Chapter 2

The Methods of Preparation of Ti-Ni-X Alloys and Their Forming

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Additional information is available at the end of the chapter

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1. Introduction

The continuous development of science and technology in all industrial sectors means connecting and usage of a wide range of new knowledge together with implementation of new modern technologies for production of materials with high functional, specific and special properties. Intermetallic compounds TiNi with shape-memory effect are an interesting group of materials. These materials are used in a wide range of industry, such as electronics, robotics, tele-communication and also in medicine and optics. Shape-memory alloys (SMA) are a group of materials characterized by shape-memory effect (SME) and superelasticity (SE), also called pseudoelasticity.

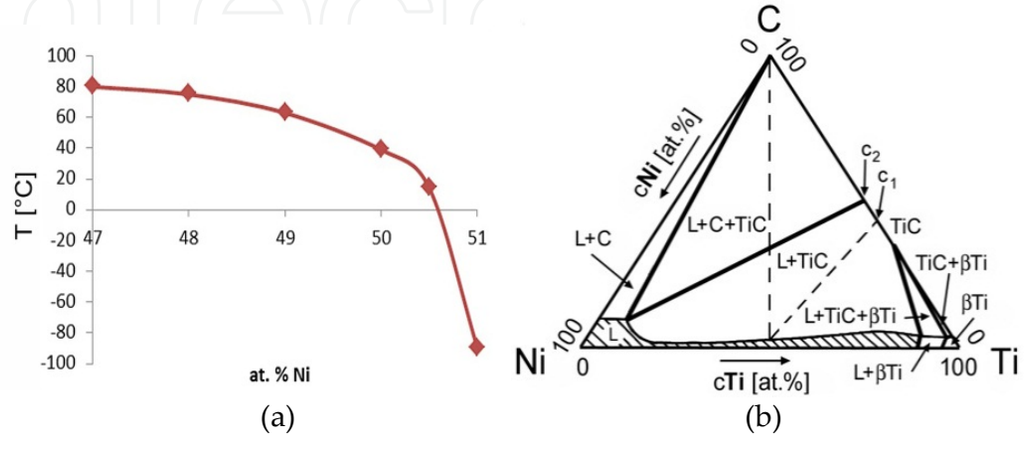
Ti-Ni binary alloys (sometimes called "Nitinol") are probably the best known from this group of materials. Nevertheless, these alloys are not always the most suitable for the particular purpose. This factor is also the reason for seeking optimized variants of these original binary systems. One of the possible solutions is to modify binary alloys by incorporation of one or more chemical elements into the production process. The resulting materials can be summed up in the term Ti-Ni-(X), where X means presence of another element. Although the best memory characteristics are usually achieved for alloys with Ni content of 49.3 ÷ 51 at. % (Raz & Sadrnezhaad, 2004), by decreasing the content of one element (Ti or Ni) to the prejudice of the third element, modified materials are obtained, while preserving some of original characteristics. Among the main characteristics, surpassing SME and SE, mechanical properties, corrosion resistance and related biocompatibility should be mentioned (Van Humbeeck, 2001) or (Duerig et al., 1999). Intermetallic equiatomic compound of nickel and titanium thus remains as the base of modified binary materials. Nevertheless, it should be stated that characteristics of Ti-Ni SMA may be significantly modified otherwise than by the appropriate choice of chemical composition, namely by forming and thermal (thermomechanical) processing. As will be

indicated later, final properties and products made of SMA are significantly influenced not only by the chosen forming technique, but also their mutual sequence. These factors together with the used technique play a major role in the manufacture of products from SMA.

2. Method of preparation

Production of Ni-Ti alloys is mostly done by vacuum melting, whilst various melting procedures are used (electron beam melting, arc melting (Ma & Wu, 2000) and (Meng, 2001), high frequency vacuum melting in a graphite crucible (Noh, 2001) or (Tsai et al., 1994), plasma melting, etc.). When Ni-Ti alloys are melted, there can be unfavourable effects, especially of gases such as nitrogen or oxygen. Other problems consist in the conditions suitable for crystallization and minimalization of micro- and macro-segregation connected with that. Also, contamination of the material by non-metallic intrusions has to be prevented (Schetky & Wu, 2005). Due to the formation of titanium carbide and titanium oxide in Ni-Ti, concentration of individual elements changes and thus so does the transformation temperature. Among other problems arising from the melting of Ni-Ti, there is the formation of low-melting point phase $NiTi_2$, which causes a strong tendency towards hot crack formation.

The basic requirement to metallurgy of these alloys is strict adherence to the chemical composition of the alloy, which is the main condition for obtaining the alloy with the required transformation behaviour. Another condition is obtaining an excellent microstructural homogeneity of the alloy, which is also a condition for functional reliability and guaranteed transformation behaviour. A deviation of about 0.1 at. % from the required chemical composition usually changes the transformation temperature by as much as 10 K. In Fig. 1a you can see the dependence of temperature of martensitic transformation on the nickel content in the alloy. There is a possibility of attenuation of concentration dependence of the martensitic transformation temperature by alloying with other elements, especially Cu, Fe, etc.



(a) (b)

Figure 1. The dependence of temperature of martensitic transformation (a) Ternary system Ti-Ni-C (b)

Based on specific requirements of applications such as actuators/sensors, temperature control, fatigue properties, etc., various alloys with the addition of a third element giving a ternary alloy were developed (Otsuka & Wayman, 1998) or (Zhang et al. 2006).

There is a certain influence of each alloying element on transformation characteristics of the alloy. For example, the addition of Hf, Zr, Au, Pd and Pt causes the increase of phase transformation temperatures, while elements such as Fe, Co, and V have the opposite effect. Similarly, hysteresis is increased, e.g., by Fe and Nb, and, on the contrary, decreased by Cu (Ramajan et al., 2005). As a consequence of alloying by other elements, the transformation sequence is also changed; e.g., at the content of Cu below 7.7 % one-stage phase transformation B2→B19′ occurs (similarly as in a binary alloy). If the content of Cu exceeds 7.7%, two-steps transformation B2→B19→B19′ takes phase (Tang et al., 2000). The alloy properties may also be significantly influenced by alloy impurities from the production process, forming, heat treatment, etc. As it was already stated, there could be an important role of gases (O_2, N_2, H_2) and carbon. In the resulting structure intrusions of the type $Ti_4Ni_2O_x$, TiO_2 etc. connected with the decrease of Ti content in the matrix can be observed. There is significant influence of these composition changes on transformation characteristics of the alloy.

Typical superelastic nitinols contain ca. 350–500 ppm of oxygen and 100÷500 ppm of carbon. The metallurgical purity (grain structure, presence of impurities etc.), of course, greatly depends on the preparation process. Ni-Ti alloys can be called high-purity alloys if they contain <100 ppm of oxygen and <20 ppm of carbon. These alloys are prepared in vacuum induction furnaces in graphite crucibles with the subsequent repeated re-melting in vacuum arc furnaces (Graham et al., 2004).

