The martensitic phase transformation in the ductile DyCu and YCu intermetallic compounds

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Abstract

DyCu and YCu are representatives of the family of CsCl-type B2 rare earth intermetallic compounds that exhibit high room temperature ductilit~~ies~~y. Phase transformation, structure, orientation relationship, and morphology of the martensites in the equiatomic compounds DyCu and YCu are examined using transmission electron microscopy (TEM). TEM studies show that the martensite structures in DyCu and YCu alloys are virtually identical. The martensite is of orthorhombic CrB-type B33 structure with lattice parameters $a = 0.38$ nm, $b = 1.22$ nm, and $c = 0.40$ nm. $(02\bar{1})$ twins were observed in the B33 DyCu and YCu martensites. The orientation relationship of B33 and B2 phases is $(11\bar{1})[112]B33 \parallel (110)[001]B2$. The simulated electron diffraction patterns of the B33 phase are consistent with ~~that~~ those of experimental observations. TEM investigations also reveal that an orthorhombic FeB-type B27 martensite with lattice parameters $a = 0.71$ nm, $b = 0.45$ nm, and $c = 0.54$ nm exists in YCu alloy. (101) twins were observed in the B27 YCu martensites.

The formation mechanism of B2 to B33~~,~~ and B27 phase transformation is discussed.

1. Introduction

Intermetallic compounds such as NiAl and FeAl are light in weight as compared with Ni and Fe-based alloys, possess excellent creep and oxidation resistance, high strength, and stiffness at elevated temperature making them potentially useful for high-temperature structural applications [1]. However, few practical uses have materialized for intermetallic compounds due to their low ductility and poor fracture toughness at room temperature. Almost all intermetallic compounds are inherently brittle [2]. There have been considerable efforts ~~for improving~~to improve the ~~room-~~room-temperature ductility of intermetallic compounds, but high ductility ~~was~~is usually observed only under ~~special~~fie conditions. The ~~room-~~room-temperature ductility of ~~the~~ polycrystalline NiAl ranges only from 0 to 2% elongation~~, which is due to~~; it possesses only three independent slip system~~s provided by~~for its <001> slip direction. The ductile-to-brittle transition temperature (DBTT) is about 673 K, at 873 K ~~the~~ polycrystalline NiAl has a plastic elongation of over 40% [3]. For CuZn compound~~,~~ the order-disorder transformation from ~~the~~ β′ to β occurs ~~at an experimental temperature of~~ around 730 K. The disordered β structure retained by quenching from high temperature is ductile, but the ordered β′ structure ~~becomes~~is quite brittle [4]. ~~The~~ Boron additions ~~of boron~~ (up to 0.4 wt.%) can increase the ductility of Al-poor (between 23 and 25 at.% Al) polycrystalline Ni₃Al with the fracture mode changing from intergranular to transgranular~~,~~. ~~while i~~In stoichiometric or Al-rich Ni₃Al~~,~~. ~~the~~ boron ~~is ineffective in improving the~~additions do not improve

2

ductility. ~~Auger analysis shows that the~~The intensity of boron segregation to grain boundaries increases and the concentration of grain-boundary ~~aluminum~~ Al decreases dramatically with decreasing bulk ~~aluminum~~ Al concentration, ~~detected by Auger analysis,~~ thereby ~~affects~~ affecting the grain-boundary cohesion [5,6]. Hydrogen-induced environmental embrittlement is considered ~~as a main reason for~~a major contributor to the low ductility of iron aluminides. Non-stoichiometric FeAl (36.5 at.% Al) shows 2.2% tensile elongation tested in air at room temperature but has 18% tensile elongation when tested in ~~a~~ dry ~~oxygen~~ O_2 [7].

A family of ductile B2 CsCl-type rare-earth intermetallic compounds, RM (R: rare earth, M: metals from groups 8-13), was discovered by Gschneidner et al. in 2003 [8]. At ambient temperature polycrystalline YAg and NdAg specimens elongate 27% and 18% [9,10]. The YCu and DyCu intermetallic compounds are nearly as ductile as YAg and NdYg with tensile elongation of 11-16%. Polycrystalline DyCu, YAg, and YCu have plane strain fracture toughness (K_{IC}) values of 26, 19, and 12 $MPa\sqrt{m}$, respectively~~, while~~. For comparison B2 NiAl ~~is~~ has a K_{IC} of only 6.4 $MPa\sqrt{m}$ [11]. RM intermetallics are line compounds, ~150 kinds are known to exist, and about two-thirds of those tested to date exhibit ~~extremely~~ ductility. The operative slip systems determined by slip trace measurements are {110}<001> and {100}<001> for YAg, YCu, YZn, and DyCu, and {110}<111> for YAg and DyCu [8,9,12,13]. {110}<001> and {100}<001> slips can ~~only~~ provide only three independent slip systems~~,~~; the operation of {110}<111> slip could provide the five independent slip systems required to meet the von Mises criterion for generalized plastic deformation

of a polycrystalline aggregate ~~and permit high ductility~~ [14].

