

Ingredient Losses during Melting Binary Ni-Ti Shape Memory Alloys

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Losses of the alloying elements during vacuum induction melting of the binary NiTi alloys were evaluated by visual observation and chemical analysis of the NiTi melted specimens and the scalp formed on the internal surface of the crucible. The results indicated that the major sources of the losses were (a) evaporation of the metals, (b) formation of the NiTi scalp and (c) the sprinkling drops splashed out of the melt due to the exothermic reactions occurring between Ni and Ti to form the NiTi parent phase. Quantitative evaluations were made for the metallic losses by holding the molten alloy for 0.5, 3, 5, 10 and 15 min at around 100°C above the melting point inside the crucible. Chemical analysis showed that there existed an optimum holding time of 3 min during which the alloying elements were only dropped to a predictable limit. Microstructure, chemical composition, shape memory and mechanical properties of the cast metal ingots were determined to indicate the appropriate achievements with the specified 3 min optimum holding time.

KEY WORDS: Shape memory alloy (SMA); Vacuum induction melting (VIM); Metallic loss

1. Introduction

Three decades of research have resulted in introduction of numerous NiTi shape memory alloy (SMA) applications^[1~3]. These developments have, however, been constrained with the high NiTi production costs due to the complications of manufacturing processes that have been presented so far^[3~6]. Vacuum induction melting (VIM) is the most common method for mass production of NiTi alloys^[6~8]. Intermetallic compounds with atomic ratios of greater (or less) than one are responsible for deviation of the alloy composition from the precise analysis required for production of a soft, formable, workable and homogenous alloy^[6,9]. Microstructural heterogeneity causes undesirable mechanical behaviors such as brittleness, rigidity and extreme hardness in the system. The alloys containing less than 49.4 at. pct of Ti are, for example, extremely hard and brittle and cannot easily bear deformation processing to reach the eventual geometric shape. It can be observed from the binary Ni-Ti phase diagram^[10] that the solubility range of the NiTi phase is very narrow below 550°C. A very small deviation from this range can cause an undesirable segregation of NiTi₂ and Ni₃Ti within the NiTi parent phase.

The presence of the NiTi₂ and the Ni₃Ti phases within the NiTi parent phase can cause the enhancement of both hardness and strength and the reduction of ductility and workability of the NiTi shape memory alloy. Transformation temperatures dramatically change, even if the compositional deviations are not too significant^[11]. These deviations can considerably affect the workability, superelasticity and shape memory effects. The exact chemical composition is, hence, an important parameter in selecting an appropriate production route for producing NiTi shape memory phase. A successful exploitation of the material is, thus, dependent on the methods of development and processing used to generate a hom-

ogeneous NiTi solid solution with exact equiatomic chemical composition^[12] without any undesirable intermetallic precipitates. Prevention of the alloying ingredients loss during the heating/melting process plays an important role in preservation of the elements and homogeneity of the produced alloy. Present study deals with evaluation of the important sources of the losses in the alloying constituents during the heating/melting process. Any achievement of the required optimal conditions for melting the NiTi shape memory alloy with pertinent specifications can help to develop a desirable raw material as smart material objects.

2. Experimental

2.1 Melting procedure

A medium frequency vacuum induction furnace (IS1/11, Lybold AG, Germany) was employed for melting the NiTi shape memory alloy. The nominal input power, frequency and voltage of the VIM furnace were 60 kW, 4 kHz and 500 V, respectively. It was found absolutely necessary to avoid contaminations from sources other than crucible, because Ni-Ti shape memory alloys are quite sensitive to impurities from the atmosphere^[13]. Furnaces constructed by isolating ceramic materials, which could not be fully degassed, are unsuitable for melting Ni-Ti even with a powerful vacuum pump.

