Development and characterization of Ti-Ni based and Ti-Ta based shape memory alloys for novel applications

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This study focused on basic research oriented towards the understanding of the interrelationship between different parameters and the properties of shape memory alloys in order to increase its potential for more applications. Specifically the parameters investigated were phase stability, internal structures and processing method. The thesis consists of two major parts and each part was divided to different chapters having specific objectives. The first part of the study involves the use of sputter-deposition method to develop novel micro-devices, such as Ti-Ni microtubes (Chapter 2) and Ti-Ni-Pt-Cu HTSMA thin films (Chapter 3). The second part (Chapter 4 to 8) of this study includes the development of Ti-Ta based bulk alloys as novel high temperature shape memory alloys with excellent cold-workability and stable high temperature shape memory effect.

In Chapter 2 a new method of fabricating superelastic Ti-Ni microtubes having an inner diameter of 50μm and a wall thickness of 6μm were successfully fabricated by sputter deposition on Cu wire (50μm diameter). It was clarified that wall thickness and microstructure were strongly influenced by the geometry of the Cu wire substrate. For example the formation of columnar grains and thickness variation were due to the relative orientation of the surface of the Cu wire with the sputter target. The columnar grains caused the microtubes to exhibit low fracture strength. In order to remove the influence of the geometry of the Cu wire on the microstructure of the microtube, the Cu wire was rotated during sputter deposition. As a result high strength superelastic Ti-Ni microtubes with dimensions of 50μm inner diameter and wall thickness of 6μm were successfully fabricated. These superelastic microtubes are attractive as micro-stents, micro-catheter and microneedle, for biomedical applications.

In Chapter 3 the sputter deposition method was used to develop Ti-Ni-Pt-Cu high temperature shape memory alloy thin films. All the as-deposited films were amorphous and require heat treatment process to crystallize the films. A crystalline phase is necessary for the films to exhibit martensitic transformation. The addition of Pt to Ti-Ni thin films were found to increase the Ms, but at the same time also increases the crystallization temperature. A lower
crystallization temperature is desired for shape memory alloy thin films to be easily integrated to micro-mechanical-electro-systems (MEMS). The addition of Cu to Ti-Ni-Pt was found to be effective to decrease the crystallization temperature and the \( M_S \) was not significantly affected. Thus quatermary Ti-Ni-Pt-Cu thin films with high temperature martensitic transformation and lower crystallization temperature (when compared to ternary Ti-Ni-Pt films) were successfully fabricated.

The second part covers Chapter 4 to Chapter 8, and concentrate on the development of a new high temperature shape memory alloy bulk specimens with excellent cold workability and stable high temperature shape memory effect \((M_S > 373 \text{ K})\). Previously the biggest limitation for \( \beta \) Ti based shape memory alloys to be considered as high temperature shape memory alloy was its sensitivity to aging above 373 K. The aging effect is due to the formation of \( \omega \) phase, which decreased the \( M_S \) and led to poor thermal stability of high temperature shape memory effect. It was found that the amount of \( \omega \) phase decreased with increasing amount of \( \beta \) stabilizers (Ta, Nb, Mo) irrespective to the type of element. However the \( M_S \) of the alloy was strongly dependent on the type element added, for example to obtain the same \( M_S \) the Ti-Ta alloy contains more \( \beta \) stabilizer elements compared to Ti-Nb and Ti-Mo. Using this idea it was revealed that for Ti-Ta alloy having similar \( M_S \) with Ti-Nb or Ti-Mo, the formation of the \( \omega \) phase by aging was significantly less. For this reason it was suggested that Ti-Ta base alloy has the potential for the development of novel high temperature shape memory alloys. Due to the scarcity of information regarding the crystallography of \( \beta/\alpha' \) martensitic transformation in Ti-Ta, this topic was also investigated in Chapter 4. Crystallographic information such as habit plane, internal twinning and the formation of unique microstructures in Ti-Ta alloys were clarified.

In order to further improve the thermal stability of the high temperature shape memory effect in Ti-Ta, the effect of addition of different ternary alloying elements was investigated. Among the ternary alloying elements it was found that the addition of Al and Sn can significantly improve the thermal stability of the high temperature shape memory effect by strongly suppressing the formation of \( \omega \) phase during aging. Furthermore the composition dependence of shape memory behavior and the effect of aging in Ti-Ta-Al were found to be dependent to the amount of Ta and Al. Composition range revealing stable high temperature shape memory effect was identified. For example Ti-27Ta-5Al exhibited extremely stable high temperature shape memory effect when compared to Ti-32Ta, which has similar \( M_S \). Lastly improvement of shape memory recovery strain and mechanical properties by short time annealing was suggested. As a result a new high temperature shape memory alloy system with excellent cold-workability and stable high temperature shape memory effect was successfully developed in Ti-Ta base alloys.

審査の結果の要旨

本論文は，形状記憶合金をミクロンサイズの領域と 100 度以上の温度範囲で利用可能な実用合金の開発を目的とし，前者として Ti-Ni 系スパッタ薄膜を取り上げ，後者として Ti-Ta 系合金を取り上げて，材料開発を行ったものである。スパッタ法を用いて，直径が 50 ミクロンのマイクロチューブ作製に成功した。成膜中の欠陥形成機構を解明し，強度を有するマイクロチューブ作製技術を開発した。また，高温形状記憶合金として，Ti-Ta 系合金に絞り込み，Al や Sn の添加で特性が安定することを見出した。これらの新規材料の結晶学的解析も行い，マルテンサイト変態の基礎も確立した。特に，高温材料は，冷間加工が可能ため，実用的にも今後多大の貢献が期待できるものであり，価値ある研究であると判断される。よって，著者は学位を受けるに十分な資格を有すると認められる。

よって，著者は博士（工学）の学位を受けるに十分な資格を有するものと認める。