Most intermetallic compounds show phase stability up to their melting temperature, deformation is mainly by the dislocation Burgers vectors of <001> type, which ~~precludes~~ seems inconsistent with their~~the room~~ room-temperature ductility [15]. ~~Concurrent~~ The ductility of RM intermetallics is thought to be attributable to concurrent dislocation slip and mechanical twinning or stress-induced martensitic transformation ~~will help to obtain high ductility in intermetallic compounds~~ [16]. Mechanical twinning ~~occurs~~ often occurs when dislocation slip ~~process~~ is restricted. Twinning ~~plays~~ can enhance ductility by reorienting regions in the crystal to~~an important role in crystallographic reorientation, and may place~~ raise the Schmid factor ~~for new~~ slip systems that had not been active during the early portion of plastic flow ~~in orientation that are favorable relative to the stress axis such that the slip can now take place~~ [17]. Metals such as hexagonal close-packed (hcp) Zr and Mg achieve high polycrystalline ductility by twinning to compensate for insufficient independent slip systems. {114} twinning results in large than 50% room temperature ductility in polycrystalline $Ti_{50}Ni_{47}Fe_3$ alloy having B2 structure [16]. The martensitic phase transformation of B2 to B19′ (monoclinic) via B19 (orthorhombic) or R (trigonal) phases has been observed in Ti-Ni-based alloys. The reversible martensitic phase transformation and the martensitic transformation twinning induced by ~~thermal~~ temperature changes or stress are responsible for their shape memory properties. Thermal expansion measurements of GdCu, TbCu, and YCu have shown~~ed~~ that martensitic structural transformation takes place at low temperature [18]. Neutron

diffraction indicated that B2 YCu undergoes a transformation at about 150 K, the martensite has a B27 FeB-type structure [19]. The martensitic transformation of B2 to orthorhombic B27 phase can also be induced by stress, and the increasing amount of B27 phase with decreasing temperature leads to a decrease in ductility [20,21].

~~The p~~Most ~~previous~~ ~~works~~ studies ~~of~~on RM intermetallic compounds have ~~been~~ focused on slip system~~s~~, ductility, and fracture toughness~~,~~; however, information about the phase stability, especially phase transformation of B2 to B33 CrB-type phase, remains ~~to be~~ limited. The present paper ~~is aimed at characterizing~~describes TEM observations and analysis of the B33 phase in DyCu and YCu intermetallic compounds ~~using TEM,~~with particular emphasis on the structure, orientation relationship, and morphology of the martensites. The implications of these findings are expected to be helpful in understanding the nature of the mechanical behavior of RM intermetallic compounds.

2. Experimental procedure

Polycrystalline DyCu and YCu alloys were made by arc melting equiatomic R and Cu in an ~~argon~~ Ar atmosphere. The nominal purity for the starting materials was 99.99 wt.% for Dy, 99.9 wt.% for Y, and 99.99 wt.% for Cu. The samples were turned over and remelted several times to achieve compositional homogeneity. DyCu single crystal was grown from the arc-melted DyCu ingot in a sealed Ta crucible by the Bridgman technique, as described more fully elsewhere ~~in reference~~[~~-~~9]. TEM specimens of both ~~alloys~~ compounds were prepared by cutting discs having diameters of 3 mm and thickness of ~0.2 mm using a diamond saw from the bulk samples.

