Modulated Structures Observed in Metastable Phase of Commercial Alloys

Byung Hak Choe, Jong Heon Shim, Chan Hee Park, Seung Eon Kim, Joo Hee Kang, and Yong Taek Hyun

Abstract**—**Metastable phase characteristics of commercial alloys including Beta Ti alloy were investigated to consider the relationship of microstructure and diffraction pattern in TEM. TEM analysis showed that the microstructure was mottled as a modulated structure, and the diffraction pattern was composed of spot streaks between main spots of a stable beta phase with specific lattice relationship. The modulated structure may be induced by short distance slip or atom movement during very short interval of STQ (solution treated and quenched) materials. It is confirmed by phase relationship between stable bcc matrix and unknown metastable phase in diffraction patterns like atherml ω phase or premartensitic transformation. The metastable phases have a common characteristic of hardened and brittle behavior because the dislocation slip is restricted by super lattice effect due to short distance atom movement at the metastable state.

Index Terms**—** Metastable phase, TEM analysis, modulated structure, premartensitic transformation, super lattice effect**.**

I. Introduction

With regard to pretransformation behaviors, Tanner and Soffa stated, in a 1988 symposium proceedings foreword, that specifically, the evolution of anomalies in phonon spectra, strain-induced scattering, modulated microstructures, etc., that often seem uniquely related to the ensuing symmetry changes, suggests that parent phases are effectively preparing themselves for the phase transformations. The prototype pretransformation behavior is, of course, premartensitic phenomena which occur in various martensitic alloys including shape memory and ferroelastic crystalline materials, and they are often characterized by a relatively small Bain strain, shear modulus softening, and a weak-to-moderate first order transition. Although much understanding has been accomplished for the pretransformation behavior during the last three decades, there seem many questions that still remain unanswered. In this work, we report pretransformation phenomena observed in four commercial alloy systems of β-C Ti, Al-Mg-Cu, Fe-Cu and Fe-N steel, and discuss possible mechanisms for the behaviors.

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II. Experimental Procedure

A β-C Ti alloy in commercial application has nominal compositions of Ti-3Al-8V-6Cr-4Mo-4Zr in weight percent. The alloy specimens were heated to 800°C in the region of β phase and then water-quenched (STQ). The quenched, metastable β phase was examined for TEM observation using a JEOL-TEM 2000FX. In addition, the microstructures of a Fe-N austenitic stainless steel (Fe-18Cr-19Mn-2Mo-0.8Si-0.9V-1N) and an Al-Mg-Cu alloy (Al-5.5Mg-0.3Cu) were also studied after solution treatment at 900°C and 550°C, respectively, followed by a water-quenching to room temperature. For a thin Fe-Cu steel (Fe-0.15C-1.5Mn-1.5Si-1.0Cu) sample of 0.8 mm thick, a solution treatment was first performed at 790˚C for 5 minutes, and annealing was followed in a salt bath at 500˚C for 20 minutes before TEM observation.

III. Results and Discussion

Modulated structure like tweed is built up in the process of solid solution and quenching, and locates in metastable state thermodynamically. The phase instability is resulted in solute supersaturation in matrix due to the restricted diffusion of solute atoms. Generally, this tweed pattern is indicative of some mesoscopic lattice deformation that anticipates the upcoming phase transition. And it is seen as a pretransitional effect in transmission electron microscopy of various materials, including shape memory alloys (NiAl, FePd, CuAu.) and high-temperature superconductors (V_3Si, Nb_3Sn), and undergoing phase separation such as steel during tempering treatments [1,2,3,4]. The typical feature of tweed in a shape memory alloy matrix was performed by Wayman [5,6]. The tweed of NiAl matrix is characterized by faint straight lines with about 10nm thickness formed at each layer boundary, and spot streaks and satellites located in the points of 1/3 and 2/3 between main spots in TEM diffraction patterns.

The crystal structures for a β-C Ti alloy formed at as quenched state were examined through electron microscope. Fig.1 shows the microstructures and selected area diffraction patterns of β-C. In the observation of optical microstructures, we could not detect any specified characterization of both martensitic shear and twin. However, the unusual structures of tweed were observed in TEM microstructures as shown in Fig.1. The microstructure of quenched β-C consists of striations of which average direction corresponds to the traces of <123> planes. The striation spacing is about 10-20nm similar with that of NiAl shape memory alloy undergone premartensitic transformation [1]. The diffuse scattering from quenched β-C has a number of features not directly related to the tweed structure. Fig.1(b) shows diffuse spots at displacements of 1/3 and 2/3 <123> from fundamental spots of bcc structure, and scattering lines not straightened. The crystal transformation in Ti-15-3 alloy exhibits also premartensitic phenomena such as streak and 1/3 spots in electron diffraction, and striations in microstructures. The microstructure also consists of striations directed to <123> and arranged with 10-20nm spacing. The diffuse spots were also seen at the positions of 1/3 and 2/3 <123> from fundamental spots of β bcc phase.

