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Internal Structure and Phase Transformation of Ti-V Alloy Fine Particles

Kouta ISHII*, Yoshito TAKEMOTO* and Moritaka HIDA*

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Fine particles of Ti-V alloy were prepared by means of arc method. and were investigated on internal structure and phase transformation using HR-TEM and EDS.

Martensite phase was observed in a particle containing comparatively low concentration of V, and ω phase was also found to exist in a nearly 15%V particle. The structure of the ω phase in the fine particle is remarkably expanded in comparison with the bulk sample, and the ω phase is unstable, so that it has disappeared in a few seconds during TEM observation.

1. INTRODUCTION

There has been considerable interest in the phase transformation of ω phase and martensite phase in metastable β-Ti alloys[1-3]. Especially the ω phase is interesting in its marked embrittlment effect[4,5]. Both the ω phase and the martensite phase have been considered that the formation of them are related to a strain field[3,6]. Many studies of the phase transformation in metastable β-Ti alloys have been concerned with the bulk samples. It has not been ascertained whether these phases could exist in fine particles of metastable β-Ti alloys in which the effect of strain field would be little in prospect. Even the reports on the fine particles of alloys are few because of difficulties in fabrication of particles containing a desired composition. Though there is a report on the fine particles of Ti-Mo alloy[7], this alloy system makes difficult in experiment. The present paper will describe internal structure and phase transformation in fine particles of Ti-V alloy using a high resolution transmission electron microscopy(HR-TEM) and an energy dispersive X-ray spectrometry(EDS).

* Department of Mechanical Engineering

2. EXPERIMENTAL

The experimental apparatus to produce the fine particles is illustrated schematically in Figure 1. In this study, Ti-V alloy is adopted because evaporation pressures and melting points of both Ti and V are approximately equal. The specimen rods of Ti-10mass%V alloy and Ti-15mass%V alloy, which were prepared by powder sintering method respectively, were attached to both electrodes in a stainless steel vacuum chamber. The anode was movable to keep a constant clearance of about 0.5mm between the electrodes. The micro-grid to capture the particles was placed at 50mm above the electrodes. Fine particles of Ti-V alloy were produced by arc discharge between the electrodes for about 0.1s under 5.3×10^4 Pa in pressure of Ar. If the arc would be generated for a long time(~2s), the tip of specimen melt down. The collection of fine particles was accordingly carried out by 20 times repetition of the short time discharge. The measurement of composition of individual particle was performed by Kevex EDS system using a micro electron beam condensed by a thick Pt aperture ($t = 360\mu m$) to suppress generation of high energy Bremsstrahlung.

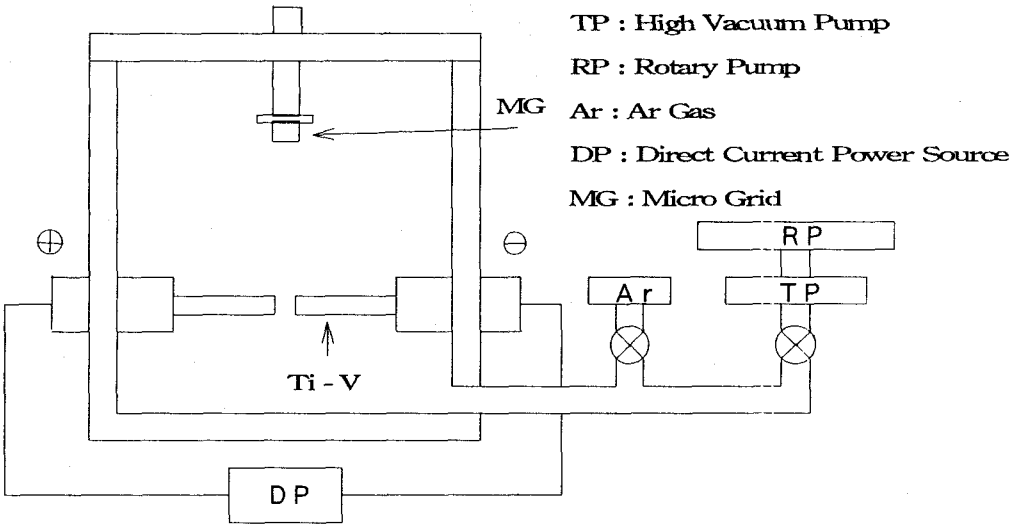


Figure 1. Illustration of apparatus to prepare the Ti - V alloy fine particles.

