# HEAT TREATMENT OF HYPO-EUTECTOID NITI ALLOY MANUFACTURED BY CGDS POWDER MIX DEPOSITION

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**Abstract**

Deposits of 92/8 at% Ti/Ni were produced by low-pressure cold spray technique using heated air as working gas. The chemical composition of the 8 mm thick was kept in hypoeutectoid concentration. Samples of the deposited material were annealed at temperatures from 500°C to 1000°C for two hours in argon protective atmosphere. Selected samples were quenched directly from the homogenizing temperature of 1000 and subsequently evolution of precipitated eutectoid was studied. Generally microstructural changes of material character during annealing were evaluated together with changes in the character of fracture behaviour and local micro hardness of the evolved phases. Microstructure and chemistry of the newly formed phases was evaluated using analytical electron microscopy. DSC study was involved in order to characterize the precipitation behaviour under eutectoid temperature. Gradual evolution of intermetallic phases by diffusion mechanism was observed. The samples general shape was preserved during the heating process although formation of Kirkendall porosity was evident. First occurrence of intermetallic phases was observed at 600°C. The evolved phases incurred by diffusion mechanism and included phases close to $Ti_2Ni$, TiNi, and $TiNi_3$.

**Keywords:** Cold Spray, reaction synthesis, intermetallics, diffusion, metallic foam

## 1 INTRODUCTION

Intermetallic phases typically exhibit strictly different crystallographic arrangement than the metallic elements form which they are constituted. Intermetallics also usually have high strength and lower ductility – characteristics that are connected to the crystal lattice type [1-3.] Manufacturing of intermetallic materials usually is limited to precise casting or casting and machining. In this study, the Cold Spray technique is used for deposition of arbitrarily shaped samples of material.

Cold Spray is a technique using gas that expands in Laval-type jet to super-sonic speeds as carrier medium for accelerating individual particles of the deposited powder which weld locally upon impact on the substrate or previously deposited particles. The fact that the particles are not melted during flight and at impact and that oxidation of the particles surface is minimal establishes this method not only as surface engineering method but also for bulk material deposition method, where high volumes of material ca be deposited [5,6].

## 2 EXPERIMENTAL SETUP

Cold Spray technique was used to deposit the analysed material. A powder previously mixed form pure Ni and Ti powders were used as feedstock. The elemental powders were mixed in the 50 at.% Ni : 50 at.% Ti ratio. Air was used as the carrier gas, temperature 300 °C and pressure 1.5 MPa. Samples in the form of bars were deposited by 20 consecutive passes of the nozzle. The resulting material had thickness of approx. 1 cm. (**Fig. 1**).

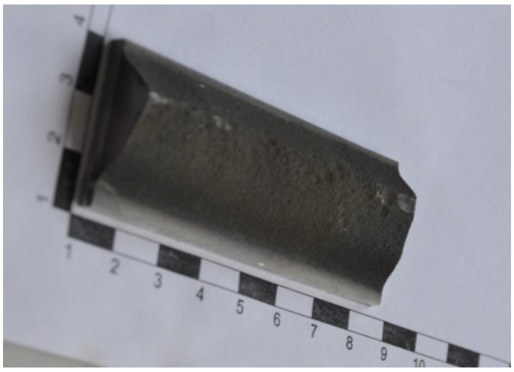

**Fig. 1** Overall appearance of the deposited material

This material was cut using low speed saw to samples 5x6x7 mm big which were then used for annealing experiments. The annealing was done in tube furnace under flowing Ar (1.2 l/min, purity 4N8) protective atmosphere. Temperature as measured directly at the sample which was placed into 100 g heavy stainless steel holder that provided homogeneous temperature field and also enabled fine control of the sample temperature. Only the deposited bi-metallic CS deposit was annealed after the Al temporary substrate was removed.

Following temperatures were used: 600, 700, 800, 900 and 1000 °C. The samples were heated relatively slow to the desired temperature; then 2 hours were used for the isothermal annealing. After two hours, the samples were left in furnace to slow cool still in the protective Ar atmosphere.

The annealed samples were fractured and one piece of the material was used to prepare a metallographic sample by standard grinding and polishing techniques. No etching was used, but colloid silica (OPS from Struers) was used for the last polishing step, which provided also visible microstructure.

