INFLUENCE OF CONDITIONS OF PREPARATION ON STRUCTURAL CHARACTERISTICS OF NI-TI ALLOYS

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VLIV PODMÍNEK PŘÍPRAVY NA STRUKTURNÍ CHARAKTERISTIKY SLITIN NI-TI

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Abstrakt

Intermetalická sloučenina obsahující cca 50 at. % Ni a 50 at. % Ti je považována za standardní paměťovou slitinu. Základním předpokladem pro metalurgii těchto materiálů je striktní dodržení chemického složení slitiny, které je hlavní podmínkou pro výrobu slitiny s požadovanými transformačními teplotami. Při použití plazmového tavení je materiál umístěn ve vodou chlazeném krystalizátoru. Tento je unášen pod plazmovým hořákem. Pro vytvoření plazmatu je používán argon. Pro tavení je nutno použít nejčistšího dostupného argonu v důsledku vysoké afinity titanu ke kyslíku. Při této metodě je dosahováno teplot až 6500 K. Chemické homogenity může být dosaženo tavením ve vakuové indukční peci. Na výslednou kvalitu ingotu má zásadní vliv materiál kelímku. Kelímky z Al_2O_3 a MgO nemohou být použity z důvodu obsahu kyslíku. Kyslík obsažený v grafitovém kelímku může být zanedbán, nicméně musí být brána v úvahu absorpce uhlíku. Slitiny na bázi Ni-Ti jsou obvykle taveny při teplotě cca 1500 °C. Pro přípravu drátů je nejvhodnější použití technologie rotačního kování v kombinaci s tažením. Cílem tváření za tepla je změna licí struktury a dosažení vhodné velikosti zrna, vhodného pro následné tažení za studena. Tento příspěvek je zaměřen na přípravu Ni-Ti slitin v plazmové a vakuové indukční peci. Následovalo rotační kování a tažení drátu, na kterém bude prováděno měření transformačních teplot slitin.

Abstract

Intermetallic compound containing approx. 50 at.% Ni and 50 at. % Ti is considered as standard shape memory alloy. The basic requirement to metallurgy of these advanced materials is strict adherence to chemical composition of the alloy, which is the main condition for obtaining of the alloy with the required transformation temperatures. At use plasma melting, material is placed into copper water-cooled mold. This is drifted by bolt under plasma burner. Argon is used as plasma forming gas. For the melting as such it is necessary to use the cleanest available argon due to high affinity of titanium to oxygen. Plasma temperature achieves at this method of melting 6500 K. Chemical homogeneity can be achieved at vacuum induction melting. Material of crucible has at this method the principal influence on quality of ingot. Crucibles made of Al_2O_3 and MgO cannot be used due to oxygen content. Oxygen contained in

graphite crucible can be neglected, it is, however, necessary to take into account absorption of carbon. Ni-Ti based alloys are usually melted at the temperature of approx. 1500 °C. For obtaining of wire it is best to use technology of swaging in combination with subsequent drawing. Aim of hot forming consists in change of casting structure and achievement of satisfactory grain size that is suitable for subsequent cold drawing. This article deals with preparation of Ni-Ti shape memory alloys in plasma furnace and vacuum induction furnace. The swaging and drawing were carried out to produce wires which will be used for measurement of transformation temperatures.

Key words: Ni-Ti shape memory alloys, plasma melting, vacuum induction melting

1. Introduction

Development of science and technology in all branches of industry means interconnection of the whole series of new findings with implementation of advanced methods at production of materials with high service properties or special properties. NiTi based inter-metallic shape memory alloys undoubtedly belong to such materials. They find application in numerous industrial and other branches, such as e.g. medicine, robotics and communication technology. [1].

Alloys with shape memory effect have generally several variants of shape memory behaviour. Generally speaking these are pseudo-elasticity, shape memory phenomenon (irreversible), reversible shape memory phenomenon and universal shape memory [2,3].