These discs were then mechanically ground to a thickness of ~60 μm, followed by dimpling to a thickness of ~20 μm using a dimple grinder (VCR Dimpler). Attempts to perforate the discs ~~were proved impossible~~ by twin-jet electropolishing using an electrolyte failed due to ~~the~~ oxidation and corrosion reaction ~~easily in~~with the electrolyte~~solutions~~. The thin foils were perforated by Ar-ion milling using a Gatan dual ion mill 600 equipped with a liquid nitrogen cooling stage at 4.5 kV, 0.5 mA, and 15° incidence angle ~~equipped with a liquid nitrogen cooling stage~~. TEM bright field (BF) imaging and selected area electron diffraction (SAED) were performed on a Philips CM 30 electron microscope equipped with a LaB_6 cathode operated at an acceleration voltage of 300 kV and a Tecnai G2 electron microscope operated at an acceleration voltage of 200 kV with a double-tilt specimen holder. The chemical composition ~~on~~of martensites was examined by energy-dispersive X-ray spectroscopy (EDXS) on the Philips CM 30. Simulation of the electron diffraction patterns was carried out with ~~the~~ Desktop Microscopic software.

3. Results

3.1 B33 martensite in DyCu

Fig. 1a is a BF TEM image showing that ~~the~~ a lamellar phase formed in the as-grown DyCu ~~single~~ single-crystal specimen. Fig. 1b is the SAED pattern of region A in Fig. 1a along the [$1\bar{1}2$] zone axis. Indexing revealed a highly ordered bcc structure with lattice parameter $a = 0.35$ nm. Thus, it is concluded that A is B2 DyCu. ~~T~~Since the SAED pattern of ~~the~~ region B in Fig. 1a did not match the patterns of the known compounds in the Dy-Cu binary phase diagram such as $DyCu_2$, Dy_2Cu_7,

Dy_2Cu_9, $DyCu_5$, and $DyCu_7$. A series of SAED patterns were taken from a single plate by tilting the DyCu TEM specimen to determine the crystal structure of ~~the~~ phase B. According to patterns in Fig. 1c-h, we deduced that this phase has the orthorhombic CrB-type structure with lattice parameters $a = 0.38$ nm, $b = 1.22$ nm, and $c = 0.40$ nm. Fig. 1c-h are SAED patterns of the orthorhombic phase correspond to [100] (Fig. 1c), [201] (Fig. 1d), [203] (Fig. 1e), [102] (Fig. 1f), [710] (Fig. 1g), and [712] (Fig. 1h) zone axes, respectively. The observation of the ~~space~~ space group forbidden (001) reflection in Fig. 1c and g is due to the effect of dynamic double diffraction. The reflections of the type $h + k = 2n + 1$ are absent, indicating C-centering of the unit cell.

In the orientation where the SAED patterns (Fig. 1c-h) were taken, the electron diffraction patterns of the orthorhombic phase along the [310] and [5$\bar{1}$0] zone axis could not be obtained during continuous sample tilting due to ~~limitation by~~mechanical limitations of the TEM goniometer. The SAED patterns from another plate along different axes are shown in Fig. 2a-c. The SAED pattern in Fig. 2c is the same as that of Fig. 1c, which is the orthorhombic phase along the [100] zone axis. Fig. 2a and b are SAED patterns of the orthorhombic phase along the [310] and [5$\bar{1}$0] zone axes. The (001) reflection in Fig. 2a is still ~~exist~~present, however, it becomes weaker in Fig. 2b, which further demonstrates that the (001) reflection appears because of double diffraction. The space group of the orthorhombic phase is *Cmcm*. The general reflection conditions for CrB-type structure are *hkl: h + k = 2n; 0kl: k = 2n; h0l: h, l = 2n; hk0: h + k = 2n; h00: h = 2n; 0k0: k = 2n;* and *00l: l = 2n*. The SAED patterns

7

indexed in Fig. 1c-h and 2a-c are in agreement with the above reflection conditions. Fig. 2d is a [100](010) stereographic projection of the orthorhombic phase displaying the rotation directions of the DyCu specimen under TEM shown in Fig. 1c-h and Fig. 2a-c. Fig. 3a and b are EDX spectra of the B2 DyCu and orthorhombic phases showing that the orthorhombic phase consists of Dy and Cu, with an Dy:Cu ratio close to 1:1. Therefore, based on crystal structure, lattice constants, and chemical composition, the orthorhombic phase is CrB-type B33 DyCu.