3. RESULTS AND DISCUSSION

3. 1. Internal Structure of Ti-V Alloy Particle

It is well known that the metastable β-Ti alloy quenched from the β field consists of β(bcc)+ ω(trig.) phases, and becomes the stable phases such as $\beta+\alpha$(hcp) by heat treatment[1)-3)].

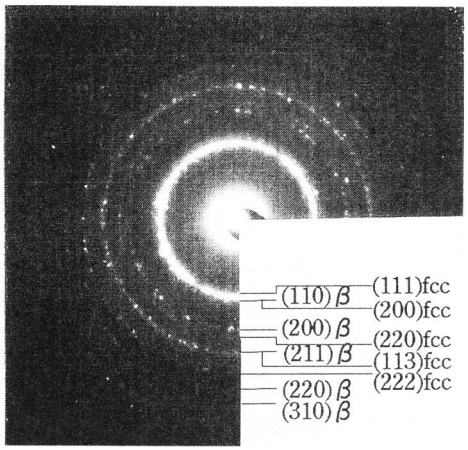


Figure 2. SADP from many fine particles of Ti-15%V alloy

Figure 2. shows the selected area diffraction pattern(SADP) obtained from many fine particles of Ti-15%V alloy. The SADP rings can be mostly indexed as the β structure, although the rings of fcc structure are recognized. The fcc structure can be considered as oxidized particles of Ti-V alloy.

Figure 3(a) and (b) show the micro beam diffraction pattern (MBDP) and the HR-TEM image of particles of 9.0%V, respectively. The MBDP was taken from the lower area in the particle indicated by an arrow in 3(a), showing $(11\bar{2}0)_{hcp}$ pattern. The lattice constants of the hcp structure were a=0.301nm and c=0.487nm which were stretched as compared with those of bulk ; a=0.291nm and c=0.463nm[8]. This effect of lattice expanding may be peculiar to fine particles. The particle in 3(b) shows martensitic stacking fault fringes of $(0001)_{hcp}$ in the upper area where would be joining to other particle. It is considered that the strain field generated by joining causes the fringes. In the bulk sample of metastable β type titanium alloys, there are two kind of phases in hcp structure, the one is α phase and the other is α' martensite. It is known that the α' martensite can be formed by quenching in the range of 5%V~11%V alloys[9]. Though the α' in the bulk can be generally distinguished from α phase with respect to a morphology which is lenticular about 100 μ m in size, it is impossible to judge from such morphology in a fine particle. However the particle may be regarded as the α' martensite in a viewpoint of composition.

Figure 4(a), (b), (c) and (d) are HR-TEM image, bright field image, MBDP and dark field image(DFI) of a particle of 15.8%V,respectively. Two kind of peculiar fringes (d=0.40nm) to the ω phase can be seen in 4(a). Such fringe is not moiré fringe which can be reproduced due to overlapping with other particle, because the particle is isolate except both ends. Moreover the MBDP shows $(110)_{\beta}$ pattern including two kind of $(11\bar{2}0)_{\omega}$ patterns. The other two kind of ω variants are unvisable from $(110)_{\beta}$ observation. An area of ω phase in the particle repeated appearance and disappearance during DFI observation. From this result, it is considered that the structure of ω phase in a fine particle is remarkably unstable. The lattice constant of β phase was a_{β}=0.330nm which was stretched as compared with that of bulk in 15%V alloy ; a_{β}=0.323nm~0.324nm[10]-[12]. From these results, it is evident that even metastable phase such as ω phase and martensite phase can exist even in a fine particle of Ti-V alloy.