2. Problems of alloys preparation

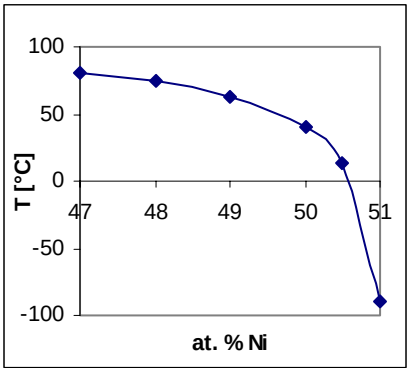

Fig.1 Influence of excess of Ni on temperature of martensitic transformation

Inter-metallic alloy containing approx. 50 at.% Ni and 50 at. % Ti is considered as standard shape memory alloy. The basic requirement to metallurgy of these advanced materials is strict adherence to chemical composition of the alloy, which is the main condition for obtaining of the alloy with the required transformation temperatures [4]. Another condition is observance of excellent homogeneity of the alloy, which also conditions functional reliability and guaranteed temperatures of transformation. Change of composition by 0.1 at. % usually leads to change of transformation temperatures even by 10 °C. Figure 1 illustrates influence of Ni contents in the alloy on temperature of martensitic transformation. It is possible to weaken

concentration dependence by alloying by other elements, particularly Cu and Fe. It is also possible to obtain in this manner more favourable mechanical properties [5]. The following methods are presently used for preparation of Ni-Ti shape memory alloys.

3. Plasma metallurgy

At use of this method material is placed into copper water-cooled mold. This is drifted by bolt under plasma burner. Argon is used as plasma forming gas. For the melting as such it is necessary to use the cleanest available argon due to high affinity of titanium to oxygen. Plasma temperature achieves at this method of melting 6500K. It is possible to use this method also for refining of initial titanium from titanium sponge [6,7]. Advantages of plasma furnaces are the following: prevention of contamination pf melted material by graphite from used electrodes and use of inert atmosphere. Possibility of creation of low-temperature plasma from any mixture of gases This enables use of oxidation, reduction of inert atmosphere as needed. Possibility of degassing of metal, since partial pressures of gases contained in metals are very low in inert gas.

Disadvantages of plasma furnaces in comparison with vacuum induction furnaces comprise lower degassing of melted metal, which depends on purity of used argon. Moreover it is necessary to take into account the fact that at melting in plasma furnace the metal absorbs larger amount of gases that it corresponds to an equilibrium state [8]. Another disadvantage of plasma melting, particularly at preparation of highly reactive metals, consist in necessity of use of highly pure argon. Commercial argon contains residues of O_2, N_2, H_2 and other gases, which lead to possible interaction of interstitial impurities with melted metal.

4. High-frequency induction vacuum melting

Chemical homogeneity can be achieved at vacuum induction melting by selection of suitable magnitude of alternating current, which influences induction and thus also mixing of the melt. Material of crucible has at this method the principal influence on quality of ingot. Crucibles made of Al_2O_3 and MgO cannot be used due to oxygen content. Oxygen contained in graphite crucible can be neglected, it is, however, necessary to take into account absorption of carbon. In reference [9] is showed, that in case of use of Ni pellets and Ti bars their arrangement in crucible is also of importance. If surface of crucible was covered with Ti discs cut from bars, then carbon contents in final metal was lower than in case of traditional random arrangement of charge. This is caused by formation of TiC layer, acting as diffusion barrier. It was ascertained that absorption of carbon is strongly dependent on temperature. Ni-Ti based alloys are usually melted at the temperature of approx. 1500 °C, below this temperature approx. 800 ppm of carbon can be absorbed. It is possible to use for melting also a crucible made of CaO. Research has shown that by use of crucible made of CaO it is possible to achieve contents of oxygen and carbon below 500 ppm [8,10,11].

