



Powder Metallurgy of NiTi-Alloys with Defined Shape Memory Properties

Martin Bram, Ariane Ahmad-Khanlou, Hans Peter Buchkremer, Detlev Stöver

Forschungszentrum Jülich GmbH
Institut für Werkstoffe und Verfahren der Energietechnik IWV-1
D-52425 Jülich, Germany

Summary

The aim of the present work is the development of fabrication processes for NiTi shape memory alloys by powder metallurgical means. The starting materials used were prealloyed powders as well as elemental powder mixtures. Three techniques seem to be very promising for shaping of NiTi compacts. Hot Isostatic Pressing (HIP) has been examined for the production of dense semi-finished components. A promising technique for the production of dense and porous coatings with an increased wear resistance is Vacuum Plasma Spraying (VPS). Metal Injection Moulding (MIM) is especially suitable for near-net shape fabrication of small components with a complex geometry considering that large numbers of units have to be produced for compensating high tool and process costs. Subsequently, thermal treatments are required to establish defined shape memory properties. The reproducibility and stability of the shape memory effect are main aspects thinking about a production of NiTi components in an industrial scale.

Keywords:

Shape memory effect, NiTi, Nitinol, powder metallurgy, Hot Isostatic Pressing, Vacuum Plasma Spraying, Metal Injection Moulding

1. Introduction:

The requirement for the occurrence of the shape memory effect is a reversible and diffusionless austenite \leftrightarrow martensite transformation. Normally this transformation is caused by a change of temperature. Additionally, in the case of a metastable austenite a stress induced austenite \leftrightarrow martensite transformation at a constant temperature is also possible (pseudoelectricity). Although different materials exist showing shape memory effects, at the present near stoichiometric NiTi alloys are of greatest scientific and economic interest (1). The transformation of these alloys occurs within

the temperature range between 50 and 100°C and strongly depends on the chemical composition (usually 48 – 51 at.-% Ni). It has been observed that a variation of the Ni content by 0.1 at.-% changes the transformation temperature by approx. 10 K (2). As indicated in the binary phase diagram (Fig. 1) there are additional stable phases (NiTi_2 , Ni_3Ti) in the above mentioned composition range beneath the main phase NiTi . These additional phases do not show any shape memory effect but their formation changes the composition of the remaining NiTi matrix. Additionally, the decreased solubility of Ni at lower temperatures lead to the formation of the finely dispersed metastable Ni_4Ti_3 phase (3). Annealing at 300 – 600°C is followed by a coarsening of this phase and finally a transformation to the stable Ni_3Ti phase occurs (3). Especially the fine Ni_4Ti_3 dispersion has a strong influence on the austenite \leftrightarrow martensite transformation.

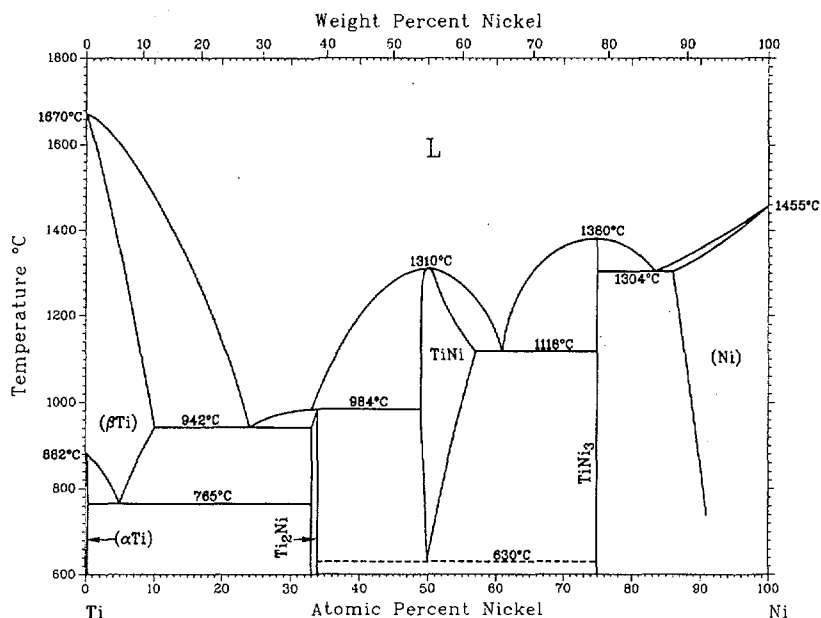


Fig. 1 Binary phase diagram of the Ni-Ti-system (4).