Light microscopy and electron microscopy were used to evaluate both fracture surfaces and the polished metallographic samples microstructure (Zeiss Z1M light microscope, Zeiss UltraPlus FEG-SEM). For chemical analysis, local and mapping EDS analyses were used (OXFORD EDS mounted on the UltraPlus). XRD analysis was used for phase occurrence determination (Philips Xpert).

Micro-hardness measurements of the individual grains and microstructure constituents were used to provide also mechanical property despite the small size of the samples. Vickers indenter and $F_1$ = 0.09807 N were used as the indenting force for 15 seconds.

## 3 EXPERIMENTAL RESULTS

The as sprayed material shows strong change in the average composition when comparing to the original feedstock composition, this has changed form 50/50 at.% Ni/Ti to 8/92 at.% Ni/Ti. The deposition efficiency of nickel in this case was much lower than that of titanium (**Fig. 2**).

The fracture surface of the as-sprayed material shows nicely that titanium, although severely deformed by the deposition process, still possess some plasticity and produces mixed ductile fracture with large areas of decohesion, whereas the nickel particles do not break at all and the fracture surfaces contain delaminated nickel particles where the nickel particles and the titanium matrix have separated. In the as-deposited state there is no connection between the nickel and titanium particles. (**Fig. 3**).

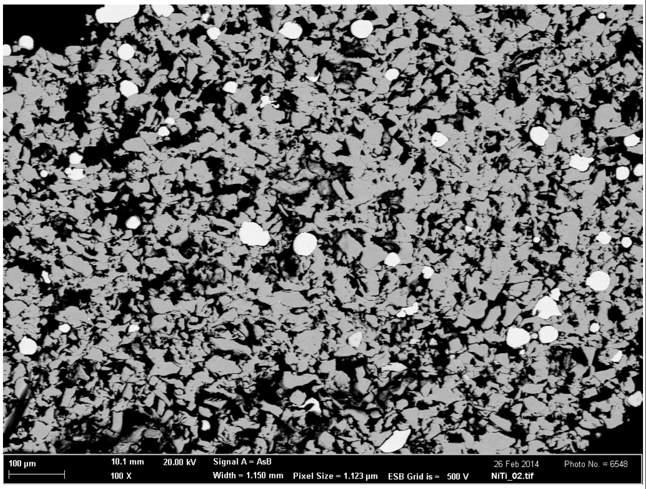

**Fig. 2** Microstructure of the as deposited material dark phase Ti, light phase Ni

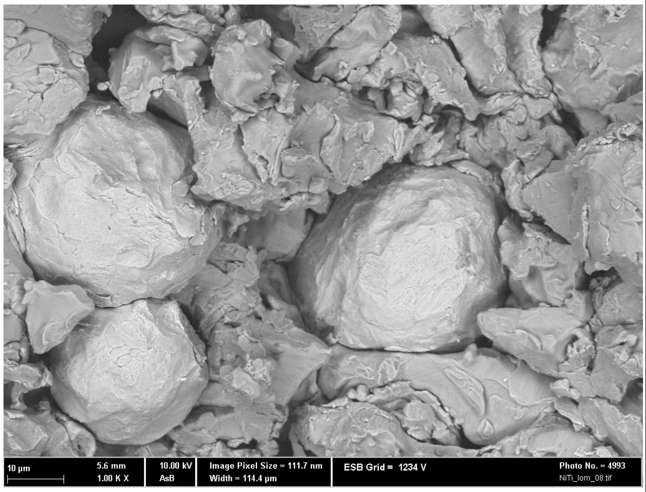

**Fig. 3** Fracture of the as deposited material

### 3.1 Annealing at 600 and 700 °C – sub eutectoid temperatures

Annealing at these temperatures caused changes in the micro hardness in individual nickel particles and also in limited extend in titanium particles, which later show increase in hardness.. This can be seen in **Table 1**. The as deposited titanium particles were too brittle for hardness measurements, later the annealed material is gradually recovering when annealed One exception in the monotonous decrease is the case of titanium particles hardness after annealing at 800 °C. The value is higher than the hardness value for 700 °C. We expect this is due to diffusion of nickel atoms into the titanium. This creates solid solution strengthened by substitution mechanism. The fracture surface character is unchanged in all samples with lower annealing temperatures. The fracture surface is composed of ductile fracture of the titanium and delamination of the nickel particles. A very limited amount of intermetallic phases was generated on the Ni-Ti interphase at both lower annealing temperatures. Point analysis showed that $NiTi_2$, NiTi a $Ni_3Ti$ were firmed in minute areas (Fig.4).