3. 2. Quantitative Analysis of Oxygen in Particles

Oxygen has a large influence on the structure in metastable β titanium alloy, as the ω phase is surppress to form by oxygen atoms. Therefore quantitative analysis of oxygen in fine particles was attempted on the EDS spectra. Figure 5 describes the process of quantitative

analysis of oxygen in particles. On the basis of EDS spectrum in low energy range, the characteristic X-ray peaks of titanium and oxygen were separated and the oxygen concentration was calculated. Figure 6(a) and (b) show the X-ray spectra of EDS obtained from a fine particle of 9.0%V and 15.8%V, respectively. Fig. 6(c) and (d) are the best fitted curves with gaussan distribution function in low energy range for 6(a) and (b). From the calculation in 6(c) and (d), the oxygen concentration of 9.0%V particle was estimated as 7.1%O, and that of 15.8%V particle was 5.4%O. The oxygen concentration for other particles was within range of 4.2%O～9.3%O. Though these values are too high in the bulk to form the ω phase, the ω phase is certainly observed in the fine particle. It is very different between bulk and fine particle in the view point of ratio of surface to volume. If fine particle would consist of the internal with low oxygen and the surface layer with high oxygen, it might give an account of the discrepancy. To simplify the calculation the following assumption was used. The shape of a fine particle of pure titanium (ρ=4.54g/cm^3) is sphere of 50nm in diameter and is covered by an oxide layer of rutile (TiO_2 : ρ=4.26). When the thickness of rutile layer is about 3nm as shown in Fig.3(a), the whole oxygen concentration of the particle becomes to be 10%O, which well explains the high concentration of oxygen in fine particles. It is considered that the internal structure of the fine particle is protected from the complete oxidization to form an oxide layer on the surface.

4. CONCLUSIONS

Fine particles of Ti-V alloy were produced by means of arc method, and were investigated on internal structure and phase transformation by HR-TEM and EDS. Martensites were observed in particles that have comparatively low concentration of 9.0%V, and ω phase was also found in a particle of 15.8%V. In addition, the latter particle could have two kind of ω variants. It was found that ω phase repeated appearance and disappearance during DFI observation. The lattice constants of matrix, martensite and ω phase expanded in fine particles. From quantitative analysis of oxygen, a fine particle had high oxygen concentration by reason of an oxide surface layer, which was within range of 4.2%～9.3%.The thickness of oxide layer calculated from these values was about 3nm and equal to that from HR-TEM observation. The internal structure of a fine particle was not affected by oxygen, because an oxide layer to protect was formed on the surface.

5. REFERENCES

(1) B.S.Hickman, J.Inst.Metals, 96(1968)330
(2) D.L.Moffat and D.C.Labalestier, Met.Trans., 19A(1988)1677
(3)M.J.Blackburn and J.C.Williams, TMS-AIME, 242(1968)2461
(4) Y.Takemoto, M.Hida, E.Sukedai and A.Sakakibara, J.Jpn.Inst.Met., 53(1989)1004

(5) J.C.Williams, B.S.Hickman and H.L.Marcus, Met.Trans., 2(1971)1913
(6)F.H.Froes, C.F.Yolton, J.M.Capenos, M.G.H.Wells and J.C.Williams, Met.Trans., 11A(1980)21
(7) Y.Takemoto, A.Sakakibara and M.Hida, Memoirs Faculty Eng., Okayama Univ., Vol. 28, No.2(1994), pp. 1-7.
(8) G.V.Raynor, *Inter. Ser. Monog. Metal Physics and Physical Metallurgy*, Vol.4(1958)
(9) M.Ikeda, S.Komatsu, T.Sugimoto and K.Kamei, J.Jpn.Inst.Met, 54(1990)743
(10) O.Nakano, J.Jpn.Inst.Met, 45(1981)653
(11) H.K.Adenstedt, Trans. ASM, 44(1952)990
(12) P.Pietroknowsky and P.Duwez, Tran.AIME, 194(1952)627