Powder metallurgy (PM) is a well known technique to adjust the chemical composition with high accuracy. Therefore, NiTi shape memory alloys were produced about 20 years by powder metallurgical means (5)(6)(7). Preferred techniques were combustion synthesis or reaction sintering (8)(9). But some disadvantages have prevented an application of PM routes for production of shape memory alloys in an industrial scale until now. In principle, NiTi alloys can be made

from elemental powders as well as prealloyed powders. In the first case the ductility of elemental powders allows the use of conventional PM equipment. After compaction the NiTi phase is formed by an exothermic reaction during the sintering process. Unfortunately, the different diffusion coefficients of Ni and Ti lead to the appearance of Kirkendall porosity (7). This effect is enhanced by partial formation of eutectic melt (β -Ti - Ni₂Ti) at 942°C (see Fig. 1). On a macroscopic level an anisotropic swelling of the pressed compacts is observed. A further disadvantage is the strong affinity of Ti and its alloys to oxygen, nitrogen and carbon during the sintering process leading to undesired formation of oxides, nitrides and carbides. This has a negative influence on the mechanical and shape memory properties (10)(11)(12).

Prealloyed powders do not show the appearance of the Kirkendall effect, but they are currently quite expensive due to the small production units: A technical problem takes place if the powder particles show a pseudoelastic behavior. The high springback of each powder particle immediately leads to a destruction of pressed compacts. Therefore, their use is restricted to methods where the shaping is done without pressure during compaction (e. g. metal injection moulding).

The present work deals with the optimization of promising techniques regarding to a subsequent transfer to industrial scales. *Hot Isostatic Pressing (HIP)* was used for the production of semi-finished parts (13)(14). This pressure-enhanced sintering technique generally leads to products with almost theoretical density and allows a direct comparison of mechanical and shape memory properties of PM parts and parts produced by melting technologies. A preferred method for the production of dense or porous NiTi coatings is *Vacuum Plasma Spraying (VPS)* due to its high deposition rate and high level of automatization (15). Potential applications of these coatings are wear resistant protective layers and biomedical functional layers. In both cases the resistance to corrosive environments is of special interest. *Metal Injection Moulding (MIM)* has high potential for the near net shape fabrication of small PM parts with complex geometries. Elemental powder mixtures are not useful for this technique due to the anisotropic swelling of the compounds during sintering. The MIM process becomes economic, if production of high quantities or compounds with complex geometry is provided.

2. Experimental:

Table 1 gives the manufacturer, the nominal particle sizes and the impurities of the powders used in this investigation. In addition, the transformation temperatures of the prealloyed NiTi powder for cooling (A_p , austenite \rightarrow martensite) and heating (M_p , martensite \rightarrow austenite) are included.

Table 1: Elemental and prealloyed powders used in this investigation.

Powder	particle size (μm)	manufacturer	oxygen (wt.%)	carbon (wt.%)	nitrogen (wt.%)	M_p ($^{\circ}\text{C}$)	A_p ($^{\circ}\text{C}$)
Ti	< 45	GfE, Nürnberg	0.225	0.039	0.014	-	
Ni	< 45	H.C. Stark, Goslar	0.376	0.035	0.032	-	
NiTi (50.9 at.% Ni)	< 22	Nanoval, Berlin	0.077	0.069	0.002	- 80	- 40

In order to obtain NiTi alloys capable of precipitation, all investigations were done with Ni-rich alloys (≥ 50.5 at.% Ni). Elemental powder mixtures were homogenized in a Turbula mixer for 24 h in a bottle without addition of grinding balls to keep impurities low. The prealloyed powder was used as delivered.

Hot Isostatic Pressing (HIP)

The HIP process was done in cylindrical stainless steel capsules (316L) using an elemental powder mixture with 50.5 at.% Ni. To avoid an excessive deformation of the capsules during the HIP process, a precompaction of the powder mixture was necessary. Therefore, cold isostatically compacted cylinders (compacting pressure 400 MPa) with approx. 70 % of theoretical density were filled into the capsules. Then the capsules were welded in vacuum. The hot isostatic pressing step was done at a pressure of 195 MPa. Regarding to the phase diagram (Fig. 1) sintering temperatures were chosen to 850, 950 and 1050 $^{\circ}\text{C}$ for 5 hours each. At 850 $^{\circ}\text{C}$ the reaction between Ni and Ti is controlled by solid state diffusion processes. A transition to liquid phase sintering takes place at 950 $^{\circ}\text{C}$ due to the appearance of an eutectic melt (Ti-Ti₂Ni-eutectic with a melting temperature of 942 $^{\circ}\text{C}$) at the reaction front. At 1050 $^{\circ}\text{C}$ the reaction is strongly influenced by liquid phase sintering. After the HIP process, the capsules were removed by machining. To avoid uncontrolled precipitations inside the NiTi phase, all samples were thermally treated in evacuated quartz glass capsules at 850 $^{\circ}\text{C}$ for 1 h (solution annealing) and then water quenched. Annealing of the quenched samples at 500 $^{\circ}\text{C}$ for 1 h was performed in order to achieve a controlled precipitation of fine dispersed Ni₄Ti₃ particles. The samples were subsequently prepared for morphological investigations, X-ray diffraction (XRD) as

