J. ISSS Vol. **2** No. 2, pp. 1-9, Sept 2013.

REGULAR PAPER

$Ni_{30}Ti_{50}Pt_{20}$ High Temperature Shape Memory Alloy (HTSMA) Wires: Processing Related Issues

K.V. Ramaiah, C.N. Saikrishna, M. Sujata and S.K. Bhaumik

Council of Scientific and Industrial Research (CSIR), National Aerospace Laboratories, Materials Science Division, Bangalore 560 017, INDIA

Corresponding author email: kvramaiah@nal.res.in

Keywords:

High temperature shape memory alloy, NiTiPt, melting, secondary processing, wire properties

Abstract

There is a growing demand for high temperature shape memory alloys (HTSMAs) for applications in areas such as aeroengines, chemical industries, and nuclear power plants, where the ambient temperature is relatively high (150-350°C). Platinum addition to binary NiTi, with Pt substituting for Ni, has been found to raise the transformation temperatures of the alloy with the advantage of retaining the transformation hysteresis in the range 25-35°C. In the present study, a NiTiPt alloy was selected for processing into the wire form for applications in the range 200-250°C. Addition of Pt of about 20 at.% to binary NiTi was required to raise the transformation temperatures of the alloy above 200°C. It was found that Pt addition significantly changed the processing characteristics of the NiTiPt alloy from those of binary NiTi alloys. For successful processing of the NiTiPt wires, it was necessary to modify the process usually followed for binary NiTi alloys. Also, additional steps were incorporated to overcome the problems inherent to this alloy system. Some of these aspects related to processing of this alloy in wire form are discussed in this paper.

1. Introduction

In recent years, there has been a growing interest for development of shape memory alloy (SMA)-based sensors and actuators for a variety of engineering applications. Among the commercially available SMAs, binary NiTi alloys have superior shape memory properties [Otsuka *et al.*, 2005, Humbeeck and Stalmans, 1998]. However, the maximum operating temperature for binary NiTi alloys is limited to about 100°C. For many applications in areas such as aeroengines, chemical industries, and nuclear power plants where the ambient temperature is relatively high (150-350°C), binary NiTi alloys are not suitable because of this limitation. Ternary alloying additions such as Hf, Zr, Pd, Pt, and Au to NiTi alloys are known to increase the transformation temperatures [Lindquist and Wayman, 1990, Noebe *et al.*, 2007, Firstov *et al.*, 2006, Ma *et al.*, 2010, Bigelow *et al.*, 2010, Kumar and Lagoudas, 2010, Noebe *et al.*, 2008, Noebe *et al.*, 2005, Rios *et al.*, 2005]. Among these, NiTiPt has emerged as a promising alloy system because of the resulting narrow transformation hysteresis, relatively better processibility and reasonably good phase and thermal stability during repeated thermal actuation [Ma *et al.*, 2010, Noebe *et al.*, 2008, Noebe *et al.*, 2005, Rios *et al.*, 2005].

Available online at www.isssonline.in/journal/02paper06pdf Paper presented at the Sixth ISSS International Conference on Smart Materials, Structures and Systems, January 03-05, 2012 (ISSS 2012) Bangalore, India.

In the recent past, significant research has been carried out towards development and characterization of NiTiPt High Temperature Shape Memory Alloys (HTSMA). Most of this research has been concentrated on alloy development and properties evaluation; very little work has been published related to processing of the alloys. Noebe *et al.* [2008, 2005] have reported the successful fabrication of NiTiPt alloy in rod form of diameter 1.1 mm by multiple hot extrusions at 900-927°C. The hot-extruded rod was further processed by cold drawing to a wire of diameter 0.5 mm. However, the issues associated with processing of this class of alloys have not been discussed in detail. In the present study, an attempt has been made to process NiTiPt alloy in wire form for applications above 200°C. It has been reported [Lindquist and Wayman, 1990, Ma *et al.*, 2010, Noebe *et al.*, 2008, Noebe *et al.*, 2005] that about 20 at% Pt addition to binary NiTi, Pt substituting for Ni, is required to obtain a NiTiPt alloy with a martensite finish temperature greater than 200°C. However, the addition of such high amount of Pt to the binary NiTi alloy not only changed the processing characteristics significantly, but also imposed number of limitations at different stages of processing. The problems that arose during processing and the additional steps incorporated to fabricate the alloy into wire form are discussed in this paper.

2. Experimental Procedure

An experimental alloy of nominal composition $Ni_{30}Ti_{50}Pt_{20}$ (at.%) weighing about 50 g was prepared by non-consumable vacuum arc melting process (VAM), using tungsten as the electrode and water-cooled copper crucible as the hearth. High-purity titanium (99.97%), nickel (99.99%) and platinum (99.99%) were used for preparation of the alloy. The cast button was homogenized at 1050°C for 24 to 72 h and furnace-cooled. Rectangular strips were cut from the homogenized button and then hot rolled at 900-1000°C in ambient atmosphere using a groove rolling mill. Following hot rolling, the alloy was subjected to cold rolling operation with intermediate annealing at 700-900°C. The final wire of diameter 263 μm was obtained by the cold wire drawing process in multiple passes, with intermediate annealing at 650-850°C.