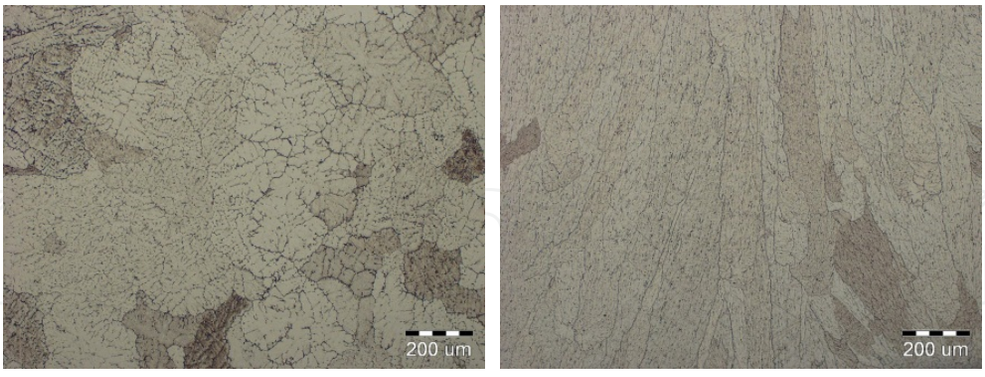
2.1. VIM – Vacuum induction melting

As has already been stated, VIM is one of the production processes used for the preparation of TiNi alloys. The technology of vacuum induction melting in graphite crucibles represents the existing key preparation method. Chemical homogeneity within this technology can be achieved by appropriate power control (and stirring of liquid alloy connected with that). When using this technology, the quality of the prepared alloy will strongly depend on the material of the crucible. Usually the mentioned graphite crucible is recommended – where the oxygen content can be neglected; nevertheless, carbon absorption must be considered here (there is a significant influence of carbon on microstructural characteristics and transformation behaviour). During the preparation of the material in a graphite crucible it was also found (Frenzel et al., 2004) that in the case of using Ni-pellets and Ti bars/disks the appropriate arrangement of the material in the crucible was important. The authors of this study have shown that although the inner surface of the crucible was covered with Ti disks, the content of carbon in the produced alloy was lower in comparison with the case of random arrangement of the charge. This phenomenon is caused by formation of a TiC layer, which acts as a diffusion barrier. It was also found that the carbon content strongly depends on temperature and time of dwell of the melt in the crucible. For this reason, a more

intensive investigation of these effects was carried out (Zhang et al., 2006). It was established that with increasing time of dwell of the melt in the crucible the melt gets enriched in carbon.

In Fig. 1b (Du & Schuster, 1998) it is possible to see more detailed information on the isothermal section (at 1500°C-temperature recommended for melting of Ni-Ti based alloys) of the Ni-Ti-C ternary system. The composition in this system is given in atomic %. It is shown that there exists a single-phase region of liquids, extends from the area of pure Ni to the area of pure Ti. There exists only a narrow two-phase area L+β-Ti which separates the area of melted material from the β-Ti phase. The diagram also shows that the melted material dissolves a certain amount of carbon (this dissolution is limited). Elementary melted Ti and C cannot coexist in equilibrium state, due to this reason a TiC carbidic phase is created. The diagram in Figure 1b also predicts the existence of three phases in thermodynamic equilibrium: pure carbon, TiC carbidic phase and melted Ni-Ti depleted by Ti. The reactions between the melt will result in a melted material with higher carbon content and certain amount of TiC. In practice we cannot expect this equilibrium.

When the molten Ni-Ti enters into contact with the graphite of the crucible, inter-diffusion causes a growth of the TiC layer and the contents of carbon in the melted alloy grows. This process includes the diffusion of carbon through a thin layer of TiC which grows on the boundary between TiC/melted Ni-Ti. On the boundary between graphite / TiC and the boundary of TiC / melted material we expect local thermodynamic equilibriums. If using a pure (unused, new) crucible for preparing the alloy, the first prepared ingot will have a higher content of carbon than the next one. This fact is in accordance with the creation of the above-listed TiC diffusion barrier. It is also recommended to perform rinse-melting before melting alloys in an unused crucible.

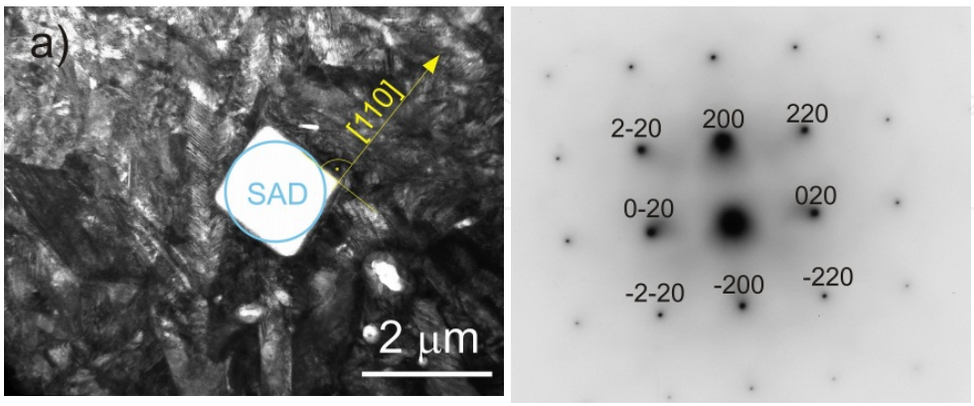


(a) (b)

Figure 2. As cast state of alloy: Ni50.6-Ti(at.%) (a), Ni46-Ti50-Co4 (b)

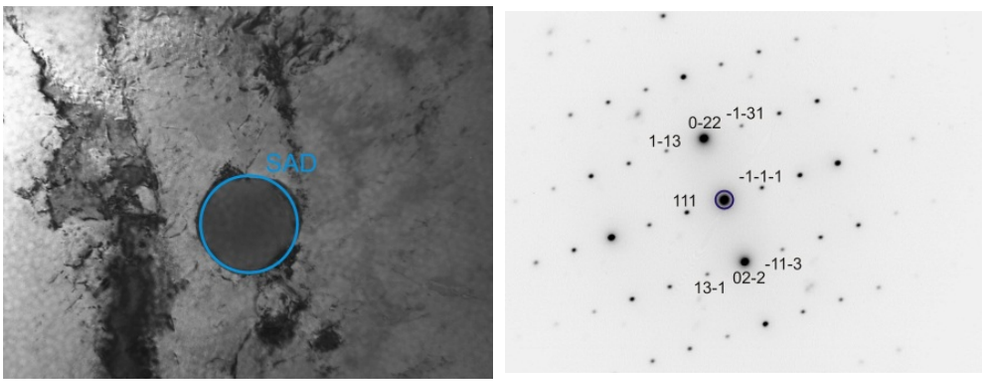
In order to define the exact influence of the used technique, an experimental study (Szurman & Kursa, 2010) with the aim of monitoring the influence of the preparation process on microstructural characteristics of Ni-Ti-(X) alloys was performed. The examples of microstructures of Ni50.6-Ti (at. %) and Ni46-Ti50-Co4 cast alloys are presented in Figs. 2a and 2b. As a consequence of the preparation of alloys in a graphite crucible, TiC type

carbide phases are visible in the alloys' microstructure. A TEM image of the TiC phase (Fig. 3a) with the appropriate diffraction is presented in Fig. 3b. Similarly as with carbides, oxide phases can also be seen in microstructures of Ni-Ti alloys. A specific example is presented in Figs. 4a, b where particles of Ti_4Ni_2O can be seen.



