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A Comparison of Chemistry and Inclusion Distribution and Morphology Versus Melting Method of NiTi Alloys

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NiTi alloys are produced by three melting methods. The first method requires compaction of nickel and titanium raw material into sections that can be joined together for melting in a Vacuum Arc Remelt unit (VAR). This ingot is melted two or more times in a VAR. The second method utilizes a Vacuum Induction Melting (VIM) unit to alloy the nickel and titanium, with the use of a graphite crucible. The resulting ingot is prepared and remelted in a VAR. The third method begins with primary melting in a vacuum Induction Skull Melter (ISM). The ISM produces ingots that are assembled into an electrode for VAR melting. For each of the melting methods, the final product depends on the quality and handling of the raw materials, the control of the process at each unit, and the preparation of the intermediate ingots for further processing. The melting method influences the final chemistry as well as the type and number of inclusions present in the final product. This study compares the chemistry and microcleanliness of product manufactured by each method to determine the appropriate melting technique that produces NiTi with the lowest residual elements, such as carbon, as well as the lowest size, and number of inclusions.

Keywords advanced characterization, biomaterials, intermetallics, primary metals, titanium

1. Introduction

Nitinol possesses unique mechanical properties that have sparked an explosion of product innovation (Ref 1, 2). The superelasticity and shape-memory properties impart characteristics that are engineered for use in human bodies as well as auto bodies.

The superelastic and shape-memory effects result from an atomic arrangement of approximately 50 atm.% Ni and 50 atm.% Ti. The alloy undergoes a martensitic/austenitic shift at a temperature determined by the alloy chemistry (Ref 3). Either the Differential Scanning Calorimetry (DSC) method or the active A_f method is used to measure the transformation temperature. The transformation temperature is sensitive to small chemical changes and is not accurately predicted by a chemistry analysis. Chemical analysis is not precise enough for transformation temperature prediction, but chemical homogeneity along the final ingot is important to the end-user of the ingot for consistent properties (Ref 4).

Inclusion size, composition, and morphology are the subjects of investigation into their effect on the physical properties of nitinol. Multiple studies have attempted to determine the effects of inclusion composition and inclusion size versus mechanical properties (Ref 5, 6, 7).

This investigation compares three melt methods (VIM/VAR, multiple VAR, and ISM/VAR) and characterizes the chemical and inclusion results.

2. Melt Method

Vacuum Induction Melting (VIM) followed by Vacuum Arc Remelting (VAR), or multiple Vacuum Arc Remelting (MVAR) are the common methods of industrial melting of NiTi (Ref 2).

When the primary melting is performed in the VIM, the use of graphite crucible results in carbon pickup during the melt. The charge material is melted quickly at a controlled temperature to minimize carbon pickup and is thoroughly mixed before pouring. The VIM ingot displays a chemical homogeneity that results in minimal transformation temperature variation from top to bottom (as good as ±3 °C). The VIM ingot is subsequently processed through the VAR (Ref 1).

When all the melt cycles are performed in the VAR, raw materials are compacted and assembled into a primary melt electrode. The VAR remelts the ingot multiple times to homogenize the chemistry. This method maintains low carbon levels by melting in a copper as against versus graphite crucible. The carbon and oxygen levels in the ingot are then only dependent on raw material control and vacuum management. The ingot varies in chemistry from top to bottom since a relatively small melt pool is mixing with the material at any time. Consequently, the transformation temperatures vary up to ±10 °C along the ingot as well (Ref 2).

3. Alternate Melting

Multiple alternate methods of melting nitinol have been attempted (Ref 2, 8, 9). As in the VAR, a method known as

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Induction Skull Melting (ISM) maintains low carbon and oxygen levels through proper raw material and vacuum management. The ISM is similar to the VIM in that the induction field mixes the metal well prior to pouring. The ISM ingots are processed singly or tested and matched with other ingots for VAR processing.