Microstructural study was carried out using optical and scanning slectron microscopy (SEM). Compositional analysis of the phases in the microstructure was carried out using an electron probe micro analyzer (EPMA). The transformation temperatures were determined using a differential scanning calorimeter with a constant heating/cooling rate of 10°C/min. Hardness was determined using a Vickers micro-hardness tester at a load of 0.5 kg.

3. Results and Discussion

3.1. Melting, Casting and Homogenization

Preparation of alloys with elements having wide difference in densities imposes restrictions in getting a homogeneous melt. In view of this, the charging sequence of the elements in the melt crucible is important. Pt having the higher density was placed at the top layer followed by Ni and Ti in the charge. Further, it was necessary to flip the button upside down and re-melt at least six times to get a macroscopically homogeneous melt. The cast button was sectioned and the composition determined at various locations (Fig.1) across the thickness to assess the quality of the cast material before further processing of the alloy (Table 1).

Figure 2 shows the microstructure of the cast button. It consists of dendritic structure indicative of inhomogeneity in microstructure. The microstructure was found to be typical of cored structure. This is in contrast with cast binary NiTi alloys which barely show dendritic structure with segregation as seen in the present alloy. Compositional analysis of NiTiPt alloy showed that there was partitioning of the elements during solidification. The interdendritic regions were rich in Ti and depleted in Pt with reference to the matrix phase (Table 2). Examination also revealed the presence of a distinct second phase, dark in appearance and rich in Ti, at the interdendritic channels (Fig.2(b)).

The microstructure described above is inhomogeneous and hence, the cast alloy was subjected to homogenization treatment at 1050°C for times ranging from 24 to 72 h. Microstructural analysis suggested that the cast alloy required at least 48 h of homogenization for dissolution of the

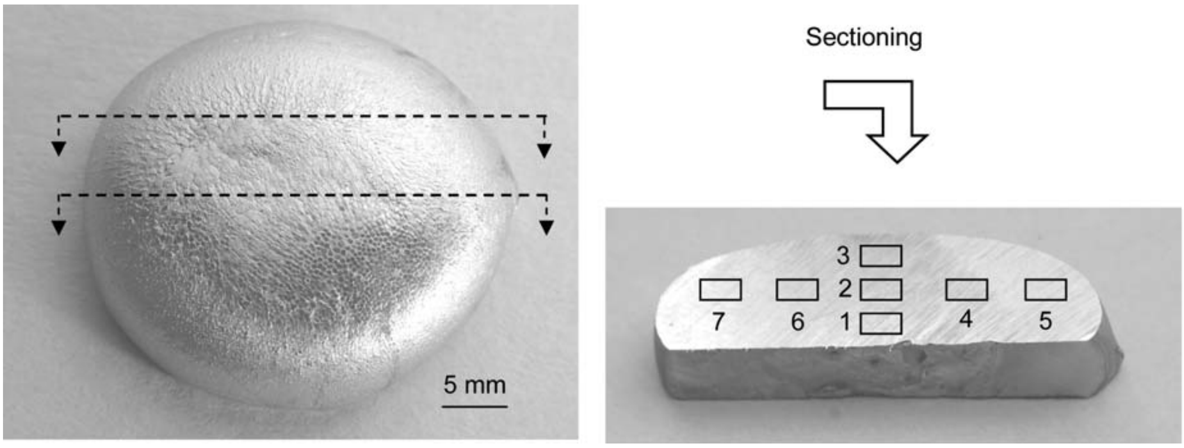


Figure 1 Photographs of cast button of $Ni_{30}Ti_{50}Pt_{20}$ alloy and its cross section on which compositional analysis was carried out

Table 1 Compositional analysis on the cross section of $Ni_{30}Ti_{50}Pt_{20}$ alloy cast button on the regions marked in Fig.1

Element	Composition, at.%						
	Region 1	Region 2	Region 3	Region 4	Region 5	Region 6	Region 7
Ti	48.8	48.8	48.9	49.3	49.1	49.2	49.7
Ni	30.0	30.4	29.8	29.4	30.4	30.4	29.5
Pt	21.2	20.8	21.3	21.3	20.5	20.4	20.8

Table 2 Composition of phases in the cast $Ni_{30}Ti_{50}Pt_{20}$ alloy

Element	Composition, at.%		
	Dendrite	Inter-dendritic region	Precipitate (dark)
Ti	50.4	52.2	68.4
Ni	27.0	32.7	18.5
Pt	22.6	15.1	13.1