well as differential scanning calorimetry (DSC) to determine the transformation temperatures.

Vacuum Plasma Spraying (VPS)

Starting material for the VPS process was an elemental powder mixture (50.8 at.% Ni). The spraying process was carried out using a facility from Sulzer Metco. Due to the high affinity of the Ti powder to oxygen and nitrogen, the spraying process was performed in a vacuum chamber (10^{-2} mbar). All substrates made of stainless steel were sandblasted to increase the adherence of the coatings. The substrates were mounted in the vacuum chamber with a spraying distance of 250 mm. Argon, hydrogen and helium and mixtures of these gases were used as plasma gases. The max. arc power was approx. 55 kW. The substrates were preheated to 850°C by the plasma arc monitoring the temperature by a pyrometer. The elemental powder mixture was fed into the plasma arc. Molten droplets of NiTi were formed and accelerated onto the substrate. Thus, a layerwise coating of the substrate was obtained. Under optimized conditions the coatings show already in the as-sprayed state the desired properties like increased wear resistance. In order to investigate a possible improvement of the desired NiTi-layer properties, thermal treatment of samples was performed at 900°C for 2 hours. However, it should be considered that annealing may lead to a change of the microstructure of the substrate. Samples were prepared for optical microscopy and XRD.

Metal Injection Moulding (MIM)

For the MIM process a gas-atomized, prealloyed NiTi powder (50.9 at.% Ni) with spherical particle shape (particle size < 22 µm) was used. Wax and binder were added to the powder and the mixture was homogenized for 4 hours using an heatable kneader. Three different feedstocks were produced. Table 2 shows the nominal composition of these feedstocks.

Table 2: Nominal composition of feedstocks used in this investigation.

	nominal composition
feedstock 1	NiTi + 34 Vol.% (wax + binder)
feedstock 2	NiTi + 28 Vol.% (wax + binder)
feedstock 3	NiTi + 28 Vol.% (wax)

The main parameters for the injection moulding process (temperature of feedstock and die, injection pressure, mass flow) were optimized regarding to uniform filling of the die. Further criteria for defect-free green bodies are the lack of macroscopic pores, shrink holes and cracks. As model geometry small rods as well as hollow cylinders were moulded. Fig. 2 shows the dimensions of the parts.

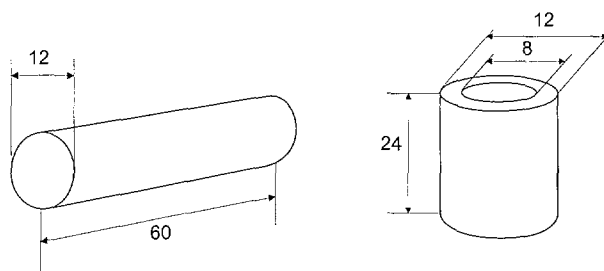


Fig. 2: Dimension of the MIM parts.

Dewaxing was achieved by thermal treatment on a sand bed. The capillary action of the sand supports the removal of wax out of the green bodies. Due to the low sintering activity of prealloyed NiTi powders, a sintering temperature above 1100°C has to be chosen to get parts with closed porosity. As an optional step, theoretical density can be achieved then by a subsequent HIP process without encapsulating (195 MPa, 1050°C, 3 h).

The microstructures of different samples were examined under an optical microscope from Olympus equipped with M.A.R.S. software and under JOEL (JSM-T300) scanning electron microscope and by energy-dispersive X-ray analysis (EDX). X-ray diffractograms were recorded using a Siemens diffractometer (D-500) with Cu-K α radiation in the angular range of $2\theta = 30 - 70^\circ$ at step rates of 0.01°/10 sec. A device from TA-Instruments (DSC 2920) was used for DSC measurements.