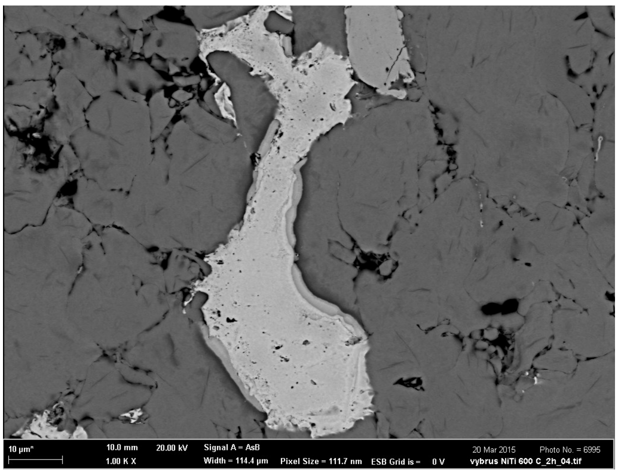

**Fig. 4** Microstructure of the material after 550 °C Darkest Al, grey $Al_{70}Fe_{30}$, lightest Fe

| Temperature | Ti particles | Ni particles |
|---|---|---|
| (°C) | HV 0.01 | HV 0.01 |
| 0 | - | 281 |
| 600 | 307 | 238 |
| 700 | 267 | 147 |
| 800 | 334 | 141 |
| 900 | 367 | 120 |
| 1000 | 326 | - |

***Table 1*** *Microhardness values of Ti and Ni particles*

### 3.2 Annealing at 800-1000 °C –above eutectoid temperature

At 800 °C new phases were formed rapidly around the nickel particles by mutual diffusion (**Fig. 5**). By local chemical analysis compositions both $Ti_2Ni$ a $TiNi_3$ were measured (**Fig.6**). 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. The diffusion speed is increased at elevated temperatures and with the possibility of beta titanium solid solution. After crossing the alpha to beta transformation temperature of titanium, the evolution of intermetallic phases was further increased.