Graphite crucibles with isolating ceramic materials packed around their periphery were used to lengthen the lifetime of the crucible at relatively high temperatures and under vigorous stirring conditions. The setup was heated twice at 150°C and twice at 550°C both for 2 h under atmosphere. The furnace was then evacuated up to a pressure of 10⁻⁵ Pa and then heated 5 times for 2 h at 1200°C under vacuum. Sponge titanium with a purity of 99.5 wt pct and cathodic nickel plates with purity of 99.9 wt pct were used for Ni-Ti melting and alloying procedures. The nickel plates were ground to re-

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move the oxide layer off their surfaces and washed with 97% pure acetone to remove any undesirable dirt. The plates were then dried at 200°C for 2 h and wrapped with pure aluminum foils to keep them away from humidity and external dirt. Accurate amounts of Ti and Ni were weighed to achieve the required Ni-45 wt pct Ti composition. After charging Ni and Ti into the crucible and evacuating chamber up to 5×10^{-6} Pa, heating was started. The temperature of the crucible was gradually increased up to approximately 1180°C. Near this temperature, Ti sponge particles reacted with Ni plates and the temperature suddenly rised. The charge materials were consequently melted in a trice, showing a temperature as high as 1450°C. The specimens were held in molten state for 0.5, 3, 5, 10 and 15 min, respectively. The melt was then cast into a mold to cool down to the room temperature under vacuum conditions.

A number of other samples were prepared using a crystal growth machine (Materials Research Company, England) equipped with a high frequency vacuum induction unit with a nominal frequency of 450 kHz, nominal voltage of 12 kV and nominal output power of 20 kW. This machine was also equipped with a transparent quartz chamber that allowed visual observation of the melt. It was, thus, helpful to observing the sources of the alloying element losses during the melting procedure.

2.2 Evaluation of the specimens

After solidification, the specimens were separated from the mold and their surfaces were ground up to 2 mm in depth. All melted specimens were ground using silicon carbide emery papers and then polished with Al₂O₃ impregnated clothes. Particle X-ray emission (PIXE) method was used to determine the chemical analysis of the solidified samples. The chemical analysis was performed using bombardment of fast protons having 2 MeV of energy. The incident diameter was around 2 mm. Two points of each sample were analyzed by this method and the average of the results obtained was calculated. X-ray diffraction (XRD) patterns of the as-cast samples were achieved at room temperature using an X-ray diffractometer (PM 9920/50, Phillips, Holland) with CuK α radiation with the wavelength of 0.15405 nm. After PIXE and XRD analysis, all specimens were etched in a 10 ml HNO₃, 2 ml HF and 10 ml CH₃COOH solution. An optical microscope (Olympus, Germany) was used to evaluate the microstructure of the as-cast samples.

3. Results and Discussion

One of the principal objectives of the current study is to identify the sources of losses of the alloying elements during vacuum induction melting process. Holding time of the Ni-Ti melt in the crucible was a crucial parameter that could change the chemical composition of the Ni-Ti melt. Properties of the Ni-Ti alloy were dramatically affected by the holding time of the melt in the crucible (0.5, 3, 5, 10 and 15 min, respectively). The chemical compositions of the melted samples were analyzed by PIXE method. A graph of the PIXE assay is presented in Fig.1. The results of the chemical analysis of the melted

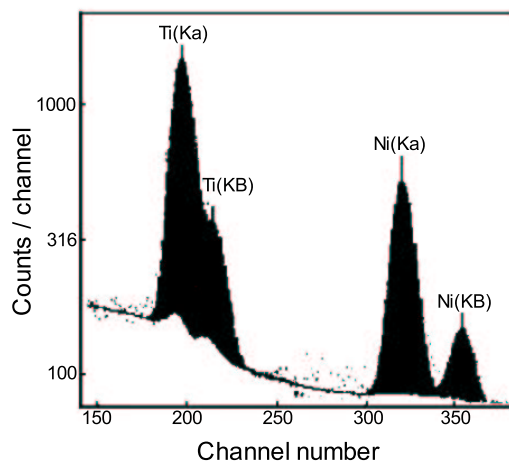


Fig.1 Typical graph of chemical analysis of NiTi sample obtained by PIXE method

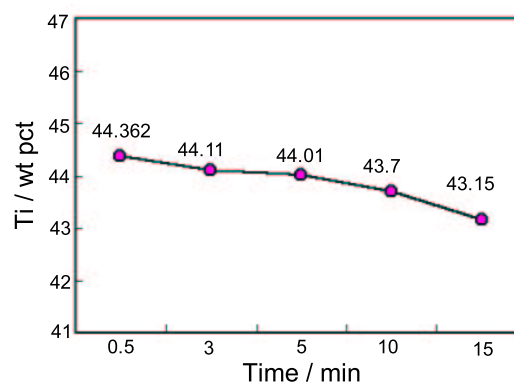


Fig.2 Graph of weight percent of titanium in melted specimens vs the holding time of melt in crucible

