Improvement of the superelasticity of Ti-Nb base shape memory alloys via alloying elements modification and heat treatment

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The aim of this study was to produce Ni-free Ti-based shape memory alloys with good superelastic properties. The Ti-Nb alloys developed by Kim et al. though exhibited superelastic properties: they possessed low critical stress for slip deformation and relatively small transformation strain. Hence, the present research concentrated on enhancing the superelastic properties of Ti-Nb alloys by addition of a third element and conducting various heat treatments. Furthermore, in contrast to other types of shape memory alloys, the alloys developed were found to exhibit anomalous mechanical and electrical properties. These anomalies were systematically studied based on microstructural observations. Finally, the stability of the superelastic properties against room temperature aging was studied, where it was found that they are sensitive to room temperature aging effect. This effect compromised the reliability of the developed alloys. The causes of this effect were determined and solutions were successfully proposed.

The first part of this study (chapter 2) concentrated on developing Ti-Nb-Mo alloys and characterizing their shape memory properties. The following conclusions can be made:

[1] The Ti-27Nb, Ti-24Nb-1Mo, Ti-21Nb-2Mo and Ti-18Nb-3Mo alloys exhibit the most stable superelasticity with a narrow stress hysteresis among Ti-Nb-Mo alloys with Mo contents of 0, 1, 2 and 3 at.%, respectively.

[2] Addition of Mo was effective in enhancing the superelastic properties of Ti-Nb alloys through increasing the critical stress for slip deformation and transformation strain.

[3] The effect of 1at. %Mo addition of the reverse transformation temperature is equal to that of 3at. %Nb. Accordingly, the total amount of β-stabilizers included in the alloy decreased. This decrease causes the stability of the beta phase with respect to omega phase to decrease and hence the alloy to become more sensitive to the formation of the omega phase.

The second part of this study (chapter 3) aimed on studying the effect of the athermal omega phase which was found to increase in volume fraction during cooling on the superelastic properties of the alloys. The following
conclusions can be made:

[1] Anomalous temperature dependence of the stress for inducing martensite was observed, where all alloys revealed a deviation from the behavior expected by the Clausius-Clapeyron relationship. This deviation is due to the formation of the athermal omega phase during cooling, which directly affects the martensitic transformation temperature and causes it to drop. Hence, the stress for inducing martensite continuously deviated from the Clausius-Clapeyron relationship on cooling.

[2] It was found that the alloy with a higher (electron to atom) $e/a$ ratio revealed a smaller deviation from the Clausius-Clapeyron relationship. This is due to the enhanced stability of the beta phase with respect to the omega phase as $e/a$ increases.

[3] Regardless to the test temperature, the consumption of the omega phase during the martensitic transformation allowed the alloys to reveal a reverse transformation stress that satisfies the Clausius-Clapeyron relationship. Accordingly, the lower the test temperature the greater the stress hysteresis.

The third part of this study (chapter 4) aimed on studying the effect of room temperature aging on the superelastic properties of Ti-Nb-Mo and Ti-Nb-Mo-Sn alloys. The following conclusions can be made:

[1] The stress for inducing martensite of a Ti-Nb-Mo alloy heat-treated at relatively low temperatures after being cold-rolled up to a 98.5% reduction in thickness was found to increase during aging at room temperature, rendering the superelasticity to be instable. TEM investigations have shown that this is due to the decomposition of the beta phase into the isothermal omega phase.

[2] It is suggested that the nonequilibrium vacancies, which were not efficiently annihilated at the low heat treatment temperature, facilitated the diffusion process and resulted in the formation of the isothermal omega phase.

[3] Addition of Sn was only partially effective in suppressing the room temperature aging effect, and the diffusion remained an operative process.

[4] Alloys heat-treated at higher temperatures revealed greater resistance against the room temperature aging effect, owing to the annihilation of the nonequilibrium vacancies.

[5] Alloys subjected to aging treatment after being heat-treated at a high temperature revealed very strong resistance against room temperature aging effect, where the superelasticity remained unaffected even after long holding time at room temperature. In addition to the annihilation of the nonequilibrium vacancies, the formation of the alpha phase during aging treatment provided the alloy with further resistance to room temperature aging effect.