(a) (b)

Figure 3. TiC phase: TEM image (a), corresponding diffraction pattern (b)



(a) (b)

Figure 4. Particle of Ti_4Ni_2O (a), corresponding diffraction pattern (b)

2.2. Plasma melting – Plasma furnace with horizontal crystallizer

This is another possible preparation process; there are, however, serious drawbacks. During this process, input elemental metals are placed in the copper water-cooled crystallizer. The crystallizer is carried by the screw below the plasma burner. Argon is used as a 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. The plasma temperature during this process reaches 6500 K (Dembovský, 1985) and (Pacholek et al., 2003). The advantage of this process can be seen in the prevention of contamination of melted material by graphite from used electrodes (crucibles); high concentration of energy, high plasma flow velocity and very quick heat transfer on the heated material ensure high speed of melting. Disadvantages of plasma furnaces in comparison with vacuum induction furnaces include lower degassing of the melted metal, which depends on purity

of the used argon. The key disadvantage of this process consists in insufficient homogeneity of the prepared alloy.

The development of plasma furnaces takes place in two main directions. Melting units working on the similar principle as common arc furnaces can be added to the first type of plasma furnaces. There is only one difference – that instead of electrodes, plasma burners are used and the furnace used to be equipped with special soil electrode carrying the current into the charge. The working space of furnaces is often designed to be vacuum-tight, which enables maintaining an ideal inert atmosphere. This type of furnace can be equipped with a relatively simple device for electromagnetic stirring of liquid metal.

The second furnace type is plasma furnaces with water-cooled metal crystallizers. As to the arrangement, the concept of these furnaces is similar to electronic furnaces, with the difference that instead of electron guns plasma burners are used and the furnaces mostly work with the pressure of an inert gas varying around 10^5 Pa. Exceptionally, there are furnaces with overpressure. In metallurgy, so-called low-temperature plasma in particular is considered, which is a system comprising a mixture of neutral particles with the prevailing number of electrons and positive ions with temperatures in orders of 10^3 to 10^4 K. The temperature of 10^5 K can be considered as the temperature of totally ionized plasma (Dembovský, 1978).

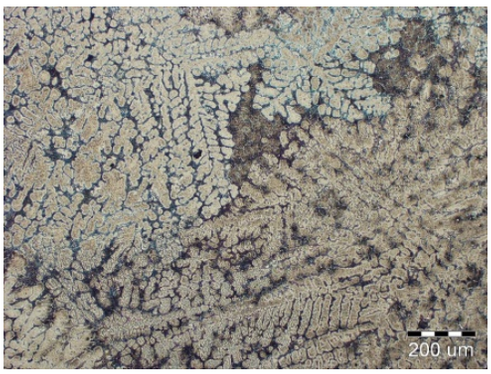


Figure 5. Microstructure of alloy Ni49.5-Ti25.5-Zr10-Nb15 (at. %), plasma

Specific experiments with melting of selected alloys Ti-Ni-(X) are described, e.g., in studies (Szurman & Kursa, 2009). Using this technique, ingots with the weight of 200–1000 g were prepared. In Fig. 5 you can see microstructure of alloy after plasma melting. As you can see, the microstructure of the alloy is highly inhomogeneous. This problem is caused by very high temperature gradients during melting. At the top of the ingot the alloy is heated to a high temperature. On the other hand, the part of the ingot which is in contact with the crystallizer is intensively cooled.

2.3. VAR – Vacuum Arc Melting

VAR technology is widely used to increase metallurgical purity of alloys prepared using standard procedures, e.g., in vacuum induction furnaces. This procedure is also known as

"consumable electrodes". Direct current is used for the formation of arc between the electrode (melted material) and a water-cooled copper crucible/crystallizer. As a consequence, the electrode tip is melted and a new ingot is formed within the water-cooled crucible. The melt during the arc vacuum melting therefore is not in contact with the graphite crucible (as it is in the case of the VIM technique with a graphite crucible/mould), thus a "more pure" product can be obtained using this method. The carbon content usually does not exceed 200 ppm (Dautovich & Purdy, 1965) or (Wu, 2001). For this technique a very high vacuum is required.

Nevertheless, there are also drawbacks of this technique – small volume of the alloy and low convection in the melt which may cause inhomogeneity of ingots. That is also the reason why this procedure is usually repeated several times. Often the VIM+VAR process is applied for the preparation of Ti-Ni-(X) alloys. VAR technology is also preferred for preparation of experimental material for basic research of Ti-Ni-(X) alloys. For example, the study (Choi et al., 2005) describes the preparation of experimental Ni-Ti alloys alloyed by Fe. In this study, the ingot prepared using this method is homogenized at 1273 K for 24 hours. In another study (Sakuma et al., 2003) heat treatment at 1223 K for 1 hour after the preparation of the material using this method is proposed. The specific regime is also mentioned in the study (Jung et al., 2003) where heating at 1100°C for 100 h was used.

2.4. EBM – Electron Beam Melting (Vertical Zone Melting)

Crucible-free zone melting – or the floating zone process known as the FZ method represents another specific preparation method. The formation of a narrow melted zone is performed using electron heating. The melting takes place in a vacuum, and values of 10^{-2} Pa are reached in this technology compared to 10 Pa in VIM technology. Using the method of electron zone melting with suitable oriented nuclei, even monocrystals of many high-melting metals – W, Mo, Ta, Nb, V, Zr, Ti, Re – can be prepared. The zone is maintained in the floating condition mainly by forces of surface tension. The zone stability depends on gravitation, surface tension and density of the melt, on material composition and also on direction of zone movement. To maintain the stability of the zone, an outer magnetic field with so-called supporting frequency is used (Kuchař & Drápala, 2000). A circular shape ingot prepared in a vacuum induction furnace is used in this case as input material. There is no risk of other contamination of the material with carbon in this technology (there is no crucible). Carbon contents are usually lower than in the case of the alloy preparation using VIM technology. Contents of gases are usually low as well because of using a high vacuum. The contamination with gases thus depends only on the quality of an input casting and tightness of the vacuum system. The disadvantage of this technology is the control of chemical composition – evaporation of some elements can be expected here during melting. Another drawback is the rather small volume of the prepared material; therefore this technology is not suitable for commercial use (Ramaiah et al., 2005).

Rather integrated results regarding (un)suitability of various methods of preparation are presented, e.g., in a recent study (Szurman & Kursa, 2009). The aim was an intercomparison

of techniques selected for the preparation of Ti-Ni-(X) alloys from the point of view of the microstructure and gas contents in the material. Also in this situation a distinct decrease of gas contents after the preparation was observed here. The specific microstructure of the prepared alloy Ni50,6-Ti (at.%) is presented in Fig. 6.