specimens are given in Fig.2. As indicated in the figure, the weight percent of Ti in the melted specimens decreased with increasing the holding time. According to the earlier investigations^[14~16] and current study, the charged materials reacted together according to the following reaction prior to melting^[17]:



This is an exothermic combustion reaction with great amount of heat released during the melting. Reaction 1 indicates the enthalpy change of the reaction.

The observations showed that the reaction started at the interface of the sponge titanium with the nickel plates. With the great amount of enthalpy that was almost suddenly released, the temperature of the charge materials sharply rose at some locations to higher than 1700°C. It gradually decreased, thereafter, to the final temperature of 1450°C. The vapor pressures of Ti and Ni at the topmost temperature of 1700°C was evaluated according to the thermodynamic correlations available^[18]:

$$P_{\text{Ti}}(1700^\circ\text{C}) = 0.867 \text{ Pa}(0.0065 \text{ mmHg})$$

$$P_{\text{Ni}}(1700^\circ\text{C}) = 14.265 \text{ Pa}(0.107 \text{ mmHg}) \quad (2)$$

The evacuated chamber had a pressure of 0.067 Pa (0.0005 mmHg) during the melting. The vaporization of Ni and Ti is, therefore, thermodynamically feasible at

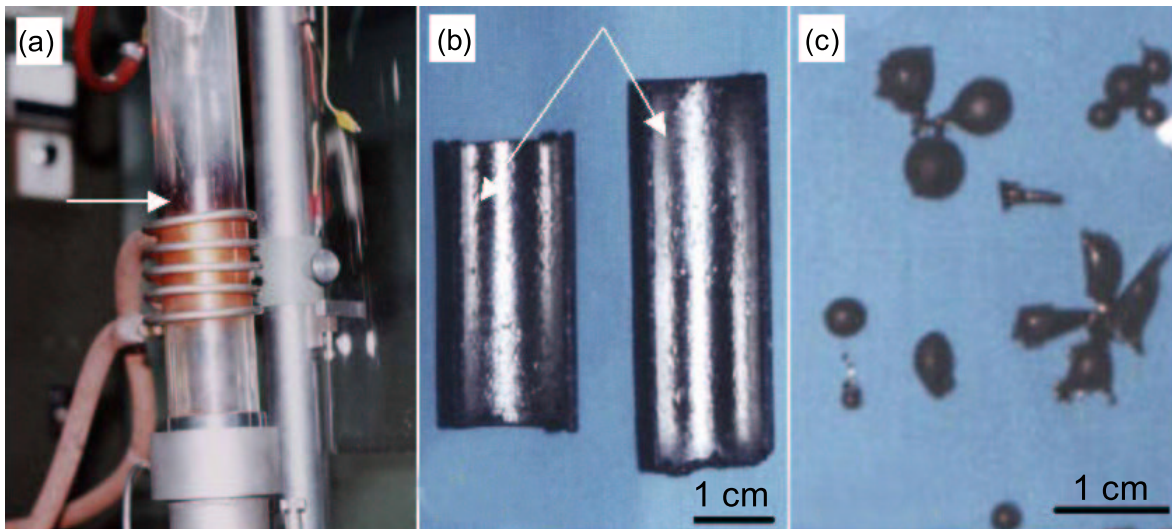


Fig.3 Sources of losses of the alloying elements during heating and melting of NiTi shape memory alloy: (a) metallic layer deposited from the Ni and Ti vapors on the interior of the quartz chamber of the high frequency induction unit (indicated by arrow), (b) solidified Ni-Ti alloy stuck to the interior of the crucible indicated by two bright arrows and (c) solidified sprinkles of the Ni-Ti alloy splashed out of the melt during heating and the combustion process

