METHODS FOR Ni-Ti BASED ALLOYS PREPARATION AND THEIR COMPARISON

Ivo SZURMAN a, Miroslav KURSA a

a Department of Non Ferrous Metals, Refining And Recycling, VŠB TU Ostrava, VŠB TU, ivo.szurman@vsb.cz, miroslav.kursa@vsb.cz

Abstract

Temperatures of phase transformations and properties of the Ni-Ti and Ni-Ti-X based shape memory alloys are in the first place highly dependent on processing technology. It is well known that only small deviation from the required composition can cause very important change of transformation behaviour. For this reason it is necessary to pay special attention to the metallurgy of these interesting alloys. At present, the Ni-Ti-(X) based alloys are mostly prepared in vacuum, and various methods of melting are used (electron-beam melting, arc melting, high-frequency induction melting). Another possibility for the preparation should be plasma melting. Complications during preparation are caused mainly by carbon, nitrogen and oxygen, which could form non-metallic inclusions. Carbon is related to the alloys mainly in the course of their preparation in graphite crucibles. Due to titanium carbide formation in Ni-Ti matrix, the concentrations of nickel and titanium are shifted, so this leads to change of the temperature of martensitic transformation. Creation of a low-melting phase Ti2Ni, which causes a distinct susceptibility to hot formation of cracks, is another issue arising during melting of Ni-Ti alloys. The presented work is focused on comparison of individual methods of preparation of the alloys mentioned above, i.e. induction vacuum melting, plasma melting and vacuum electron-beam melting.

1. INTRODUCTION

Phenomenon of shape memory was observed for the first time in an equi-atomic inter-metallic compound of TiNi in 1963 [1]. Ni-Ti based alloys are highly sensitive to the composition. A deviation of 0.1 at. % from the required composition can change here the transformation temperature even by 10 K [2, 3]. The alloys alloyed by other elements have this concentration dependence of temperature of martensitic transformation lower. However, in these ternary or quaternary alloys different transformation sequences occur in comparison with the binary alloys. These multi-component systems generate also weaker forces at transformation [4, 5]. Typical raw materials for preparation of Ni-Ti based alloys are pure titanium (sheet, rod) and electrolytic nickel [6]. Ni has usually lower contents of interstitial impurities. Typical superelastic nitinols contain 350-500 ppm of oxygen and 100-500 ppm of carbon. It is possible to describe Ni-Ti alloys as super-clean, if they contain < 100 ppm of oxygen and < 20 ppm of carbon. Such alloys are usually prepared by high frequency induction vacuum melting in graphite crucible combined with re-melting in a vacuum arc furnace [7].

The present key technologies for preparation of Ni-Ti and Ni-Ti-Me alloys are realised mostly in vacuum. They use various methods of melting (electron beam melting, arc melting [8, 9], induction high frequency melting in vacuum in a graphite crucible [10 - 13]). Next very interesting method is plasma melting. Arrangement of charge in the crucible is also very important at vacuum high frequency induction melting [14, 15]. It was established that if the surface of the crucible is covered with Ti disks, the content of carbon in the produced alloy is reduced 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 found that absorption of carbon is strongly dependent on temperature. Extensive experiments concerning preparation of alloys in a graphite crucible were carried out. It was established that with the increasing time of dwell of
the melt in the crucible the melt gets enriched in carbon. Increase of carbon contents occurs also at increase of temperature of melting. Oxygen penetrates into material at melting in a graphite crucible particularly from input raw materials, or from furnace atmosphere [16, 17]. Preparation of highly pure and special alloys, to which shape memory Ni-Ti based alloys undoubtedly belong, by plasma metallurgy requires use of defined controlled atmospheres. It is necessary to ensure high purity of inert gases. The most commonly used gas in plasma metallurgy is argon. It is used for stabilisation of the arc discharge of plasma burners. It is a medium for heat transfer to re-heated material and it forms after decomposition of low-temperature plasma also a protective working atmosphere in a plasma furnace [18]. Preparation of an alloy by electron beam melting [19] is also one of the interesting methods. Contamination of the alloy by carbon is prevented thanks to melting of the material in a vertical arrangement of uplift. Electron furnace operates on the principle of zone melting – floating zone melting. Input material consists of an ingot prepared in a vacuum induction furnace. Content of carbon is usually 4 - 10x lower than at the VIM technology. Content of oxygen is usually very low due to working vacuum, which in this case achieves 10^{-2} Pa as compared with 10 Pa at vacuum induction melting. Contamination by oxygen therefore depends mainly on purity of the input material. Drawback of this technology consists in control of chemical composition. This issue is caused by possible evaporation of the alloy components. Another drawback is small volume of the alloy, so it can be stated that this technology is not suitable for commercial use. Objective of this procedure was to reduce content of gases and carbon in an alloy.

