A transmission electron microscopy study of phase compatibility in low hysteresis shape memory alloys

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Ni-Ti represents the best known shape memory alloy (SMA), today widely used for medical device manufacturing and numerous other applications. Despite the important amount of scientific work already done on Ni-Ti and other SMAs, the understanding of certain important technological properties such as hysteresis and fatigue, have long eluded scientists and engineers, limiting the potential for applications. This is exemplified with the occurrences of Ni-Ti medical-device fracture, along with large temperature/stress hysteresis which are detrimental for many applications. Recent findings [1] have however shed some light on the underlying processes generating hysteresis. These show a strong correlation between hysteresis and phase compatibility between austenite and martensite for the several alloys studied. The compatibility is described by the middle eigenvalue λ_2 of the transformation matrices mapping austenite to one of the martensite variants. As the compatibility between the two phases increases (i.e. $\lambda_2 \rightarrow 1$), the hysteresis is λ_2 and the behavior is universal. A theory [2] developed in the frame of the non-linear theory of martensite supports also this viewpoint.

The present work focuses on the TEM investigation of ternary $Ti_{50}Ni_{50-x}Pd_x$ and $Ti_{50}Ni_{50-x}Au_x$ alloys in which different amounts of Pd/Au substitution on Ni lead to special ratios between the austenite and martensite lattice parameters. As the compatibility between the two phases increases, a change in the microstructure is observed (figure 1). Away from the compatibility condition with $\lambda_2 > 1$, martensite plates contain twin laminates which are the result of stress accommodation at the austenite-martensite habit plane. Electron diffraction shows that the fine twinning occurs along the predicted lattice invariant shear (1-11) type I mode. When perfect compatibility is satisfied, as for Pd/Au content around 11at.%/13at.%, plates composed of a single variant can develop. It shows a strikingly different microstructure determined by the local nucleation conditions and the ensuing growth of twinless martensite plates.

The interface between austenite and a single variant of martensite was studied by highresolution and conventional electron microscopy. The atomically sharp, defect free, low energy configuration of the interface (figure 2) suggests that it plays an important role in the lowering of hysteresis. In-situ TEM experiments also show that the coherency strain of the martensite-austenite interface is not relaxed by twinning or other defects during phase transformation thus minimizing the loss of elastic energy at the interface. Finally, dynamical modeling of the martensitic transformation using the phase-field micro-elasticity model within the geometrically linear theory succeeded in reproducing the change in microstructure as the compatibility condition is satisfied. 1. J. Cui et al., Nature Materials 5 (2006) 286-290.

2. Z. Zhang, S. Müller, R. D. James, Energy barriers and hysteresis in martensitic phase transformations, submitted to Acta Materialia.

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 $Ti_{50}Ni_{35}Au_{15}$ $\lambda_2=1.0018$

Figure 1. Change of microstructure with composition is shown in the bright field images (a)-(c) for $Ti_{50}Ni_{50-x}Pd_x$. Fig. (a) shows internally twinned martensite plates, (b) shows a smaller twin ratio in the plates and (c) a twinless plate when the compatibility condition is satisfied. SAD patterns (d, e) correspond to plates A and B in (a), respectively, showing a (111) type I twinning. Fig. (f) shows a twinless martensite plate in $Ti_{50}Ni_{35}Au_{15}$ which has a λ_2 close to 1 and presents a microstructure similar to $Ti_{50}Ni_{39}Pd_{11}$.



Figure 2. HREM picture of an exact austenite-martensite interface. The upper part is the B19 phase in [010] orientation, the lower part the B2 phase in [011] orientation. A simulation of the interface and the trace of the habit plane are added to the picture. The $(011)_{B19}$ (blue line) and $(01-1)_{B2}$ (red line) planes join seamlessly at the interface despite the small rotation of the martensite and a misfit in lattice plane spacing as indicated in the enlargement of the inset.