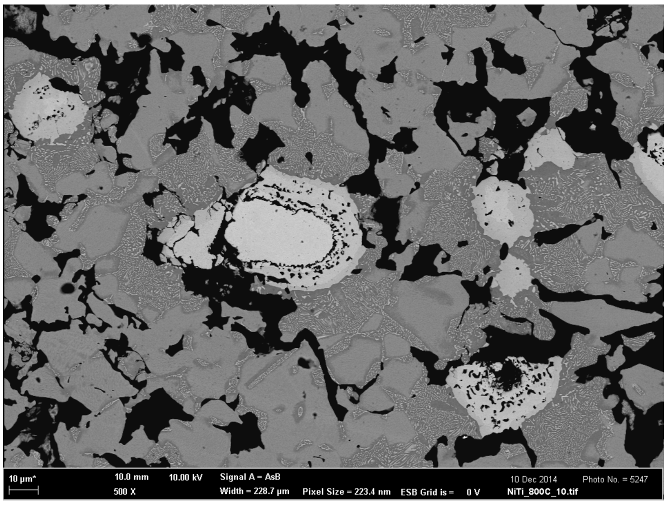


**Fig. 5** Microstructure of the material after 800 °C
Darkest Ti, lightest Ni and intermetallics

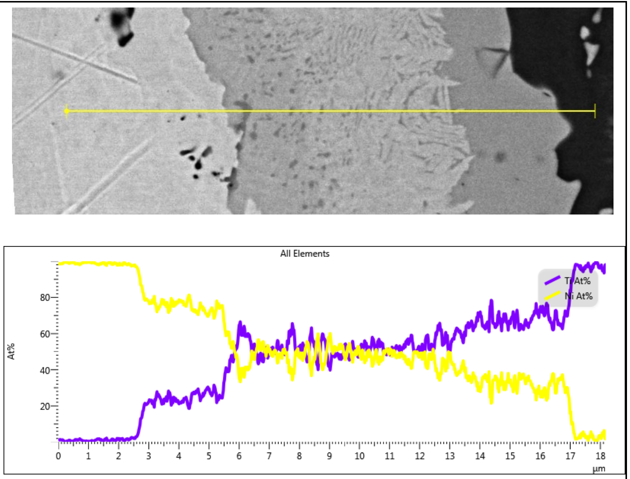


**Fig. 6** Analysis of the intermetallics formed at 800 °C

The next annealing temperature – 900°C is above the transformation temperature of beta titanium (882°C). While solubility of nickel in alpha titanium is very low , in beta titanium it is above 10 %, which greatly promotes diffusion and new phases formation. (**Fig. 7**). The titanium particles get enriched by nickel and gradually form network of eutectoid microstructure of α-Ti a $Ti_2Ni$. (**Fig. 7**). This composition was confirmed by EDX analysis. (**Fig. 8**). The nickel particles are surrounded by rings of intermetallic phases and porosity. Parts of the nickel particles can be still seen unreacted. The matrix of this material consists of alpha titanium and eutectoid mixture. The fracture is of predominantly cleavage mechanism in titanium areas. Eutectoid delamination between individual phases is possible in the areas of decomposed solid beta solution. (**Fig. 9**). Large amounts of porosity can be seen on the fractured surface and also in section of the microstructure. This corresponds to the original porosity of the as-deposited material. Only the shape of the porosity is changed to be more round and the individual titanium particles are well joined together.

At 1000°C, nickel is fully dissolved in beta titanium matrix. The microstructure at room temperature is formed by titanium the eutectoid mixture and intermetallic phase $Ti_2Ni$ **(Fig. 10 and 11).** The sample exhibits uniform and homogeneous character. The pores are nearly round which correspond with high diffusion rates.