the topmost of temperature 1700°C . Our observations showed that vaporization of Ti and Ni increased drastically at the start of the combustion reaction. The vapors were then deposited at the interior of the silica chamber. A picture of the layer deposited on the interior of the crystal growth chamber is shown in Fig.3(a). This layer was analyzed by using PIXE method and the results indicated that the layer consisted of 76.81 wt pct Ti and 23.17 wt pct Ni. Figure 2 indicated that the weight percent of titanium in the liquid phase decrease with increasing holding time of the melt in crucible. The chemical analysis of the metallic layer deposited at the interior of the quartz chamber indicated that despite the larger vapor pressure of nickel as compared to that of titanium (see Eq.(2)) the weight percent of titanium was larger than that of nickel. It was inferred, therefore, that the metallic loss was too complicated to be simply evaluated by a mere thermodynamic term. More details were thus required to be considered including the kinetic parameters of the evaporation process so a more realistic view could be provided.

The surface of the sponge titanium was much larger than that of nickel plates. The free surface for titanium evaporation was, therefore, much bigger than that for nickel. A larger mass per unit time was, therefore, vaporized from the titanium surface than that from the nickel exterior. This caused the weight percent of titanium in all of the melted specimens to be lower than that in the initial mixture, *i.e.* 55 wt pct Ti.

Another source for discrepancy was high chemical reactivity of titanium in liquid state. This caused titanium a high affinity with the graphite crucible^[19]. According to the ternary Ni-Ti-C equilibrium system^[20], titanium carbide could exist at the temperatures used in this research. Examinations revealed that TiC existed at the crucible/metal interface^[12]. TiC formation at the crucible interior caused the losses of titanium from the liquid phase and decreased the dissolved titanium content

of the solidified metallic phase. With a holding time of 5 min, the titanium weight percent of the scalp was 63.07, much greater than the initial percentage of titanium in the charge material. This effect was enhanced by increasing the holding time of the liquid phase inside the crucible, as shown in Fig.2. Figure 3 shows the Ni-Ti layer condensed on the interior of the quartz chamber. It indicated the alloy layer that had solidified at the graphite crucible interior.

Another important source of the alloying element losses from the Ni-Ti liquid phase was the sprinkling of the droplets. A number of solidified droplets are shown in Fig.3(c). The very fast exothermic combustion reactions caused the sprinkling of droplets from the NiTi melt.

With increasing the holding time of the vigorously stirring melt inside the graphite crucible, both the amount of contaminating agents and the losses of alloying elements got bigger^[12]. Vacuum induction stirring could cause, however, a homogeneity enhancement in the Ni-Ti melt. Different holding time was, hence, practiced to reach an optimum uniformity in the liquid phase^[12]. It was found that 3 min is the optimum holding time for reaching acceptable homogeneity with minimum contaminants.

A sample was also melted in a medium frequency vacuum induction furnace with the holding time of 3 min. It was cast subsequently into a cold steel mold under the same vacuum condition. Chemical composition of three points of the cast ingots (bottom, middle and top of the ingot) was analyzed by PIXE method. Results are indicated in Table 1.

The shape memory effect of Ti-Ni alloy appeared in the 43.942 to 45.467 weight percent titanium range^[8]. As indicated in Table 1, the weight percent of titanium in three analyzed points are within the same range. Ambient temperature structural analysis with X-ray showed that the following phases presented in the as-cast samples:

Table 1 Chemical analysis of three points (bottom, the middle and top) of Ni-Ti cast ingot with holding time of 3 min in a medium frequency vacuum induction system

Location of analysis	Ti/wt pct	Ni/wt pct
Bottom	44.018	Bal.
Middle point	44.329	Bal.
Top	44.005	Bal.