5. Technology for forming of alloy

For obtaining of wire it is best to use technology of swaging in combination with subsequent drawing. Aim of hot forming consists in change of casting structure and achievement of satisfactory grain size that is suitable for subsequent cold drawing. Hot forming is effected at temperatures of approx. 800 °C, when material has appropriate formability and formation of oxides is not so pronounced yet. Bars are forged on forging machines to final minimal diameter

from 10 mm to 2.3 mm. If there is required wire of smaller diameter, drawing operation is applied, which enables obtaining of final diameters of wire down to 0.1 mm. Obtained deformation strengthening can be removed by inter-operational annealing in protective argon atmosphere. Temperature of inter-operational annealing is usually in the interval between 600 °C – 800 °C. It is also necessary to use lubricants at drawing, such as water modified by mixing with graphite admixture, MoS_2, oil based lubricants or soda soap. Drawing dies made of sintered carbide (WC - Co), but mainly diamond dies are used for drawing [12, 13, 14].

6. Experimental procedures and results

Two technological processes were used for melting. The first process consisted in use of plasma metallurgy with vacuum induction melting. At the first process we used also crucibles made of Al_2O_3, which are usually not recommended for melting. The second process consisted in preparation of alloys just by single operation, namely by high-frequency induction vacuum melting in graphite crucible. We prepared for the experiment two types of alloys: A - (Ni49.8 - Ti50.2 at. %) and B - (Ni49 - Ti50 - Cu1). The following materials were used as initial raw materials: cathodic Ni 3N (other impurities - C 0.035 %, Fe 0.031 %, Al 0.011 %), plasma re-melted Ti 2N8 (other impurities - C 0.026%, Fe 0.012 %, Al 0.012 %, O_2 0.0219 %, N_2 0.018 %), conductive Cu 4N.

1) Experimental alloys were made with use of plasma melting. Technological parameters of melting were the following: speed of movement of tray under the plasma burner: 2 $cm.min^{-1}$, argon flow (4N5) 27 $l.min^{-1}$, duration of melting 1 h, output characteristics: I = 500 – 700 A , U = 42 V and input power 30 kW. Length of ingots was 400 mm, mass 850 g. This was followed by induction re-melting in corundum crucible stabilised by TiO_2 and casting of material into Cu ingot mold with diameter of 20 mm and length 300 mm without pre-heating. Parameters of vacuum melting were the following: Vacuum 2.10^{-5} MPa. After melting the furnace was filled with argon (4N5) to the pressure of 600 kPa. Melting was performed at frequency of 4 kHz and furnace input power was 14 kW. After preparation samples were taken and complete metallographic documentation was made. We used an etching agent with this chemical composition - $5H_2O$: $4HNO_3$: 1HF. Microstructures of alloys A1, B1 are shown in Figures 2 - 5. We made also chemical analysis of phases by energy dispersive micro-analyser EDAX. Chemical analysis are summarised in tables 1 and 2. We made also determination of gas contents after plasma and also vacuum melting. Contents of gases are given in the table 3.

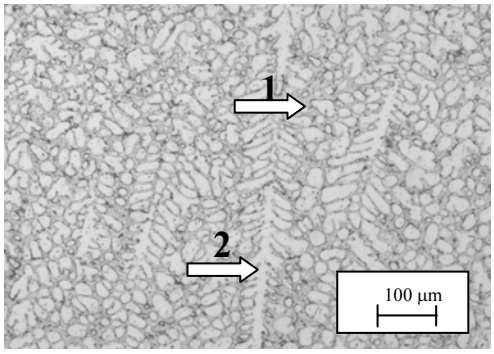

Fig.2 Microstructure of alloy A1, plasma melting

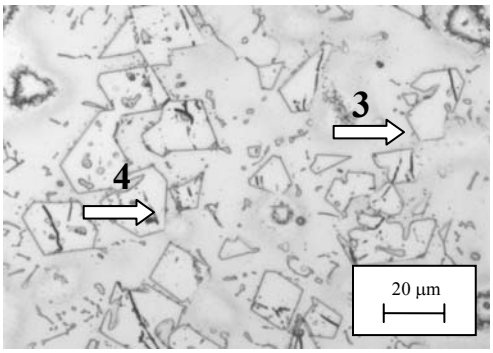

Fig3 Microstructure of alloy A1, induction melting

Table 1 Chemical composition pf phases for the alloy A1

Element	amount in the area [at. %]			
	1	2	3	4
Ni	76.02	56.83	54.18	35.33
Ti	23.98	43.17	45.82	64.67
total	100	100	100	100

