

SHS as Possible Alternative Production Route for $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ SMA: Advantages and Limitations

Paola Bassani¹, Enrico Bassani¹, Berk Keskin², Bora Derin²

¹CNR ICMATE Institute of Condensed Matter Chemistry and Technologies for Energy, Lecco, Italy

²Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering,
Department of Metallurgical and Materials Engineering, Istanbul, Turkey

Abstract

Shape memory alloys are extremely interesting smart materials, that can be employed in several applications, from biomedical to automotive field. Their use is limited primarily because of their costs related not only to alloy production but also to processability. Recently, costs reduced due to increased number of producers, and new production technologies are tried in order to achieve nearly net shape products. Among these processes SHS could be considered. NiTi can be produced by SHS even if limitations are encountered due to secondary phases formation, but limited studies are available about processability of ternary alloys through SHS.

In this study the characteristics of NiTiCu shape memory alloys produced by SHS are presented. Microstructural investigation revealed the presence of NiTiCu matrix phase, characterised by shape memory properties, together with secondary phases which do not present any transformation. Calorimetric analyses were performed in order to assess transformation temperatures. XRD investigation performed at room temperature, above and below transformation temperatures helped in the identification of the type of phase transformation. Results were compared with typical properties of conventionally produced NiTiCu alloys, and possible applications are also discussed.

1. Introduction

Among Shape Memory Alloys, only NiTi alloys are widely commercialised, due to its excellent performances as superelastic material, and recovery properties coupled with good mechanical properties, corrosion resistance and biocompatibility. In order to fulfill specific applications, also ternary alloys have been developed, for use in non – medical applications. Among them, $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ alloys have been developed as they provides narrow transformation hysteresis, useful for actuators [1-4].

Another characteristic of ternary NiTiCu alloys is higher damping capacity compared to binary alloys, that could allow their usage in damping applications [5]. An alternative, less expensive and faster production route, with respect to conventional one (that start from ingot melting) could let to wider usage of

such alloys in non biomedical application: Self propagating High temperature Synthesis (SHS) can satisfy such requirements.

SHS process has been already considered for NiTi alloys production. To author's knowledge, however, most of the research studies on SHS-produced NiTi alloys are related to binary composition, as through SHS process, porous NiTi could be obtained for biomedical application. A lack of information do exist about the effect of ternary element addition to Ni-Ti reaction.

In this work, combustion synthesis of ternary $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ alloys have been attempted. The produced specimens were characterised by SEM (Scanning Electron Microscope) coupled with EDXS (Energy Dispersive X-ray Spectroscopy) detector, X-ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC) analyses.

2. Experimental procedure

A range of $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ compositions were considered, in which Ni is increasingly substituted by Cu, at fixed Ti atomic content ($X= 5,10,15,20,25$). Pure (above 99.5%) Ni, Ti and Cu powders were mixed in a turbula mixer for 12 hours under Argon atmosphere. Pellets were pressed under the pressure of 60 MPa into cylinder of about 15mm height and 12.8 mm diameter, with a relative density of about 65% .

The pelleted samples were inserted in a batch reactor, in which they can be preheated. Three level of preheating were considered (240°C-330°C-420°C). Tungsten wire was used at top of the compacted samples in order to trigger the combustion reaction. The reactor was swept by Argon few times to avoid oxidation of samples. All the experiment were recorded by HD camera.

The reacted pellets were cut longitudinally: one half was prepared for microstructural investigations through conventional metallographic grinding and polishing. The other half was further sectioned in order to prepare DSC specimen weighing about 100mg. Thermal analyses were performed with Q100 DSC (TA Instruments)(analyses performed between -150°C and 200°C, two cycle for each specimen). SEM analyses were performed with a Field Emission SEM (SU70, Hitachi), coupled with EDXS detector (Thermo

Scientific). XRD analyses were performed with a diffractometer (Panalytical X'Pert Pro) using Cu K_{α} radiation operating at 40 kV and 30 mA in the 15-100 2theta range. The diffractometer was equipped with a TTK-450 (Anton Paar) heating/cooling chamber. X-ray patterns were acquired at 25 °C. Additionally, on selected samples, XRD analyses were performed also at 200°C, in order to get information on fully austenitic structures.

