
Effects of VIM frequency on chemical composition, homogeneity and microstructure of NiTi shape memory alloy

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The concentration distribution and microstructure of NiTi shape memory alloys produced in vacuum induction furnaces operating at high and medium frequencies are compared with those of materials melted in vacuum resistance furnaces. The production procedure consisted of charging pure metals into a graphite crucible; raising the temperature to 1450°C under vacuum; holding the materials in high and medium frequency induction and resistance furnaces for 3, 5, and 120 min under vacuum; and allowing alloys to solidify in the crucibles under the same vacuum. The procedures in each of the three furnaces were made as similar as possible. Chemical composition, microstructure, and surface hardness of alloys were determined at different locations along the length of solidified specimens. Standard deviations in chemical analyses and hardness numbers were taken as criteria for specimen homogeneity. Results indicate that a high vacuum induction furnace operating at medium frequency is an appropriate equipment for melting NiTi shape memory alloys of the desired homogeneity, microstructure, and hardness.

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Keywords: TiNi, Shape memory alloy, Homogeneity, Vacuum induction melting, Vacuum resistance melting

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Introduction

Desirable behaviours, such as shape memory effect, pseudo-elasticity, biocompatibility, and corrosion resistance¹ have resulted in the introduction of Ti–Ni shape memory alloys (SMAs) as an important family of memory materials having numerous industrial uses including aerospace and bioengineering applications.^{2,3} Commercial production processes involve both non-melting methods, such as powder metallurgy,^{4–7} and melting methods, such as vacuum induction melting (VIM).^{8–10} The latter have, in the past, been used almost exclusively for commercial mass production of these alloys.

An important characteristic is susceptibility to the exact chemical composition and vulnerability to the processing history of these alloys.^{10–13} Desirable memory properties can, in general, be obtained with 49–50.7 at.-%Ti. Binary alloys containing less than 49.4 at.-%Ti are extremely hard and brittle.^{14–16} This can be observed from the Ti–Ni phase diagram shown in Fig. 1, which indicates a relatively narrow compositional variation for low temperature intermetallic TiNi phase. A small variation in the chemical analysis would result in precipitation of other intermetallic compounds such as Ti₂Ni, Ti₂Ni₃, Ti₃Ni₄, and TiNi₃^{12,13} in the alloy matrix, which causes enhancement of both hardness and strength, and reduction of ductility and workability of the alloy.^{14–18} Obtaining a uniform chemical composition in the TiNi cast ingot is of great importance because the variation of composition can cause changes in workability, ductility, strength, hardness, and martensite to austenite and austenite to martensite transformation temperatures along the solidification path.^{19–21} A 0.1 wt.-% increase in nickel content of the alloy, for example, can decrease the martensitic start transformation temperature by more than 20°C.²²

Because of the considerable difference in density as well as reactivity of titanium and nickel constituents, the raw materials do not tend to dissolve rapidly into each other to form the desired TiNi intermetallic phase at the initial stages