3. Results and discussion:

Hot Isostatic Pressing

Fig. 3 shows the microstructure of HIPed samples depending on the sintering temperature. Phase compositions marked in Fig. 3a were examined by EDX. After 5 hours at 850°C unreacted Ti as well as intermediate phases (NiTi₂, Ni₃Ti) are still visible, but NiTi is already present as the major phase. As expected, intermediate phases surround elemental phases leading to core-shell structures. This microstructure is typical for diffusion-controlled reaction sintering. With increasing sintering temperature a homogenization of the microstructure occurs (Fig. 3b). Liquid phase sintering at 1050°C leads to the most homogeneous microstructure, where large areas of intermediate phases do not longer exist (Fig. 3c). The expected precipitation of Ni-rich phases (Ni₄Ti₃) in the NiTi matrix is unverifiable by optical microscopy.

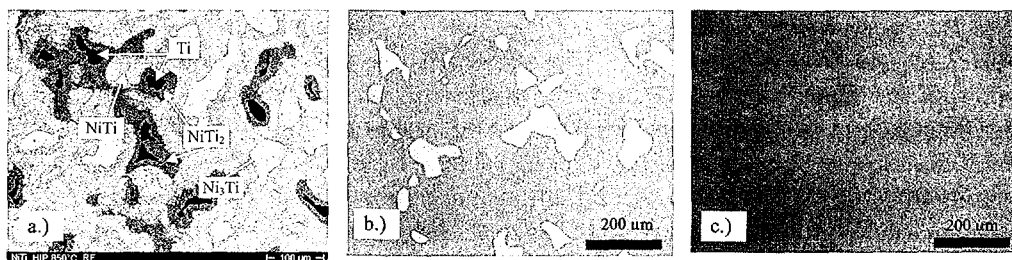


Fig. 3 Microstructure of NiTi samples made of elemental powder mixtures. The samples were HIPed at a.) 850°C b.) 950°C c.) 1050°C for 5 hours each at 195 MPa.

Due to the obtained homogeneity all samples used for further investigations are HIPed at 1050°C. For economic reasons, a decrease of the holding time (5 hours) was aspired. Anyhow, the decrease (e.g. 3 hours) resulted in the formation of transition phases again – similar to Fig. 3b – and was not realized (16).

To investigate the influence of Ni-rich precipitations in the NiTi matrix on the temperatures of the reversible austenite \leftrightarrow martensite transformation, samples were solution treated at 850°C, then water-quenched and subsequently annealed at 500°C. The diffraction patterns of the different annealing steps are given in Fig. 4.

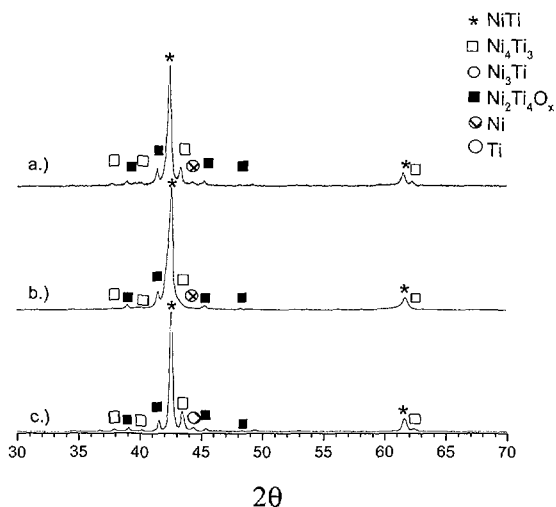


Fig. 4: Diffraction patterns of NiTi samples HIPed at 1050°C, 195 MPa, 5 hours a.) after furnace cooling b.) solution treatment at 850°C, water-quenched c.) annealed at 500°C, water-quenched.

The DSC measurements reveal the temperatures for the reversible transformation of austenite (A) to martensite (M). The sensitivity of the DSC equipment ranges between -150 and $+150^{\circ}\text{C}$. Therefore, phase transformations outside this range were not detectable. Fig. 5 shows an example of DSC measurement for a sample annealed at 500°C for 1 hour (water-quenched). Table 3 summarizes the results of DSC measurements. Obviously, a strong influence of the Ni_4Ti_3 precipitations exists. Whereas the solution-treated sample do not show any phase transformation in the measuring range, the precipitation of Ni_4Ti_3 causes an austenite \rightarrow martensite transformation at 9°C (cooling) and the reversible transformation at 12°C (heating).