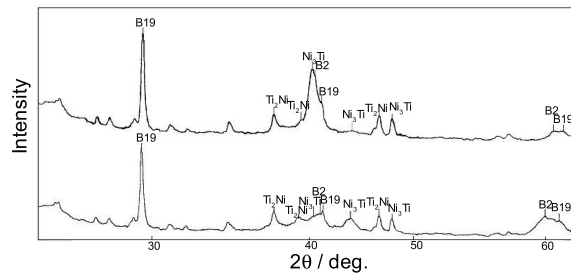


Fig.4 X-ray diffraction pattern of two as-cast Ni-Ti samples with melt holding time of 10 min (upper) and 3 min (lower)

- (1) martensite (B19),
- (2) austenite (B2),
- (3) Ti_2Ni ,
- (4) Ni_3Ti .

XRD patterns of two Ni-Ti as-cast samples with holding time of 3 and 10 min are comparatively presented in Fig.4. Presence of both martensite and austenite phases at the ambient temperature shows that this temperature is within the M_s and M_f temperatures of the Ni-Ti cast samples. As indicated in Fig.4, the appearance of Ti_2Ni and Ni_3Ti phases in the as-cast sample indicates that there are local changes in the chemical composition of the samples due to the segregation of the semi-stable phases during the solidification of the as-cast sample. These variations were obviously caused by the segregation of Ti_2Ni and Ni_3Ti phases from the NiTi equiatomic phase. Figure 4 indicates that the intensity of the Ti_2Ni and

Ni_3Ti peaks in the specimen with the holding time of 10 min is greater than those with the holding time of 3 min. This is due to the greater titanium losses observed in the samples with 10 min holding as compared with the as-cast ingots with 3 min holding. This finding is due to the greater deviation that occurs in the chemical analysis of the sample with respect to the equiatomic NiTi alloy when the holding time gets longer. Results of the chemical analysis on the formation of these phases can simply be assessed based on the equilibrium Ti-Ni phase diagram^[10].

Optical microscope photographs of an as-cast Ni-Ti ingot and a cold-rolled specimen are illustrated in Fig.5. Chemical analysis and XRD patterns of the cast ingots showed that the predominant phase produced during melting and subsequent processing was the intermetallic NiTi compound. From the equilibrium diagram of the Ni-Ti system, this phase is stable at higher temperatures. At lower temperatures, a disorder-order transition occurs at a temperature between M_s and M_f resulting in the formation of martensite phase. Austenitic and martensitic NiTi phases were both present in our samples even after cooling to the room temperature. The micrographs shown in Fig.5 indicate, for example, the surface relief of the martensitic phase at the room temperature used for our metallographic studies as well as the flat regions indicating the austenitic phase (Fig.5).

For evaluation of the shape memory effect of the as-cast Ni-Ti sample, the recovered angle of a deformed sample *vs* temperature was measured and the results are given in Fig.6. As indicated in this figure, the as-cast specimen recovers its initial shape by an increasing temperature. The sample can thus show an acceptable shape memory effect even in the as-cast state. Rolling of the ingot from a thickness of 10 mm to a thickness of 1.5 mm with a 0.65 strain in each rolling stage showed that the alloy was quite workable. Cracks did not occur during hot rolling as indicated in literature [13]. The cast ingot could, therefore, offer acceptable workability accompanied with desirable shape memory effects. Produced