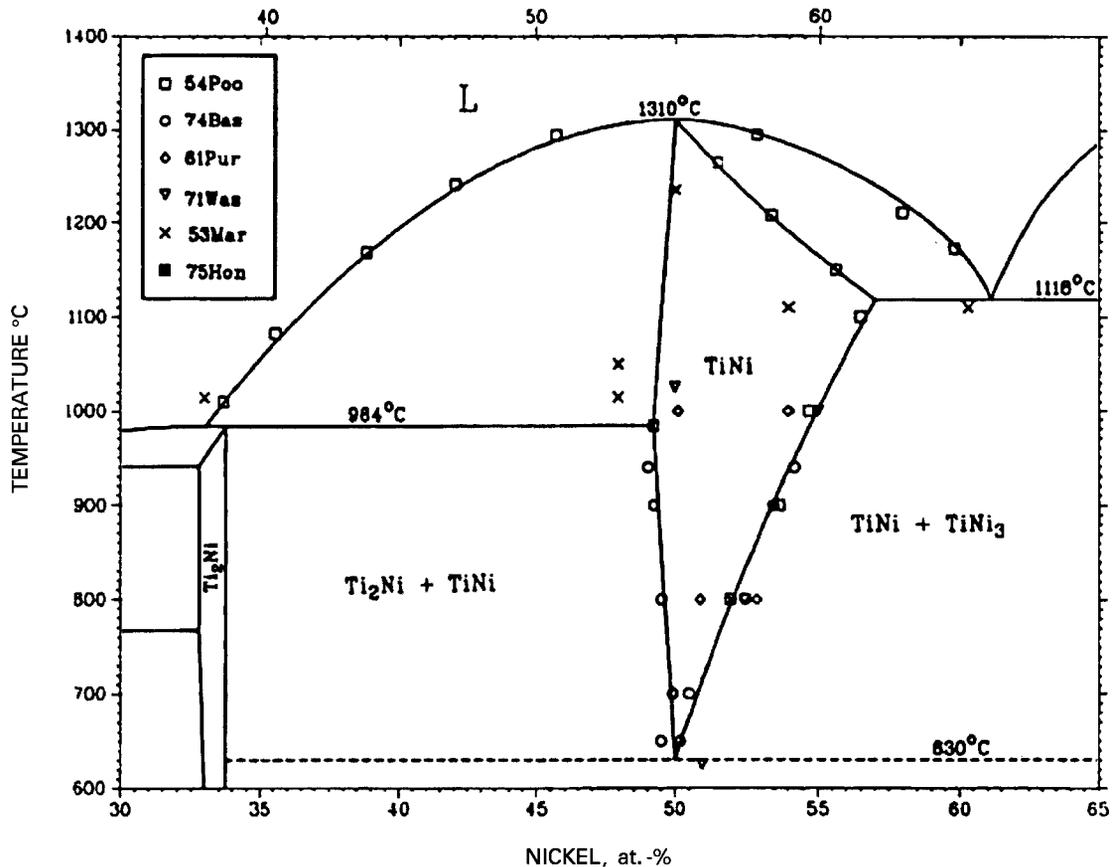
of melting. As a result, the composition of the liquid phase tends to deviate from that of the equiatomic TiNi, and undesirable phases such as Ti₂Ni, Ti₂Ni₃, Ti₃Ni₄, and TiNi₃ segregate within the principal TiNi phase.¹⁵ Strong mixing is, hence, required in order to obtain a homogeneous liquid phase. Because of the small diffusion coefficients as well as the large reactivity of the titanium, the solidified alloy requires a relatively long homogenisation time.^{1,22,23}

Absorption of oxygen and nitrogen during heating, melting and annealing can also dramatically influence the mechanical properties and workability of TiNi samples.¹¹ Highly vacuumed furnaces should, therefore, be utilised to produce workable TiNi ingots.²⁴ High frequency induction furnaces can reduce this undesirable effect by decreasing the contact times of materials with the environment. Rapid melting and rapid solidification can each reduce the detrimental gas absorption effects.²⁵

Work on alternative production methods is important in order to determine the optimum melting conditions to achieve a homogeneous TiNi cast phase. This paper deals with the most recent findings obtained in the author's laboratory on the influence of molten metal residence time, stirring and heating rate imposed on the liquid phase retained in a graphite crucible inserted inside experimental inductive or resistance heating units.

Experimental procedure

Nickel samples were cut from cathodic plates with a purity of 99.9%. They were polished and then washed with 97% pure acetone to remove any oxide scale and contamination that might have remained on their surface. They were then dried at 200°C for 2 h and wrapped with pure aluminium foil to keep them away from humidity and contamination. A balanced amount of sponge titanium particles of purity 99.95 wt.-% and nickel samples of cathodic plates of purity 99.9 wt.-% were carefully weighed and charged into graphite



1 Ti-Ni binary phase diagram¹

crucibles prepared for the production of Ti-55 wt-%Ni shape memory alloy.