3. Results

3.1. SHS experiments

All the tested conditions let to completely reacted specimen. The shape features of the specimens are collected in table 1, while an example of lognitudinal section appearance, for $Ni_{35}Ti_{50}Cu_{15}$ specimens is reported in Figure1. At the lower preheating temperature the specimens generally reacted preserving their shape and size, while internal porosity reorganized. Naked eye visible pores were formed that often reached the surface, resulting in a rough surface of the specimens, but also small, micrometric pores were formed. A general trend was observed at increasing pre-heating temperatures: the number of pores decrease, their size increase and eventually, no pores are present and the samples loose its cylindrical shape and collapsed. This latter event can be easily explained by excessive heating of the specimen that led to very high content of liquid phase in the specimens, that could not retain the cylindrical shape. $Ni_{50-x}Ti_{50}Cu_x$ alloys show different sensitivity to preheating temperature: it can be observed that for low amount of copper addition, porous structure can be preserved, while above 20% Cu addition, the samples preserved a rather cylindrical shape, even if with a reduced porosity and shrinkage of upper part of the specimen were observed.

Table 1: $Ni_{50-x}Ti_{50}Cu_x$ samples morphology

X	Pre-heating temperature		
	240°C	330°C	420°C
5	Big pores	Porous	Melted
10	Big pores	Big pores	Big pores
15	Big pores	Big pores	Partly collapsed
20	Slightly shrunked	Slightly shrunked	Slightly shrunked
25	Slightly shrunked	Slightly shrunked	Slightly shrunked

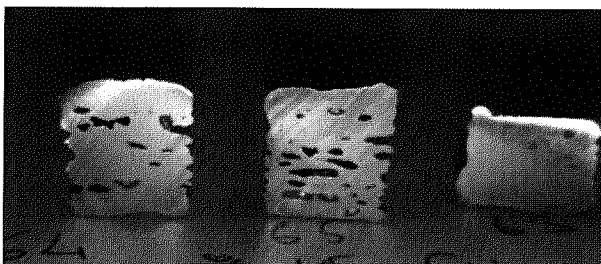


Figure 1: Longitudinal section of $Ni_{35}Ti_{50}Cu_{15}$ specimen, preheated, left to right, at 240-330-420°C.

3.2. Specimen characterization

DSC analyses

For every composition, DSC analyses were performed on the samples preheated at 330°C (603 K). All the specimens showed the presence of a martensitic transformation characterized by narrow hysteresis (between direct and inverse transformation, that did not vary between first and second cycle. Main features (Martensite formation start temperature M_s , Austenite formation finish temperature A_f , enthalpy of transformation on cooling dH_c) are presented in table 2. Two examples are also shown in Figures 2 and 3: in the first case a two-step transformation can be appreciate, where only the first peak is well defined (between 65 and 53°C), the second starts at about 53°C but its end is not well defined. The second example (figure 3) reports a single step transformation.

Table 2: $Ni_{50-x}Ti_{50}Cu_x$ DSC analyses main features

X	5	10	15	20	25
M_s [°C]	61.5	64.1	69.6	73.7	74.7
A_f [°C]	86.6	72.5	75.9	78.5	79.5
dH_c [J/g]	18	3.5	0.6	7.3	9.8

Irrespective of Cu content, M_s is in the range 60-75°C, as expected for $Ni_{50-x}Ti_{50}Cu_x$ alloys. More interestingly, dH_c values vary a lot: for X=10 and 15 a two-step transformation is present, those ending temperature could not be defined with a sufficient degree of certainty: an underestimation of spread of the transformation led to underestimated dH_c values.

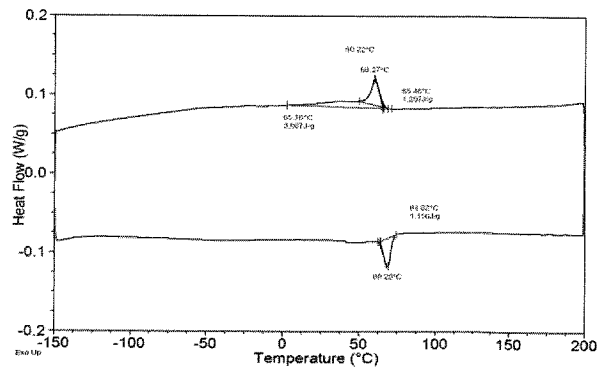


Figure 2: DSC analysis for $Ni_{40}Ti_{50}Cu_{10}$, preheated at 330°C

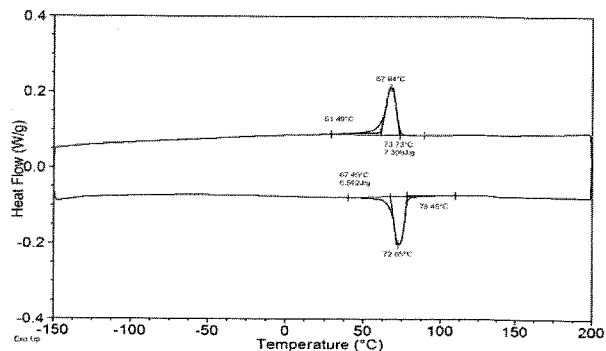


Figure 3: DSC analysis for $Ni_{30}Ti_{50}Cu_{20}$, preheated at 330°C

XRD analyses

All XRD spectra show the presence of B19 peak accompanied by B2, and B19' peak. Due to the broad aspect of the peaks, a detailed phase analyses can't be performed: in most cases a single broad peak is observed in the theta region where peaks from two or more phases are expected.