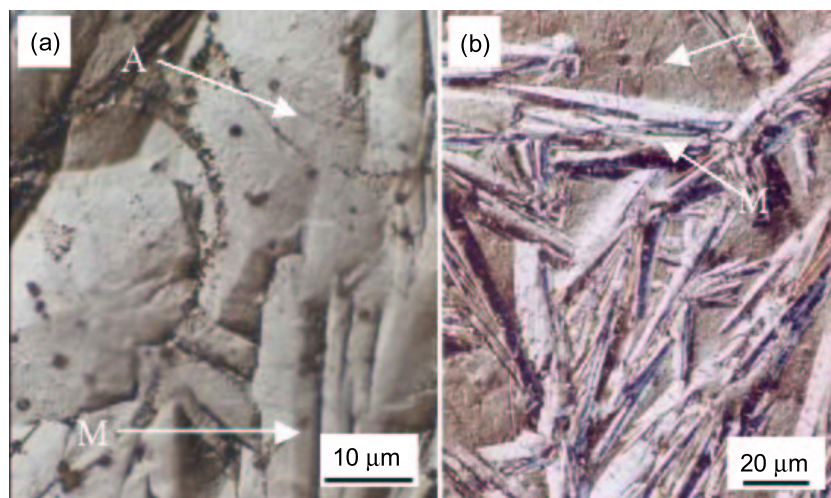


Fig.5 Microstructures of the produced Ni-Ti alloy taken with polarized light (at magnifications of) (a) 1000 for as-cast ingot and (b) 500 for cold rolled specimen. Martensitic phase is indicated by M and austenitic phase by A

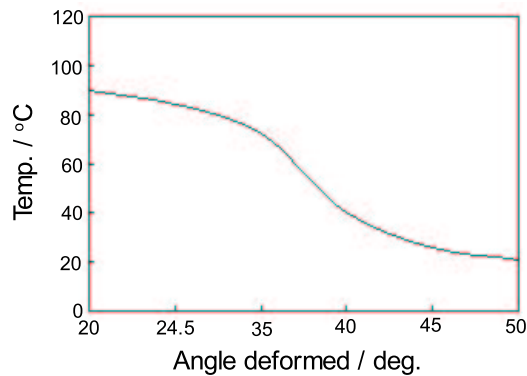


Fig.6 Angle vs temperature of the deformed specimen cut from as-cast Ni-Ti ingot

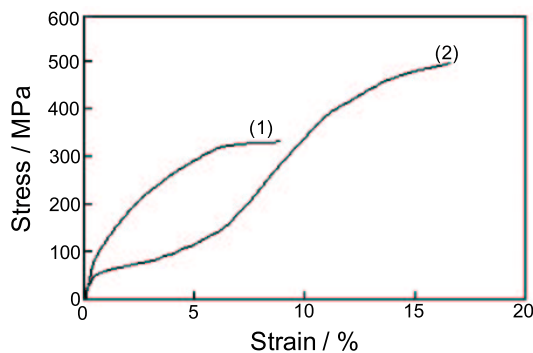


Fig.7 Stress-strain curve of Ni-Ti specimens at room temperature: (1) after cold rolling to 1 mm thickness and (2) after annealing at 600°C for 60 min and then quenching in iced water

Ni-Ti plate was then cold rolled into a sheet with the thickness of 1 mm. Tensile properties of the shaped alloy samples were also evaluated through the following stages:

(1) after cold-rolling,

(2) after annealing of cold-rolled sheet at 600°C for 60 min and its subsequent quenching in iced water.

The stress-strain curves of the Ni-Ti sheets are given in Fig.7. As seen in the figure, there is no plateau in the stress-strain curve of the cold rolled specimen. After annealing, however, a plateau arises in the stress-strain curve. Annealing removes, therefore, the cold rolling effects from the specimens and the Ni-Ti specimens showed the pseudoelastic properties usually observed at the ambient temperature. Appearance of plateau area in stress-strain curve indicated that Ni-Ti samples had good superelastic property at the room temperature.

Results of the chemical analysis and the microstructural and mechanical evaluation of hot and cold rolled Ni-Ti as-cast ingots indicate that 3 min holding time is sufficient to produce cast ingots with desirable shape memory and mechanical properties in the as-cast state.

4. Conclusions

(1) The losses of the alloying elements during melting binary Ni-Ti shape memory alloys were evaluated

through visual observation and chemical analysis with PIXE method. In all Ni-Ti melted specimens some metallic losses of the alloying elements were observed.

(2) Evaporation of Ti and Ni elements under vacuum, sprinkling of droplets after start of the combustion reaction and sticking of metallic compounds on the interior of the crucible were found to be the major sources of the losses of alloying elements.

(3) Results of chemical analysis indicated that 3 min holding time was enough for achieving the Ni-Ti homogenization, required chemical composition and the shape memory specifications.

(4) The Ni-Ti as-cast ingots inductively stirred for 3 min inside the hot crucible showed suitable microstructure, chemical composition, workability, shape memory effect and mechanical strength.

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