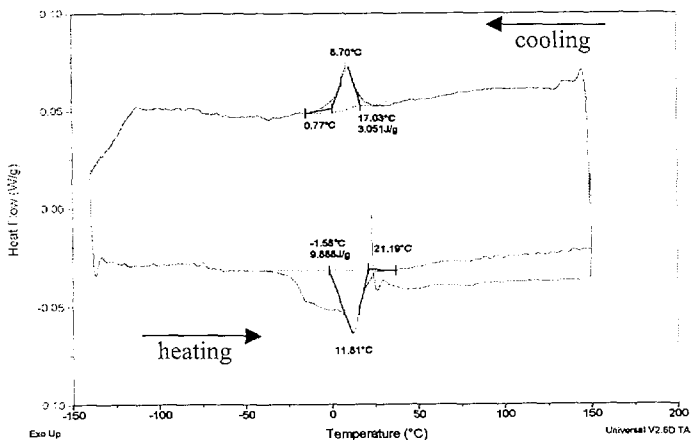


Fig. 5: DSC measurement of HIPed NiTi samples (1050°C , 195 MPa, 5 h) annealed at 500°C , 1 h. The precipitation of Ni_4Ti_3 is responsible for the appearance of phase transformations.

Table 3: Transformation temperatures of HIPed NiTi samples (1050°C , 195 MPa, 5 h) heat treated at 500°C and solution treated at 850°C , each 1h (water-quenched).

Sample	M_s ($^{\circ}\text{C}$)	M_m ($^{\circ}\text{C}$)	M_f ($^{\circ}\text{C}$)	A_s ($^{\circ}\text{C}$)	A_m ($^{\circ}\text{C}$)	A_f ($^{\circ}\text{C}$)
HIP 1050°C $500^{\circ}\text{C}/1\text{h}$	17	9	1	-2	12	21
HIP 1050°C $850^{\circ}\text{C}/1\text{h}$	-	-	-	-	-	-

M: martensite, A: austenite, Index - s: start, m: middle, f: finish

A comparison of the microstructure, transformation temperatures and mechanical properties of HIPed and melted NiTi samples is subject of further investigations to determine the influence of the production route on the shape memory effect. As an example of use in near future flexible couplings for damping and load limitation purposes will be machined from semi-shaped HIP products and applied in a suitable test rig.

Vacuum Plasma Spraying (VPS)

In Fig. 6 the microstructure of plasma sprayed NiTi coatings is given. In the as-sprayed state the coating shows the typical lamellae microstructure caused by the spraying process. After cooling down stresses occur in the layer due to the high cooling rates, the different thermal expansion coefficients (TEC) of coating and substrate and the different TEC of the various stable phases. As worst case microcracks were formed between the lamellae (Fig. 6a). Subsequent thermal treatment (900°C, 2 h) leads to reduced stresses and a homogenized microstructure (Fig. 6b). Additionally, healing up of some microcracks was observed.

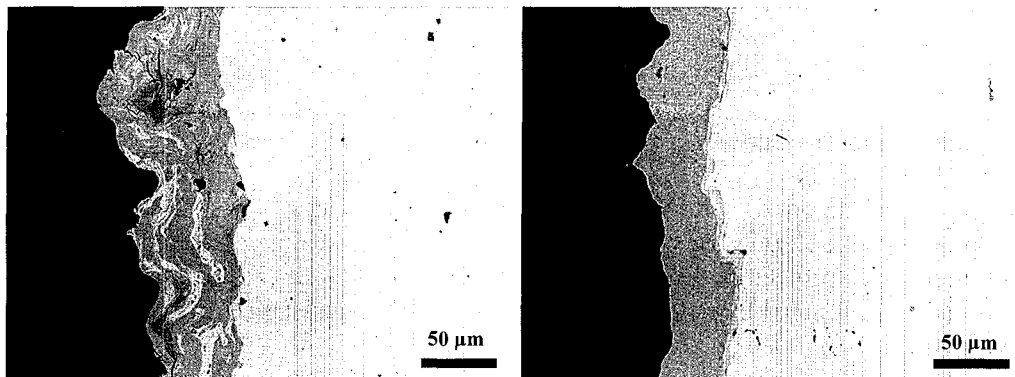


Fig. 6: Microstructure of plasma-sprayed NiTi-coatings onto a steel substrate **a.)** as sprayed state **b.)** annealed at 900°C, 2 h.

The diffraction patterns of as-sprayed as well as thermal treated samples are given in Fig. 7. As indicated in Fig. 7a elemental Ni and Ti are already clearly reduced in the as-sprayed state. After the subsequent thermal treatment at 900°C for 2 hour no elemental Ti is detectable but pure Ni is still apparent (Fig. 7b). However, the existence of pure Ni makes this layers unattractive for biomedical applications. Compared to the investigated HIP samples the content of transition phases (Ni₃Ti,

NiTi₂) and mixed oxides (Ni₂Ti₄O_x) is much higher. The high oxidation rate is probably caused by the low vacuum of the VPS chamber (10⁻² mbar).