Since there are strongly dynamic interactions between electrons and matter when samples ~~were~~ are examined under TEM, electron diffraction may provide ~~wrong signs for~~erroneous determination~~s of~~ the crystal structure. Therefore, the comparison between the calculated and experimental electron diffraction patterns could ~~give an indication of~~confirm the correctness of the proposed structure. Based on the CrB structure, we considered that B33 DyCu ~~have~~has four Dy atoms and four Cu atoms in the unit cell. The Dy atoms occupy the positions of (0, 0.146, 1/4), (0, 0.854, 3/4), (1/2, 0.646, 1/4) and (1/2, 0.354, 3/4), and those of Cu (0, 0.44, 1/4), (0, 0.56, 3/4), (1/2, 0.94, 1/4), and (1/2, 0.06, 3/4). Fig. 4 shows the simulated electron diffraction patterns of the CrB-type DyCu phase. The computer diffraction patterns of [100] (Fig. 4a), [201] (Fig. 4b), [203] (Fig. 4c), [102] (Fig. 4d), [710] (Fig. 4e), [310] (Fig. 4f), [5$\bar{1}$0] (Fig. 4g), and [712] (Fig. 4h) are displayed. The (001) spots in [100], [710], [310], and [5$\bar{1}$0] zone axes, and ($\bar{1}$02) spot in [201], ($\bar{3}$02) spot in [203], and ($\bar{2}$01) spot in [102] zone axes are systematic extinctions. The presence of the (001) and ($\bar{2}$01) reflections is the result of double diffraction in Figs. 1 and 2 in the experimental

8

observations. Nevertheless, the simulated electron diffraction patterns are in good agreement with the experimental observed patterns, which provides strong support for the proposed structure.

The superposition of the SAED patterns of the orthorhombic B33 DyCu phase along [100] zone axis and B2 DyCu phase along [401] zone axis (Fig. 5a) shows that the B33 and B2 DyCu have the orientation relationship of $(02\bar{1})[100]$B33 $\parallel$ $(010)[401]$B2. Fig. 5b and c are composite SAED patterns of the B33 and B2 phases from other areas showing the orientation relationships of $(11\bar{1})[101]$B33 $\parallel$ $(110)[11\bar{1}]$B2, and $(13\bar{2})[201]$B33 $\parallel$ $(120)[2\bar{1}1]$B2, respectively. The stereographic projection of the crystallographic orientation relationship of B2 $[401](010)$ and B33 $[100](02\bar{1})$ is shown in Fig. 6a and b. The angles of the crystal directions of $[2\bar{1}1]_{B2}/[401]_{B2}$, $[1\bar{1}1]_{B2}/[401]_{B2}$, $[201]_{B33}/[100]_{B33}$, $[101]_{B33}/[100]_{B33}$ are 26.9°, 45.6°, 27.8°, and 46.5°, respectively. The angles of the crystal planes of $(120)_{B2}/(010)_{B2}$, $(110)_{B2}/(010)_{B2}$, $(13\bar{2})_{B33}/(02\bar{1})_{B33}$, $(11\bar{1})_{B33}/(02\bar{1})_{B33}$ are 26.6°, 46°, 26.2°, and 46.9°, respectively. Therefore, the three orientation relationships of $(02\bar{1})[100]$B33 $\parallel$ $(010)[401]$B2, $(11\bar{1})[101]$B33 $\parallel$ $(110)[11\bar{1}]$B2, and $(13\bar{2})[201]$B33 $\parallel$ $(120)[2\bar{1}1]$B2 observed in Fig. 5 are almost equivalent. Besides, the angles of the crystal directions of $[001]_{B2}/[401]_{B2}$, and $[112]_{B33}/[100]_{B33}$ are 75.9°, and 75.4°, the orientation relationship between B33 and B2 phases could be described as $(11\bar{1})[112]$B33 $\parallel$ $(110)[001]$B2. We will show how the B33 structure forms from B2 lattice based on the above crystallographic orientation relationship, slip systems and dislocation structure [12] later in the Discussion section.