2. EXPERIMENTAL

For the experiments two alloys were chosen: A (Ni50.6 – Ti49.4 at. %) and B (Ni49.8 – Ti42.2 – Zr8 at. %). Alloy preparation was realized with use of plasma melting, vacuum induction melting in a graphite crucible and by electron beam melting in vacuum. Before preparation all the raw materials were thoroughly mechanically and chemically cleaned. For the purposes of metallographic testing the samples were abraded with paper containing abrasive material SiC, polished by water suspension of Al_{2}O_{3}. Microstructure was developed by an etching agent 1HF : 4HNO_{3} : 5H_{2}O, observation of microstructure and taking pictures of it was realised on the microscope Olympus GX 51, equipped with the digital camera DP 12. SEM was realized on the JEOL JSM 6490 LV microscope. Determination of quantity of gases was made by thermo-evolution method on the instrument LECO TC 436. Content of carbon was determined by spectrometry with use of the instrument SpectroMaxx.

2.1 Plasma melting

Plasma furnace can be used for melting of materials with T_{M} < 3400°C. The heat necessary for melting of metal is generated by the plasma burner. Temperature of plasma achieves at this method of melting 6500 K. Ar of purity 4N6 is mostly used as a plasma forming gas. Parameters of the melting were the following: Ar flow – 27 l.min^{-1}, input power 30 kW, rate of feed of the mould was 2 cm.min^{-1}. In this manner the ingots with mass 200 - 1000 g were prepared, in dependence of the type of the mould. After preparation the gases (N_{2} and O_{2}) and also C were determined in material. Results are presented in table 1. Microstructures of the alloys prepared in plasma furnace are shown in figures 1 and 2.
2.2 Vacuum induction melting

This method of preparation was realised in the furnace Leybold Heraeus IS1/FFF. Well proven graphite crucible was used for vacuum melting. Prior to melting itself a flushing melting was made with use of binary Ni-Ti alloy in order to create a TiC layer, the purpose of which was explained above. A separate crucible was used for each alloy. Material was also appropriately arranged in the crucible. Melting was realised with use of the following parameters. First, the furnace was evacuated to a low residual pressure and then filled with Ar (6N). Afterwards the furnace was evacuated. This procedure was repeated three times. Input power of the furnace was approx. 15 kW. This was followed by filling the furnace with Ar (6N) to a pressure of several kPa and casting of material into an ingot-mould with inner diameter of 10 mm, height 300 mm. Mass of the ingot was 210 g. Microstructures of the prepared alloys are shown in figures 3 and 4. The preparation was also followed by determination of gases (N₂ a O₂) and of C in material. Results are presented in table 1.

<table>
<thead>
<tr>
<th>alloy</th>
<th>melting</th>
<th>O₂ [wt. %]</th>
<th>N₂ [wt. %]</th>
<th>C [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>plasma</td>
<td>0.0970</td>
<td>0.0155</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>vacuum</td>
<td>0.0651</td>
<td>0.0041</td>
<td>0.039</td>
</tr>
<tr>
<td></td>
<td>electron beam</td>
<td>0.0857</td>
<td>0.0420</td>
<td>0.020</td>
</tr>
<tr>
<td>B</td>
<td>plasma</td>
<td>0.1042</td>
<td>0.0144</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>vacuum</td>
<td>0.0818</td>
<td>0.0037</td>
<td>0.037</td>
</tr>
</tbody>
</table>
2.3 Electron beam melting

Used electron furnace works on the principle of vertical zone melting with floating zone. For melting in the electron furnace an ingot was used, which was prepared in high frequency induction vacuum furnace. Preparation of the ingot was realised in full compliance with the chapter 2.2. Ingot surface was abraded and etched by HF. Melting was realised under the pressure of 8.10^{-3} Pa. Voltage was 6.4 kV at 28 mA. Rate of feed of the zone was 3 mm.min^{-1}. During melting a slag appeared on the surface of the bar. Due to the fact that the obtained results were not very satisfactory, the electron beam melting was realised only on the alloy A (binary) twice. Microstructure of the alloy after EBM is shown in figure 5.