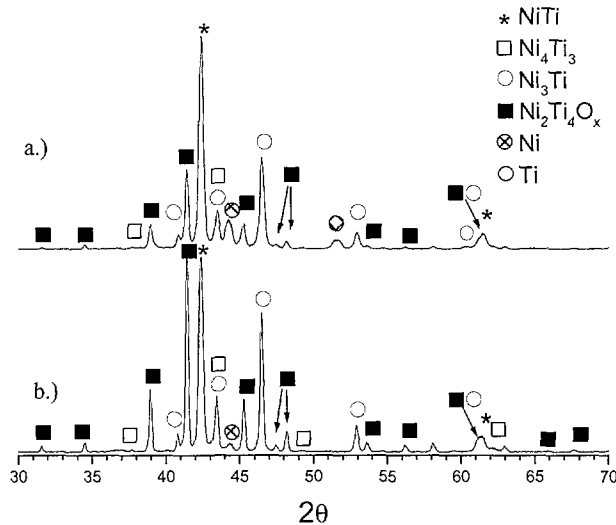


Fig. 7: Diffraction patterns of plasma sprayed NiTi coatings a.) as sprayed b.) annealed at 900°C, 2 h.

It has been reported that NiTi shows an improved wear resistance due to its pseudoelastic deformation behavior. Therefore, plasma sprayed coatings are discussed as protection against abrasive loads as well as cavitation effects (15)(17)(18). Related experiments to estimate the wear resistance of plasma sprayed NiTi coatings are done by now.

Metal Injection Moulding (MIM)

MIM process was optimized to achieve dense NiTi parts without extensive formation of oxides and carbides caused by uncompleted debinding. The first step of the improvement was the development of a suitable feedstock. The content of wax and binder plays an important role. Samples with approx. 34 vol.% wax and binder are susceptible to massive failures. After debinding large cavities and pores are still visible (Fig. 8a). The reduction of wax and binder content to 28 vol.% leads to an improved die filling behavior without obvious failures (Fig. 8b). Samples produced only by using wax do not show a sufficient green strength. Therefore, they are not suitable for further investigations.

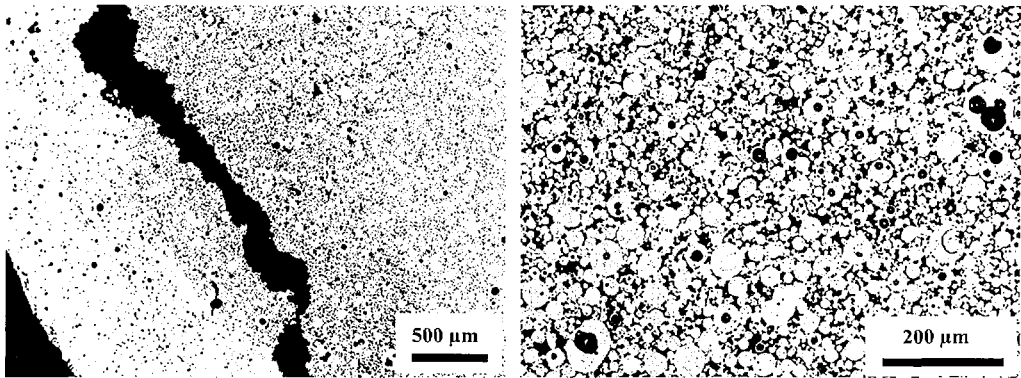


Fig. 8: Influence of wax and binder content on the die filling behavior **a.)** 34 vol.% wax and binder **b.)** 28 vol.% wax and binder.

Whereas the dewaxing of the MIM parts could be done by conventional techniques using a sand bed, the low sintering activity of prealloyed NiTi powders required an optimization of the sintering process. It was observed that a sintering temperature above $0.9 \cdot T_m$ (melting point of NiTi) was necessary to get a closed porosity, which is a prerequisite for mechanical stability of sintered parts. Another problem is related to the production process of the NiTi powders by gas atomization. Approx. 5 % of the powder particles are hollow spheres (see Fig. 8b). Pores inside of powder particles remain nearly unchanged during the sintering process even at temperatures above $0.9 \cdot T_m$. Therefore it was impossible to achieve theoretical density by pressure-less sintering (Fig. 9a). In case of closed porosity a subsequent capsuleless HIP process (1050°C , 195 MPa, 3 h) led to theoretical density (Fig. 9b).