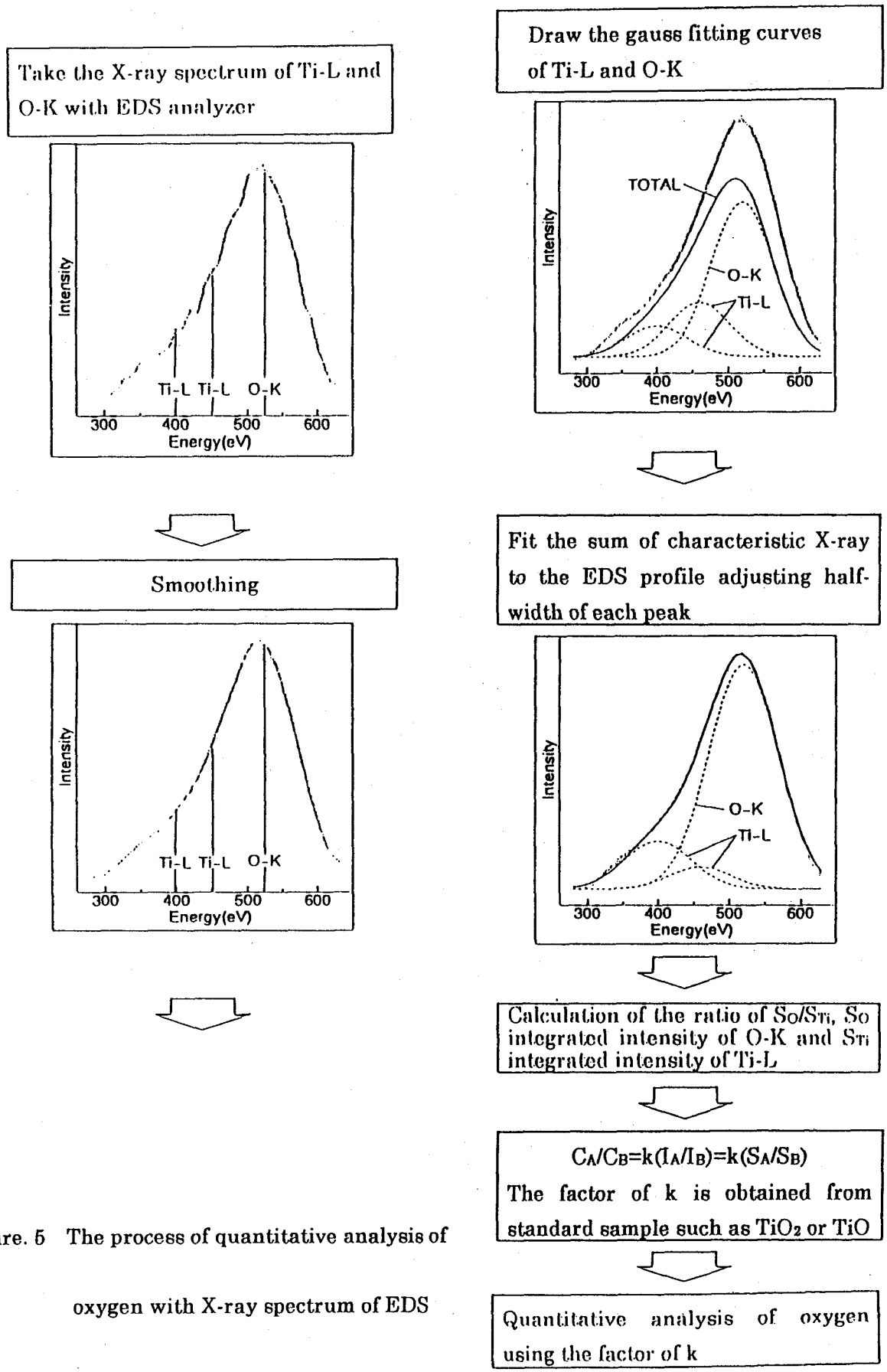
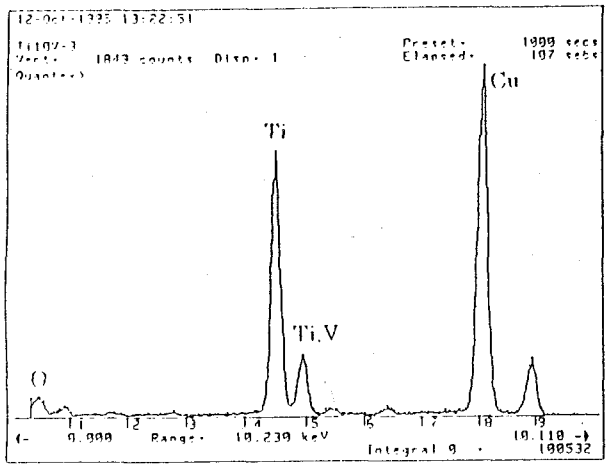
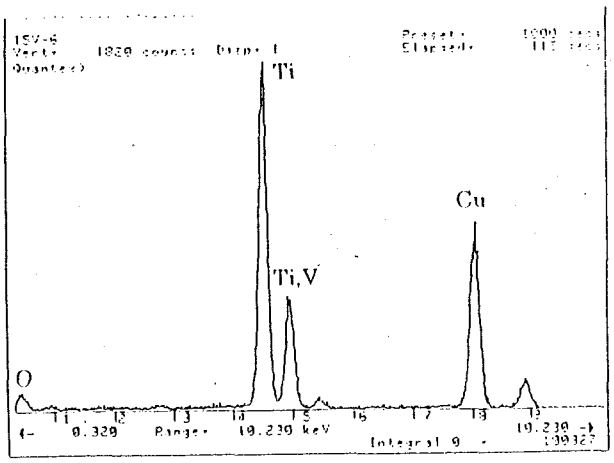