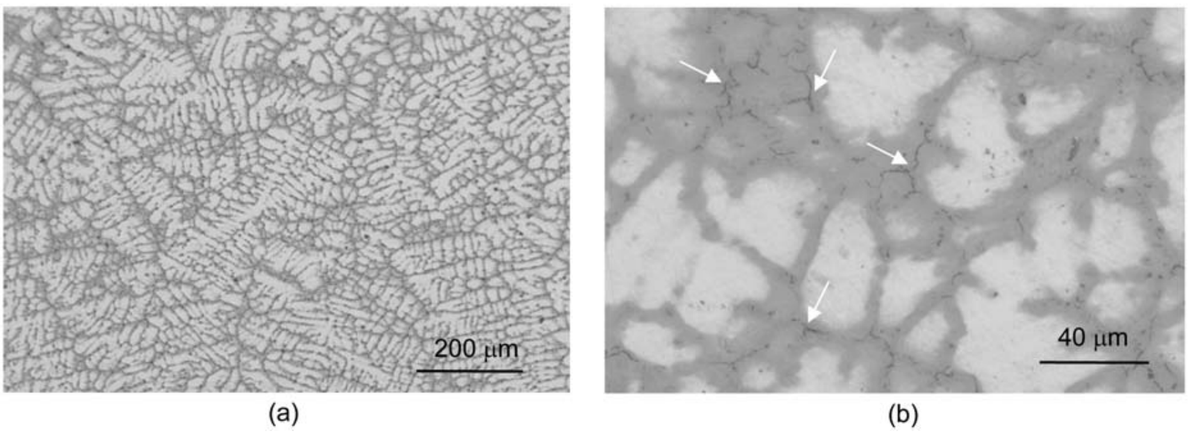


Figure 2 Optical microstructures showing (a) cast structure, and (b) partitioning of alloying elements at the inter-dendritic regions and a distinctive dark phase (arrows)

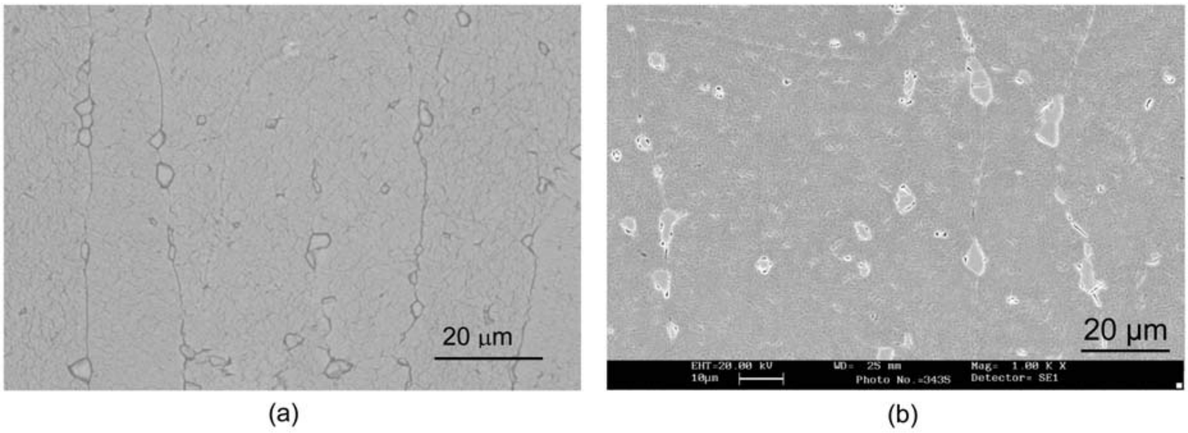


Figure 3 Homogenized microstructure of $Ni_{30}Ti_{50}Pt_{20}$ alloy showing uniform distribution of Ti_2(Ni,Pt) precipitates: (a) optical microstructure, and (b) scanning electron microstructure

Table 3 Compositional analysis (at%) of the matrix and precipitate phase in the alloy after homogenization

Element	Matrix phase			Precipitate phase		
	Analysis 1	Analysis 2	Analysis 3	Analysis 1	Analysis 2	Analysis 3
Ti	48.1	48.0	48.9	65.2	65.1	65.1
Ni	30.2	30.1	29.2	15.4	15.6	15.7
Pt	21.7	21.9	21.9	19.4	19.3	19.2