The ISM process utilizes a water-cooled copper crucible that is loaded with charge material. An induction coil surrounds the copper crucible. The copper crucible is constructed of copper "fingers" that are separated by thin layers of di-electric. This allows the field produced by the induction coil to couple with the charge materials. The coupling of the charge material with the induction field is inefficient when compared to other melt methods, and therefore, ISM units must use high power (up to 1150 kW) for melting (Ref 10).

A melt in the ISM progresses as follows. The melter cleans the crucible and charges the raw material into the crucible. After evacuation of the chamber and the application of power, the charge melts rapidly, undergoing vigorous stirring and mixing. The liquid metal solidifies, and when in contact with the copper crucible effectively results in the melting of the alloy within a solid skin of the same composition, i.e., without any contaminant pick-up. When the first melt is poured from the ISM, a layer of solidified metal coats the surface of the crucible, and subsequent melting of the same alloy is conducted without removing the skull. Some authors have suggested that the ISM method be studied for high-purity nitinol production (Ref 1).

4. Experimental Setup

The Metalwerks melting facility has produced common NiTi compositions for some time. The experimental procedure followed proprietary standard operating procedures. Procedures that did not previously exist for nitinol on VIM and VAR furnaces were developed and standardized for the experiment. Every effort is adopted to maintain similar raw material and melting conditions for each process path.

High-purity electro-refined titanium crystal from the same lot and electrolytic nickel from the same lot were obtained for use in the melting of ingots during all the three processes (the nickel was minimum 99.97% pure and the electro-refined titanium was minimum 99.99% pure). Three melts of 45.36 kg each were formulated for the VIM and for the ISM. A 136.08-kg ingot was formulated for the first VAR melt.

The VIM utilized a new graphite crucible to produce three ingots from three individual melts. The melts were sequential and poured into molds sized for assembly to melt in the VAR.

The first ISM ingot poured was not equal in weight to the charge makeup, since the melt formed the skull for the subsequent two melts. The ISM melts were sequential and poured into the same size molds as were the VIM ingots for VAR processing.

The preparation of VAR compacts was considerably more complicated. The titanium crystal and the nickel were weighed on the same scale as the material for the other units. Packets of mixed Ti and Ni were weighed for the target composition. Each packet weighed 2.27 kg. The material was placed in a titanium-lined tube and compressed into cylinders of the same diameter as the primary VIM and ISM ingots. The compressed piece was removed from the tube, and the compacts were prepared for assembly.

Table 1 Ingot chemistries

Ingot	C%	O%	Ni%	Ti%
ISM/VAR—Top—V1608683	0.013	0.024	55.50	44.42
ISM/VAR—Bottom—V1608683	0.013	0.026	55.07	44.85
VIM/VAR—Top—V1608684	0.028	0.021	55.75	44.15
VIM/VAR—Bottom—V1608684	0.038	0.025	55.29	45.59
Twice VAR—Top—V1608690	0.015	0.031	45.73	54.15
Triple VAR—Center—V1608693	0.013	0.029	46.96	52.98

The VAR electrode of welded NiTi compacts did not possess sufficient strength to be loaded into the VAR as a single piece. The electrode was cut into two pieces and melted. The resulting two ingots were joined and remelted. This ingot was cut into sections and reassembled to further mix the ingot chemistry by melting a third time.

5. Experimental Results

The ingots from the VIM and the ISM were analyzed (as detailed in Table 1), and the chemistries conformed to ASTM F-2063-05. The ingot chemistries were consistent with formulation aims. Conversely, the ingot produced by triple-VAR of compacted raw materials did not meet ASTM F-2063-05 for Ni and Ti. This is likely due to inhomogeneous raw material arrangement of the Ti and Ni in the primary electrode. Second, inadequate mixing of the raw materials in the smaller melt-pool of the VAR caused segregation of the Ti and Ni (which is visually apparent in Fig. 7).

The ISM/VAR and VIM/VAR ingots were heat-treated, then forged on an in-house GFM. The ingots were forged to a bar size of 34.29 mm (1.35″) and cut to obtain samples for microcleanliness analysis. Because of multiple remelting, the size of the triple-VAR ingot was not compatible with the GFM, and it was sent to an outside conversion source. The ingot broke apart during forging. Sections from this ingot were cut into sections to attempt lab-scale processing for limited data analysis. The ingot sections were not formable, therefore processing was stopped. The ingot sections were sent for microstructural analysis to determine the phases present (Fig. 7).