Fig. 7a is a BF TEM image showing that ~~a~~ Vvee-shaped morphology was observed (in the upper right portion of that image?   I'm not sure I'm looking at the right region. AR). Fig. 7b is a SAED pattern from region C. Indexing indicated that it is B2 structure along the [10$\bar{2}$] zone axis~~,~~; again the region marked C ~~has been~~ prove~~d~~s to be B2 DyCu. The SAED patterns of the ~~plates~~ regions marked as D and E are shown in Fig. 7c and d. Careful~~ly~~ indexing reveals that ~~plates~~ regions D and E are B33 DyCu phase along [$\bar{1}$12] and [1$\bar{1}\bar{2}$] zone axes, respectively. Fig. 7e is a composite of SAED patterns taken from the interface between C and D in Fig. 7a. The electron diffraction reveals that the orientation relationship of the B33 with B2 DyCu is (02$\bar{1}$)[$\bar{1}$12]B33 ‖ (010)[10$\bar{2}$]B2. This orientation relationship is equivalent to (11$\bar{1}$)[112]B33 ‖ (110)[001]B2. Fig. 7f ~~is~~ shows ~~SEAD~~ SAED patterns taken at the interface between D and E regions in Fig. 7a. The double diffraction patterns in Fig. 7f indicate that the B33 crystal is ~~exhibits~~ twin~~ning~~ned. The twins have a (02$\bar{1}$) plane and are related by a 180° rotation. No internal twinning was observed in the B33 plates. The plates shown in Fig. 7a indicate that the plates are in the edge-on orientation according to the double diffraction in Fig. 7f.

Fig. 8a is a BF TEM image showing that the grain size of the polycrystalline DyCu specimen was smaller than 500 nm. The SAED pattern in Fig. 8b from one of the DyCu grains along the [001] zone axis indicated that polycrystalline DyCu is still a high~~ly~~ ordered structure with lattice parameter a = 0.35 nm. Careful inspection reveals the presence of plate structure in the polycrystalline DyCu specimen as shown in Fig. 8c. Fig. 8d ~~is~~ shows the composite patterns of the plate and the B2 DyCu

matrix illustrating that the plate is CrB-type B33 DyCu along [101] zone axis~~, and the~~ ~~with an~~ orientation relationship of $(11\bar{1})[101]$B33 $\parallel$ $(110)[11\bar{1}]$B2.

3.2 _B27 and B33 martensites in YCu

~~A~~ Fig. 9a shows a BF TEM image of the microstructure of the polycrystalline YCu specimen revealing that bands or platelets ~~appeared is shown in Fig. 9a~~are present. Both the B2 YCu matrix (region marked F) and the bands were identified by the SAED patterns. Fig. 9b is the SAED pattern of the B2 YCu (region F) along [001] zone axis, which indicates an ordered B2 structure with lattice parameter $a = 0.35$ nm. The SAED pattern from ~~a~~ one of the band~~s~~ is shown in Fig. 9c~~,~~; indexing indicates that the bands ~~has~~ have an orthorhombic FeB-type B27 structure with lattice parameters $a = 0.71$ nm, $b = 0.45$ nm, and $c = 0.54$ nm. The observed bands are twin-related ~~of~~ to the orthorhombic phase. A twinning plane coincides with the observed (101) plane of the orthorhombic FeB-type lattice. This ~~can be~~is supported by the composite~~s~~ SAED patterns shown in Fig. 9d.

Fig. 10a is a BF TEM image showing that plates having similar morphology as in Fig. 7a occur in polycrystalline YCu ~~specimen~~. The SAED patterns of the plate and B2 YCu are shown in Fig. 10b and c, respectively. Indexing reveals that the plate also has an orthorhombic CrB-type B33 structure with lattice parameters $a = 0.38$ nm, $b = 1.22$ nm, and $c = 0.40$ nm. Therefore, similar B33 martensite forms in YCu alloy. The composite SAED patterns of the B33 and B2 phases in Fig. 10d ~~showing~~ have the orientation relationship ~~of~~ $(11\bar{1})[101]$B33 $\parallel$ $(110)[11\bar{1}]$B2.

4. Discussion

11

~~Alternative~~ In addition to the~~to~~ dislocation slip <u>occurring during</u> ~~modes of~~ plastic deformation<u>,</u> there ~~could~~ <u>can also</u> be mechanical twinning and stress-induced martensitic phase transformation [22]. Twinning can re-orient portions of a grain to facilitate further dislocation motion, thereby compensating <u>for</u> inadequate numbers of independent slip systems [17,23]. Moberly et al. reported that {114} twinning in polycrystalline B2 $Ti_{50}Ni_{47}Fe_3$ alloy results in <u>more</u>~~large~~ than 50% ~~room-~~<u>room-</u>temperature ductility [16]. TEM examination indicated no evidence of twinning in B2 structured DyCu and YCu. In the present research the TEM studies reveal that B27 FeB-type martensite forms in YCu alloy, and B33 CrB-type martensites form in YCu and DyCu alloys. No B27 FeB-type phase was observed in DyCu alloy. First-principle calculations have been used to examine the phase stability in YCu and demonstrated that YCu exhibited little energy differences between the B2 and B27 phases. The energy of B27 structure is lower than that of B2 structure, by an amount of 0.038 eV per formula unit, thus the formation of B27 YCu is thermodynamically favorable [21]. The lattice parameters of the B27 YCu martensite determined from SAED patterns are in good agreement with that measured by neutron diffraction by Ritter et al. [19] and X-ray diffraction by Oertel et al. [20]. The martensitic transformation temperature of B2 YCu to B27 YCu begins at about 150 K, and the reverse transformation at about 500 K [18]. The ductility of YCu is lowered with the increasing amount of B27 phase. A drastic decrease in ductility sets in at about 160 K when a massive thermally induced transformation starts, which corresponds to <u>the</u> DBTT [20].