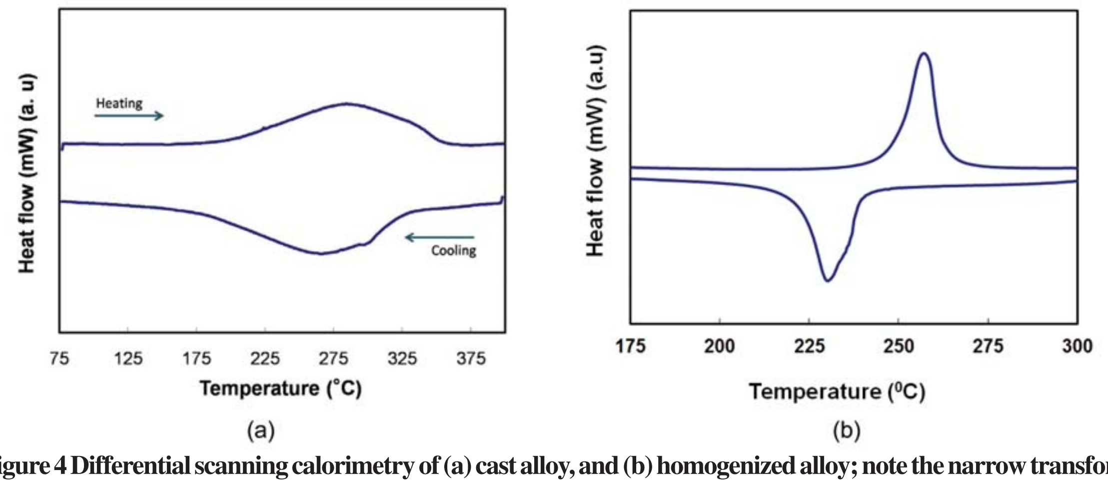


Figure 4 Differential scanning calorimetry of (a) cast alloy, and (b) homogenized alloy; note the narrow transformation range after homogenization

dendritic structure (Fig.3). After homogenization, the matrix was found to be uniform in composition, close to that of the nominal composition of the alloy. Importantly, a distinct precipitate phase of type Ti_2(Ni, Pt), predominantly at the grain boundaries, was observed (Table 3). The presence of similar second phase particles in the microstructure has also been reported by Noebe *et al.* [2008, 2005].

The DSC study showed that the cast alloy has a very wide transformation range of about 150°C (Fig. 4(a)), which is not the true characteristic of this alloy system. Further, the transformation range while heating and cooling almost coincided with each other. A wide transformation range is expected when the alloy is chemically inhomogeneous on a micro-scale, representing a material with a mixture of NiTiPt phase of varying

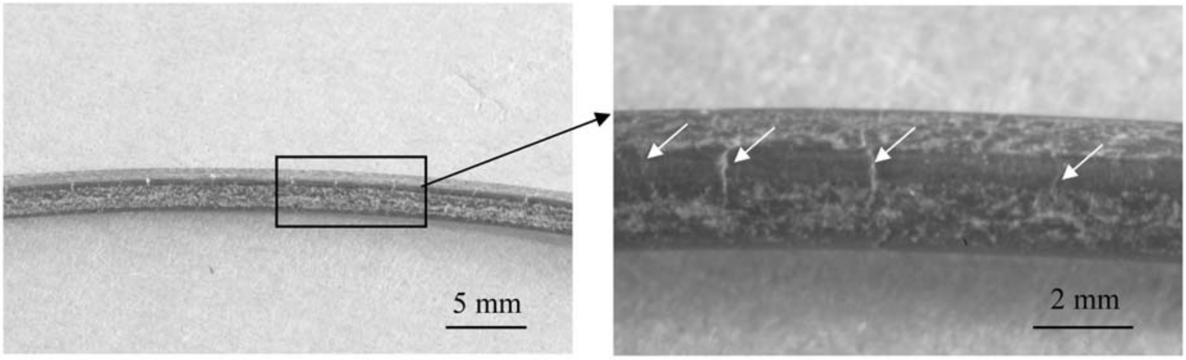


Figure 5 Photographs showing shallow surface cracks in hot rolled wire rod of $Ni_{30}Ti_{50}Pt_{20}$ alloy

compositions. Homogenization treatment resulted in a NiTiPt matrix of uniform composition (Fig.3 and Table 3). This is evident from the DSC scan (Fig.4(b)) wherein the transformation width is reduced to 23-26°C in confirmation of what has been reported in the literature [Noebe *et al.*, 2005].

3.2. Hot and cold rolling

A strip of cross section 5 x 5 mm^2 was machined from the homogenized alloy and subjected to hot rolling operation at 900-1000°C in ambient atmosphere. In comparison with the binary NiTi alloy, the NiTiPt alloy was found to have substantially inferior workability. For example, the NiTi binary alloy can be deformed at 900°C to at least 40% reduction in cross section in a single pass without encountering any surface or edge cracking. Experimental study revealed that such high deformation is not possible in case of the NiTiPt alloy. A maximum of 10-15% reduction was possible in a single pass, and even with this deformation, surface or edge cracking could not be avoided completely (Fig.5).

For reducing its cross section further to facilitate subsequent wire drawing process, the hot-rolled wire rod was subjected to cold rolling operation with intermediate annealing at 700-900°C. However, because of the presence of surface or edge cracks and inferior workability of the NiTiPt alloy in general, it was not possible to perform cold-rolling of the hot-rolled wire rod.

