NiTi-(Cu-Fe) Shape Memory Alloys Produced by Combustion Synthesis

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Abstract

This study investigates the effect of addition of some elements such as Fe and Cu to the well-known shape memory alooy NiTi by conbustyion synthessis method. In addition to the experimental study, Gibbs energy minimisation method was used for the thermochemical calculations with appropriate alloy database. The experimental products were characterised by using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) to investigate the shape memory effects of the alloys.

1. Introduction

NiTi is the most diffused among Shape Memory Alloys due to its excellent performances as superelastic material, and recovery properties coupled with good mechanical properties, corrosion resistance and biocompatibility. It can be used in several application field, from biomedical to aerospace applications. NiTi is available as sheet, tubes or wire. Increased interest in porous NiTi has rised in the last years as possible bone replacement meterial and high damping material, due to apparent reduction of Elastic modulus shown by porous structures. Porous NiTi can be produced by high temperature sintering under controlled atmosphere, or by additive manufactoring., both requiring generally long times, and that can lead to relatively coarse microstructure and reduced performances. It can be produced also by combustion synthesys method, with much shorter production times [1-4]. Unfortunatly several studies shown that not only NiTi is produced but also secondary phases, that show no shape memory effect, and can be detrimental for biomedical applications (Ni_3Ti) [5]. Evaluation of secondary phases that forms in NiTi produced by combustion methods is hence of interest. NiTi can be alloyed with Fe and Cu without loosing Shape Memory properties. The addition of a third element modifies the sinthesys reaction of NiTi and consequently phase formation. Combustion synthesis were attempted for different ratio of Fe and Cu that sobstituted Ni in NiTi equiatomic alloy. Reactions were studied from themochemical point of view with Factage Thermochemical Software [6], and produced specimen were analysed by SEM, XRD, and DSC analyses.

2. Experimental procedure

Two composition were selected: $Ti_{0.5}Ni_{0.4}Cu_{0.075}Fe_{0.025}$ and $Ti_{0.5}Ni_{0.4}Cu_{0.025}Fe_{0.075}$, atomic ratios. Pure (above 99.5%) Ni, Ti, Fe and Cu powders were mixed in a turbula mixer for 12 hours under Argon atmosphere. Pellets were pressed under the pressure of 70 MPa into cylinder of 15mm height and 12 mm diameter.
The pelleted samples were inserted in a batch reactor. Preheating temperature was monitored by using two thermocouples: two values were used (230 and 430 °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.

Table 1: Samples composition and preheating temperatures

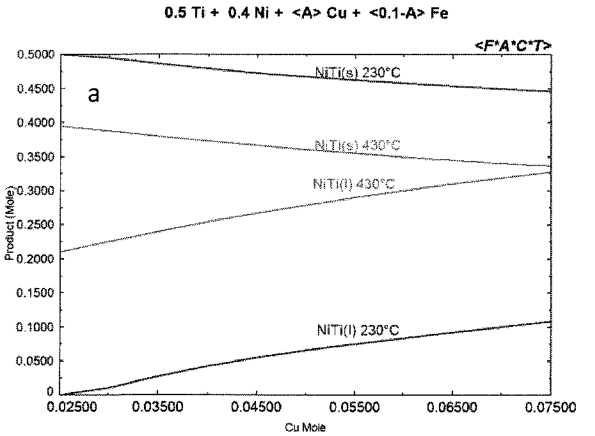
Sample composition (%at)	Preheating Temperature(°C)	
	230	**430**
%2,5Cu-%7,5Fe	NTC1	NTC2
%7,5Cu-%2,5Fe	NTC3	NTC4

The reacted specimen were longitudinally cut in two halves. XRD measurements and SEM observations were performed on one of the longitudinal section after metallographic preparation. The other part of the sample was cut in order to prepare specimens with a mass of about 100mg for DSC analyses.

3. Results

3.1 Thermochemical Calculations

The Factage Thermochemical Software was used to predict adiabatic temperature (T_{ad}), and to estimate the effect of preheating temperature. Results are presented in Figure 1. In the investigated range, increasing Fe content increases solid phase ratio and also T_{ad}.
Noticeably, a marked difference in liquid phase ratio is observed at the two considered preheating temperature: far more liquid phase is present when considering the higher preheating temperature.