Before charging, the empty crucibles were heated to 1200°C under 10^{-1} mbar pressure for 10 min to reduce any chance of crucible gassing during the subsequent heating and melting. This was found to be beneficial to keeping the vacuum pressure as low as possible during the melting operation. Subsequent to melting, solidification was achieved inside the furnace under the same vacuum as used during the melting process (10^{-4} to 10^{-5} mbar).

Three different melting units were used to produce the SMA samples.

1. A high frequency vacuum induction unit made by Materials Research Co. of England with a nominal frequency 450 kHz, nominal voltage 12 000 V and nominal output power 20 kW.

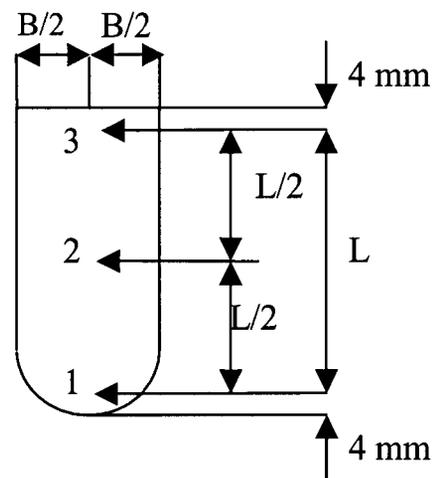
2. A medium frequency vacuum induction unit made by Leybold AG Co. of Germany with a nominal frequency 4 kHz, nominal voltage 500 V and nominal output power 60 kW.

3. A vacuum resistance furnace made by Weinert Company of Germany with tungsten rod elements, nominal voltage 380 V, nominal power 210 kW, and actual output power 152 kW.

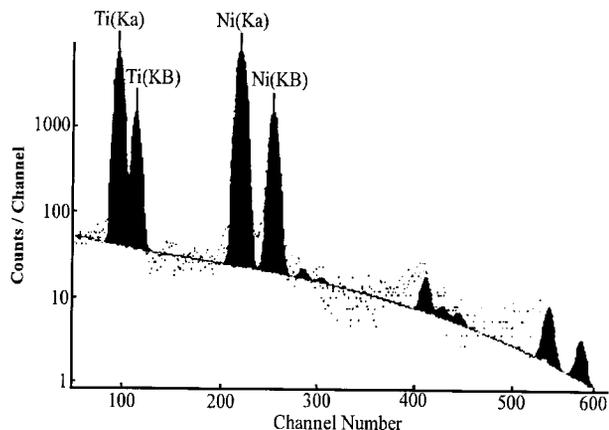
When temperature reached 1183°C, titanium-nickel reaction started to produce a large amount of heat that helped to speed up the melting operation. After reaching a temperature of 1450°C, the charge materials were molten in the VIM furnaces. The materials were held in the molten state for either 3 min in the medium frequency vacuum induction furnace and 5 min in the high frequency vacuum induction furnace under steady stirring conditions to try to ensure homogenisation within the liquid phase. The materials were then cooled down to room temperature to produce a solid ingot usable for chemical, metallographic, and hardness measurements.

The situation in the resistance furnace was somewhat different. Due to the negligible mixing rate, the molten material had to be kept for about 2 h at 1450°C under 10^{-6} mbar vacuum to reach an acceptable homogeneity, and then it was cooled to room temperature to produce the ingots needed for chemical, metallographic, and hardness measurements.