The microcleanliness analyses for all the samples were performed on 50 fields of view at 500×, with methodology adhering to ASTM F-2063-05. Backscattered Electron Imaging (BEI) was used to perform the inclusion analysis. This method can distinguish between lower and higher atomic weight elements that contribute to the inclusions' composition. Lower atomic weight compositions appear lighter. However, through this technique, the voids adjacent to the inclusions were highlighted as part of the microcleanliness analysis. The inclusion plus void total were compared with the requirements of ASTM-F-2063-05. This was conducted in this manner to eliminate completely the defects found in the material.

As mentioned previously, the triple VAR ingot was not usable for microcleanliness analysis. Table 2 summarizes the results for the inclusion analysis for the other two ingots.

Table 3 further details the distribution of inclusion sizes for each ingot.

Table 4 details the dimensions of the largest inclusions.

Table 2 Inclusion maximums by ingot

Ingot	Diameter	Maximum dimension of porosity + non-metallic inclusions	Maximum %area of inclusions and porosity in one field of view	Total number of inclusions + voids	Total number of voids
(ISM/VAR) V1608683	34.29 mm	40.0 μm	1.4%	4,817	135
(VIM/VAR) V1608684	34.29 mm	28.3 μm	1.0%	12,236	54
(triple VAR) V1608693	~20 mm rectangular	NA	NA	NA	NA

Table 3 Inclusion distribution by ingot

	(ISM/VAR) V1608683		(VIM/VAR) V1608684	
Size range, μm	Void	Void + inclusion	Void	Void + inclusion
1.0-3.9	124	4,466	50	11,152
4.0-7.9	10	7	4	967
8.0-11.9	0	157	0	96
12.0-19.9	1	47	0	20
20.0-29.9	0	2	0	1
30.0-39.0	0	2	0	0
>39.0	0	1	0	0
Total	135	4,682	54	12,236

Table 4 Further dimensional breakdown of inclusions

Ingot	Length, largest dark feature, μm	Breadth, longest dark feature, μm	Area, longest dark feature, μm^2
ISM/VAR—V1608683	40.0	5.1	107.0
VIM/VAR—V1608684	28.3	3.1	32.8

6. VIM/VAR Analysis

The microcleanliness of the VIM/VAR ingot revealed primarily carbon-containing inclusions. The inclusions were generally globular and small. The inclusions were mostly carbide inclusions with some mixed carbide/intermetallic inclusions. The percent of voids versus the total number of inclusions was 0.44%.

The image of the longest inclusion in the VIM/VAR ingot is seen in Fig. 1.

Another typical carbide/void inclusion is seen in Fig. 2 at a higher magnification.

The EDS analysis of a typical inclusion in this forged ingot section is shown in Fig. 3.

7. ISM/VAR Analysis

The microcleanliness evaluation of the ISM/VAR ingot revealed primarily NiTi inclusions. There were two classes of these inclusions: smaller inclusions that were globular in nature, and larger inclusions that were angular. The ISM/VAR sample contained one inclusion/void 1 μ longer than the permissible limit by the ASTM standard. The percent of voids versus the total number of inclusions was 2.88%, compared to the 0.44% in the VIM/VAR ingot. Figure 4 shows the longest inclusion observed in the ISM/VAR ingot.