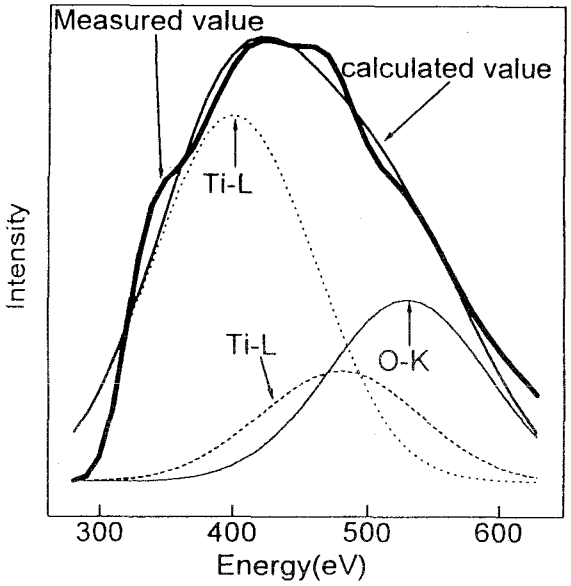
Figure. 5 The process of quantitative analysis of oxygen with X-ray spectrum of EDS



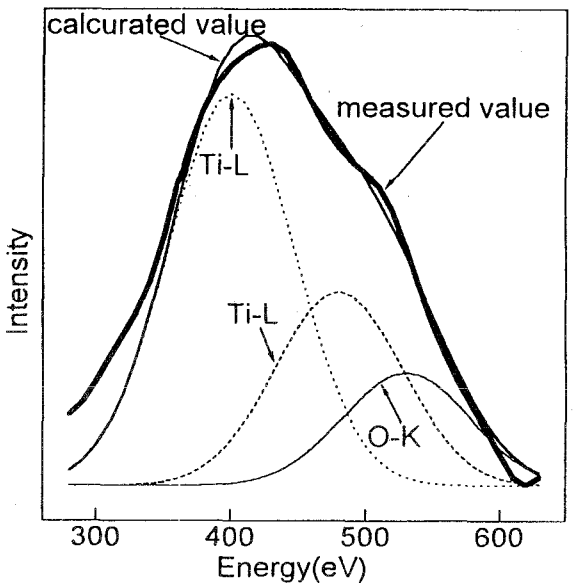
(a)



(b)



(c)



(d)

