Process, Features and Applications of **Shape Memory Alloys**

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Preface

The purpose of the book is to provide a glimpse into the dynamics and to present opinions and studies of some of the scientists engaged in the development of new ideas in the field from very different standpoints. This book will prove useful to students and researchers owing to its high content quality.

Alloys, which when deformed can return to their original shape once heated are called shape memory alloys (SMA). The field of shape memory alloys over the past few years has evolved as a significant topic of study. The complexity of relationship between properties and structure has always interested researchers and is mostly associated with the fact that strong multidimensional interactions occur in these alloys. This is reflected by initial researches on thermal and mechanical induced phase transformations and also latest developments emphasizing on magnetically induced structural changes. Applications of shape memory alloys offer innovative aspects which have drawn significant industrial interest attributing to its singular behavioral characteristics. These have led to the subject of shape memory alloys acquiring a position of great interest for undergoing research and studies in various fields varying from crystallography and thermodynamics to mechanical evaluation of electrical and chemical properties. The book includes recent researches and studies in this field. It encompasses various aspects of shape memory alloys like processing, novel applications and relationship between structure and properties.

At the end, I would like to appreciate all the efforts made by the authors in completing their chapters professionally. I express my deepest gratitude to all of them for contributing to this book by sharing their valuable works. A special thanks to my family and friends for their constant support in this journey.

Editor

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Chapter 1

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

Radim Kocich, Ivo Szurman and Miroslav Kursa

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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.

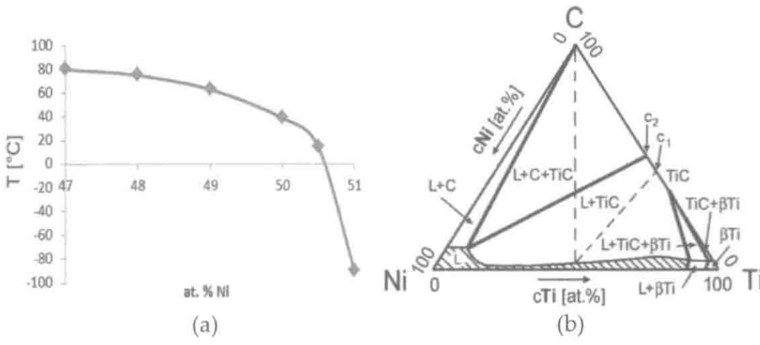


Figure 1. The dependence of temperature of martensitic transformation (a) Ternary system Ti-Ni-C (b)

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.

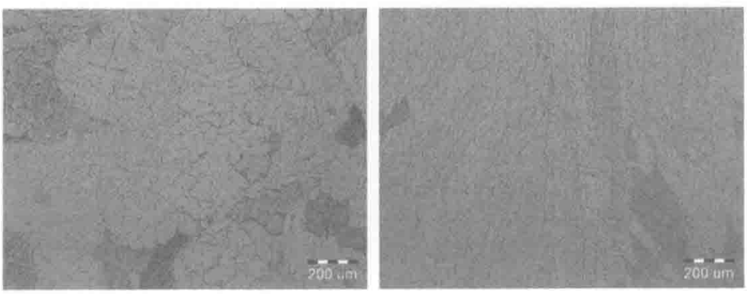
Typical superelastic nitinols contain ca. 350–500 ppm of oxygen and 100÷500 ppm of carbon. The metallurgical purity (grain structure, presence of impurities etc.), of course, greatly depends on the preparation process. Ni-Ti alloys can be called high-purity alloys if they contain <100 ppm of oxygen and <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.

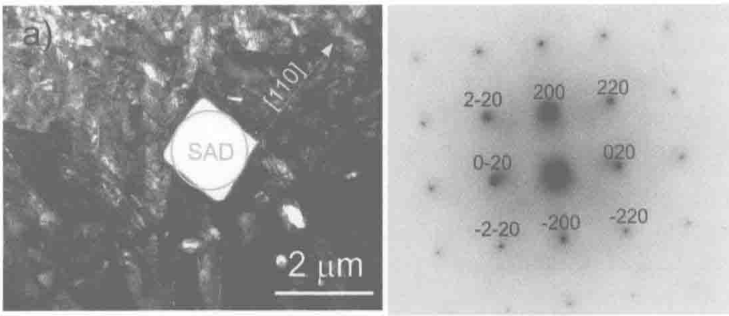
When the molten Ni-Ti enters into contact with the graphite of the crucible, inter-diffusion causes a growth of the TiC layer and the contents of carbon in the melted alloy grows. This process includes the diffusion of carbon through a thin layer of TiC which grows on the boundary between TiC/melted 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)

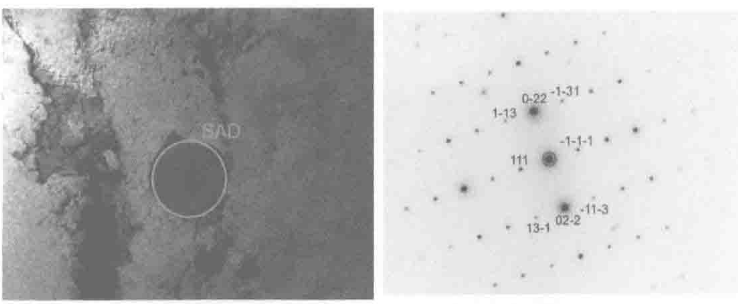
Figure 2. As cast state of alloy: Ni50.6-Ti(at.%) (a), Ni46-Ti50-Co4 (b)

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).

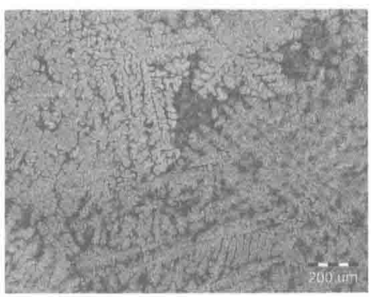


Figure 5. Microstructure of alloy Ni49.5-Ti25.5-Zr10-Nb15 (at. %), plasma

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