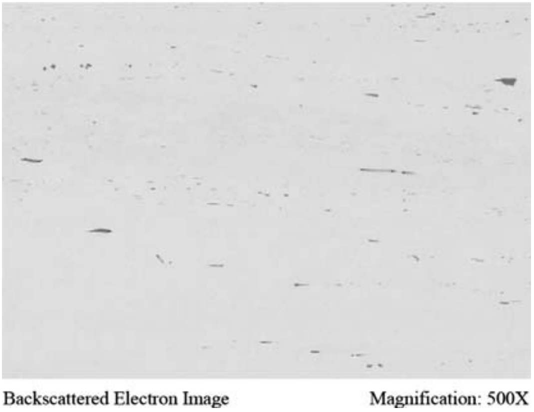

Fig. 1 Longest inclusion in Vim/Var ingot

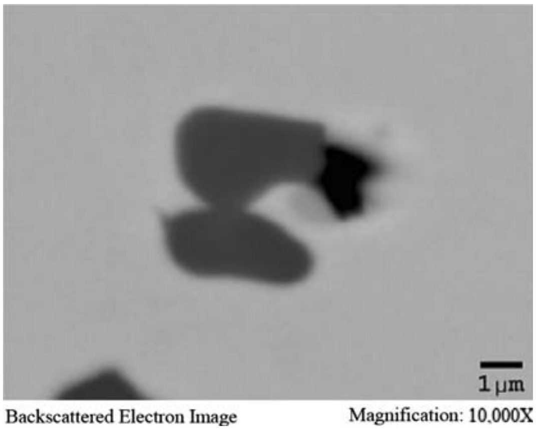

Fig. 2 High magnification VIM/VAR inclusion

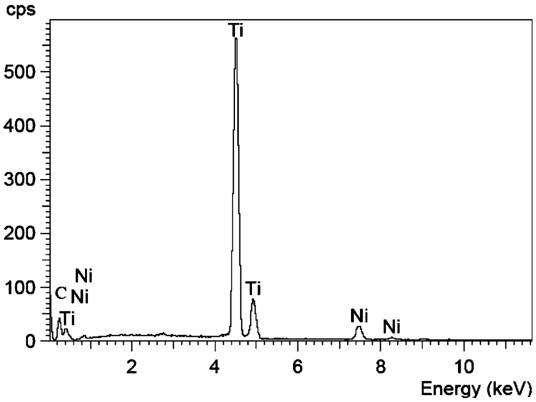

Fig. 3 EDS analysis VIM/VAR ingot

Fig. 4 ISM/VAR inclusions—500×

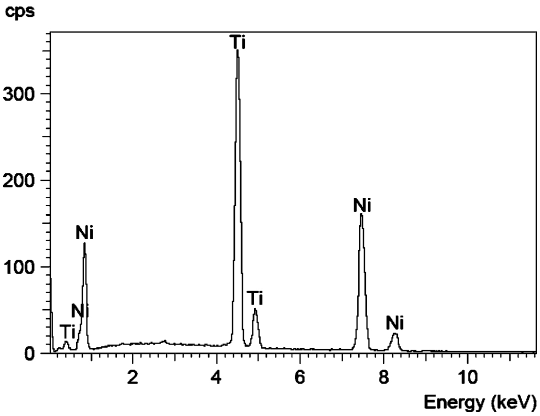

Fig. 5 EDS analysis of ISM/VAR inclusion

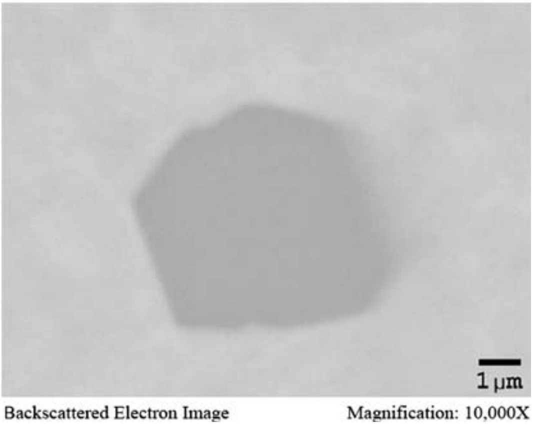

Fig. 6 A globular inclusion in ISM/VAR ingot

Figure 5 shows the EDS analysis for the typical inclusion in this ingot. The analysis reveals no carbon signature.

A second image of typical inclusion morphology is shown, minus an adjacent void (Fig. 6).