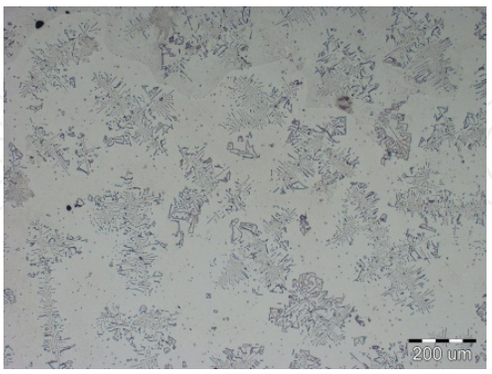


Figure 6. Microstructure of alloy Ni50.6-Ti (at. %), EBM

2.5. Preparation of alloys using powder metallurgy

Powder metallurgy is an important and suitable method for the production of the mentioned alloys. Methods of atomization were developed for preparation of powder metals with precise control of composition. However, the biggest problem with these alloys is oxygen and carbon content. The content of oxygen can be up to 3000 ppm, but it can be decreased by careful treatment to 1500 ppm (Schetky & Wu, 2005). It is well known that with increasing content of impurities (especially oxygen and carbon), transformation temperatures are decreased and a brittle secondary phase is formed (Mentz et al., 2008). Subsequently, the composition of NiTi matrix (depletion by Ti) is significantly influenced by oxide and carbide intrusions and thus can cause degradation of functional and mechanical properties, which was also confirmed, e.g., in the study (Mentz et al., 2006). Other methods are hydridation, pulverization and mechanical alloying (Wu, 2002).

The method for preparation of Ni-Ti alloy using powder metallurgy is described in the study (Mentz et al., 2008). At first, the alloy was prepared by authors using a classical VIM melting from high-purity input raw materials, then atomization with 6N argon followed. The obtained powders were sealed into evacuated capsules made from stainless steel and then compacted using the HIP method. It was also found that each technological step is accompanied by increased content of impurities (oxygen and nitrogen). In the study (Bertheville & Bidaux, 2005) the authors performed the preparation of Ti-rich Ni-Ti alloy from elementary powders – Ni and TiH_2. In another study (Zhu et al., 2005), preparation of Ni-Ti alloy by sintering in argon from elementary Ni and Ti powders is described. Another method of preparation is then described in the study (Mousavi et al., 2008), where a method of mechanical alloying is described. The Ni-Ti alloy was prepared from elementary powders in a planetary ball mill under atmosphere of Ar. During sintering of Ni and Ti, a significantly exothermic reaction takes place so that the heat generated during the process is used for the formation of the intermetallic compound TiNi.

Elemental powders can also be sintered using "combustion" synthesis or explosion. In the first case, a laser can be used as an external energy source (Bertolino et al., 2003). As for explosive sintering, the reaction takes place after explosion during the temperature rise. Another method is based on the passage of an electric current of suitable value under optimal voltage. It was found that the optimal current density is 2822–5290 $kA.m^{-2}$. The observed sintering times were within the range 5÷40 min (Locci et al., 2003). Ni-Ti materials prepared from powder metals are very porous and contain other intermetallic compounds such as Ti_2Ni and Ni_3Ti.

3. Forming of SMA

Apart from the already mentioned influence of the selected preparation method of SMA, final properties and behaviour of SMA will be also determined by next processing including heat treatment. This means not only the chosen method of forming, but also a sequence of given forming operations. Also the influence of applied regimes of heat treatment should be considered. All the mentioned factors have their own partial effect in formation of final properties of SMA-based materials. With admixture elements, such as Cu contained in binary NiTi alloys, martensitic transformations are considerably shifted and at the same time also mechanical or thermomechanical characteristics of SMA are changed, as can be seen, e.g., in the study (Liu, 2003). Hand-in-hand with forming or heat processing, strengthening and healing processes are also important. Several studies are known, e.g. (Gili et al., 2004) or (Morgiel et al., 2002), which confirm the importance of chemical composition (Cu content) during dynamic recrystallization, esp. near borders of grains. On the other hand, other studies (Nam et al., 1990) bring information on formability of SMA when Ni was substituted by Cu. If Ni is substituted by Cu up to the content of ca. 10% (i.e. binary NiTi alloy will be modified to Ti-40Ni-10Cu), then the phase transformation will take place in two steps and these alloys will be much more deformable in the martensitic state than original NiTi alloys. Despite these findings it is still valid that when Cu content exceeds the limit 10 at.%, Ni-Ti-Cu alloys exhibit a rather low formability.

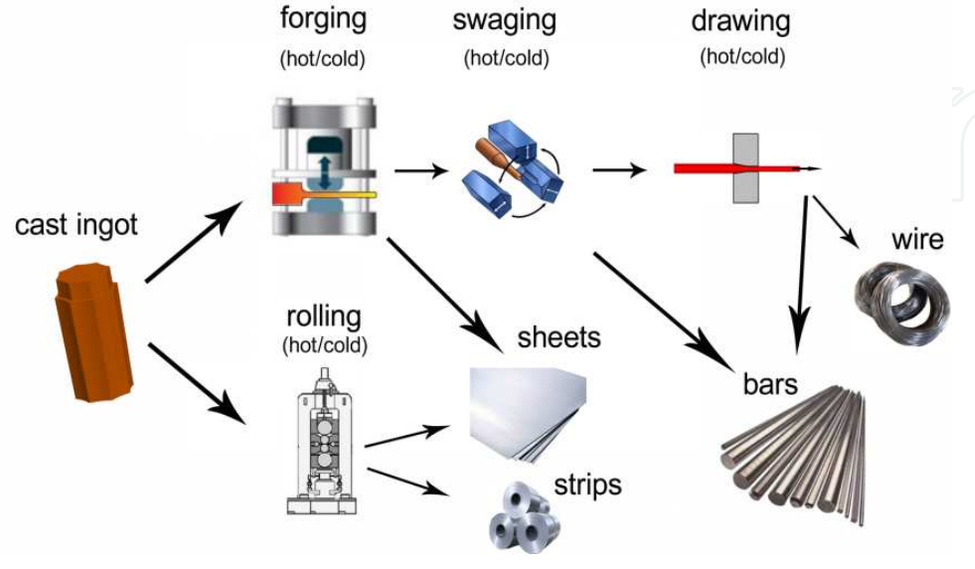


Figure 7. Scheme of basic forming operations used for plastic deformation of SMA

The chosen method of forming together with the method of heat processing is directly proportional to achieved characteristics. Although SMA are mostly used in the form of thin belts, wires or pipes (Kursa et al., 2005), all these products are produced by forming from original cast ingots. Ingots in the cast state are characterized by a very low formability and usually only a small or no memory or superelastic effect. With subsequent hot or cold forming these properties are modified. In Fig. 7 you can see a scheme of basic distribution of forming operations which are usually used for plastic deformation of SMA. Similarly as in other materials, the main aim of hot forming is to change the dimensions and shape of cast ingot, together with modification of its unfavourable microstructure. For the "destruction" of the original dendritic structure, some deformation depending on the cross section of the treated ingot should be applied. It is not unusual for the real size of the applied strain which will provide the required changes to reach values of around 90%. High degrees of deformation performed as hot forming are often also conditioned by requirements arising from the consecutive cold forming, during which such significant reductions of cross section cannot be realized (Ramaiah et al., 2005). Nevertheless, especially recently, when an explosion of unconventional forming techniques occurred, it can be said that intensities of applied strain can reach, and in practice do reach, much higher values than 100%. It should be stated that in these cases it is a shearing deformation where no significant changes in cross section occur. The main aim of these unconventional forming techniques is to achieve structural modification with the effort to deform materials at temperatures as low as possible.