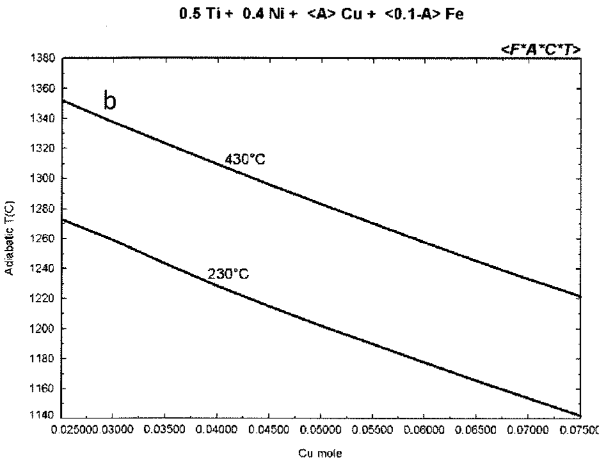


Figure 1: a)Cu(and Fe) mole ratio vs Preheating b)Cu(and Fe) mole ratio vs T_{ad}

3.2 Combustion synthetized specimen results

The specimens preheated at the lower temperature, namely NTC-1 and NTC-3, did not propagate to the end point, whilst the other specimen were completely reacted. Reacted specimens can be observed in Fig.2; noticeably, among NTC1 and NTC3, the latter, which should have the lowest T_{ad}, is also the less reacted specimen. Reduction of height due to partial densification can also be observed. The latter is more pronounced in specimen NTC4, which should have the higher liquid phase content among the four tested conditions.

Only the completely reacted specimens were further analyzed.

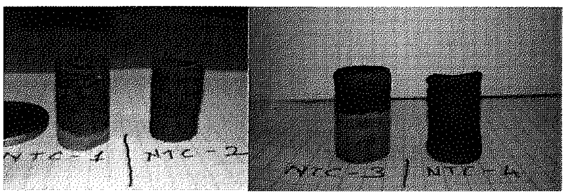


Figure 2: a)NTC-1 and NTC-2 at 230 and 430°C b) NTC-3 and NTC-4 at 230 and 430°C respectively

The results of the XRD analyses for NTC2 and NTC4 are given in Figure 3. Main peaks can be associated to cubic parent phase of NiTi, and Ti_2Ni secondary phase. The results of DSC analysis showed the presence of typical thermoelastic martensitic transformation of shape memory alloys, even if characterised by wider tranformation temperature ranges than binary NiTi. Transformation temperature range of the two specimen are different: NTC-4 shows higher transformation temperatures (Martesite starting temperature: about 53°C) than NTC-2 (Martesite starting temperature: about 15°C). This is consisten with known effect of Cu addition [4] and Fe addition [7] to NiTi.

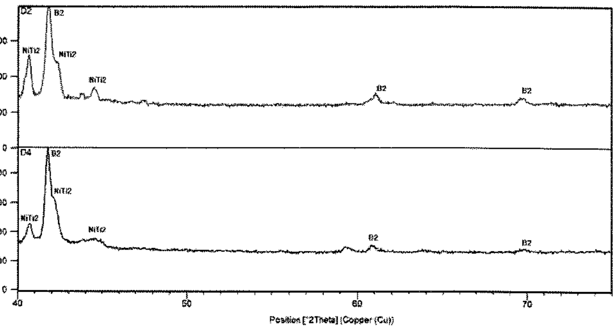
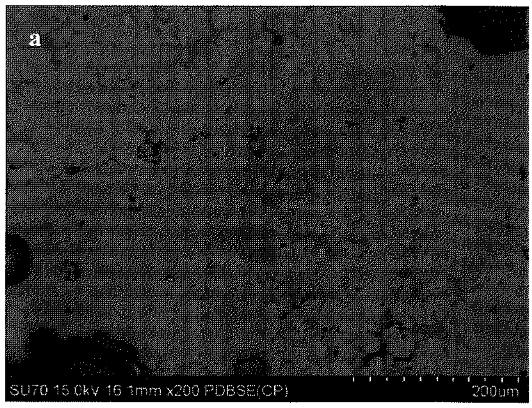