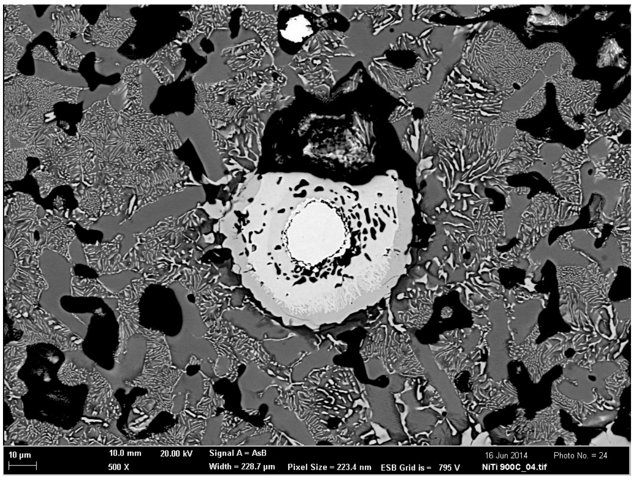

**Fig. 7** Microstructure of material annealed at 900 °C

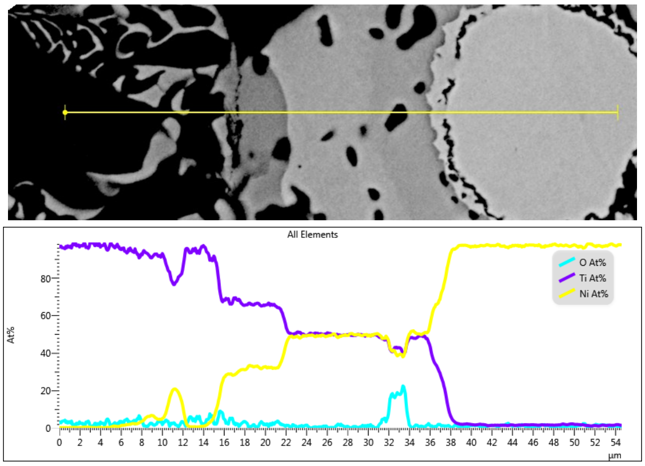


**Fig. 8** Analysis of the intermetallics formed at 900 °C

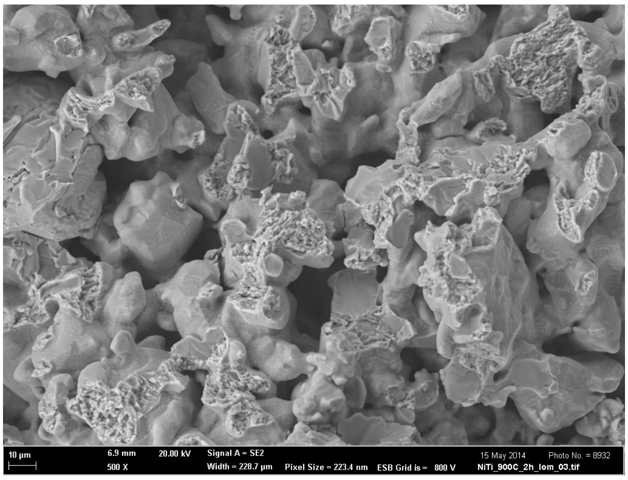

***Fig. 9** Fracture of material annealed at 900 °C*

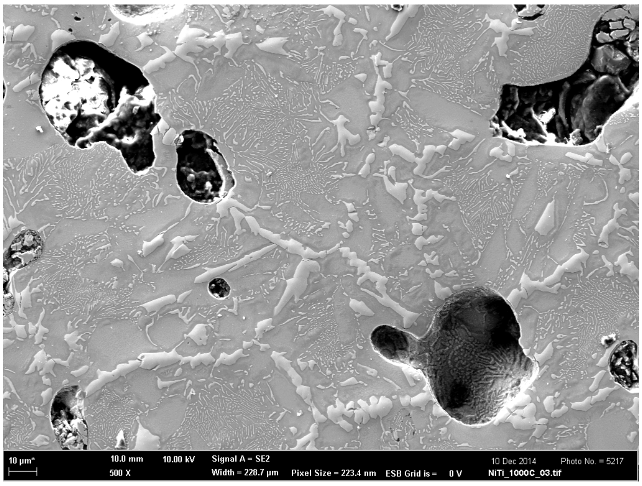

**Fig. 10** Microstructure of material annealed at 1000 °C

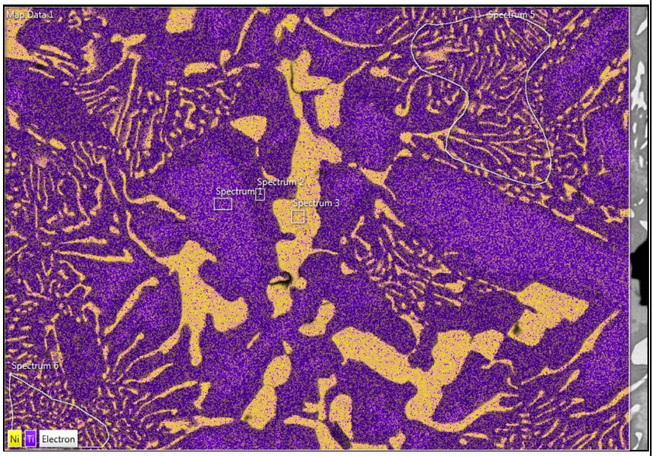


**Fig. 11** EDX map of nickel (yellow ) and titanium (magenta) in material annealed at 1000°C

## 4. SUMMARY

The samples annealed at lower temperatures of 600 and 700 °C exhibit already minor new phases formation. Gradual change of local hardness of the nickel and titanium particles was observed, which can be attributed to deformation strengthening healing and then by solid solution strengthening of titanium. The generation of new phases is in accordance with the previously published works [7-8].

Homogeneous microstructure of eutectoid accompanied by $Ti_2Ni$ intermetallic and titanium solid solution was generated after high temperature annealing. All samples had microstructure with porosity. First there was the porosity generated during deposition between the titanium particles. This gradually changed shape as the titanium particles welded and the sharp angle voids begun to change to more rounded shape. It may be considered that this was motivated by the minimization of free surface energy in the material [9-11]. The porosity appeared to be of open type, so the material is in the form of solid metallic sponge. The porosity mainly originates in the depositing porosity; however some Kirkendall porosity mainly at medium temperatures around 800 and 900°C could be seen around the nickel particles [12-13].

The porous intermetallic material manufactured by this approach can be used further for matrix reinforcement by melt infiltration or simply as is for filtering or catalyst support for high temperatures taking advantage of the high temperature resistance of the intermetallic phases and the high specific surface of the open porosity.

## CONCLUSIONS

Ni Ti intermetallics were created by annealing of elemental powders cold spray deposit. Uniform porosity materials were created at repeated attempts. Since the cold spray technique allows to form any shapes and sizes of the deposits, the material can be considered for technical applications rather than similar products achieved by pressing or free powder reactions.

## ACKNOWLEDGEMENTS

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