An examination of the cross section of the hot rolled wire rod showed the presence of surface cracks. The crack surfaces were found to be covered with an oxide layer (Fig.6). Such oxide layer is unavoidable during conventional hot-working operation. In case of the NiTi alloy, if such cracks and/or surface oxide layer is present, they can be removed by chemical cleaning. But, such a treatment was found to be ineffective in case of the NiTiPt alloy. On the contrary, because of the presence of noble metal Pt in the alloy, the chemical treatment was found to have adverse effect on the surface preparation meant for facilitating further processing of the alloy to wire form.

Investigation of the surface of the hot-rolled wire rod revealed that, beneath the surface oxide layer, there develops a region which is rich in Pt and Ni, and depleted in Ti. The hardness of this surface layer was found to be very high (760 HV) compared to the bulk hardness of 265 HV of the alloy (Fig.7). In comparison, the surface layer of binary NiTi alloy, hot-rolled under similar conditions, showed a hardness value of ~540 HV. It has been found that the surface diffusion characteristics of NiTiPt alloy is significantly different from that of the NiTi alloy in oxidizing atmosphere because of the presence of noble metal, Pt, in the former. It has been established that it is the presence of the hard surface layer which makes the NiTiPt alloy vulnerable to the generation of surface and edge cracks during hot- as well as cold-rolling processes. A detailed analysis on this aspect has been reported elsewhere [Ramaiah *et al.*, 2010].

3.3. Wire drawing

The wire drawing of the hot-rolled wire rod was unsuccessful. Wire breakage was unavoidable even with 10% reduction in cross section because of the presence of surface defects. Attempt to remove either the surface cracks or the surface oxide layer by chemical etching was found to have an adverse effect,

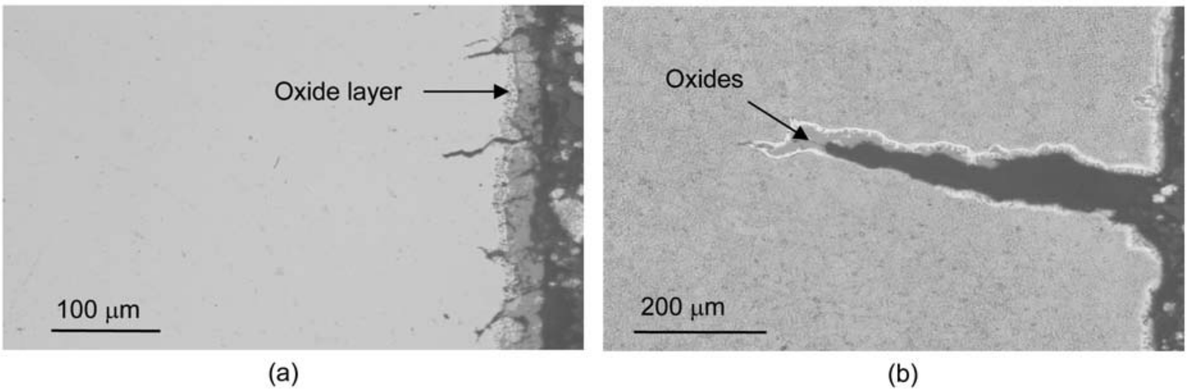


Figure 6 Optical microstructures of the cross section of the hot-rolled wire rod showing (a) surface oxide layer and cracks, and (b) crack surface covered with an oxide layer

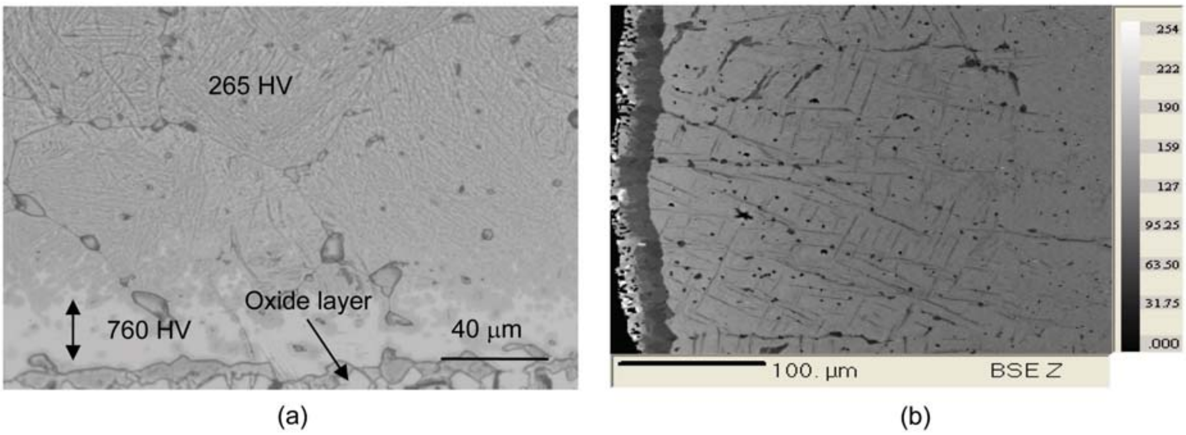


Figure 7 (a) Optical microstructure, and (b) back scattered electron image showing a hard layer beneath the surface oxide

and it degraded the surface condition further. Hence, the surface oxide layer and the surface defects were removed by mechanical means. Following this, it was possible to perform the cold wire drawing operation.

