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Exploration, Characterization and Optimization of Ti-Cr-Sn Novel Superelastic Alloys in Sn-rich Region

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Thesis outline

The objective of the present thesis is to develop novel Ti-based superelastic alloys which exhibit the large lattice deformation strains near the human body temperature and room temperature for practical biomedical applications. Then, Sn-rich region in the Ti-Cr-Sn ternary system was widely and systematically explored by conventional metallurgical approach. At first, the lattice deformation strain and the martensitic transformation behavior were investigated, and candidate alloys were identified. Second, the superelastic properties of the candidate Ti-Cr-Sn superelastic alloys were systematically characterized and compared in terms of their microstructure, lattice deformation strain and superelastic behavior including critical stress for slip and shape recovery strain. Third, to obtain the improved superelastic properties, solution treatment conditions were systematically changed and optimized. Finally, yttrium addition to Ti-Cr-Sn superelastic alloy was systematically investigated to achieve better mechanical properties though grain refinement, dispersion strengthening of second phase formation and impurity oxygen level reduction. Then, a material design for promising β-Ti superelastic alloys is described. The major conclusions of present thesis that obtained in each chapter are summarized as follow;

Chapter 2: Effects of Cr and Sn Contents on Martensitic Transformation and Deformation Behavior of Ti-Cr-Sn Alloys

The effects of Cr and Sn additives on the lattice deformation strain, martensitic transformation temperature, and deformation behavior of Sn-rich Ti-Cr-Sn alloys were systematically explored for a wide range of alloy compositions: Ti-(1.5~4.0)Cr-(6.0~9.0)Sn (mol%). The lattice deformation strain values ($|\eta_1|$, η_2, and η_3) were calculated based on the lattice parameters of the martensite α″ and parent β phases. The rates of change of η_2 with Cr and Sn content were determined: −0.79%/mol% Cr and −0.56 %/mol% Sn, respectively. The reverse martensitic transformation temperature (A_s and A_f) changed with Cr and Sn content at rates of approximately −190 K/mol% Cr and −141 K/mol% Sn, respectively. The deformation behavior of Ti-Cr-Sn alloys at room temperature (RT: 298 K) changed from SME to SE with increasing Cr and Sn contents. Especially, Ti-2.5Cr-8.5Sn, Ti-3.0Cr-7.5Sn, Ti-3.0Cr-8.0Sn, Ti-3.5Cr-7.0Sn, and Ti-4.0Cr-6.5Sn alloys exhibited SE at RT and possessed large η_2 values that exceeded 6.32%. Moreover, it was revealed that the addition of Cr and Sn can decrease the martensitic transformation temperature considerably without significant reduction of lattice deformation strain in comparison with other additional elements in the literature. Therefore, it is concluded that Cr and Sn are effective alloying elements for developing superelastic β-Ti alloys with a large lattice deformation strain at RT.

Chapter 3: Microstructure, Lattice Deformation Strain and Superelastic Properties of Ti-Cr-Sn Alloys

The microstructures, texture distribution, lattice deformation strains, and superelastic properties were characterized and compared using the solution-treated Ti-2.5Cr-8.5Sn, Ti-3.0Cr-7.5Sn, Ti-3.5Cr-7.0Sn, and Ti-4.0Cr-6.5Sn superelastic alloys which found in Chapter 2. It was found that all the alloys consist of single β-phase at RT by X-ray diffraction analysis, and that the formation of athermal ω phase observed by transmission electron microscopy seemed to be suppressed with decreasing Cr contents and increasing Sn contents. Mechanical tests revealed that the larger superelastic recovery strains (ε_{SE}) over 3.6% were obtained in Ti-2.5Cr-8.5Sn and Ti-4.0Cr-6.5Sn alloys than those in the others. Although there was no significant difference in martensitic transformation temperature and critical stress for slip deformation (σ_{CSS}) between Ti-2.5Cr-8.5Sn and Ti-4.0Cr-6.5Sn alloys, the highest value of ε_{SE} for 4.0% was obtained in Ti-4.0Cr-6.5Sn alloy due to their well-developed $<011>_{\beta}$ texture component. Moreover, both Ti-2.5Cr-8.5Sn and Ti-4.0Cr-6.5Sn alloys exhibited the almost perfect SE and maintained lager than 4.5% shape recovery strain after 100 cycles of repetitive loading-unloading tensile tests to keep a maximum applied strain of 5.0%. The superior SE behaviors were due to their considerably high values of η_2, ε_{SE}, and σ_{CSS} than the previously reported β-Ti SE alloys. Finally, from the viewpoint of Sn content, Ti-4.0Cr-6.5Sn alloy with lower Sn content is judged to be the best superelastic alloy in the Ti-Cr-Sn ternary system.