In all spectra, B19(002) peak at about 40.1° can be observed at room temperature: the same peak can not be observed in XRD collected at 200°C , demonstrating complete inverse transformation from martensite to austenite. The comparison of the curve at room temperature with ones at high temperature allow also to assess the presence of considerable amount of secondary phases. An intense peak can be observed at about 42° - 43° . The peak can be indexed as the sum of many contribution: B2(110), B19(020) and B19(111), and also peaks from secondary phases. At the different temperatures, the peak evolves in term of intensity and width, due to the different contributions of the phases, rather than to disappear.

Small peaks related to $\text{Ni}(\text{Cu})_3\text{Ti}$ and $\text{Ti}_2\text{Ni}(\text{Cu})$ secondary phases can also be observed between B19(002) and the big peak describe above.

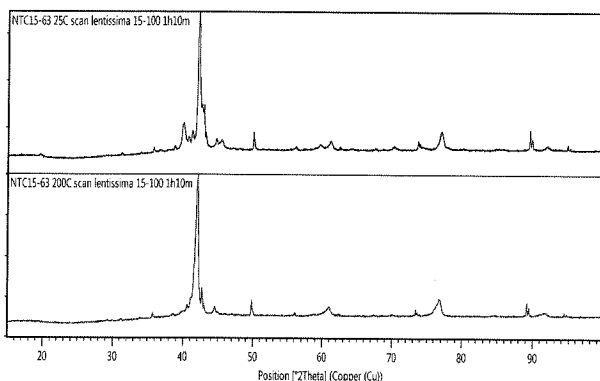


Figure 4: XRD pattern of $\text{Ni}_{35}\text{Ti}_{50}\text{Cu}_{15}$, preheated at 330°C (vertical axe: counts [a.u.], horizontal axe: 2θ [°]). Analyses performed at room temperature (blue curve) and 200°C (red curve).

SEM and EDXS analyses

SEM observation with secondary electron (SE) detector confirmed the presence, in specimen with low amount of Cu, of micrometric pores in addition to bigger ones that could be observed by naked eye (Figure 5).

All the specimen displayed similar features, even if in different amounts for each composition. EDX analyses evidenced that the composition of the matrix, especially for high Cu content is not homogeneous: Cu content range over 10-15%. The matrix of the specimen present a relative ratio of element that varies

between $\text{Ni}_{50-x}\text{Ti}_{50}\text{Cu}_x$ type, (nominal composition) to $\text{Ni}_{50-x/2}\text{Ti}_{50-x/2}\text{Cu}_x$ type, in which Cu substitutes both Ni and Ti, quite different from nominal one. Relief effects due to selective polishing of martensitic structure were observed (Figure 6): they are typical of martensitic structures.

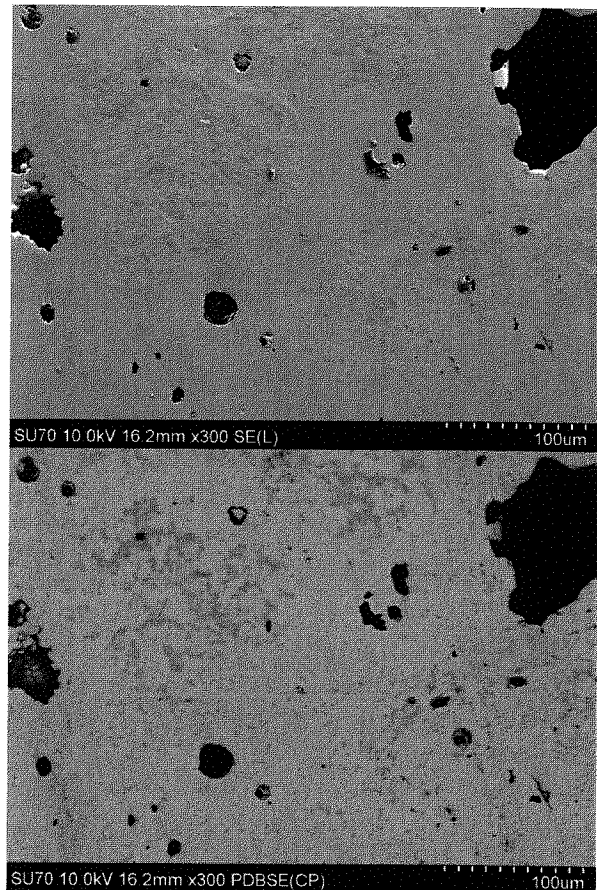


Figure 5: SEM micrographs of $\text{Ni}_{40}\text{Ti}_{50}\text{Cu}_{10}$, preheated at 330°C : up) SE micrograph (sensitive to topography), down) BSE micrograph (sensitive to composition). Nominal magnification 300x

Besides the matrix, other secondary phases can be observed, whose appearance with Back Scatter Electron detector (BSE) is either brighter (rich of heavy elements, namely Cu and Ni) or darker (rich of light elements, Ti and possibly C, O).