As mentioned earlier, the workability of the NiTiPt alloy is significantly inferior to that of the NiTi alloy. Hence, to avoid any wire breakage, the deformation during each pass of wire drawing was limited to only 10-15%, with intermediate annealing at 650-850°C. It is worth mentioning here that in case of NiTi wire, cold deformation up to 40% is possible in each pass with intermediate annealing at 650°C [Saikrishna *et al.* 2009, Ramaiah *et al.*, 2006].

Prevention of the formation of a hardsurface layer during intermediate annealing of the NiTiPt alloy is important. Otherwise, this surface layer generates cracks during cold drawing, and these cracks slowly propagate into the material as the wire drawing process proceeds. This eventually leads to fracturing of the wire when the diameter decreases with each successive wire drawing operation. Therefore, intermediate annealing of the wire in controlled atmosphere is a necessary step to avoid this problem. This is in contrast to the binary NiTi alloy wherein a thin surface oxide layer is desirable on the wire surface. In this case, the surface oxide layer acts as the lubricant which facilitates not only wire-drawing but also helps in improving surface quality [Suzuki, 1998]. But, to process the NiTiPt wires successfully with good surface condition, it is necessary not only to control process parameters stringently but also to incorporate additional steps which sometimes are unconventional. Figure 8 shows a $Ni_{30}Ti_{50}Pt_{20}$ wire of diameter 263 μm processed in the authors' laboratory following the methodologies described above.

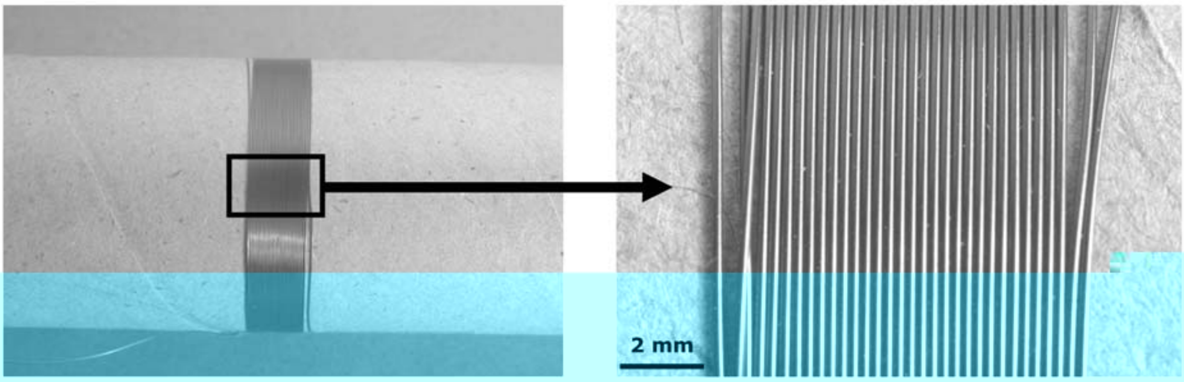
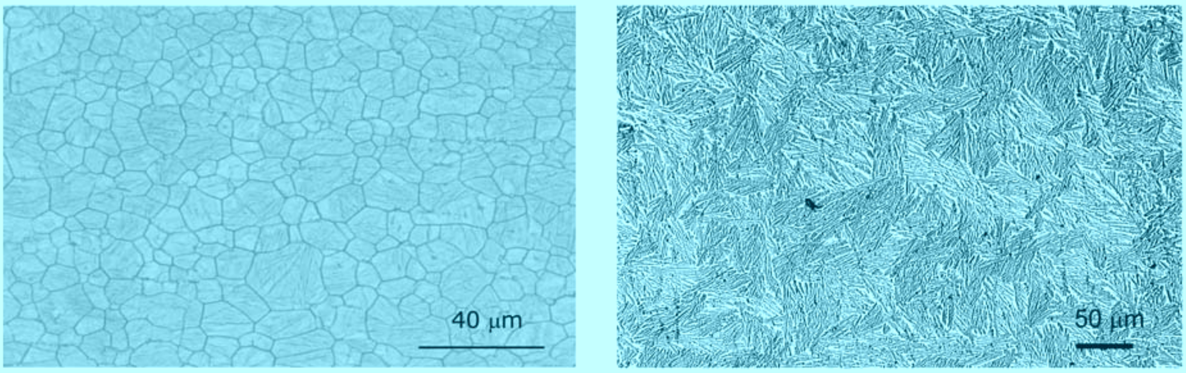


Figure 8 Photograph showing $Ni_{30}Ti_{50}Pt_{20}$ wire of diameter 263 mm of 5 m length processed in authors' laboratory



(a) (b)

Figure 9 Optical microstructures of (a) $Ni_{30}Ti_{50}Pt_{20}$ and (b) NiTi wires