Figure 6. X-ray spectra of EDS obtained from a fine particle of (a)9.0%V and (b)15.8%V, and best fitted curves with gaussian distributeion function in low energy range for 6(a) and (b)

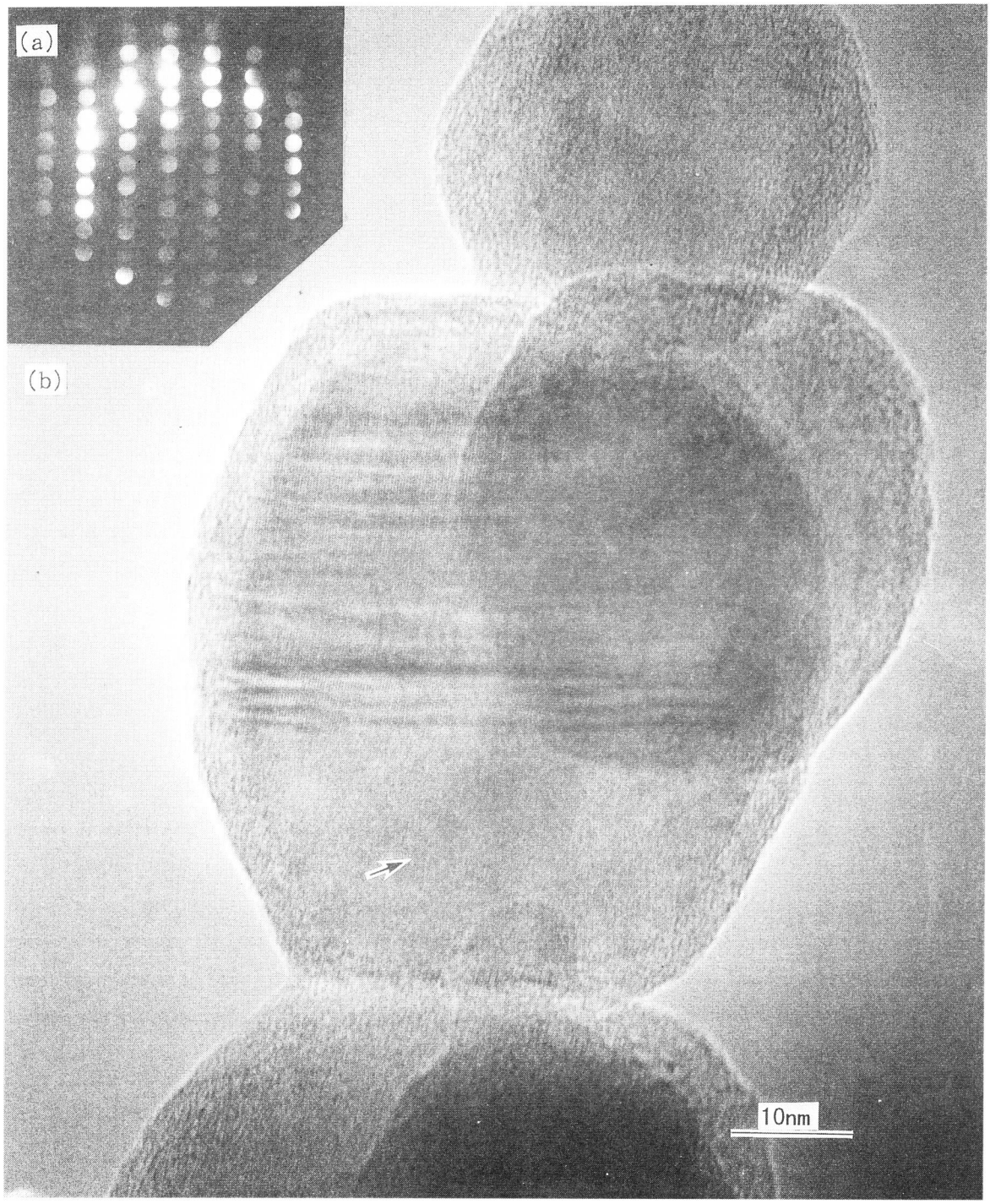


Figure 3. Particle of Ti-9.0mass%V (a)MBDP and (b)HR-TEM image, beam // 〔$11\bar{2}0$〕
The particle has stacking faults of (0001).

