FORMATION OF SINGLE PHASE NiTi SHAPE MEMORY ALLOY VIA SOLID STATE PROCESSING IN REDUCING ENVIRONMENT

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Notations	**Descriptions**
ASTM	American society for testing and materials
BSE	Back-scattered electron
Ca	Calcium
CaH_2	Calcium hydride
CaO	Calcium oxide
DSC	Differential scanning calorimetry
EDS	Energy dispersive spectroscopy
H, H_2	Hydrogen, hydrogen gas
HIP	Hot isostatic pressing
MEMS	Micro-electro-mechanical systems
Mg	Magnesium
MgH_2	Magnesium hydride
MgO	Magnesium oxide
MT	Martensitic transformation
Ni	Nickel
NIH	National institute of health
NiTi	Nickel titanium (equiatomic)
O	Oxygen
SEM	Scanning electron microscopy
SHS	Self-propagating high temperature synthesis
SMA	Shape memory alloy

SPS	Spark plasma sintering
Ti	Titanium
TiH_2	Titanium hydride
TMA	Thermomechanical analyser
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	Descriptions
A_s	Austenite start temperature
A_f	Austenite finish temperature
A_p	Austenite peak temperature
M_s	Martensite start temperature
M_f	Martensite finish temperature
M_p	Martensite peak temperature
ΔG	Gibbs free energy change
ΔG_c	Chemical free energy change
ΔE_{ir}	Irreversible energy change
ΔE_{el}	Elastic strain energy change
ΔH	Enthalpy change
$\Delta H_{A \rightarrow M}$	Enthalpy change for austenite to martensite transformation
$\Delta H_{M \rightarrow A}$	Enthalpy change for martensite to austenite transformation
T	Temperature
T_o	Equilibrium transformation temperature
$T_{A \rightarrow M}$	Critical temperatures for the forward transformation
$T_{M \rightarrow A}$	Critical temperatures for the reverse transformation
ΔS	Entropy change
A, B2	Austenite
M, B19'	Martensite
R	R-phase

P	Density
σ_o	Equilibrium transformation stress
σ_y	Yield stress
α, β	Lattice parameter
α-Ti	Alpha-titanium
β-Ti	Beta-titanium
Å	Angstrom
K_α	K-alpha (energy level)
wt%	Weight percentage

PEMBENTUKAN FASA TUNGGAL ALOI INGATAN BENTUK NiTi MELALUI PERSEKITARAN PENURUNAN KEADAAN PEPEJAL

ABSTRAK

Perkembangan pesat aplikasi terutamanya dalam bidang perubatan dan kejuruteraan menuntut kepada pembangunan NiTi berstruktur nobel yang mana memerlukan teknik pemprosesan alternatif, selain dari teknik konvensional secara peleburan. Sintesis berkeadaan pejal merupakan teknik pemprosesan alternatif untuk menghasilkan NiTi berstruktur nobel seperti struktur poros dan juga struktur nobel yang lain. Sementara sifat memori bentuk NiTi yang unik adalah satu kelebihan, tiada tercatat percubaan yang berjaya dalam menghasilkan fasa aloi tunggal NiTi yang mempamerkan transformasi martensitik yang baik. Kebanyakan produk yang terhasil melalui kaedah sintesis keadaan pejal mempunyai struktur mikro yang kompleks melibatkan pembentukan fasa lain seperti Ti_2Ni dan $TiNi_3$. Fasa-fasa ini tidak mempunyai transformasi martensitik, justeru menjejaskan sifat memori bentuknya. Selain itu, pembentukan oksida boleh menghalang kepada pembentukan fasa aloi tunggal NiTi. Oleh yang demikian, kajian ini bertujuan untuk mengkaji keadaan yang membolehkan terbentuknya fasa aloi tunggal NiTi yang mempunyai sifat transformasi martensitic yang optimum dan juga mengenalpasti rintangan kepada pembentukan fasa aloi tunggal NiTi ini. Dalam kajian ini, serbuk campuran Ni-Ti dan Ni-TiH_2 disintesiskan dalam aliran argon dan persekitaran terkawal menggunakan serbuk CaH_2 dan MgH_2 sebagai agen penurunan in-situ. Pelbagai parameter seperti suhu pensinteran, masa, komposisi, dan rawatan haba pasca pensinteran digunakan untuk mengkaji kesan kepada pembentukan fasa aloi, sifat