After solidification, specimens were removed from the crucibles and their surfaces removed to a depth of 2 mm. Specimens were then mechanically polished for 0.3 mm. Three points on each specimen were marked Points 1, 2, and 3, as indicated in Fig. 2. Chemical analysis, metallography, and hardness numbers were similarly determined for these



2 Schematic diagram of TiNi casting ingots showing locations 1, 2, and 3 of samples used for comparison of alloy composition and properties



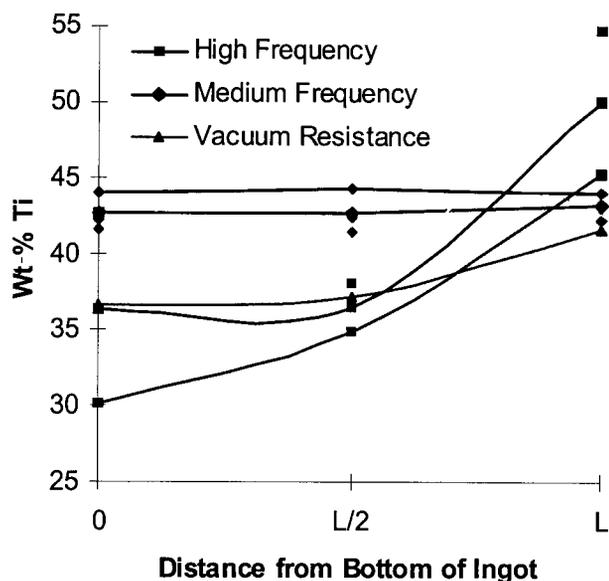
3 PIXE chemical analysis of specimen 1H melted in a high frequency vacuum induction furnace

three points on all samples. Results were compared to determine the effect of the production procedure on the physicochemical properties of the samples produced.

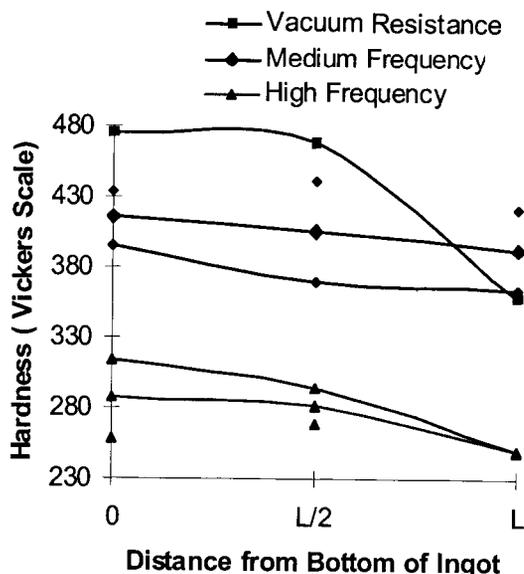
Chemical analysis was made by a particle induced X-ray emission (PIXE) method in which the specimens were bombarded with fast proton particles having 2 MeV energy. The incident diameter was around 2 mm. Vickers hardness was measured using an Instron–Wolpert device at 13.6 kg force. After mechanical polishing, the samples were etched for 10 s with a solution containing 40 vol.-% nitric acid, 10 vol.-% hydrofluoric acid and 50 vol.-% distilled water. Metallographic micrographs were taken with an Olympus optical microscope. The intermetallic compounds were analysed using a 45 kV WDS system at 45 kV scanning electron microscope (model JXA–840, JEOL, Japan).

Results

Figure 3 shows a typical example of PIXE chemical analysis obtained for specimens produced during this research. Effects of the method of melting on the chemical composition of the sample at different locations are demonstrated in Fig. 4. It is seen from the curves that the type (and