The conventional treatment (forming) of SMA is usually divided into more stages. A frequent sequence of individual operations consists in melting, casting, hot swaging, cold rolling and drawing. Especially during cold forming techniques it is common to insert heat treatment between partial operations. So it is obvious that the transformation behaviour of a particular alloy will be influenced by each of these mentioned operations. In the first stages (melting, casting), there is an already mentioned factor of chemical composition. However, the production process itself can be performed in several various ways with different influence on the studied characteristics, which is documented by a high number of performed studies (Frenzel et al. 2004 and Zhang et al., 2005 and Frenzel et al., 2007a). Regardless of the chosen technique of melting, increased attention should be paid in all techniques to minimization of additional elements, especially oxygen and carbon. These elements have negative influence on the memory effect and also on the brittleness of the particular alloy, which is not without perceptible consequences, especially during the stage of forming.

During alloy forming, which is usually performed in the temperature range 300÷900°C, in addition to the present admixtures, defects in the crystal lattice also begin to come to light. To be more specific, both point defects and changes in the dislocation density begin to activate, which will significantly influence healing and precipitation processes (Frenzel et al., 2007b) or (Kocich et al., 2007). In binary NiTi alloys at around temperatures of 400°C the softening process begins, while at temperatures of 900°C formability (elongation) of alloys determined by tensile tests can exceed 100%. Although SMA at these temperatures exhibit

relatively good formability, during alloy forming some cracks may appear, especially near the edges. Usually bars or plate slabs are prepared by forming (forging, rolling). The deformation behaviour of SMA can probably be considered optimal in the temperature range near 800°C. Just these temperatures lie in the range where the alloys are workable and at the same time oxidation of their surface is not as massive as at higher temperatures (Wu, 2001). If forming temperatures are too high, the mentioned oxidation takes place and with increasing temperature the degradation of the material increases as well. The consequence of these processes is formation of very stable oxide layers which are often a part of the surface and cause destruction of the material due to the formation of cracks. When SMA is heated to the temperature 900°C, the alloy tends to be brittle because of occurrence of the Ti_4Ni_2O phase.

After hot forming of alloys, heat treatment is very often applied. The influence of annealing temperatures or cooling rate after annealing is already known very well; more detailed information on partial modes can be found, e.g., in the study (Standring et al., 1980). Generally it can be said that longer annealing times cause higher A_f temperatures (austenite finish). It is known that an increase of transformation temperatures (A_s, A_f) depends on the technology used for the preparation (machining) of SMA and is caused by temperature-induced stresses and defects. High M_s temperature is attributed to incomplete transformation during heating. The mentioned heat treatment is used for optimization of physical and mechanical properties together with maximization of shape memory effect and pseudo-plastic behaviour. The main reason for performed heat treatment after forming is thus modification of transformation temperatures for specific applications. When compared to the relatively wide interval of forming temperatures, the range for annealing temperatures is considerably narrower (300° – 525°C). The times used for annealing are usually in the order of minutes (5–30). Relatively stable resulting transformation temperatures are documented for annealing at temperatures of about 500°C and times shorter than 10 minutes (Liu et al., 2008). With increasing time of annealing A_f temperature increases and stress decreases. Increase of A_f is usually accompanied by depletion of the NiTi matrix by Ni, which is precipitated in the form of precipitates.

3.1. Swaging

As has already been mentioned before, one of the first forming procedures used for plastic deformation of cast ingot is swaging. Swaging is a forming process characterized by a very high rate of deformation (i.e. potential possibilities for the production are 4–6 pieces per minute). It is usually performed on swaging machines. There are many significant advantages of swaging, among them, e.g., possible high reduction of cross section at relatively low energetic costs, significantly dimensionally more precise forged pieces, higher surface quality and considerable improvement of mechanical properties of these products. This process has been known about for a relatively long time, which is also documented by many published studies. One of the main aims of these studies is to find a method of detection of pressure distribution on contact surface during individual deformations

(Zhang, 1984). Individual approaches consider various assumptions related to the parameter of applied energy (Choi et al., 1997 and Canta et al., 1998) or to the course of metal flow (Standring et al., 1980) or (Wang et al., 2005).

Swaging can be divided into two main groups. The first group is hot swaging; the second one cold swaging. Both named groups are procedures characterized by high efficiency and they can be used both for the production of full bars and differently shaped pipes. Swaging is a process which can be described using gradual (incremental) deformations, and is widely applicable for the production of engineering parts such as disks, rings, gear shafts, etc. The main difference between cold and hot swaging is in the working temperature of the process and also the used lubrication (in cold swaging).

However, it is generally known that high-temperature swaging, when compared to the original state of SMA after homogenization, need not necessarily cause a significant difference in reached transformation temperatures. On the other hand, e.g., after cold rolling, there is a distinct (usually full) suppression of phase transformation. It should be noted however that even short annealing of such a deformed state will be enough to restore the memory effect. The annealing will unblock obstacles which prevent the mentioned transformation process and the transformation can proceed again. Although the values of transformation temperatures in the state after hot forming and in the original state are not very different, there are considerable differences in the structural arrangement. During forming, a distinct decrease in grain size occurs, which also determines the final mechanical properties of individual states. Based on the size and type of applied strain, this value after forming can be increased to twice the original value.

3.2. Rolling

During hot rolling, individual grains of SMA forming the structure are deformed and simultaneously recrystallized, which preserves their equiaxed microstructure. At the same time the deformation reinforcement is compensated. The source material is usually in the form of cast semiproducts such as plate slabs, bars or ingots, or semiproducts after forming (e.g., by previous swaging, etc.). Heating of SMA is usually performed in electric furnaces, since SMA semiproducts are generally of small dimensions. In contrast to swaging, there is not such a massive generation of deformation heat to maintain the working temperature of formed components or its slight increase. Although during rolling the temperature as a consequence of deformation changes depending on the deformation rate, it is not enough to compensate the heat loss to the environment or into the tools. That is why for most SMA products (semiproducts small in dimensions) there is a serious danger of going under the recrystallization temperature during the hot rolling itself. The temperature of formed semiproduct after rolling should be near the range from 50 to 100°C above the recrystallization temperature to ensure sufficient heat for the process. In the event of failure to comply with this condition, intermediate heating must be performed before the subsequent reduction. There are relatively many published experiments in the field of rolling focused on the effect of ausforming (forming in the region of austenite) or

marforming (forming in the area of martensite). For example, the deformation behaviour of binary NiTi alloys during hot pressure or hot tensile tests is mapped (Dehghani & Khamei, 2010 and Morakabati et al., 2010). Suzuki in (Suzuki et al., 1999) states that significant increase of hot formability can be achieved in NiTi alloys by forming at temperatures of 900° – 1000°C, but there is the drawback of the above mentioned surface oxidation.

When hot rolling is carried out, cold rolling usually follows. Cold rolling of SMA is a process which is much more difficult than the same hot process. The main factor that complicates this procedure is the absence of healing processes which are activated at increased temperatures. During cold rolling, in the course of deformation solidification of SMA takes place and consequently formability of materials decreases. Other influences include a higher value of deformation resistance when compared to hot rolling. Just as a consequence of the limited formability of SMA, microcracks may appear during cold rolling in rolled products. It should be stated that it can occur even at low reductions of height (~20%). In cases when the final wire is produced by cold rolling in calibres (with diameters usually lower than 5 mm) the forming should take place in more stages. That is why a higher amount of passes is necessary to obtain the final wire. Probably the main reason for usage of cold rolling is to obtain dimensional accuracy and also the high surface quality of products prepared in this way. A side effect of cold forming (rolling) is suppression of the shape memory effect, while there is an increase of strength properties and a decrease of plastic properties.