8. Triple VAR Ingot

The microstructural/microcleanliness analysis for the triple-VAR ingot could not be completed, because of a dual-phase microstructure that possessed a matrix with a dark appearance. This dark phase is likely composed of NiTi intermetallic compounds with islands of the lighter NiTi alloy. The dark phase propagated cracks through the ingot structure (Fig. 7).

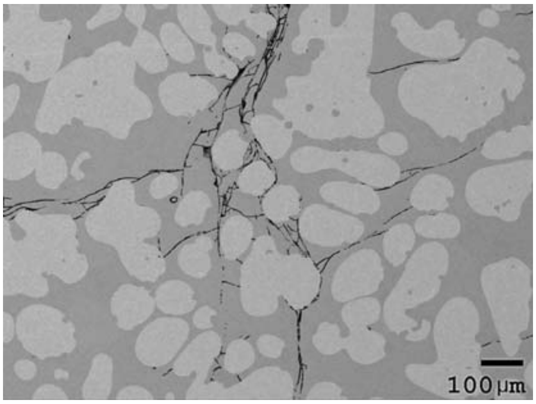

Fig. 7 Triple VAR ingot structure

9. Summary/Conclusion

The production of Nitinol ingots adopting three melt paths, VIM/VAR, VAR/VAR/VAR, and ISM/VAR, was undertaken to compare the effect of each method on the chemistry and inclusion content of the final material. Single lots of Ti and Ni were divided equally for use in each process. The nickel purity was minimum 99.97% and that of electro-refined titanium minimum 99.99%.

The ingot produced by compaction and multiple VAR melting was not usable. The ingot was melted three times from NiTi compacts, but the composition and physical properties were poor. The resulting electrode was extremely brittle and exhibited a segregated microstructure (Fig. 7). The microstructure manifests evidence of inadequate molten mixing and homogenization of the ingot, possibly because of the compaction method. Even though this process path is widely used in the production of nitinol, the processing of this ingot in this experiment did not result in a usable ingot. Further development of materials, electrode compaction methods, electrode assembly, and melting parameters is required for successful melting of NiTi by multiple-VAR in this facility.

The composition of the ingots produced by the ISM/VAR versus the VIM/VAR process demonstrates that the VIM ingots possess higher carbon than ingots produced by ISM, keeping the raw materials the same. The compositions varied from top to bottom on both the ISM/VAR and VIM/VAR ingot. This resulted from using input ingots regardless of composition for the purpose of this experiment. The ingots were welded together end-to-end to form the VAR melt electrode. The variation of the chemistry from each set of three ingots resulted from the first ingot melted by each unit. Further study is needed to determine improved methods to produce a “first ingot” from the ISM and VIM that is close to the target chemistry.

A comparison of the inclusion characteristics for the VIM/VAR versus the ISM/VAR product shows that the ISM/VAR process produces nitinol with low carbon content and inclusions with undetectable C content in this experiment (Fig. 5).

The VIM/VAR product contained higher carbon and the inclusions were composed mostly of Ti and C. While the VIM/VAR ingot possessed 2.6 times the total number of inclusions and relative to the ISM/VAR ingot (Table 3), the ISM/VAR ingot displayed larger inclusions composed of hard NiTi intermetallic compositions. The larger intermetallic inclusions were angular, and these inclusions resulted in a larger amount of voids in the adjacent matrix. The total reduction of the ingots from VAR through the GFM was 77.5%, which may not have been sufficient to break up the NiTi inclusions and heal voids.

The fraction of voids was 2.88% in the ISM/VAR ingot versus 0.44% in the VIM/VAR ingot. The voids were adjacent to the intermetallic inclusions, primarily the larger inclusions. The largest defect was a combination of an inclusion and a void. As pointed out above, the number of voids is proportional to the number and distribution of "hard" intermetallic NiTi inclusions.

It is hypothesized that the number, distribution, and size of the inclusions in the ISM/VAR were negatively affected by thermal conditions prior to forging. Future investigations will focus on the relationship between ingot melting and forging parameters and the resulting inclusion morphology and composition.

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