The B33 martensites are relevant to many shape memory B2 compounds with significant ductilities [24]. TEM investigation indicated that the CrB-type B33 martensites form in $Zr_{50}Pd_{35}Ru_{15}$ alloy, the lattice parameters of the B33 phase are $a = 0.33$ nm, $b = 1.02$ nm, and $c = 0.45$ nm. SAED patterns revealed that the orientation relationship between B33 and B2 phases is $(100)[010]B33 \parallel (010)[101]B2$. Mechanical twinning of {114}-type observed in B2 structure, <100>-type slip, and martensitic phase transformation were found to be responsible for the enhanced room temperature ductility of 6.6% elongation in the B2 structured $Zr_{50}Pd_{35}Ru_{15}$ alloy [22,25]. In $Zr_{50}Co_{39}Ni_{11}$ alloy the lenticular B33 martensites having lattice parameters $a = 0.33$ nm, $b = 0.97$ nm, and $c = 0.42$ nm were observed together with the B2 parent phases. The orientation relationship between the B33 martensite and B2 parent phase is determined to be $(021)[100]B33 \parallel (010)[001]B2$. (021) twins exist in the lenticular B33 martensites [26]. In the present investigation the $(11\bar{1})[112]B33 \parallel (110)[001]B2$ orientation relationship was observed indicating that the B33 martensites might form on the {110} B2 planes along the <001> direction by shuffle. The orientation relationship between B33 and B2 phases discussed above is analyzed by the coincidence site lattice model [27], we may suppose that two lattices of B33 phase in [112] direction of B33 are superimposed on one lattice of B2 phase in [001] direction of B2. The lattice mismatch along this orientation is $\delta = (2d(112)B33-d(001)B2)/d(001)B2,$ and which is about 1.2%. The results show that smaller lattice mismatches suggesting would be consistent withthe low internal stress between B33 and B2 phases.

The previous worksPrevious research has have shown that the dominate dominant slip systems in RM intermetallic compounds are {110}<001> and {100}<001>. The {110}<111> slip was also found to be active in DyCu, YAg, and YCu [8-13]. Based on the criterion of von Mises for generalized plastic deformation of a polycrystalline aggregate, the <001> dislocation slip can only provide onlys three independent slip systems, and the operation of <111> dislocations will satisfy the necessary von Mises requirement of five independent slip systems [14]. TEM observation indicated that the <001>-type dislocations were considerably more common than that of <111>-type dislocations. The observation of <001>-type dislocations is consistent with the Ab ab initio calculation that the unstable stacking fault energies for <001> slip on both {110} and {100} planes are quite small [21]. François et al. [15] showed that B2 to B33 transformation requires no macroscopic shear, but can occur by stacking faults. Ab initio calculations demonstrated that the energy differences between B2, B27, and B33 phases are quite small in YCu and DyCu showing that the B33 and B27 phases are competitive with the B2 structure. Instead of shearing {110} planes along the <001> directions, pairs of {110} planes are shifted in alternating <001> directions, the B33 phase is thus formed [24]. The martensitic phase transformations may dissipate the energy near a tip and play an important role in deformation properties of DyCu and YCu intermetallic compounds. Since the DyCu and YCu TEM foils were milled on a cooling with stage cooled by liquid nitrogen, we are not sureone cannot be certain to what extent that the martensitic transformation observed is was induced by stress or by low

temperature~~thermally induced to which extend~~ [23].