Chapter 4: Effects of Solution Treatment on Microstructure and Superelastic Properties of Ti-4.0Cr-6.5Sn Alloy

In order to optimize the heat-treatment condition for the achievement of superior SE in Ti-4.0Cr-6.5Sn alloy, the effects of solution treatment condition on microstructure characteristics and superelastic properties were systematically investigated by changing solution treatment temperature and duration time. Regardless of texture distribution, the higher value of ε_{SE} was obtained when the solution-treated Ti-4.0Cr-6.5Sn alloy possess the relatively high values of $\sigma_{CSS} / \sigma_{SIMT}$ and $\varepsilon_{CSS} - \varepsilon_{SIMT}$. Moreover, the optimized solution treatment condition was determined to be temperature of 1213 K and time of 3.6 ks for Ti-4.0Cr-6.5Sn alloy and the highest ε_{SE} value of 4.5% was obtained due to its highest values of $\sigma_{CSS} / \sigma_{SIMT}$ and $\varepsilon_{CSS} - \varepsilon_{SIMT}$.

Chapter 5: Effects of Yttrium Addition on Microstructure, Phase Constitution, Shape Memory Effect and Mechanical Properties of Ti-2.5Cr-8.5Sn Alloy

The formation of fine-dispersed Y_2O_3 particles was attempted through the reaction between yttrium (Y) and solute oxygen (O) for the effective β-grain refinement using Ti-2.5Cr-8.5Sn alloy. Then, the effects of Y addition on microstructure, martensitic transformation temperature and mechanical properties were investigated by varying Y content up to 1mol%. Since element Y possesses the high affinity with O and low solubility in Ti alloys, Y_2O_3 oxide was preferentially formed by consuming the residual oxygen in the matrix through the scavenging effect when Y content was ranged up to 0.15 mol%. Then, the β-grain size became effectively smaller with Y content due to the well-dispersed Y_2O_3 oxides. When Y content exceeded 0.15 mol%, Y_5Sn_3 intermetallic phase was also formed in addition to Y_2O_3 oxides. The deformation behavior changed from SE to SME at RT with increasing Y content. The change in deformation behavior is considered by the increase in martensitic transformation temperature, since Y addition absorbs and consumes O and Sn atoms in the β matrix. As for the effect on mechanical properties, the ultimate tensile strength was significantly raised from 788 MPa (Y-free) to 1120 MPa (0.15Y addition). This improvement is judged to be achieved not only by the effective β-grain refinement but also dispersion strengthening of Y_2O_3 oxide particles.

In conclusion, several Ti-Cr-Sn superelastic alloy compositions which exhibit the large lattice deformation strain of 6.32% near the human body temperature were successfully developed as the candidate for practical biomedical applications. Especially, Ti-4.0Cr-6.5Sn superelastic alloy is considered to be promising alloy composition compare to other superelastic β-Ti alloys. Moreover, superelastic recovery

strain that exceeds 4.5% was obtained in Ti-4.0Cr-6.5Sn alloy when the solution treatment was performed at 1213 K for 3.6 ks. Finally, not only the effective β-grain refinement but also improved mechanical properties were obtained through the formation of fine-dispersed Y_2O_3 particles in Ti-Cr-Sn superelastic alloy. This findings demonstrate that the strengthening methods through fine-dispersed Y_2O_3 particles can be applicable to other superelastic β-Ti alloys for obtaining the improved mechanical properties.