With increasing content of Ni, rolling is more and more difficult and when the limit of 51 at.% of Ni is exceeded, any rolling of NiTi alloys is extremely difficult. The main reason is considerable deformation reinforcement. As is obvious from the more experimental results, yield strength of annealed NiTi alloys is usually lower than 100 MPa, but already after deformation of 40% this limit increases to values of about 1000 MPa. If the deformation continues, it would be very probable that cracks in the material would appear or even destruction of the material would take place. Intermediate annealing must therefore be performed before the next forming. This will cause a decrease of strength properties and a partial recovery of plastic properties. The just mentioned combination of deformation-healing (annealing) causes refinement of the final structure as a result. The temperature of intermediate annealing and its length will accordingly be the key parameters for the microstructure development. Generally it can be said that the temperature of intermediate annealing is lower than the temperature necessary for hot forming and usually is about 600°C (Wu, 2002).

It is known that during cold forming (rolling) the increase of the volume fraction of martensite is much higher than during hot rolling. Relatively many experimental studies focused on thermomechanical processing of SMA and mapping the effects of rolling and subsequent annealing, e.g. (Kurita et al., 2004), confirm this knowledge. It can be briefly stated that the higher the annealing temperature is, the lower content of retained martensite you will find. However, this fraction can be present in SMA even at relatively high temperatures, which is also documented in numerous studies (Brailovski et al., 2006 and Lin

& Wu, 1994). The reason is the presence of dislocations which slow down its conversion to austenite during post deformation annealing. The potential softening during annealing can be considered in three ways (mechanisms): a) dislocation recovery after which retransformation of martensite to austenite takes place (at temperatures of about 400°C), b) particle stimulated nucleation (PSN) at middle temperatures (~500°C), c) recrystallization of the matrix at high temperatures (~600°C). The needed level of deformation ensuring stable shape memory and superelastic behaviour of SMA (during cold rolling) is usually above 90% (Kim et al., 2006).

Among other drawbacks of rolling, there is only a small possibility of controlling the grain morphology or texture at adequate refinement of the microstructure. These are substantial effects which can influence the shape memory characteristics. Generally it can be stated that in the case of the requirement to maximize the shape memory effect, the best solution is to use the NiTi alloy in the state after hot rolling. In the case of the requirement to obtain high strength and hardness at acceptable reversible deformation, the NiTi alloy should be used after cold rolling.

These were not the only reasons for the impulse for researching the effect of unconventional forming techniques on deformation behaviour, or transformation characteristics of SMA. Especially in recent times there is a significant effort during research regarding the application of Severe Plastic Deformations (SPD) in memory materials. Among other applied techniques within the group of SPD, there is e.g. High Pressure Torsion (HPT) technology, or the Equal Channel Angular Pressing (ECAP) process. It was already confirmed several times by experiments that these techniques are a very effective tool for influencing the transformation characteristics, cyclic stability SMA and simultaneously relatively easy control of the texture of these formed materials (Kockar et al., 2010).

3.3. SPD processes

As has already been stated, most of the characteristics of SMA are mainly based on reverse martensitic transformation, which is controlled by chemical composition, microstructural parameters and also the method of preparation. The possibility to control functional properties of materials based on Ni-Ti alloys using thermomechanical treatment can be improved through microstructural refinement, which is documented in many studies, e.g. (Sergueeva et al., 2003). It is most desirable to obtain the structure characterized by very small grain (subgrain) size – ultra fine grain (UFG) structure. Nevertheless, it is necessary to simultaneously preserve exceptional properties of memory alloys.

It is known that TiNi-based materials characterized by a very small grain size can be prepared via three methods. The first method is chilling of cast. The second one consists in the preparation using SPD methods and the third one is then the combination of conventional techniques and subsequent annealing. Using the first and the second method enables one to obtain a fine-grained structure with the grain size in the range of 200–600 μm. If conventional forming with subsequent heat treatment will be used, then generally a larger grain size can be achieved compared to both of the previous variants. Nevertheless, a

significant advantage of this method is obtaining a relatively equiaxed structure, although with a little larger grain size than in the case of SPD. A distinct difference between the conventional and unconventional method of forming is mainly in the intensity of applied strain. During conventional forming, only limited degrees of deformation can for technological reasons be applied on the formed material during one forming cycle. In addition to that – as has already been discussed above – this process should usually be performed at higher working temperature.

The principle of SPD processes is based on repeated application of high degrees of plastic deformation during individual forming cycles. This fact, together with relatively low applied temperature when these processes occur, is behind the structural refinement during SPD. The result of such deformations is equiaxed structures characterized by a relatively high amount of grains with high angle misorientation. In addition to these features, the structures can also be described by the presence of subgrains with high dislocation density (especially after ECAP). However, it must be noted that the materials prepared using SPD also contain areas with high internal stress, at least when compared to cast materials. In the case of HPT, it is possible to obtain even amorphous states which, after subsequent annealing, are transformed into nanostructural arrangements. Based on the selected regime, the final grain (subgrain) size can be expected then. The applied annealing of SMA is usually in the temperature range of 200÷400°C. This is, at the same time, the interval of relatively stable grain size, nevertheless there is a significant decrease of dislocation density inside grains. With increasing temperature (~500°C) the grain size is increased to twice the original value, while grain boundaries are also much better defined. The reason of this increase is in the course of healing processes.

3.3.1. High pressure torsion

Localization of applied strain can thus be achieved using large plastic deformations. One of the first suggested and so far the most effective SPD method is the high pressure torsion process (HPT) (Fig. 8). It should be stated that in spite of certain limitations, deformation behaviour of a wide range of materials can be studied with this process. The consequence of the application of SPD is the destruction of the crystal lattice with subsequent transformation to the amorphous state. Accumulated dislocations or grain boundaries are the main driving force of the amorphization process. High density of dislocations may cause formation of amorphous bands thanks to shear deformation instability. In SMA, especially in NiTi-based alloys, a strong crystallographic texture is formed (Frick et al., 2004). In the following course of the process, refinement of grains and simultaneously amorphization are observed. This continues up to the full amorphous state of the formed material volume. According to this study and others, even the nanostructure formed like that contains characteristics of the texture, while in this state no directional deformation occurred. Individual nanograins exhibit preferred orientation which corresponds with orientation of nanograins preserved in the structure after HPT. A certain explanation may be knowledge assigning this influence to nanocrystals thanks to which heterogeneous nucleation occurs.

It should be noted that such a structural state is stable only at low temperatures. For these reasons HPT is usually performed at room temperature or even lower. However, findings on the dependence between M_s temperature and formation of nano-crystalline structure in SMA materials based on NiTi are very important. If the deformation temperature during SPD is lower than the corresponding M_s temperature of the formed alloy, then there is a high probability of formation of nano-crystalline structure. If the deformation temperature is between the M_s temperature and the highest temperature of the beginning of martensitic transformation influenced by deformation (M_d), then the probability of the nanostructure formation is lowered. If the deformation temperature is higher than the M_d temperature, the probability of the nanostructure formation is very low. If after SPD post-deformation annealing is applied, then a submicrocrystalline structure is formed.