4 Effect of method of melting on chemical composition of TiNi alloy measured at different locations on the sample

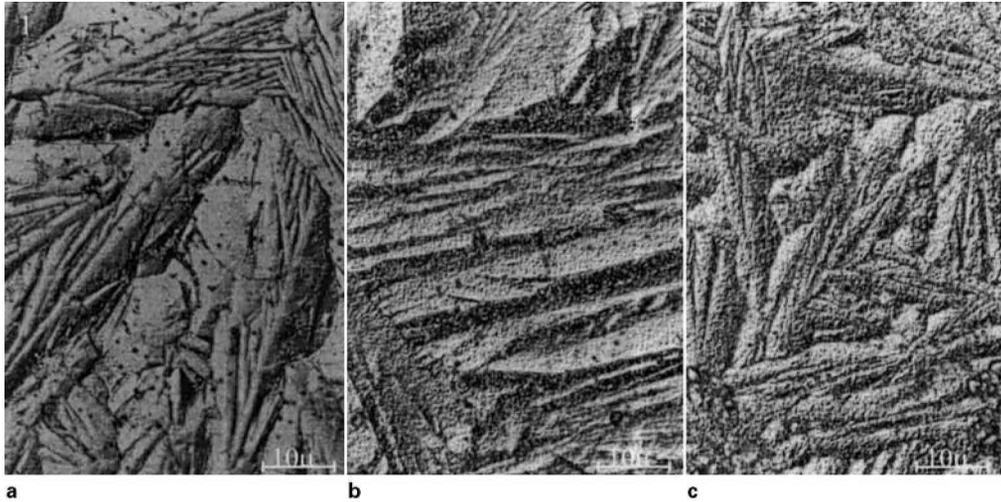


5 Effect of method of melting on Vickers hardness number of TiNi alloy measured at different locations on the sample

thus frequency) of the melting unit has a considerable influence on the chemical composition of the solidified sample. Long melting times followed by a lengthy homogenisation melt holding process do not lead to a uniform concentration distribution or to an appropriately preserved weight of materials. Large metallic loss is observed due to both vaporisation and oxidation of the titanium constituent of samples.

In induction furnaces, however, the materials behave differently. Due to the greater heating rates, the average titanium loss is lower in both the medium and high frequency furnaces used in this research. Figure 4 shows that maximum homogeneity was obtained with the medium frequency melting unit. This can be attributed to the best mixing conditions during the melting process being produced in the medium frequency induction unit. The lower homogeneity of samples melted in the high frequency induction furnace can, therefore, be attributed to the poorer mixing conditions prevailing during the faster melting operation, which do not provide enough time for homogenisation of the melt.

The nearly stagnant liquid phase that exists in the vacuum resistance furnace requires lengthening of both melting and liquid holding times so that the high melting point sponge pieces can simultaneously diffuse into and help to liquefy the high temperature hard melting materials utilised in this research. Figure 5 compares Vickers hardness numbers determined at the different locations shown in Fig. 2 for specimens produced in each of the different melting units. The lower hardness numbers obtained with the high frequency induction furnace are due to the faster melting process, which reduces the chance of contaminant absorption. Some of these contaminants can be non-metallic elements, such as oxygen, carbon, and nitrogen¹¹ absorbed from the melt environment, which reduce the workability of samples.¹² Another source of hardness increase is deviation of the chemical composition from that of equiatomic TiNi intermetallic phase.¹³ This can result in the formation of hard intermetallic phases such as Ti₂Ni and TiNi₃, which have significant adverse effects.¹³ Lower titanium loss and closer chemical composition of the melt to that of equiatomic TiNi intermetallic phase resulted in reduction of hardness numbers in the upper part of all specimens. The formation of other intermetallic compounds is demonstrated in Figs. 6, 7, and 8, and presents more details of