3. RESULTS AND DISCUSSION

The performed experiments revealed that technology of plasma melting for preparation of the Ni-Ti and Ni-Ti-Me based alloys has its advantages, but also some drawbacks. An alloy prepared in plasma furnace contains usually considerable amount of gases (oxygen and nitrogen) as shown in table 2. One great
advantage of this method is elimination of danger of carbon contamination from material of crucible. The key drawbacks comprise high non-homogeneity with unsatisfactory distribution of alloying elements, as well as their unsuitable shape forming operations resulting from the shape of the mould. Technology of plasma melting was not found to be the most suitable for preparation of Ni-Ti and Ni-Ti-Me based alloys, due to the necessity of the following operation – vacuum high frequency re-melting in graphite crucible and casting into a mould (usually rod or bar) suitable for the next forming operations (hot swaging and cold drawing). Microstructures of the alloys, prepared in the above mentioned plasma furnace, are usually highly inhomogeneous, which is documented namely by the Fig. 1a, 2a. This problem is caused by very high temperature gradients during melting. At the top of the ingot, the alloy is preheated to high temperature. On the other hand, the part of the ingot, which is with contact with copper, intensively cooled (see fig 2a). The SEM image of the alloy A (Fig. 1b) shows TiNi matrix and Ti$_2$Ni phases. On the SEM image of the alloy B (Fig. 2b) dominant TiNi matrix, Ti$_2$Ni phases and small TiNiZr phases are visible.

Melting in vacuum induction furnace in a graphite crucible proved successful at preparation of these materials. The longer dwell of the melt in the crucible leads to higher carbon contamination of the alloy, so for this reason the dwell was reduced to a minimum. After vacuum induction melting, the microstructures of the alloys are significantly more homogeneous (see Fig. 3a and 4a) than microstructures of the same alloys, melted in plasma furnace (Fig. 2a). As it can be seen very well on the ingot cross section, characteristic micro-structure is related to the heat output from the graphite mould during cooling of the alloy. For preparation of alloys with satisfactory low content of oxygen and nitrogen it is necessary to use available raw materials with the lowest possible content of gases, and also high purity argon with the purity of at least 6N. The alloys after melting in graphite crucible contain very often TiC type carbide phases. Fig. 3b presents the SEM image of the alloy A. Here the dominant TiNi matrix is visible and therefore the Ti$_2$Ni phases are shown. Carbide particles cannot be seen due to the used magnification of the microscope. TiC type particles are approx. 2 μm in diameter after preparation in vacuum induction furnace. Fig. 4b shows SEM image of the alloy B. As in the previous case, the TiNi matrix is here very well visible, the phase Ti$_2$Ni is documented too. Besides these mentioned phases, light TiNiZr phase was observed, too.

Very interesting situation occurs after EBM. Fig. 5a shows different types of micro-structures in the alloy A after VIM and EBM. On the longitudinal section, the boundary between VIM and EBM parts of the ingot is also visible. Microstructure of the alloy A after electron beam melting can be characterised as cellular (Fig. 5b). Microstructure is at all places of cross section almost identical. In the Fig. 5c, SEM of alloy B is presented. Only two phases are visible there, TiNi matrix and Ti$_2$Ni phases. In this case too (similarly as in the case of plasma melting), this technique cannot be fully recommended. In this case, however, it is necessary to supply at first the input material in the form of an ingot prepared in high frequency induction vacuum furnace.

From the viewpoint of content of gases the best results were obtained at melting in vacuum induction furnace. In the alloy from electron beam furnace, where we expected reduction of content of gases, this in fact did not happen. This fact probably corresponds with the observed slag formation during melting. It will be necessary to further verify this method in the future work. In the plasma furnace the gas Ar 4N6 was used. Use of Ar of higher purity (6N as compared to 4N6) could ensure reduction of content of gases in the alloys. From the viewpoint of carbon contents the best situation was, as it could have been expected, after plasma melting. The highest carbon content was found, again as expected, in the alloys prepared in high frequency induction vacuum furnace in a graphite crucible. In this case carbon is usually bound in the form of TiC. In case of the electron beam melting the initial carbon content from induction re-melted ingot was also reduced. The obtained quantity of carbon can be estimated as satisfactory.
4. CONCLUSIONS

- Two types of alloys were prepared (binary and ternary) by different methods - plasma furnace, high frequency induction vacuum furnace and electron beam furnace. Microstructures of alloys were examined by optical and scanning electron microscopy.
- After evaluation of experiments it was established that microstructures of alloys after plasma melting were highly inhomogeneous, but carbon content was much lower than in the alloys prepared by other methods.
- The question of gas contents is in this case also arguable. In the case of electron beam melting the advantage of use of this method for reduction of gas content was not confirmed. Carbon content is here satisfactory.
- Preparation of the alloys in high frequency induction vacuum furnace in combination with casting of the alloy into graphite moulds seems to be the most suitable method due to the fact that material with satisfactory characteristics for the needs for forming operations can be prepared just by one melting operation.

ACKNOWLEDGEMENT

The presented results were obtained within the frame of solution of the research project MSM 6198910013 „Processes of preparation and properties of high-purity and structurally defined special materials“, and grant project GA 106/09/1573 „Optimisation of chemical composition, structural characteristics, mechanical properties of NiTi alloys for bio-mechanical applications“.

LITERATURE