Figure 3: XRD Analysis for samples %7,5Cu-%2,5Fe (NTC 2) and %2,5Cu-%7,5Fe (NTC 4) when the preheating temperature is 430°C



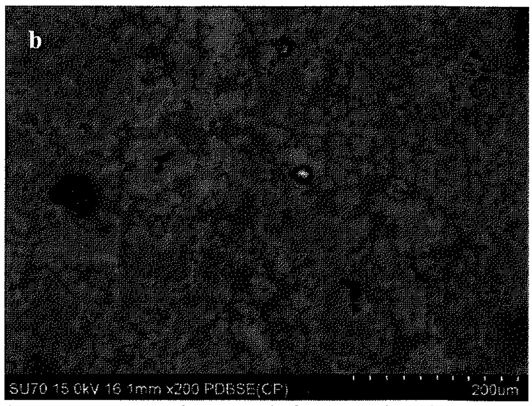


Figure 4: SEM micrograph for samples a) %2,5Cu-%7,5Fe (NTC 2), b) %7,5Cu-%2,5Fe NTC-4)

SEM observation revealed a quite complex microstructure: back scattered detector micrograph clearly show lack of homogeneity on microscopic scale. Aas can be appreciated in Figure 4, the microstructure is characterised for both samles of wide pores but also micrometric pores (black areas): local enrichment of heavy elements (Fe, Cu, Ni) is present (light grey areas), with irregular shape.

EDXS (Energy Dispersion Xray Spectrometry) analyses revealed a relative homogeneous composition at macroscale, corresponding to the nominal composition of the specimens, whilst severe segregation could be observed on microscale.

Examples are reported in Figure 5 and Table 2 for specimen NTC2, and Figure 6 and Table 3 for specimen NTC4.

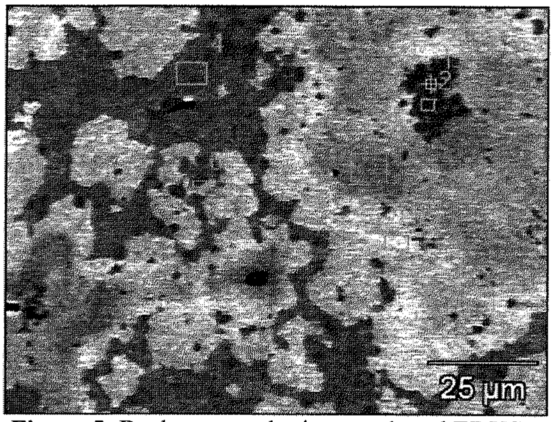


Figure 5: Back scattered micrograph and EDXS analised areas for samples %2,5Cu-7,5Fe (NTC2)

(at %)	*Ti*	*Ni*	*Fe*	*Cu*
NTC2_pt1	58,19	25,01	16,8	
NTC2_pt2	56,21	28,1	15,69	
NTC2_pt3	48,56	39,77	11,67	
NTC2_pt4	67,48	31,28	1,24	
NTC2_pt5	49,83	45,68	1,67	2,82
NTC2_pt6	60,26	36,22	1,14	2,39
NTC2_pt7	47,70	43,96	5,25	3,08

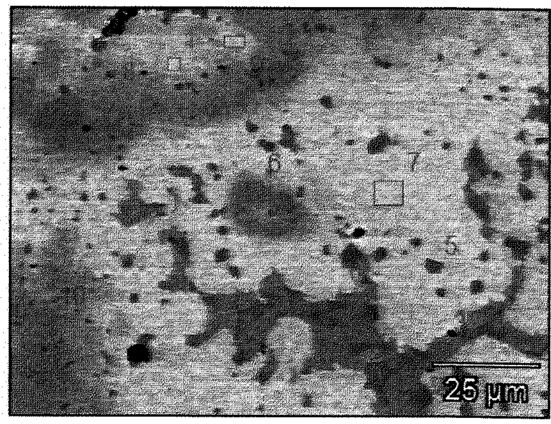
Table 2: EDXS results for regions depicted in Figure5 for sample %2,5Cu-%7,5Fe (NTC2)

For the specimen with lower Cu content, most of the analyses revealed a content of Ti rather close to 50%at. Noticeably, no region with very low Ti content that could recall Ni_3Ti phase or similar, was noticed. Region with composition close to Ti_2Ni intermetallic can be observed.