In the plasma melted alloy A1, the area 1 corresponds to intermetallic compound $TiNi_3$. Area 2 correspond to non-stoichiometric phase TiNi. In the alloy A1 re-melted by induction the matrix is formed by non-stoichiometric phase TiNi and coarse angular particles (4) correspond to the phase Ti_2Ni, which caused subsequent problems at forming.

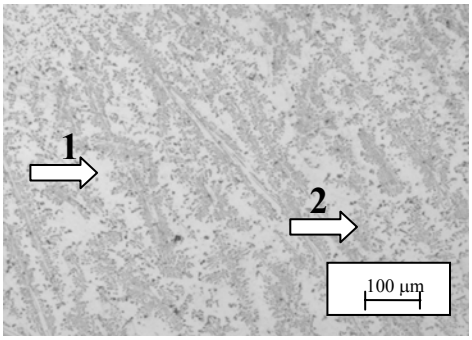

Fig.4 Microstructure of alloy B1, plasma melting

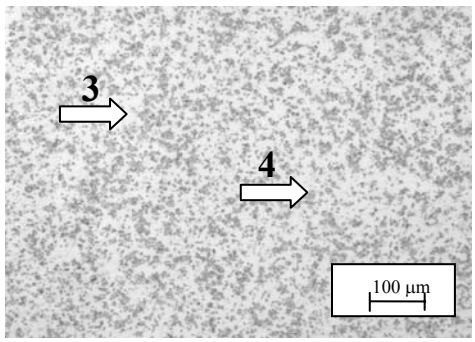

Fig.5 Microstructure of alloy B1, induction melting

Area 1 in the plasma melted alloy B1 corresponds by its chemical composition to the phase Ti_2Ni and dark formations (2) are of the type TiNi, here was determined also higher contents of Cu. In the induction re-melted alloy B1 the matrix (3) corresponds to the phase TiNi and minor angular formations (4) are again formed by problematic phase Ti_2Ni. Copper is again contained in greater extent in the matrix.

Table 2 Chemical composition of phases for the alloy B1

Element	amount in the area [at. %]			
	1	**2**	**3**	**4**
Ni	32.79	47.13	52.24	35.28
Ti	66.23	49.93	46.21	63.56
Cu	0.98	2.93	1.55	1.16
total	100	100	100	100

Table 3 Measured contents of gases in alloys made according to the scheme 1

alloy	plasma		induction	
	% O_2	% N_2	% O_2	% N_2
A1	0.0369	0.0003	0.8185	0.0045
B1	0.0602	0.0004	0.2872	0.0031

2) Experimental alloys were formed by high-frequency induction vacuum melting, only Ti sponge was plasma re-melted. Melting ran under similar output characteristics. Graphite crucible was used and ingot molds with diameter of 10 mm and length of 100 mm made of the same material. They were again not pre-heated. Preparation was followed by taking of samples and making of complete metallographic photographic documentation. We used again the same etching agent as in previous case. Photographs of microstructures are shown in figures 6-11. We made again chemical analysis of composition of alloys' phases by energy dispersive micro-analyser EDAX. Analyses of composition of phases are summarised in tables 4 and 5. We determined also contents of gases, which are given in the table 6.

Next step consisted of making of wire for experimental measurement of transformation temperatures. Initial structure of the casting was at the first stage forged by swaging at temperature of 800 °C to diameter of 2,3 mm. This was followed by drawing of wire suitable for measurement with diameter of 2 mm. Both alloys are formed at room temperature by monoclinic martensite B19′. All the samples of wire were after drawing subjected to normalising (850°C vacuum/30 min/water). During the forming itself there were continuously taken samples for making of complete metallographic photographic documentation. Etching of samples of drawn wire was made by etching agent of this composition 1HF : 5HNO_3 : 5CH_3COOH, the use of which enables observation of martensite. Lastly we evaluated influence of technology of preparation on carbon contents in final material. Picture of microstructures of final wire are given in figures 10 and 11.