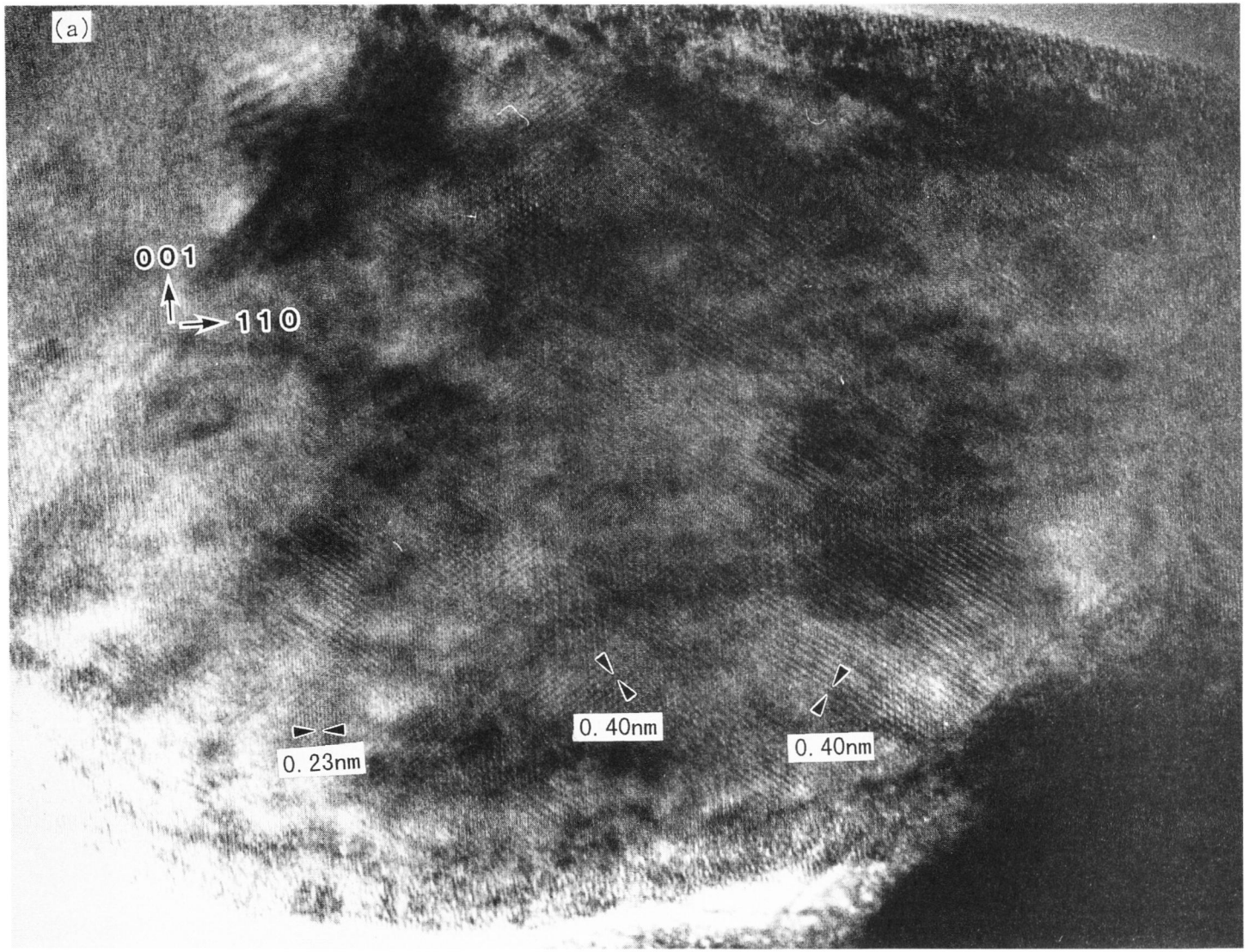
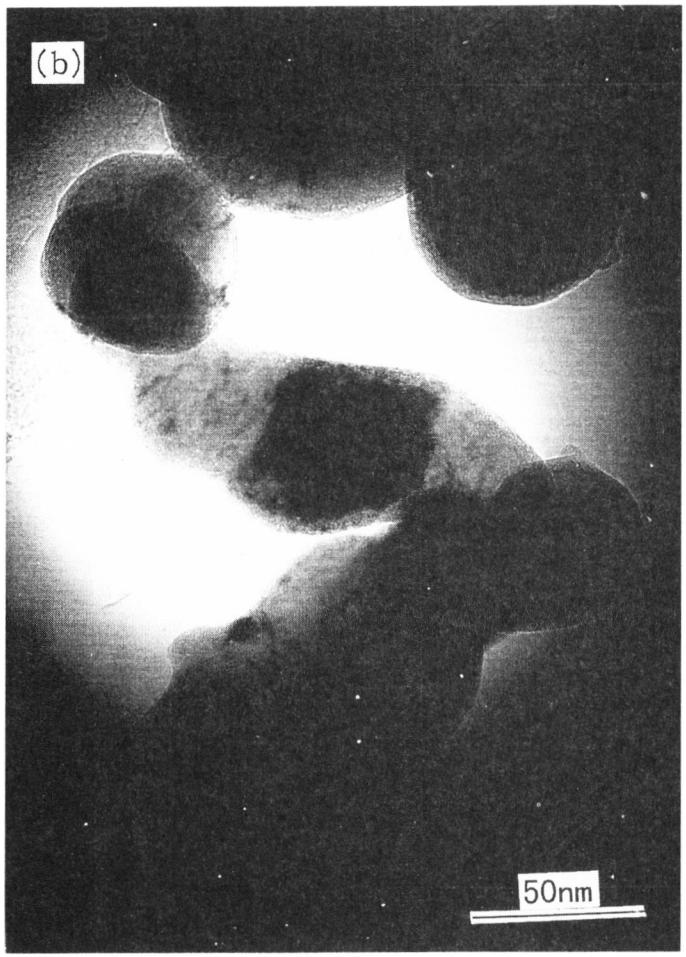
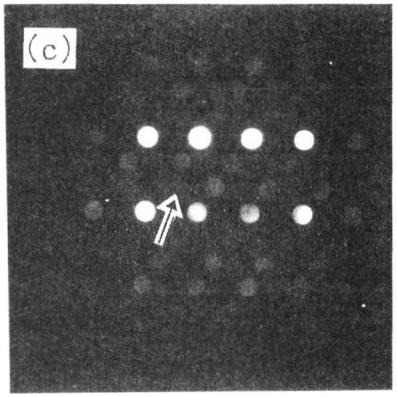
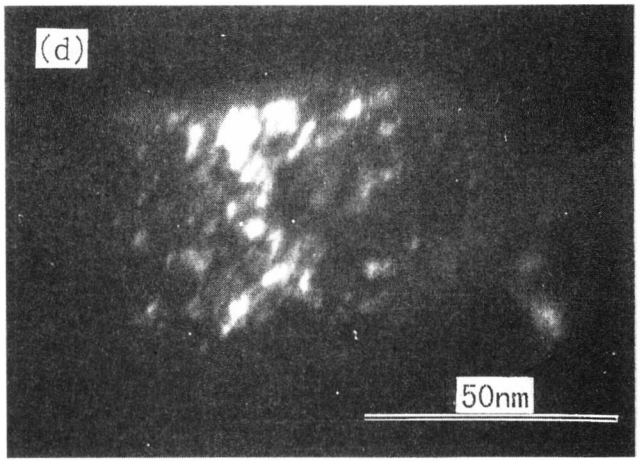


Figure 4. (a)HR-TEM image of Ti-15.8mass%V alloy particle showing two kind of ω fringes (0.40nm)







(b)Bright field image in low magnification, (c)MBDP of the particle in (a),
and (d)DFI image using the spot indicated by an arrow in (c)