a position 1; b position 2; c position 3

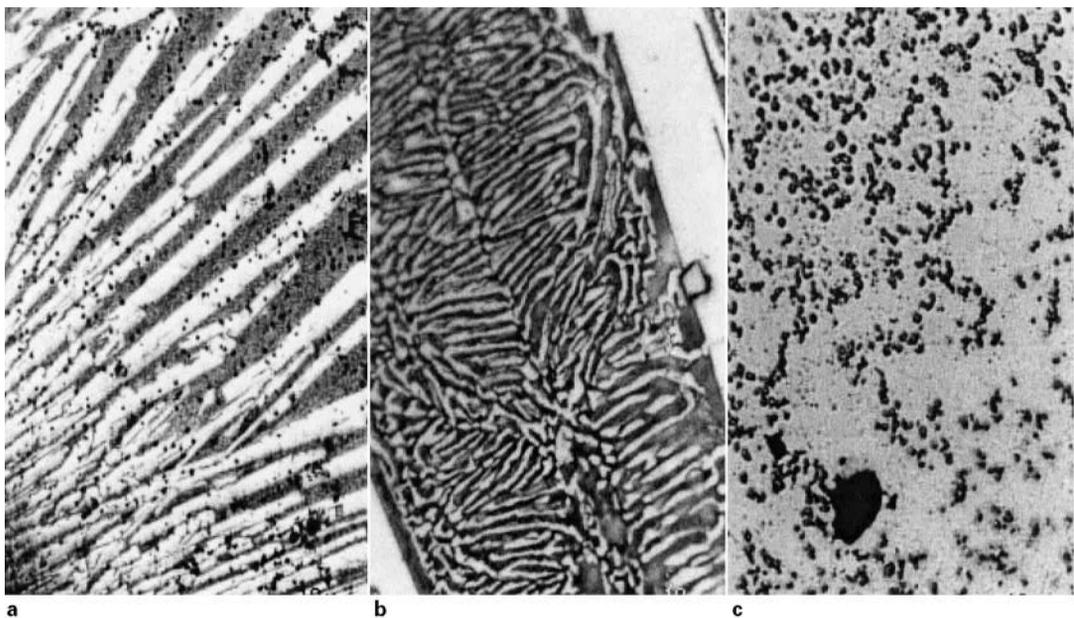
6 Micrographs at different locations in as cast specimens melted in vacuum medium frequency furnace taken at magnification of 1000 with polarised light

hardness numbers obtained at different levels in the solidified melts. Figure 6 compares microstructures obtained at three different locations on specimen 3M melted in the medium frequency furnace. Micrographs show a martensitic surface relief, which was stable at the room temperature used for metallographic sample studies. Due to the good mixing conditions followed by rapid solidification of the specimens, a homogeneous microstructure with excellent shape memory behaviour is observed in these specimens. From the equilibrium diagram and the analysis results, it is obvious that the predominant phase must be TiNi, which is martensitic at room temperature, when equilibrium conditions prevail in the system.

Figure 7 shows the differences in microstructures at the bottom, middle, and top of specimen 1H melted in the high frequency VIM furnace. The microstructure consists of a large bladelikey phase embedding a eutectic phase inside it. This large bladelikey phase was semiquantitatively studied using a WDS electron microscope. Results showed the

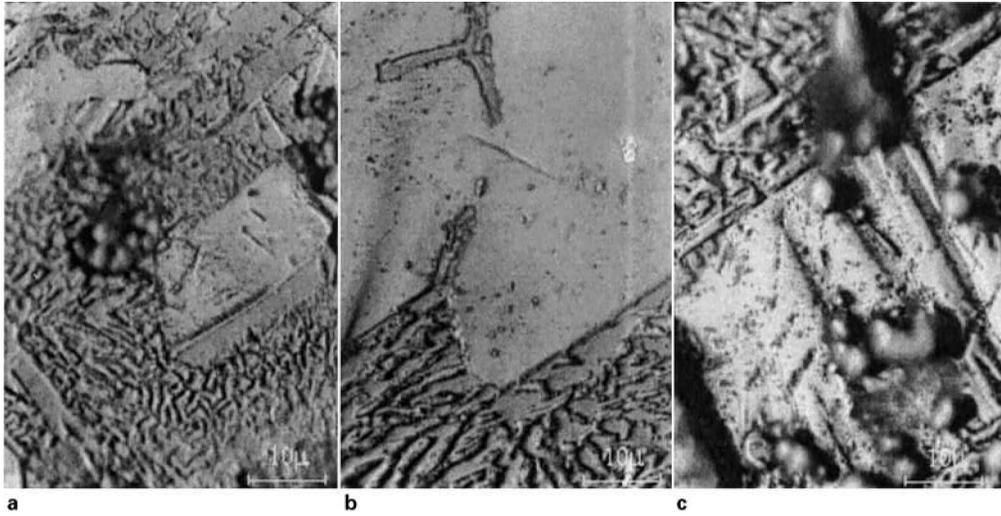
bladelikey phase titanium content to be around 22.5 wt-%Ti. The white blades are of the TiNi₃ phase depicted on the right side of the equilibrium diagram plotted in Fig. 1. It is expected that this latter phase is partly responsible for the hardness increase, workability decrease, and shape memory reduction effects seen in the non-uniform specimens melted in the high frequency VIM furnace.¹⁵ The chemical composition at point 3 of specimen 1H deviates from that of a uniform NiTi alloy, indicating a low hardness number, as indicated in Fig. 5. This may be due to the large differences between the densities of the raw materials that may either keep them separate or cause gravitational segregation during melting.