5. Conclusions

TEM investigations of DyCu and YCu intermetallic compounds have shown that phase transformation of B2 to B33 ~~take place~~occurs in both DyCu and YCu, and B2 to B27 transformation occurs in YCu. The CrB-type B33 martensites formed in DyCu and YCu have similar orthorhombic crystal structures with lattice parameters of $a = 0.38$ nm, $b = 1.22$ nm, and $c = 0.40$ nm. $(02\bar{1})$ twinning was observed in the B33 martensites. The B33 martensite has an orientation relationship $(11\bar{1})[112]$B33 $||(110)[001]$B2 with the B2 phase. The simulated electron diffraction patterns of the B33 phase are in accordance with that of experimental observations demonstrating the accuracy of the crystal structure determination. TEM analyses showed the presence of FeB-type orthorhombic B27 YCu martensites in YCu alloy with lattice parameters $a = 0.71$ nm, $b = 0.45$ nm, and $c = 0.54$ nm. In B27 martensites (101) twins exist. The phase transformation of B2 to B33 might be viewed as pairs of $\{110\}$ planes ~~are~~ shifted in alternating $<001>$ directions. The present research provides a direct approach for examining the stability of DyCu and YCu intermetallic compounds.

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17

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Figure captions

Fig. 1. BF TEM image (a) showing lamellar phase in single crystal DyCu specimen, SAED patterns of (b) the B2 DyCu (region marked A) along $[1\bar{1}2]$ zone axis, and B33 CrB-type DyCu (region marked B) along the (c) [100], (d) [201], (e) [203], (f) [102], (g) [710], and (h) [712] zone axes.

Fig. 2. SAED patterns of the B33 DyCu along the (a) [310], (b) $[5\bar{1}0]$, and (c) [100] zone axes in single crystal DyCu specimen, and (d) [100](010) stereographic projection of the B33 phase showing the rotation route under TEM.

Fig. 3. EDX spectra of (a) the B2 and (b) B33 DyCu phases in single crystal DyCu specimen.

Fig. 4. Simulated electron diffraction patterns of the B33 phase along the (a) [100], (b) [201], (c) [203], (d) [102], (e) [710], (f) [310], (g) $[5\bar{1}0]$, and (h) [712] zone axes.

Fig. 5. Composite SAED patterns of the B33 and B2 DyCu phases in single crystal DyCu specimen showing the orientation relationships (a) $(02\bar{1})[100]$B33 ∥ (010)[401]B2, (b) $(11\bar{1})[101]$B33 ∥ $(110)[11\bar{1}]$B2, and (c) $(13\bar{2})[201]$B33 ∥ $(120)[2\bar{1}1]$B2.

Fig. 6. Stereographic projection of (a) B2 [401](010), and (b) B33 $[100](02\bar{1})$, large circles represent crystal direction indices and smaller circles represent crystal plane indices.

Fig.7. BF TEM image (a) showing the V-shaped B33 DyCu martensites in single crystal DyCu specimen, SAED patterns of (b) the B2 DyCu (region marked C) along $[10\bar{2}]$ zone axis, the B33 martensites along the (c) $[\bar{1}12]$ (region marked D), (d) $[1\bar{1}\bar{2}]$ (region marked E) zone axes, (e) the B2 and B33 DyCu showing the orientation

relationship of $(02\bar{1})[\bar{1}12]$B33 ∥ $(010)[10\bar{2}]$B2, and (f) composite electron diffraction showing $(02\bar{1})$ twinning.

Fig. 8. BF TEM images showing (a) the grain size, and (c) the B33 martensites in polycrystalline DyCu specimen, SAED patterns of (b) the B2 DyCu along [001] zone axis, and (d) the B2 and B33 DyCu showing the orientation relationship of $(11\bar{1})[101]$B33 ∥ $(110)[11\bar{1}]$B2.

Fig. 9. BF TEM image (a) showing the bands (B27 FeB-type YCu) in polycrystalline YCu specimen, SAED patterns of (b) the B2 YCu (region marked F) along the [001] zone axis, (c) B27 YCu along the $[0\bar{1}1]$ zone axis, and (d) composite electron diffraction showing (111) twinning in B27 YCu.

Fig. 10. BF TEM image (a) showing lamellar B33 CrB-type YCu in polycrystalline YCu specimen, SAED patterns of (b) the B2 YCu along the $[11\bar{1}]$ zone axis, (c) B33 YCu along the [101] zone axis, and (d) the B2 and B33 YCu showing the orientation relationship of $(11\bar{1})[101]$B33 ∥ $(110)[11\bar{1}]$B2.