EDS studies was also conducted on sample NTC-4 (7.5% Cu - 2.5% Fe). Apparently higher Ti content fluctuation can be observed: regions with composition close to Ti2Ni can be easily found, as well as region with Ti content well below 50%at. Also in this case no composition close to $(Ni, Fe, Cu)_3Ti$ can be observed; on the contrary a phase with chemical composition approximately $Ti_1Ni_1(Cu,Fe)_1$ can be observed.

In both samples, matrix with Ti content cose to 50% is accompanied with a relatively higher Ni content than nominal composition, and a mixture of Cu and Fe, in which the Fe/Cu ratio is lower than nominal composition.

This can justify the transformation temperatures obtained from DSC analyses: a ternary alloys with more than 5% Fe has generally transformation temperature well below 0°C: the addition of Cu, those transformation temperatures stabilization effect is well known [2], contributes in limiting the decrease of transformation temperaturews for sample NTC4.



Sample (at %)	*Ti*	*Ni*	*Fe*	*Cu*
NTC4_pt1	34,84	35,31	15,89	13,96
NTC4_pt2	47,57	26,56	21,07	4,79
NTC4_pt3	66,15	30,3		3,55
NTC4_pt4	66,21	18		15,79
NTC4_pt5	61,16	34,24		4,61
NTC4_pt6	47,65	31,13	17,46	3,76
NTC4_pt7	50,77	41,42		7,81
NTC4_pt8	44,36	32,72	19,52	3,4
NTC4_pt9	34,66	35,46	16,49	13,4
NTC4_pt10	47,16	31,02	18,25	3,57

Figure 6: Back scattered micrograph and EDXS analised areas for samples %7,5Cu-%2,5Fe (NTC4)

Table 3: EDXS results for regions depicted in Figure6 for samples %7,5Cu-%2,5Fe (NTC4)

4. Conclusions

Two quaternary NiTiFeCu shape memory alloys were produced successfully by combustion synthesis: reaction was completed only if sufficiently high preheating temperature was used.

1) Thermodynamic calculations allowed to verify that for increasing preheating temperature and Cu content, the liquid phase content at reaction temperature is increased., thus resulting in increased densification of the specimen.

3) Homogeneity at macro-scale is obtained. Ti_2Ni, Fe or Cu enrichment regions are found at micro size as a results of SHS process.
4) DSC analyses revealed the presence of reversible Austenite to Martensite transformation, which strating temperatures are 15 to 53 °C respectively for NTC2 and NTC4. Higher Cu ratio increases A to M transformation temperatures.

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References

[1] W.J. Moberly, K.N. Melton in Engineering Aspects of Shape memory alloys, Butterworth-Heinemann ed.
[2] T.H. Nam, T. Saburi, K. Shimizu, Cu-content dependence of shape memory characteristics in Ti-Ni-Cu alloys, Mat.Trans JIM vol 31 No 11 1990
[3] H. Tobushi, A. Ikai, S. Yamada, K. Tanaka, C. Lexcellent Thermomechanical Properties of TiNi shape meory alloys, J. de Phys. IV, C1, suppl. au J. de Phys. III, vol 5, 1996
[4] Otsuka, K. and R. Xiabing, Physical metallurgy of Ti–Ni-based shape memory alloys. Progress in materials science 50.5, 2005: p. 511-678.
[5] P. Bassani, S. Panseri, A. Ruffini, M. Montesi, M. Ghetti, C. Zanotti, A. Tampieri, A. Tuissi, Porous NiTi shape memory alloys produced by SHS: microstructure and biocompatibility in comparison with Ti_2Ni and $TiNi_3$, Journal of Material Science: Materials in Medicine 25 (2014) 2277-2285.
[6] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melançon, A.D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, M-A. Van Ende, FactSage thermochemical software and databases, 2010–2016 Calphad, Vol. 54, September 2016, Pages 35–53
[7] Z. Zhang, J. Frenzel, K. Neuking, G. Eggeler, Vacuum Induction Melting of Ternary NiTiX (X=Cu, Fe, Hf, Zr) Shape Memory Alloys using Graphite Crucibles, Materials Transactions, 47 (2006) 661-669.