fig. 27). Iron particles were delaminated from nickel particles also after 500 ˚C. Nickel particles shown more ductile behaviour. At higher temperature iron particles are partially dissolved into nickel

particles and almost whole fracture surface had ductile behaviour (fig. 28). Marks of brittleness were found on cracks and microcraks and some delamination still could be found..

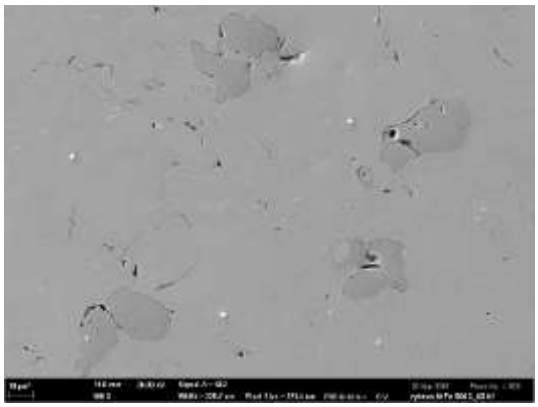

***Fig. 23**: Microstructure of the sample annealed at 500 ˚C*

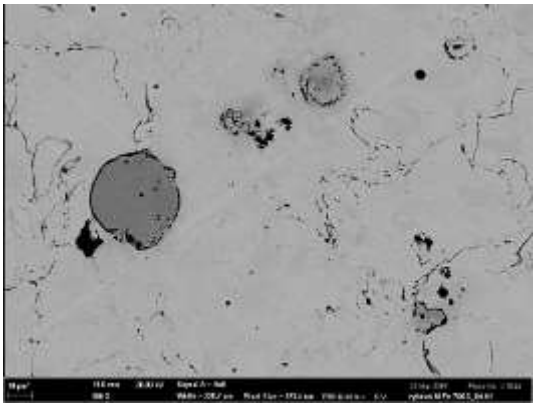

***Fig. 24**: Microstructure of the sample annealed at 700 ˚C*

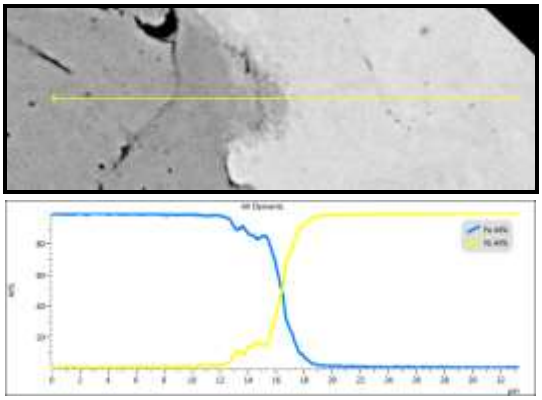

***Fig. 25**: Linescan analysis made on the sample annealed at 500 ˚C*

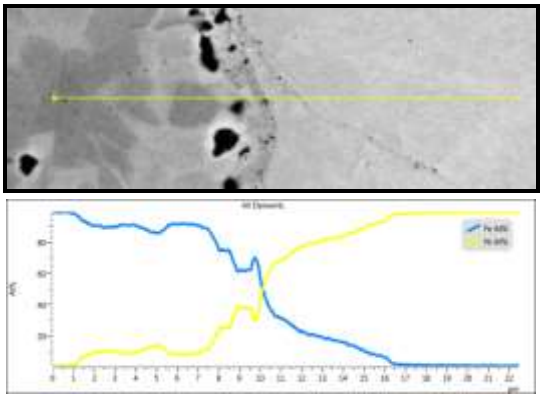

***Fig. 26**: Linescan analysis made on the sample annealed at 700 ˚C*

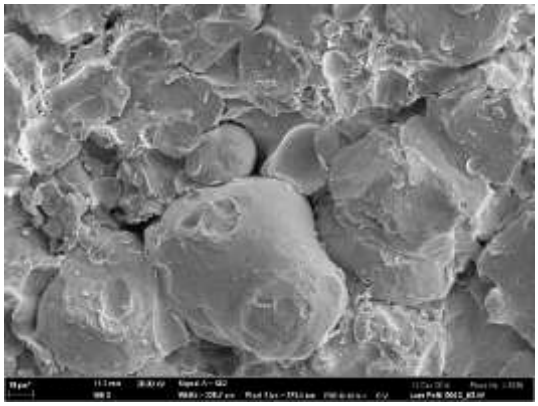

***Fig. 27**: Fracture of annealed material at 500 ˚C*

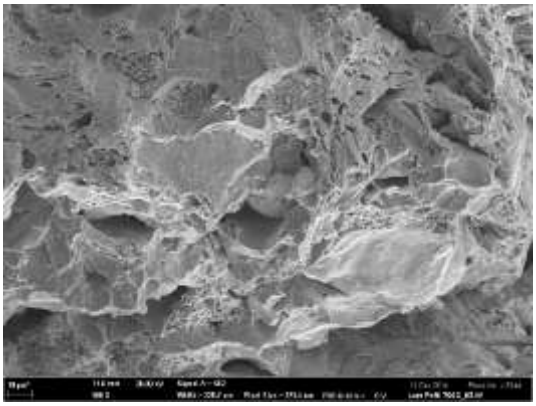

***Fig. 28**: Fracture of annealed material at 700 ˚C*

5. SUMMARY

Three different samples of three binary systems were prepared by the cold spray technique.. After analysing the as-deposited microstructure, the samples were subjected to a reactive diffusion heat treatment for two hours at different temperatures . After heat treatment, the microstructures were observed again using SEM.

The Al - Fe alloy showed a standard exothermic reaction between iron and aluminium while forming intermetallics. Samples of FeAl annealed at 550 ˚C already exhibited intermetallic phases on the interfaces of iron and aluminium particles. Mixtures of intermetallic phases with significant amounts of the lamellar

structure of FeAl + $FeAl_2$ were formed at 600 ˚C. Maximum of porosity was reached at 600 ˚C. Generally the intermetallic phases had very high values of micro-hardness.

In the Cu – Fe mixture, very limited mixing in solid state was ensured which follows the practically immiscible nature of the FeCu system. In FeCu system, pores evolved during annealing. Although the mutual solubility is minimal, solid solution was formed in iron particles with about 3 -10 at.% of Cu and precipitates of iron rich phases were found in copper. Although mixing and precipitation was achieved, micro-hardness was decreasing with increasing temperature for iron and copper particles. The fracture mode had changed with increasing annealing temperature. At lower temperature there occurred ductile fracture in copper particles and iron particles were delaminated from copper particles. At the highest temperature the fracture had practically only ductile character.

The structure of Fe-Ni deposit material recovered from improper deposition parameters with higher temperature. The amount of microcracks and cracks diminished while porosity was higher witrh higher annealing temperature. Mixing areas could be observed with some solid solution presence.

CONCLUSION

For Fe-Al and Fe-Cu, the cold spray approach with subsequent heat treatment may be considered as technically applicable technique for deposition for reactive mixtures in arbitrary shapes. Intermetallics with repeatable microstructure and porosity could be generated. Possible catalytic behaviour of the resulting material will be evaluated. For Ni-Fe system first the proper deposition parameters need to be evaluated so that the material may be deposited without the large amounts of cracking shown in this paper. Only then the material may be evaluated again for diffusion reaction testing.

ACKNOWLEDGEMENTS

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