## Microstructure and phase decomposition of α' martensite in Ti-V-Al alloys studied by TEM and STEM

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Ti-V alloys composed of  $\alpha$ ' martensite posses lower Young's modulus and higher strength, and show a good machinability for cold groove rolling [1]. Recent study on Ti-V-Al alloys revealed the increase of Young's modulus and Vickers hardness by ageing at 300-400°C. However, according to x-ray diffraction, the structure of these annealed alloys is  $\alpha$ ' single phase and the origin of the observed age hardening still remains an open question. In this study, microstructure of  $\alpha$ ' martensite in Ti-V-Al alloys and its decomposition on ageing were studied by high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM).

Ti-12mass%V-2mass%Al alloys were prepared by arc melting in an argon atmosphere using high purity Ti, V, and Al, followed by homogenization at 1150°C for 24h. The homogenized buttons were solution treated at 950°C for 2h, and then quenched into ice water. Ageing conditions for the quenched alloys were 300 and 400°C for 24h. The microstructure of these alloys were studied by using an FEI Titan 80-300 (S)TEM operating at 300 kV with a FEG and a CEOS image corrector. We adopted negative third-order spherical aberrations (typically,  $C_s = -1\mu m$ ) for HRTEM observation. HAADF-STEM images were observed with a detector inner angle greater than 60 mrad.

As-quenched alloys showed the acicular structure of  $\alpha'$  martensite phase (hcp). Reflections of the small amount of the retained  $\beta$  phase (bcc) were also found on the selected area electron diffraction (SAED) patterns of the as-quenched alloys. However, an apparent decomposition of  $\alpha$ ' martensite was not detected until up to 400°C. The maximum Vickers hardness was obtained for alloys after ageing at 400°C. STEM-EDS elemental mapping revealed the phase decomposition of  $\alpha$ ' martensite towards  $\alpha+\beta$  phases (Figure 1, aged at 500°C). The vanadium contents were distributed in a wide compositional range between 1 and 38 mass% as shown in the histograms (statistical error: 1-4% for V-K). Note that the Vickers hardness was decreased by the phase decomposition at 500°C. Figure 2 shows (a)SAED pattern, (b)bright field (BF) TEM image, and (c)HRTEM image of typical {1011} type twin of  $\alpha$ ' martensite after ageing at 400°C for 24h. No apparent precipitates were recognized at the twin boundaries. HRTEM image of the decomposed  $\alpha/\beta$  interface is shown in Fig.3. Moiré fringes at the interface region indicate the overlapping of two phases or grains with slightly different orientations. Fourier spectra shown in the inset explain the crystallographic orientation relationship between  $\alpha$  (hcp) and  $\beta$  phases as follows:  $[01\overline{1}1]_{\alpha} \| [001]_{\beta}, (\overline{1}10\overline{1})_{\alpha} \| (110)_{\beta}$ . This orientation relationship is close to the Burgers relationship (misorientation~2deg). The present results suggest that the phase decomposition of  $\alpha$ ' martensite may be a key issue for the observed age hardening of  $\alpha$ '-type Ti-V-Al alloys.

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**Figure 1.** (a) HAADF-STEM image and (b,c,d) STEM-EDS elemental maps of the Ti-12%V-2%Al alloy after ageing at 500°C for 24h. Histograms of V-content for the alloys aged at 400°C and 500°C are shown in (e) and (f), respectively.



**Figure 2.** (a)SAED pattern, (b)BF-TEM image, and (c)HRTEM image of  $\{10\overline{1}\}$ -type twin of  $\alpha$ ' martensite after ageing at 400°C for 24h.



**Figure 3.** (a)HRTEM image, (b,c) Fourier spectra, and (d)BF-TEM image of  $\alpha/\beta$  interface after ageing at 500°C for 24h.