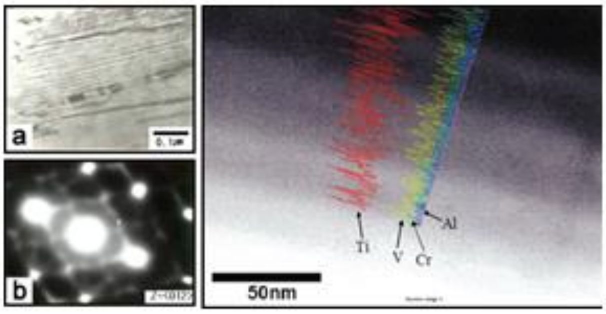

Fig.1 (A) Tweed Structure, (B) Diffraction Pattern Along <012>, And (C) TEM/EDS Analysis Showing Concentration Profiles Of Ti (Red), V (Yellow), Cr (Green) And Al (Blue) Across The Tweed Lines.

The crystal structures for Fe-N austenitic stainless steel, Fe-Cu steel and Al-Mg-Cu alloy formed were examined through electron microscope. Fig.2 and Fig.3 show the microstructures and selected area diffraction patterns of the three alloys.

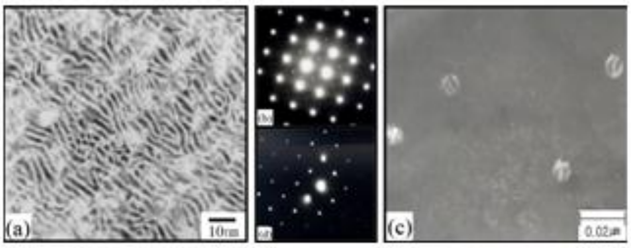

Fig.2 (A) & (B); A Modulated Structure And Its Ordered Diffraction Pattern Of Z=<001> In STQ State, And (C) & (D); Fcc E-Cu Precipitation And Diffraction In An Aged State

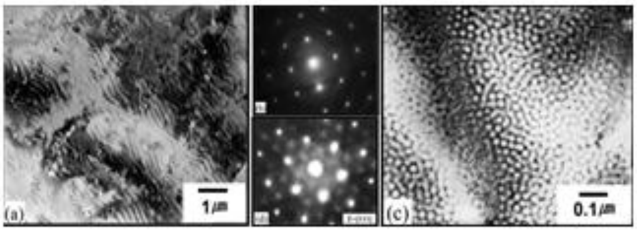

Fig.3 (A) & (B); A Modulated Structure And Its Ordered Diffraction Pattern Of Z=<001> In STQ State, And (C) & (D); Fcc E-Cu Precipitation And Diffraction In An Aged State

The formation of the superlattice reflections, which were found at 1/3 and 2/3 positions between two fundamental reflections is due to the superlattice structure formation of the parent cubic structure. The basic concept of this structure began with Peierls, who suggested that hypothetical one-dimensional metal could lower its energy by means of a distortion which changes the lattice periodicity [5,6]. The transformation is associated with coherent motion of atoms to produce lattice distortion of the original bcc lattice, and the necessary distortion produces ortho-hexagonal lattice from the bcc lattice. Kartha reported the simulation about tweed structure with a lattice distortion between square and rectangular (cubic and tetragonal), or between tetragonal and orthorhombic structure [4]. These configurations were generated by a Monte Carlo simulation based on the continuum elasticity model of a system undergoing a square to rectangular martensitic transformation, where transformation strain has been coupled to a dsordered composition field. It was found that the tweed pattern arises because the compositional disorder intrinsic to any conspires with the natural geometric constraints of lattice to produce a frustrated, glassy phase [4,7]. It was also reported that, in most cases, the appearance of tweed is concurrent with other anomalous phonon dispersion, that also appear in the vicinity of the martensite temperature upon cooling higher temperature, concluding that large amplitude vibrations were responsible for diffracted streaks characteristic contributed from tweed structures [7].