Figure 8 shows the differences in microstructures at the bottom, middle and top of a specimen melted in the resistance furnace. The microstructure shows large heterogeneity in the phases present and, therefore, in composition of the sample. All three micrographs show large TiNi₃ layers with TiNi–TiNi₃ eutectic phase solidified between them.



magnification a 50; b 200; c 1000

7 Micrographs of as cast specimens melted in vacuum high frequency furnace taken at different magnifications with polarised light



a position 1; b position 2; c position 3

8 Micrographs of the as cast specimens melted in vacuum resistance furnace at different locations taken at magnification of 1000 with polarised light

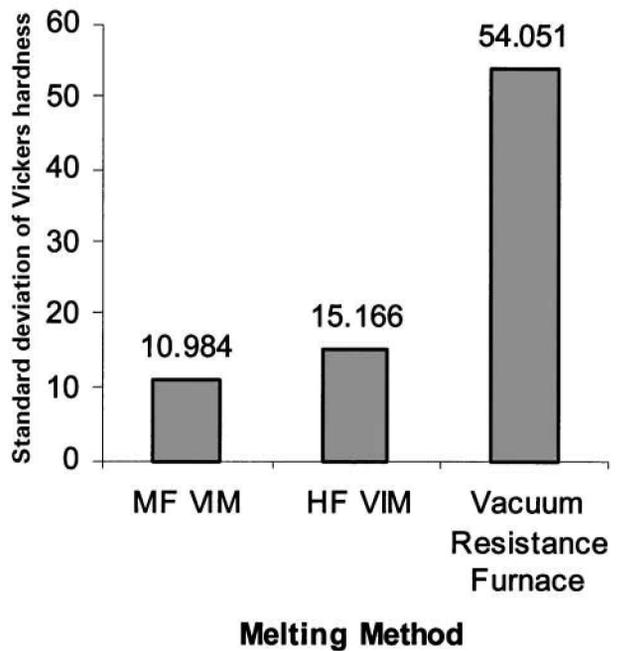
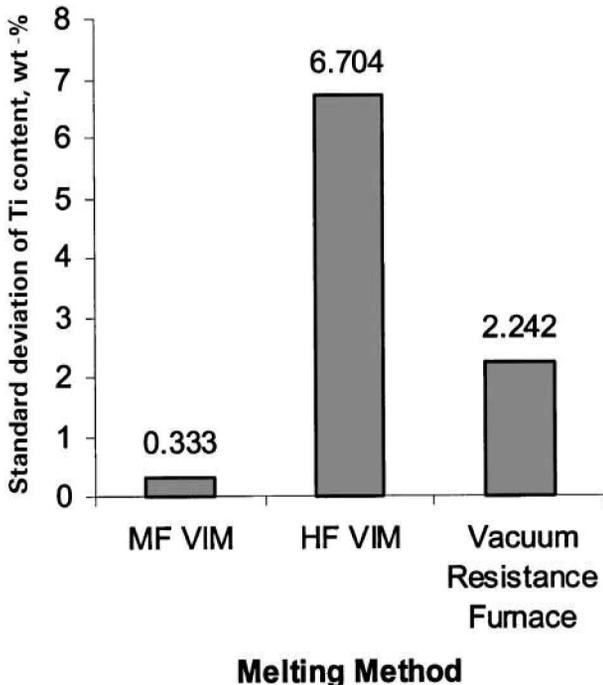
The standard deviations of the chemical analysis as well as the hardness data at different locations of the specimens were taken as two representative criteria for determination of the effect of the method of melting on the homogeneity of specimens. The deviations were evaluated using equation (1)