Table 4 Properties of a 263 µm diameter $Ni_{30}Ti_{50}Pt_{20}$ wire*

Transformation Properties		
Martensite start temperature (M_s)	-	238°C
Martensite finish temperature (M_f)	-	223°C
Austenite start temperature (A_s)	-	249°C
Austenite finish temperature (A_f)	-	262°C
Transformation hysteresis (A_f - M_s)	-	24°C
Mechanical Properties		
Yeild strength ($M^{\#}$)	-	800 MPa
Ultimate tensile strength ($M^{\#}$)	-	1200 MPa
Percent elongation to failure	-	9%
Functional properties		
Recoverable strain (max)	-	2.9%
Recovery stress (max)	-	725 MPa

* Wire with 25% cold work and annealed at 600°C for 30 min; #M: martensite phase

3.4. Microstructure and wire properties

Figure 9 shows the microstructure of the $Ni_{30}Ti_{50}Pt_{20}$ wire with 25% cold work, followed by annealing at 600°C for 30 min. For a comparison, the microstructure of a NiTi wire having a similar processing history is also shown. It can be seen that the grain size achievable in the NiTiPt wire was significantly smaller (8-10 µm) than that (usually 30-40 µm) in NiTi wire. The transformation, mechanical, and functional properties of a typical $Ni_{30}Ti_{50}Pt_{20}$ wire are given in Table 4.

4. CONCLUSIONS

In this study, processing of the $Ni_{30}Ti_{50}Pt_{20}$ alloy in wire form was attempted. Experiments were conducted from melting through processing of wires. The response of this alloy to processing was found to be significantly different from that of the NiTi alloy. For successful processing of NiTiPt wire with satisfactory microstructure, transformation behaviour, and mechanical and functional properties, it was necessary to overcome a few problems associated inherently with this class of alloy. This also necessitated the introduction of additional steps which were rather unconventional. A NiTiPt wire of diameter 263 μm with 25% cold work was successfully processed in the authors' laboratory. Further study is necessary to optimize the thermo-mechanical processing parameters for achieving improved static and functional properties in the wire through microstructural engineering. Based on the results of this study, the following major conclusions can be drawn.

(a) Cast NiTiPt alloy is chemically and microstructurally inhomogeneous. Therefore, homogenization treatment of the cast alloy is mandatory to make the alloy amenable to satisfactory hot working. In case of $Ni_{30}Ti_{50}Pt_{20}$, homogenization at 1050°C for about 48 hr is required to obtain a chemically homogeneous alloy.

(b) After homogenization, the microstructure consists of a NiTiPt matrix with a precipitate phase of Ti_2(Ni,Pt), predominantly at the grain boundaries.

(c) The workability of the NiTiPt alloy is significantly inferior to that of the NiTi alloy. The maximum deformation that the alloy can sustain at 900-1000°C without generation of major surface defects is 10-15% per pass. The same is true during cold wire drawing process as well, with the intermediate annealing temperature in the range 700-900°C.

(d) During hot working and intermediate annealing, the NiTiPt alloy forms a very hard layer beneath the surface oxide layer, which promotes generation of surface defects in the form of cracks during hot and cold working processes. Unlike the NiTi alloy, chemical etching is ineffective in the removal of these surface defects as well as the hard layer.

(e) Surface preparation by mechanical means, intermediate annealing in controlled atmosphere, and limiting the deformation to 10-15% in each pass during cold drawing are mandatory for the successful fabrication of NiTiPt wire with good surface condition, and satisfactory mechanical and functional properties.

ACKNOWLEDGEMENTS

The work presented in this paper was carried out with the financial support under National Programme on Micro and Smart Systems (Grant No. NPMaSS:Proj San:PARC#1:3). The authors are thankful to the Head, MSD, and the Director, NAL, for permission to publish this work. The help received from M. Madan and R. Bhuvana at various stages of characterization is acknowledged.

REFERENCES

Bigelow, G.S., Padula-II, S.A., Garg, A., Gaydosh, D., Noebe, R.D., 2010, Characterization of ternary NiTiPd High-Temperature Shape-Memory Alloys under load-biased thermal cycling, Met. Trans. A, 41:3065-3079.

Firstov, G.S., Humbeeck, J.V., Koval, Y.N., 2006, High temperature shape memory alloys problems and prospects, J. Intell. Mater. Sys. Struct, 17:1041-1047.

Humbeeck, J.V., Stalmans, R.,1998, Characteristics of shape memory alloys, In: Otsuka, K., Wayman, C.M., (eds), Shape memory materials, Cambridge University Press, London, 174-177.

Kumar, P.K., Lagoudas, D.C., 2010, Experimental and microstructural characterization of simultaneous creep, plasticity and phase transformation in $Ti_{50}Pd_{40}Ni_{10}$ high-temperature shape memory alloy, Acta Mater., 58: 1618-1628.