The model of charge density wave (CDW) can be also applied to the explanation for the premartensitic behaviors in beta-Ti alloys. A charge density wave (CDW) is a static modulation of the conduction electrons, which is a Fermi-surface-driven phenomenon usually accompanied by a periodic lattice distortion [5]. Fig.4 shows a commensurate charge density wave. A favorable Fermi surface geometry is required for the formation of a CDW. Depending upon the phenomenon that the period of CDW corresponds to triple of a lattice constant of the cubic parent phase, the 1/3 superlattice reflections seem to be interpreted by the CDW theory. This modulation wave vector with the k values of $\pi/3a$ and $2\pi/3a$ will modify the Fermi surface by creating energy gaps at such "nested" portions as shown in Fig.4 (c) [8].

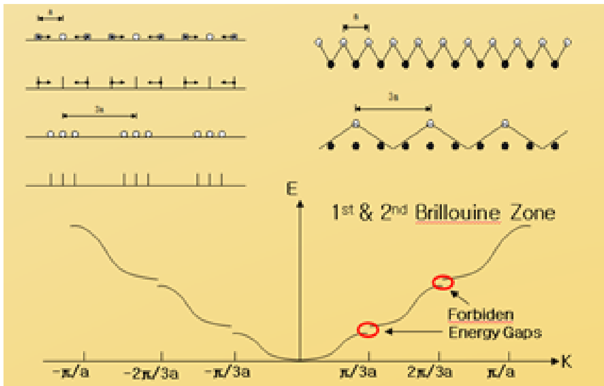

Fig.4 (A) Lattice Displacement Wave (LDW), (B) Charge Density Wave (CDW) And (C) Fermy Surface Creating Energy Gaps At 1st And 2nd Brillouine Zones.

If the nested portion of the Fermi surface is large enough, the energy gained by creating the energy gaps may overcome that lost to the lattice distortion. This means that the triple commensurate CDW may occur naturally and thermodynamically. A CDW accompanied by atomic displacements or a lattice distortion, which is a static displacement wave or condensed phonon mode, has been studied by diffraction techniques such as electron or X-ray diffraction [9]. Therefore this lattice distortion may affect the formation tweed structures, spot streaks and satellites of beta Ti alloys, inflicting diffraction streaks and XRD peak broadening. The diffraction broadening is caused by lattice vibration and softening, correlated to λ as vibration amount in real lattice space and k/Xλ as Fourier transition vector in reciprocal space [9].

IV. Conclusions

We described the electron microscopic investigation of an as-quenched β-C (Ti-3Al-8V-6Cr-4Mo-4Zr) of beta Ti alloy and Fe-N austenitic stainless steel, Fe-Cu steel and Al-Mg-Cu alloy. The commercially available alloys exhibited anomalies at in the as quenched state including tweed microstructures of thin layers, and extra spots and diffuse streaking in electron diffraction patterns. The mottled tweed microstructures and the extra spots in diffraction were interpreted as arising from transitional premartensitic phases intermediate between the parent beta phase and the martensite. The transformation is associated with coherent motion of atoms to produce lattice distortion of original bcc lattice. The premartensitic structure may results in fine precipitates during aging treatment, as offering multiple nucleation sites for aged precipitates at its highly distorted boundaries.

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References

[1] G. M. Michal, P. Moine and R. Sinclair, Acta Metallurgica, 30, 125 (1982).
http://dx.doi.org/10.1016/0001-6160(82)90052-9
[2] P. Moine, G. M. Michael, and R. Sinclair, Acta Metallurgica, 30, 109 (1982).
http://dx.doi.org/10.1016/0001-6160(82)90051-7
[3] Y. Yamada, Proc. Int. Conf. on Martensitic Transformations, Japan Inst. Metals, 89 (1986).
[4] S. Kartha, Physical Review B, 52 (1995) 803.
http://dx.doi.org/10.1103/PhysRevB.52.803
[5] I. M. Robertson and C. M. Wayman, Metallurgical Transactions A, 15A, 1353 (1984).
http://dx.doi.org/10.1007/BF02648564
[6] C. M. Hwang, M. Meichle, M. B. Salamon and C. M. Wayman, Res Mechanica, 10, 1 (1984).
[7] A. Silberstein and P.C. Clapp, Physical Review B, 38 (1988) 9555
http://dx.doi.org/10.1103/PhysRevB.38.9555
[8] A. Silberstein and P.C. Clapp, Physical Review B, 38 (1988) 9555.
http://dx.doi.org/10.1103/PhysRevB.38.9555
[9] K. Enami, T. Yoshida and S. Nenno, Proc. Int. Conf. on Martensitic Transformations, Japan Inst. Metals, 103 (1986).