It was already mentioned that at specific temperature regimes set during annealing the alloy can crystallize into grains with the size (10–40 nm). The specific temperature range where NiTi alloys are stable is 250° – 300°C (Prokoshkin et al., 2005). With increasing temperature of annealing, the final nanostructure will be "coarser". Total amorphization of the structure is usually achievable only in cases when the deformation temperature is lower than the martensite start temperature (M_s). Rate of the structure amorphization is influenced to large extent by the applied pressure during HPT. Higher imposed pressure suppresses the tendency to form an amorphous structure from nanostructure and as well to form nanostructure from deformably reinforced dislocation structure, as confirmed by the study (Prokoshkin et al., 2005). The probable reason is a decrease of M_s temperature, due to higher values of pressure deformations.

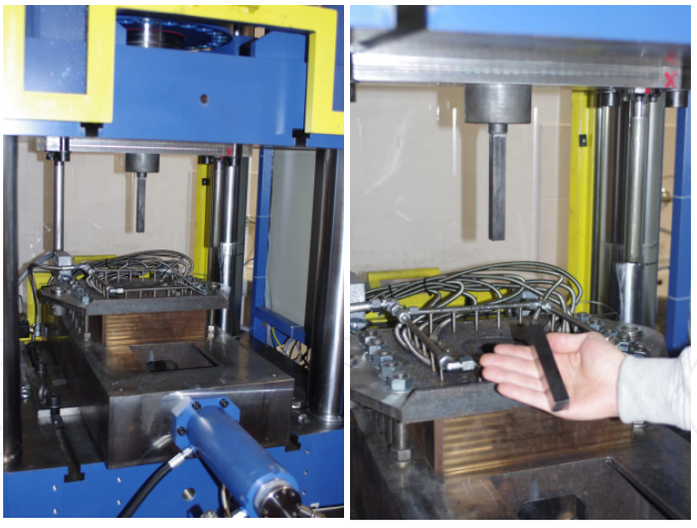
Materials processed using HPT and subsequent heat treatments usually reach very high strength properties (strength higher than 2 GPa). Surprisingly, relatively high plastic characteristics are also preserved (elongation at break up to about 40%) (Sergueeva et al., 2003). There are also assumptions to obtain super-plastic behaviour of NiTi alloys. Although the HPT technology appears to be a suitable candidate for positive modification of the properties, it is in principle excluded from commercial use by its main drawback (very small samples)-see Fig. 8b.

(a) (b)

Figure 8. Machine for HPT process (a) detail of processed sample (b)

3.3.2. Equal channel angular pressing

It was necessary to process larger volumes of products, which has led to looking for alternative ways of HPT substitution. One possible candidate for meeting the scheduled targets appears to be the equal channel angular pressing process (ECAP). In Fig. 9a you can see the assembly for practical application of this technique. It must be noted that, in contrast to HPT, various shapes of material sections can be processed here (Fig. 9b). As it was already mentioned, there is an effort when using SPD techniques to decrease the working temperature, because it is known that with decreasing deformation temperature the final grain size in the final structure of the treated material also decreases. Since SMA are characterized by a relatively high deformation resistance, the ECAP process – in contrast to HPT – should be performed at temperatures relatively higher. The most suitable range of forming temperatures found in experiments is 400° – 500°C. Amorphization of the structure, however, cannot occur in this temperature interval. This fact also determines higher size of final grains when compared to HPT technique. The size of the grain is usually decreased to a value that lies in the region of 200–300 nm. Although even in this case the strength properties are significantly increased while preserving relatively good plastic properties, these values are lower when compared with the state after HPT. Also the combination of ECAP and thermomechanical treatment is among tested procedures for another reduction of the grain size. To be more specific, cold rolling was applied after previous angular pressing (Pushin et al., 2006).



(a) (b)

Figure 9. Machine for ECAP process (a) detail of assembly and processed sample (b)

NiTi alloys are very sensitive to the exact chemical composition, which is manifested even during their deformation using SPD techniques. For example, in the study (Khmelevskaya et al., 2001) the binary $Ni_{50}Ti_{50}$ alloy absolved 12 passes (ECAP) at the temperature 500°C, or 8 passes at the temperature 400°C; in the case of $Ni_{49.3}Ti_{50.7}$ alloy, only 3 passes could be applied, since the material exhibited relatively low formability and it was destroyed.

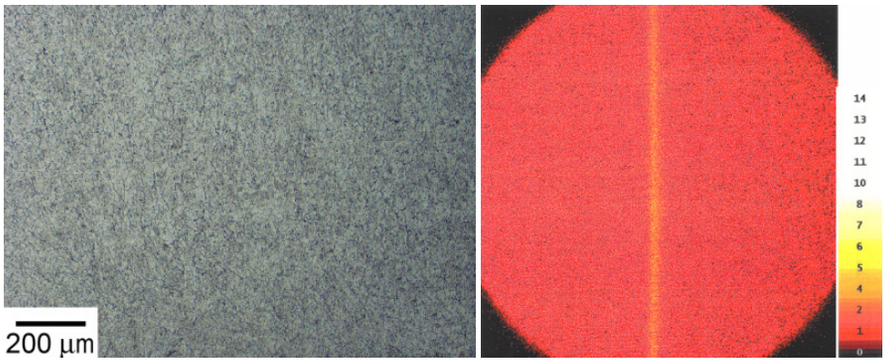
The reason for the formation of a fine-grained structure is probably the proceeding recrystallization process which causes gradual increase of disorientation of subgrain boundaries up to the formation of high-angle grain boundaries (HAGB). As to the ability of reversible deformation, its value after ECAP is comparable to the value obtained after application of conventional forming techniques (cold rolling) followed by heat treatment. It is documented, e.g., by the already mentioned study (Khmelevskaya et al., 2001) where the value of such deformation was determined to be ~7%. It should, however, be noted that the temperature interval of the memory effect after ECAP is narrower and also with lower values than after cold rolling. Similarly as after HPT, the temperature stability of SMA by annealing was tested up to temperatures of 500°C. Similarly, also after ECAP, SMA appeared to be stable, but significant reduction of dislocation density occurred. Increasing temperature caused an increase of grain size.

Generally it is known that cooling of NiTi alloys below the M_s temperature leads to higher formation of coarse-grained structure (50÷80) μm of the R phase. As confirmed by the study (Pushin & Kondratjev, 1994), cooling of coarse-grained monocrystals of B2 NiTi alloys below the M_s temperature leads to the formation of R-martensite with rhombohedral (or hexagonal) lattice. In the case of occurrence of other admixtures in binary and multiphase alloys, formation of monoclinic B19′martensite takes place during cooling below the M_s temperature. In particular, occurrence of elements such as Cu, Pd, Pt or Au during cooling of the alloy below the M_s temperature leads to formation of orthorhombic martensite B19 (Pushin, 2000). Generally it can be said that martensitic transformation on the microstructural level is caused by the presence of microtwins, while on the level of internal areas of grains it is caused by the formation of coherent crystals.