martensitik, perubahan ingatan bentuk dan juga sifat mekanikalnya. Sintesis menggunakan Ni-Ti tidak menghasilkan fasa aloi tunggal NiTi, justeru tiada nilai entalpi yang menjadi ukuran untuk sifat martensitiknya. Penggunaan serbuk TiH_2 menggantikan serbuk Ti berjaya meningkatkan jumlah peratusan fasa aloi tunggal NiTi dengan nilai entalpi iaitu ≤13 J/g. Walaubagaimanapun, nilainya agak kecil jika dibandingkan dengan nilai ideal untuk NiTi. Puncanya adalah disebabkan oleh pengaruh pengoksidaan yang menghalang pembentukan fasa aloi tunggal NiTi. Sintesis NiTi menggunakan serbuk Ni-TiH_2 dan CaH_2 sebagai agen penurunan in-situ, berjaya menghasilkan fasa aloi tunggal NiTi dengan nilai entalpi sebanyak 25 hingga 26 J/g, iaitu bersamaan dengan nilai entalpi yang ideal untuk NiTi. Analisis pada permukaan spesimen menunjukkan ada perubahan yang ketara dalam mengurangkan lapisan oksida yang terbentuk, justeru meminimumkan kesan terhadap ketidakseimbangan unsur-unsur Ni-Ti untuk tindakbalas pembentukan fasa aloi tunggal NiTi. Ini menjadikan sintesis melalui persekitaran tanpa oksigen membolehkan terbentuknya fasa aloi tunggal NiTi. Selain dari pertimbangan termodinamik yang kerap dibincangkan menjadi faktor terhalang pembentukan fasa aloi tunggal NiTi, penyelidikan ini berupaya mewujudkan fakta bahawa pengoksidaan memberikan kesan ketara kepada pembentukan fasa aloi tunggal NiTi disintesiskan dalam keadaan pejal.

FORMATION OF SINGLE PHASE NiTi SHAPE MEMORY ALLOY VIA SOLID STATE PROCESSING IN REDUCING ENVIRONMENT

ABSTRACT

The fast growing application especially in medical and engineering fields demands the development of novel-structured NiTi which requires an alternative processing technique, other than the conventional melt-casting method. Solid state synthesis is an alternative processing technique that has been attempted for producing novel-structured NiTi such as porous NiTi and other novel forms. Whilst shape memory effect is a unique advantage of NiTi shape memory alloy like, no successful attempt so far to produce single phase NiTi with good transformation. NiTi produced via solid state synthesis have complex microstructures involving multiple phases of Ti_2Ni and $TiNi_3$. These phases do not exhibit martensitic transformation and jeopardise the shape memory behaviour of NiTi. Apart from that, the formation of oxides may hinder the formation of single phase NiTi. Therefore, this research examines the processing conditions that produce single phase NiTi with optimum transformation behaviour and also identifies the possible obstacles for forming single phase NiTi. This study synthesised Ni-Ti and Ni-TiH_2 powder mixtures in flowing argon and reducing environment using CaH_2 and MgH_2 powder as the in situ reducing agent. Several effects of parameters such as sintering temperature, time, composition, and post-sintering were studied and a systematic comparative investigation was performed on phase formation, transformation behaviour, shape memory effect, and deformation behaviour of the sintered specimen. Elemental powder sintering of Ni-Ti did not result in single phase NiTi and no distinct peaks of martensitic transformation were observed on the sintered specimens. The use of TiH_2 to replace Ti increased the volume fraction of NiTi and displayed martensitic transformation peaks, albeit with low transformation heat (≤13 J/g) revealing that oxidation is an active obstacle in producing single phase NiTi. Synthesis of Ni-TiH_2 in reducing the environment, especially the use of CaH_2 as an in situ reducing agent, resulted in the formation of single phase NiTi with enthalpy change of ~25-26 J/g, similar to melt-cast NiTi alloys. The surface analysis showed a significant reduction in oxide formation, thus minimising the effects on balanced composition between Ni and Ti. This reflects that an oxygen-free environment allows unhindered Ni-Ti reaction, which leads to the formation of single-phase NiTi. This work established the fact that, other than the thermodynamic considerations often being discussed in similar work as obstacles to single phase formation, oxidation appears to have profound effects on single phase formation in NiTi synthesized in solid state.