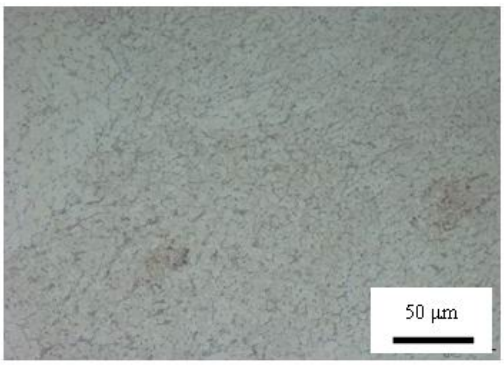

Fig.7 Microstructure of the alloy B2, induction melting

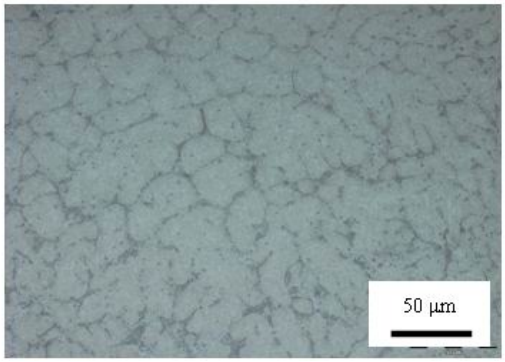

Fig.6 Microstructure of the alloy A2, induction melting

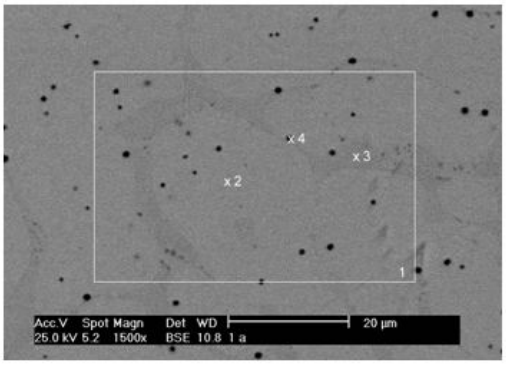

Fig.8 Microstructure of alloy A2, induction, electron microscope

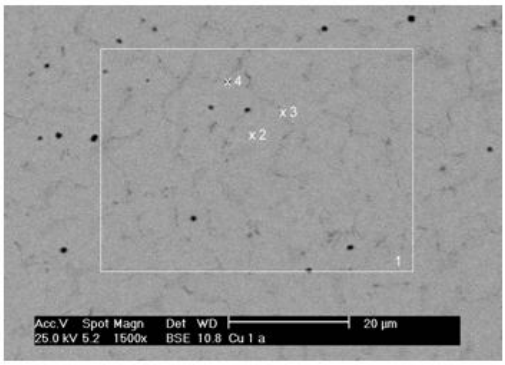

Fig.9 Microstructure of alloy B2, induction, electron microscope

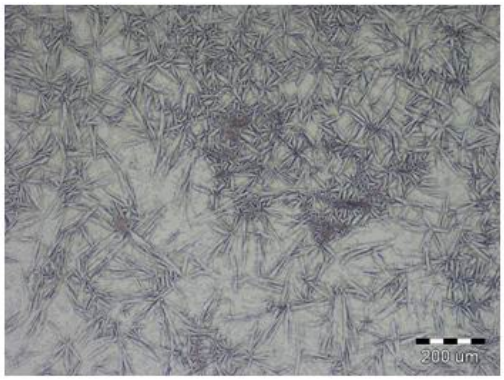

Fig.10 Microstructure of the alloy A2, drawn after rotational forging, martensite