Martensitic phase transformation thus usually takes place from cubic B2 high-temperature phase (austenite) to monoclinic B 19′ phase (martensite). This process is accompanied by high deformation. According to the results from the experiment (Waitz et al., 2004), if the grain size in SMA is in the region of nanometers, then the high density of grain boundaries will act as a significant obstacle during mentioned transformations. There are two main reasons why martensitic transformation in nanomaterials is suppressed. The decrease of transformation temperatures depending on the decrease of grain size follows from the mentioned study. It was also proved that full suppression of martensitic transformation takes place when the grain size is smaller than 50 nm. From the point of view of phase stability, these small grains have a significant influence on morphology of martensite (Waltz, 2005).

Thanks to the experiment performed with the Ni50.4Ti alloy, the specific influence of forming on transformation characteristics and also on microstructure development was mapped. The experiment describes the problem of combination of conventional forming techniques together with unconventional ones. For forming, SMA characterized by the content of O_2 (0.0624 wt.%) and N_2 (0.0039 wt.%) was used. The content of carbon (0.055 at.%) was determined using spectrometry. The diameter of the cast was 20 mm and the cast length 350 mm. Then homogenization at the temperature of 850°C is followed by subsequent cooling.

The forming itself was suggested in the first phase using swaging then pressing using the ECAP technique was performed. Swaging was performed at the temperature of 850°C. During swaging, the strain was applied gradually in individual reductions. The total strain applied on the cross section was 66 %. On the contrary, the ECAP technology was applied on SMA at the temperature of 290°C. Because of possible "negative" influence on the temperature fluctuation of the formed material, the pressed samples were placed in the steel "cans". For the ECAP, matrix with the angle 105° between individual canals was used; the extrusion speed was set to 1 mm/s. The extrusion itself consisted of two performed passes, where Bc was chosen as the deformation path. In particular, the influence of intensities of applied strain in relation to mechanical and thermophysical properties and the course of healing processes were studied. To be able to determine the mentioned effect, heat treatment was carried out after the performed deformation. In addition to optical microscopy, RTG diffraction was also used for evaluation of changes. The differences between after swaging followed by ECAP are obvious from the attached photos (Fig. 10).



(a) (b)

Figure 10. Ni50.4Ti alloy (swaged+ECAPed) : microstructure (a), diffraction fringe (b)

To be able to specify the differences caused by applied strain, it was necessary to perform heat treatment of the deformed materials. These annealing using selected temperature regimes (550°C/15 min, 600°C/15 min, 650°C/15 min, 900°C/15 min) should provide information on the influence of the accumulated deformation on the beginning of corresponding processes, especially recrystallization.

The azimuthal profile of diffraction lines of the NiTi alloy confirms that all mosaic blocks (DCA-diffraction coherent areas of crystallites) in the structure after ECAP are smaller than 10 µm (Fig. 10b). The DCA are regions that scatter coherently. These areas are defined by borders where is high dislocation density. Within the framework of the mosaic blocks, the moving dislocations face minimal resistance. Inside the mosaic blocks is much less of dislocations than on the borders of blocks, that is why the mosaic blocks are called as dislocationless cells (areas) in the crystallites. Nevertheless, this predication is not quite accurate because one of obstacle in these blocks for dislocation movement is Peierls – Nabarro stress (i.e. dislocation is moving through the mosaic block, so that mosaic block must have at least one dislocation). This labeling (dislocationless blocks) is commonly used, important factor is that inside of the mosaic blocks is considerably less of dislocation than on

its boundaries. Due to this matter (low dislocation density inside of mosaic block) can X-ray be diffracted coherently (that is why the mosaic blocks are also often marked as Coherent Scattering Regions – CSR´s). The presence of blocks smaller then 10 μm was confirmed by XRD. Generally may be noticed that mosaic blocks (obtained by XRD) are not the same as grains observed by optical microscopy. Mosaic blocks can be seen by presence of reflections on XRD patterns. In the case of the large block presence will be its reflection large as well. Since cannot into the diffracted volume be much of big mosaic blocks present, there will be their reflections on diffraction lines clearly separated. If will be mosaic block small there will be much of their reflections in diffracted volume. That is why individual reflection are overlapping (they are not separated i.e. reflection is continuous). More detailed information about this technique can be found for example in (Hindelah & Hosemann, 1988).

As a consequence of recrystallization processes after annealing of the extruded alloy at temperatures of 600°C and higher in the structure blocks larger than 10 μm were formed, while after the same length of time annealing at lower temperatures all mosaic blocks remained smaller than 10 μm. It should be noted that the size distribution of mosaic blocks was bimodal (i.e. blocks larger than 10 μm and blocks smaller than 10 μm). This means that coarser crystallites contain more nickel than smaller crystals. The reason is the asymmetry of the area in the phase diagram of titanium – nickel formed by a solid solution of TiNi. Microinhomogeneity of the alloy also influences mechanical properties of the alloy. The dispersion of such elementary composition and thus lattice parameters of individual mosaic blocks in the structure causes so-called microstrain (strain of the 2nd order) influencing the dynamics of dislocations, but also nucleation and growth of microcracks. These strains of the 2nd order also influence shifts of walls of mosaic blocks and thus the course of recrystallization of the alloy. The authors of the experiment performed with the Ni50.6Ti alloy also arrived at similar results (Kocich et al., 2009).

It means that even with very thoroughly conducted preparation of material based on shape memory alloys, microinhomogeneities may be formed. As concerns the forming technologies as such, it can be stated that after completed rotary forging (swaging) the initial grain size and therefore also the ensuing properties were substantially changed. The ECAP process also proved its influence on the final appearance of the micro- and substructure. The differences are even apparent in the number of passes; if material passed through the matrix only once, then no mosaic blocks smaller than 10 μm occurred in the structure, however, influence of the second pass can be seen here, when the samples of the NiTi alloy already contained bi-modal composition. The temperature that appeared to be the starting temperature for initiation of re-crystallisation was 600°C.

4. Conclusions

For some specific purposes, the exclusivity of binary shape memory alloys should be modified by the addition of another element. These prepared Ti-Ni-X based materials are currently very progressive materials. As has already been indicated, their final properties will, to a great extent, be determined by the chosen element. To a great extent, it is thus the

factor of chemical composition; nevertheless that is not the only one. A significant influence in the sense of the effect on transformation characteristics together with other properties was also demonstrated for the preparation method. There is an outstanding dependence on used forming technology and their relationship or thermomechanical conditions play an important role. During conventional forming, the deformation behaviour of SMA binary systems is relatively well known. As seems to be the case, multiphase SMA are very sensitive to even small deviations from the required chemical composition. These nuances can be observed through the shifts in recrystallization temperatures, which also means the shifts in their optimum forming temperatures.

Particularly at this time there is intensive research of use of unconventional forming techniques for SMA. Although it is already known that when using these procedures, in contrast to conventional forming, it is possible to obtain structures characterized by grain size of nanometers, the procedure is currently not optimized for practical applications. The effectiveness of procedures based on applications of large plastic deformations consists mainly in a distinct decrease of grain size. There is also an obvious benefit in controlled textures of deformed SMA, which can also be utilized with regard to required final properties.

Although studies monitoring behaviour of multiphase Ti-Ni-X based systems exist, a generally known method for the preparation of SMA is not still available. In the future there should be actions related to preparation of specific alloys with verified behaviour. It is obvious that hand-in-hand with the above mentioned there should also be development focused on the preparation and target modification of properties of these materials.

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