The MIM process of Ti-alloys is always critical regarding to the remaining impurities, especially oxygen and carbon. Fig. 10 shows the content of impurities after the different processing steps. Due to the fact that the starting powder had a low level of impurities, the further increase caused by the MIM process could be acceptable. The influence of high oxygen and carbon levels on the shape memory effect is not clear at the moment and will be subject of further investigations.

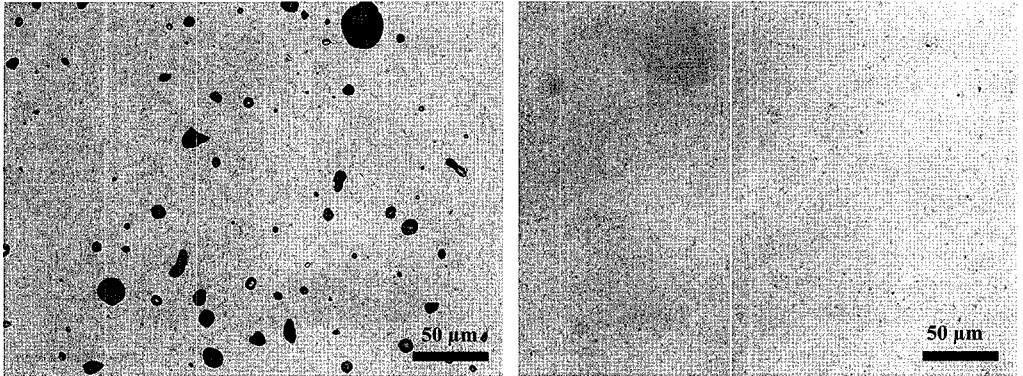


Fig. 9: Sintering of MIM parts a.) pressure-less sintering at temperature above $0.9 \cdot T_m$ leads to closed porosity of approx. 5 % b.) subsequent HIP (1050°C, 195 MPa, 3 h) leads to theoretical density.

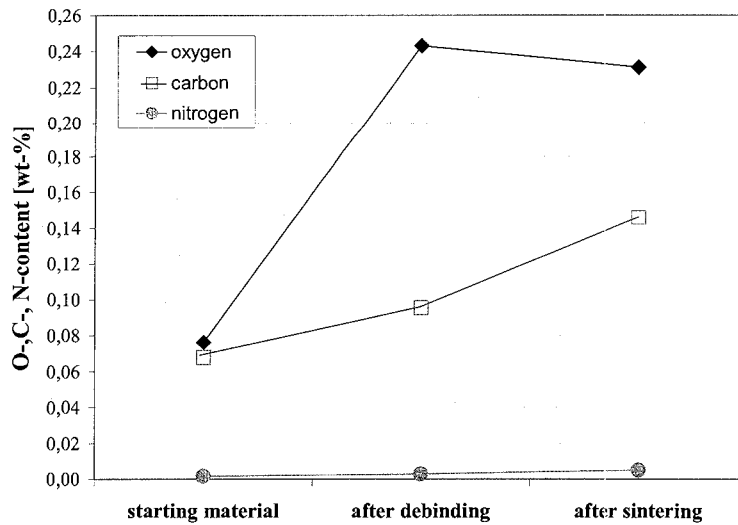


Fig. 10: Impurities of MIM parts after different processing steps

4. Conclusion:

Shape memory properties of NiTi-alloys are strongly influenced by the chemical composition and the thermal treatments. Powder metallurgy PM is a well known manufacturing route regarding to an exact adjustment of chemical compositions. Therefore, three promising PM techniques were investigated regarding to a manufacturing of NiTi-compounds with defined shape memory properties.

Hot Isostatic Pressing (HIP) was used to produce semi-finished NiTi-parts from elemental powder mixtures. The optimization of HIP parameters (1050°C, 195 MPa, 5 h) led to an homogeneous microstructure with NiTi as main phase. Further thermal treatments were necessary to achieve a controlled precipitation of the Ni₃Ti₄ phase. Then an reversible austenite → martensite transformation was observed, which is prerequisite for shape memory effects. A comparison of shape memory and mechanical properties of melted as well as hot isostatic pressed NiTi alloys is subject of the present work.