Lindquist, P.G., Wayman, C.M., 1990, Shape memory and transformation behaviour of martensitic Ti-Pd-Ni and Ti-Pt-Ni alloys, In: Duerig, T.W., Melton, K.N., Stockel, D., Wayman, C.M. (eds), Engineering aspects of shape memory alloys, Butterworth-Heinemann, London, 58-68.

Ma, J., Karaman, I., Noebe, R.D., 2010, High temperature shape memory alloys, Inter. Mater. Rev., 55:304-309.

Noebe, R., Biles, T., Padula, S., 2007, NiTi-Based High-Temperature Shape-Memory Alloys: Properties, Prospects, and Potential Applications, In: Soboyejo, W.O., Srivatsan, T. S. (eds), Advanced Structural Materials: Properties, design optimization and applications, Taylor &Francis Group, Boca Raton, FL, 145-186.

Noebe, R., Draper, S., Gaydosh, D., Garg, A., Lerch, B., Penney, N., Bigelow, G., Padula II, S., Brown, J., 2008, Effect of thermomechanical processing on the microstructure, properties, and work behaviour of a $Ti_{50.5}Ni_{29.5}Pt_{20}$ high temperature shape memory alloy, in Proc. Inter. Conf. SMST, 2006, California, USA, ASM International, 409-426.

Noebe, R., Gaydosh, D., Padula II, S., Garg, A., Biles, T., Nathal, M., 2005, Properties and potential of two (Ni,Pt)Ti alloys for use as high-temperature actuator materials, In: Armstrong, W.D. (eds), Smart struct. and mater. 2005: Active Materials: behavior and mechanics, Proc. SPIE, 5761, Bellingham (WA): SPIE, 364-375.

Otsuka, K., Ren, X., 2005, Physical Metallurgy of Ti-Ni-based shape memory alloys, Prog. Mater. Sci., 50: 511-678.

Ramaiah, K.V., Saikrishna, C.N., Sujata, M., Bhuvana, R., Madan, M., Bhaumik, S.K., 2010, Development of NiTi-base high temperature shape memory alloy (HTSMA): Microstructural Study and Phase Analysis of NiTiPt Alloy, NAL Report No: NAL-M-1-272/2, July 2010, 1-30 (restricted).

Ramaiah, K.V., Saikrishna, C.N., Bhaumik, S.K., Bhattacharya, A., Nandy, T.K., Sagar, P.K., 2006, Melting and processing of Ni-Ti shape memory alloys, Metals Mater. Process.,18:411-420.

Rios, O., Noebe, R., Biles, T., Garg, A., Palczer, A., Scheiman, D., Seifert, H.J., Kaufman, M., 2005, Characterization of Ternary NiTiPt high temperature shape memory alloys, In: Armstrong, W.D. (eds), Smart structures and materials 2005: Active Materials: behavior and mechanics, Proc. SPIE, 5761, Bellingham (WA): SPIE, 376-387.

Saikrishna, C.N., Ramaiah, K.V., Allam Prabhu, S., Bhaumik, S.K., 2009, On Stability of NiTi wire during thermo-mechanical cycling, Bull. Mater. Sci., 32:343-352.

Suzuki, Y., 1998, Fabrication of shape memory alloys, In: Otsuka, K., Wayman, C.M. (eds), Shape memory materials, Cambridge University Press, London, 137-138.

K. Venkata Ramaiah received B.Tech. degree in Metallurgical Engineering from National Institute of Technology, Warangal in 1999 and M. Tech degree in Materials and Metallurgical Engineering from Indian Institute of Technology, Kanpur in 2002. Currently, he is working as Principal Scientist in the Materials Science Division of CSIR-NAL, Bangalore and pursuing Ph.D. degree at IIT, Kanpur. His research interests include processing and development of NiTi-base shape memory alloys for low and high temperature applications.

C.N. Saikrishna obtained B.E. in Mechanical Engineering from Siddaganga Institute of Technology, Tumkur in 1998 and M.E in Mechanical Engineering from Vellore Institute of Technology, Vellore in 2002. Currently, he is working as Senior Scientist in the Materials Science Division of CSIR-NAL, Bangalore. His research interests include design of shape memory actuators, processing of NiTi-base shape memory alloy wires for actuator applications.

Dr. M. Sujata is a Senior Principal Scientist in the Materials Science Division of CSIR-NAL, Bangalore. Dr. Sujata received Ph.D. degree in Materials & Metallurgical Engineering from Indian Institute of Technology, Kanpur in 1996. Her research interests include failure analysis and accident investigation, aerospace materials, and shape memory alloys.

Dr. S.K. Bhaumik is a Chief Scientist in the Materials Science Division of CSIR-NAL, Bangalore. He obtained Ph.D. degree in Metallurgical Engineering from Indian Institute of Technology, Kanpur in 1992. Dr. Bhaumik has been working in the area of failure analysis of engineering structures & systems, and development & processing of NiTi base shape memory alloys. He is an author of over 70 research papers and 1 book.