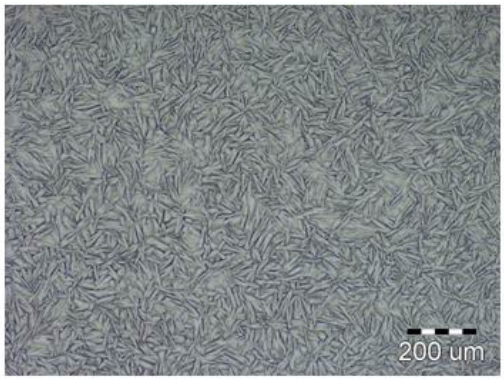

Fig.11 Microstructure of the alloy B2, drawn after rotational forging, martensite

It is visible from microstructures of alloys prepared by vacuum induction melting in graphite crucible and cast into graphite ingot molds (i.e. according to the scheme 2) that are considerably more homogenous than microstructure of previous alloys. Alloys A2 and B2 are formed predominantly by the phase TiNi, however, there are visible dark small formations of the size of several μm, which contain increased amount of carbon. These particles correspond to carbides, or to compound titanium carbonitrides. Occurrence of these particles and their impact on transformation and microstructural characteristics was already discussed in previous works [7, 15]. In all alloys carbon contents after casting was also observed. Carbon contained in the alloy causes formation of undesirable titanium carbides, as it was already mentioned. Determined contents are given in the table 7. In both types of alloys there were observed higher contents of carbon after melting in a graphite crucible and casting into ingot mold made of the same material.

Table 6 Measured gas contents in alloys made according to the scheme 1

	induction	
alloy	**% O_2**	**% N_2**
A2	0.2698	0.0097
B2	0.2309	0.0196

Table 7 Carbon contents in alloys

alloy	**% C**	**alloy**	**% C**
A1	0.036	***B1***	0.05
A2	0.039	**B2**	0.053

7. Conclusion

Objective of the experiment was to prepare two types of alloys and then to produce from them wire with diameter of approx. 2 mm for subsequent experiments with measurement, monitoring and modifications of transformation temperatures.

After plasma melting the alloy is often non homogenous, as it follows from the principle of this method. Alloy is on one hand prepared at very high temperatures and on the

other hand it is intensively cooled. Figures 2 and 4 show typical microstructures obtained by plasma melting. For improvement of homogeneity of the alloy it was therefore necessary to make vacuum induction melting. Figures 3 and 5 show microstructures after induction melting and casting into Cu ingot mold. On photos angular particles are visible, which correspond to Ti_2Ni. Due to occurrence of this phase it was impossible to perform swagging. Even at very small pass reductions (approx. 5%) there occurred total destruction of material.

The alloys obtained by the second technological process have a completely different characteristic. Alloy is prepared by a single melting in one furnace unit. It is visible from the enclosed microstructures that the alloy is much more homogenous than in the previous case, particles of problematic phase Ti_2Ni were not observed anymore. These alloys could be formed without any greater problems. Figures 10 and 11 show microstructures of wires after drawing. They show also characteristic martensitic structure.

It is obvious from results of measurement of gas content that the lowest content of oxygen and nitrogen was found in the alloys after plasma melting (A1, B1). It was found after induction melting that gas contents in alloys had increases approx. ten times. This was cause by used of unsuitable crucible made of Al_2O_3. At filling of furnace before casting it would have been more appropriate to use argon of higher purity. At preparation of the alloys A2, B2 only in induction furnace there has also occurred gasification of metal. Graphite crucible is more suitable for melting as such, oxygen contents is lower than in alloys A1, B1. There has occurred, however, increase of nitrogen contents. It can be seen from the results of measurement of carbon contents that the alloys A2, B2 contain more carbon than the alloys A1, B1. This amount is, however, not so important to arrive to a conclusion that use of graphite crucible for melting of Ni-Ti alloys is not appropriate. It follows from the obtained results that the most suitable technology of preparation consists of preparation of Ni and Ti in a plasma furnace, where gas contents is reduced, followed by vacuum re-malting in graphite crucible and casting under protective atmosphere of high purity argon.

Acknowledgements

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