Morphology varied from phase to phase. Dark phases are present as polygonal particles or branched particles with rounded shape, whilst bright phases are present as acicular particles of wide areas with convex irregular boundary.

EDXS analyses confirmed that different phases formed. Dark ones are of the type $\text{Ti}_2(\text{Ni,Cu})_1$. Relative ratio between Ni and Cu varied from 1-2 to 6-8 discontinuously: possibly different crystal structures are related to these different composition. Bright phases are characterized by high Ni and/or Cu content: in this case relative ratio between Ni and Cu varies, but in a more continuous way, between lower than 1 (Cu rich) to 8-9.

Detailed analyses of such secondary phases was beyond the scope of the work.

For the specimen with the higher Cu content ($X=20, 25$) bright regions with very high Cu could be detected, in which Copper content above 60% at. was measured.

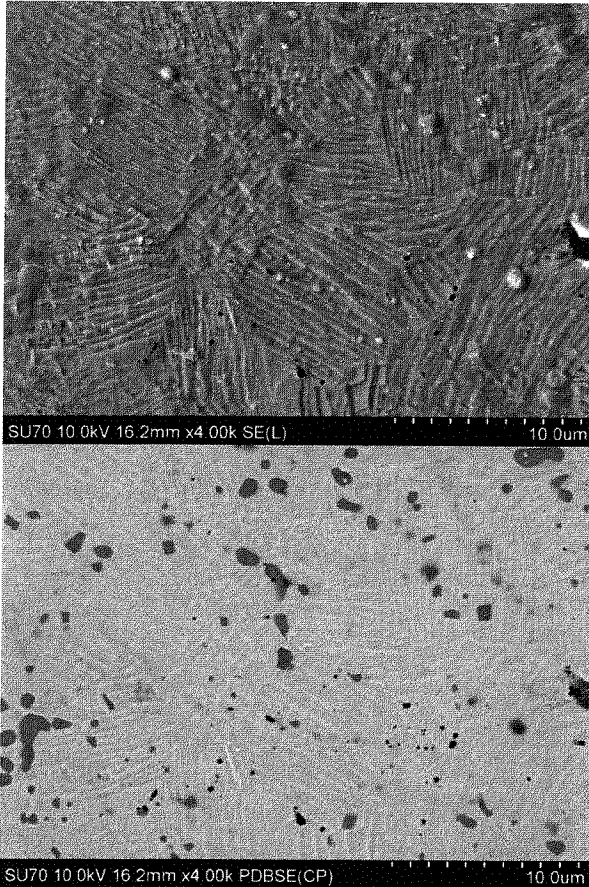


Figure 6: SEM micrographs of $Ni_{40}Ti_{50}Cu_{10}$, preheated at $330^{\circ}C$: up) SE micrograph (sensitive to topography), down) BSE micrograph (sensitive to composition). Nominal magnification 4kx

4. Conclusions

Experimental tests confirmed the feasibility of SHS production of $Ni_{50-x}Ti_{50}Cu_x$ alloys with shape memory properties. The produced alloys showed a certain degree of inhomogeneity and also the presence of secondary phases, confirmed by XRD, SEM and EDXS analyses. DSC analyses showed one or two step martensitic transformation. Literature survey confirms the presence of two phase transformation in $Ni_{50-x}Ti_{50}Cu_x$ alloys, even if limited at Cu content from 6 to 15%. The analyzed samples show the presence of two stage transformation also for Cu content above the mentioned range. Possibly the transformation sequence is B2-B19 (M)- B19' (M'). Some of them can be ascribed to as modification of binary Ti_2Ni or Ni_3Ti , with Cu substituting for Ni or both Ni and Ti. EXD analyses confirm the presence of such phases. Moreover, it was verified that the matrix of the system

for high Cu content, is not constant but show strong differences of Cu content, that replace Ni.

Despite these complex microstructural features, martensitic transformation was detected. As damping properties depend from several factors, among which phase boundaries and twin boundaries in martensitic structures, possibly these material could possess promising damping properties, obtained with a very simple production method.

Mechanical properties and damping properties will be tested in order to confirm such assumptions.

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