$$\sigma = \sqrt{\frac{\sum x^2 - \frac{\sum x^2}{n}}{n}} \dots \dots \dots (1)$$

where σ is the standard deviation, x the variable measured and n the number of measurements. The results are demonstrated in Figs. 9 and 10. It is obvious from these figures that the optimum results with the melting/casting conditions specified in this research are obtained from the VIM medium frequency furnace, as discussed throughout this section.

Discussion

The density of pure nickel is 1.96 times that of pure solid titanium.²⁶ The raw materials used in this research were pure titanium sponge particles and nickel cathodic plates. The differences in their densities were, therefore, substantial. In the vacuum resistance furnace, gravity is the major force exerted on the materials being charged. A gravity dependent mass transfer effect (i.e. natural convection) is, therefore, the most important phenomenon helping the formation of a homogeneous liquid phase.²³ Gravity forces can also cause separation of the heavier metal (nickel) from the lighter one (titanium) in these furnaces. In the resistance furnace, the difference in the density of raw materials causes their separation during the alloying process. Precipitation of heavier nickel atoms in the solidification stage is also



9 Standard deviations of titanium content of as cast samples produced in different melting furnaces

10 Standard deviations of hardness numbers of as cast samples produced in different melting furnaces

feasible for the same reason.^{27,28} The melting temperature of titanium is 1660°C, while that of nickel is 1450°C. It is, therefore, inferred that the alloying process can be controlled with the dissolution of solid titanium into the liquid nickel phase, which needs large interdiffusion rates. Alloying these elements thus needs mechanisms for facilitation of mass transfer processes in the liquid as well as solid phase, these usually being controlled by natural convection as well as diffusion in resistance furnaces. These processes take much longer than those occurring in vacuum induction units, where electromagnetic forces overcome gravity^{29,30} and stir the melt by forced convection processes.^{32,33} The materials heated in the induction units are, therefore, mixed more vigorously than those heated in the resistance furnace and produce macrohomogeneities in the cast TiNi ingots.⁹ Liquid phase stirring in an induction unit is directly proportional to the induction power of the furnace, and is inversely proportional to the square root of its frequency.²⁹ This is due to the lower liquid resistance to eddy currents as well as the deeper reference depth that exists at lower frequencies.²⁶ As a result, liquid stirring and homogeneity are more favourably achieved in lower frequency induction units that provide enough power for fast melting of the charged materials.

A comparison of the chemical analyses of the samples shown in Fig. 4 indicates that the ingots produced in the medium frequency furnace are more homogeneous than those melted in the high frequency induction unit. The deviations in chemical compositions given in Figs. 9 and 10 also indicate better mixing of the melts in the medium frequency induction furnace. The lower deviations observed for the vacuum resistance furnace with respect to the high frequency induction unit (Fig. 9) are, however, due to the much greater homogenisation time of the former.

Conclusions

1. The method of melting has a great influence on the microstructure and homogeneity of the TiNi ingots produced.

2. Because of the large differences in density and melting temperature of the sponge titanium particles and the nickel pieces, vigorous mixing is required to produce a homogeneous TiNi memory alloy with suitable microstructure.

3. Powerful electromagnetic forces induced in VIM units result in the production of forced convection mass transfer mechanisms, which help to produce a homogeneous ingot with a more suitable microstructure.

4. The high radio frequency that exists in the high frequency induction furnace results in reduced mixing of the melt compared with the medium frequency induction furnace and causes lower homogeneity of the materials melted.

5. Medium frequency induction melting was found to be an appropriate method for the production of a suitably uniform alloy with the desired homogeneity.

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