Vacuum Plasma Spraying (VPS) of elemental powder mixtures was determined to produce NiTi-coatings onto steel substrates with increased wear resistance. In the as-sprayed state NiTi could be already detected by diffraction patterns, but this phase is accompanied by elemental Ni, Ni₃Ti and Ni₂Ti₄O_x. After a thermal treatment at 900°C for 2 h a homogenization of the lamellar microstructure takes place, but the aforementioned phases are still present. Measurements of the wear resistance of NiTi-coatings in the as sprayed state and after annealing are done at the moment.

Metal Injection Moulding (MIM) of prealloyed NiTi powders was optimized regarding to the development of suitable feedstock and production route. The result of this optimization was the manufacturing of NiTi-compounds with a simplified test geometry (rods and hollow cylinders). Pressureless sintering at temperatures above 0.9·T_m (melting point of NiTi) led to a closed porosity of approx. 5 vol.%. Theoretical density was achieved by a subsequent HIP process (1050°C, 195 MPa, 3 h). The possibility of near net shape production combined with a high potential of automation suggests the MIM process for an industrial production of complex shaped NiTi compounds.

Literature

- (1) E. Hornbogen, Shape memory alloys, Pract. Metallogr. 26 (1989) 270
- (2) H. Funakubo, Shape memory alloys, New York, Gordon & Breach (1986), 99

- (3) M. Nishida, C. M. Wayman, T. Honma, Precipitation processes in near-equiatomic TiNi shape memory alloys, *Met. Trans.*, 17A (1986) 1505
- (4) Phase diagrams of Binary Nickel Alloys, Ed. P. Nash, ASR international (1991) 342
- (5) Y. Sekiguchi, K. Funami, H. Funakubo, Y. Suzuki, Study on the hot pressed powder metallurgy of a NiTi shape memory alloy, *J. Phys. C4* (1982) 279
- (6) W. A. Johnson, J. A. Domigue, S. R. Reichman, *J. Phys. C4* (1982) 285
- (7) M. Igharo, J. V. Wood, Compaction and sintering phenomena in titanium-nickel shape memory alloys, *Pow. Metall.* 28 (1985) 131
- (8) V.I. Itin, V. E. Gyunter, S. A. Shabalovskaya, R. L. C. Sachdeva, Mechanical properties and shape memory of porous Nitinol, *Mater. Charac.* 32 (1994) 179
- (9) N. Zhang, P. B. Khosrovabadi, J. H. Lindenhovius, B. K. Kloster, *Mater. Sci. Eng. A150* (1992) 263
- (10) W. J. Buehler, J. V. Gilfrich, R. C. Wiley, *J. App. Phys.* 34 (1963) 1475
- (11) P. Olier, F. Barcelo, J. L. Bechade, J. C. Brachet, E. Lefevre, G. Guenin, Effects of impurities content (oxygen, carbon, nitrogen) on microstructure and phase transformation temperatures of near-equiatomic TiNi shape memory alloys, *J. Phys. C5* (1997) 143.
- (12) Y. Sugo, S. Hanada, T. Honma, *Bull. Res. Inst. Min. Dress. Metall. Tohoku Univ.* 41 (1985) 35
- (13) M. D. McNeese, D. C. Lagoudas, T. C. Pollock, Processing of TiNi from elemental powders by hot isostatic pressing, *Matr. Sci. Eng. A280* (2000) 334
- (14) A. Ahmad-Khanlou, B. Fuchs, D. Wurzel, M. Bram, H.P. Buchkremer, D. Stöver, Characterization of hot isostatic pressed elementary powder mixtures of NiTi shape memory alloys, to be published in *Proc. Materials Week* (2000)
- (15) A. P. Jardine, Y. Field, H. Herman, shape memory effect in vacuum plasma sprayed NiTi, *J. Mater. Sci. Lett.* 10(1991) 943
- (16) O. A. Hamed, H. P. Buchkremer, B. B. Radojevic, D. Stöver, Synthesis and properties of Ni₅₀Ti₅₀ shape memory alloys from elemental powders, in *Proc. PM²TEC99*, Vancouver, Canada (1999).
- (17) K.S. Zhou, D.Z. Wang, M. Liu, A study of the cavitation erosion behaviour of a Ti-Ni alloys coating, *Surf. Coat. Tech.* 34 (1998) 79
- (18) H. Hiraga, T. Inoue, H. Shimura, A. Matsunawa, Cavitation erosion mechanism of NiTi coatings made by laser plasma hybrid spraying, *wear* 231(1999) 272

Acknowledgement

This work is supported by the Deutsche Forschungsgemeinschaft DFG and is part of the Sonderforschungsbereich SFB 459 (Formgedächtnistechnik) of the Ruhr-Universität Bochum. Thanks to all colleagues in Bochum and for the financial support.