

DIRECTIONAL SOLIDIFICATION OF TiAl ALLOYS WITH HIGH Nb CONCENTRATIONS FOR ALIGNING LAMELLAR MICROSTRUCTURES

Haruyuki Inui¹, Yuji Omiya¹ and David R. Johnson²

¹Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501,
Japan

²School Materials Engineering, Purdue University, 1289 MSEE Building, West Lafayette,
IN 47907-1289, U. S. A.

Keywords: TiAl, Lamellar structure, Directional solidification, Seeding, Creep strength

Abstract

The TiAl/Ti₃Al lamellar structure of TiAl alloys with high Nb concentrations (up to 8 at.% Nb additions) has been successfully aligned parallel to the growth direction through directional solidification by using an appropriately oriented seed from the TiAl-Si system (Ti-43Al-3Si) on the basis of the recently proposed method to predict the appropriate alloy compositions with the concept of 'Al-equivalent'. The value of Al-equivalent for Nb is found to be constant up to 3 at.%Nb but is variable depending on the amount of addition above 3 at.%Nb because of a curvature of the α/β primary phase boundary in the Ti-Al-Nb system. These DS ingots with the lamellar structure all aligned parallel to the loading axis exhibit a very nice balance of mechanical properties such as yield strength, tensile ductility and creep properties, leading to a possibility of alloy design of high property level.

Introduction

Two-phase TiAl (γ) alloys with the lamellar structure have attracted considerable interest as a new-class of light-weight high-temperature structural material [1-4]. Using the so-called PST (polysynthetically twinned) crystals in which only a single lamellar grain is contained, we have demonstrated that the lamellar structure exhibits significant anisotropy in strength and ductility; these mechanical properties strongly depend on the lamellar orientation with respect to the loading axis [5,6] The most significant implication from the studies on PST crystals is that the best balance of these mechanical properties is obtained when the lamellar boundaries are parallel to the loading axis [6]. In this case, tensile yield strength greater than 400 MPa and tensile elongation greater than 10 % are usually obtained. In order to take the advantage of this plastic anisotropy of the lamellar structure, we have proposed directional solidification (DS) processes by which the lamellar orientation is controlled to align parallel to the growth direction [7-9]. Since the lamellar structure forms from the α (disordered h.c.p.) phase upon cooling with the Blackburn orientation relationship of $(0001)_{\alpha} // (111)_{\gamma}$ and $\langle 1120 \rangle_{\alpha} // \langle 110 \rangle_{\gamma}$, control of the lamellar orientation can be achieved by controlling the orientation of the α phase. The orientation of the α phase can be controlled during solidification by using a seed from the TiAl-Si system. In the TiAl-Si system at a composition of Ti-43Al-3Si (all compositions are given in atomic percent), the α phase is the primary solidification phase and the original

orientation of the lamellar structure can be maintained after heating to and cooling from the α single-phase region, making seeding of the α phase possible. The lamellar orientation for ingots of Ti-43Al-3Si can easily be aligned by directional solidification when using an appropriately oriented seed [7]. However, it is still possible to use this material for seeding alloys of different compositions even though the β (disordered b.c.c.) phase is the primary solidification phase as exemplified for binary alloys with compositions ranging from Ti-46~48Al [8,9]. Based on these results, we have proposed a way to predict alloy compositions appropriate for aligning the lamellar microstructure of DS ingots with a seed material of Ti-43Al-3Si, introducing the concept of 'Al-equivalent' [10], as summarized in the next section. We have further extended this method to cover alloying elements with a high solid-solubility such as Nb and Ta [11,12], which are believed to be beneficial to improving creep and oxidation properties once large amounts are added [2].

Here, we first review the prediction method of alloy compositions appropriate for aligning the lamellar structure and then describe how the method can be extended to alloying elements of high solubility. After showing the DS experimental results that verify the validity of the prediction method, we show the mechanical properties as well as the oxidation resistance of TiAl DS ingots with high Nb as well as high Ta concentrations.

DS Seeding Technique for Aligning the Lamellar Structure of TiAl Alloys

Appropriate Alloy Compositions

It is possible to align the lamellar microstructure by the DS seeding technique if the continuous growth of the α phase on top of the Ti-43Al-3Si alloy seed crystal is allowed. This can occur if the alloy composition is close to the boundary that separates the α primary-solidification region from the β primary-solidification one but is a little smaller in Al concentration than the boundary composition, as aligning the lamellar microstructure is successful for binary alloys in the composition range of Ti-46~48Al [9]. Our preliminary results of evaluation indicate that under quasi-steady state growth condition, there is a sufficiently large driving force for the α phase to nucleate at the solidification front for Ti-47Al (β -primary) whereas the driving force for nucleation for the γ phase is comparable to or a little higher than that for the α phase for Ti-49Al (α -primary). This indicates that the continuous growth of the α phase can occur during solidification for Ti-47Al even the primary solidification phase is β but that for Ti-49Al in which the primary solidification phase is α , accidental nucleation of the γ phase disturbs the continuous growth of the α phase, resulting in unsuccessful alignment of the lamellar structure. For Ti-45Al, nucleation of the β phase with by far a larger driving force evidently disturbs the continuous growth of the α phase.

Then, we can predict compositions of multi-component TiAl alloys that are appropriate for aligning the lamellar structure by the DS seeding technique through evaluating the shift of the α/β primary-solidification phase boundary upon alloying with respect to the corresponding composition in the binary system so that the continuous growth of the α phase is allowed. The shift can quantitatively be evaluated by introducing the concept of 'Al-equivalent' that corresponds to the extent of the shift of the boundary in Al concentration per 1 at.% addition of alloying element (Figs. 1(a) and (b)). The value of Al-equivalent is either negative or positive depending on whether alloying element of concern is α - or β -stabilizer, respectively. The method of experimental determination for 'Al-equivalent' will be described in the next section. Once values of Al-equivalents

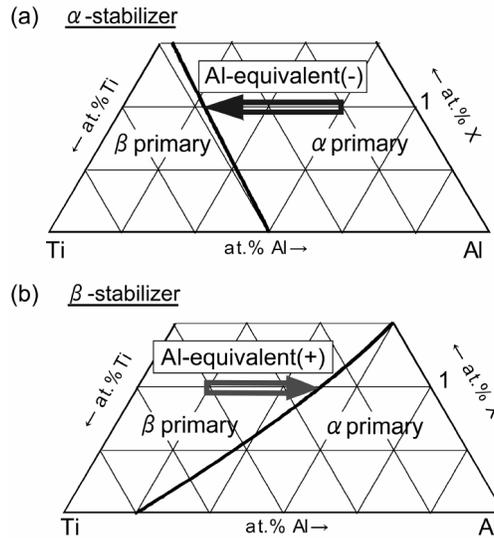


Fig. 1. Definition of Al-equivalent for alloying elements of (a) α -stabilizer and (b) β -stabilizer.

for alloying elements of concern are determined, alloy compositions (Al concentration: c_{Al}) appropriate for aligning the lamellar structure upon alloying can be calculated based on the following equation,

$$c_{Al} = 47 + aX_{eq} + bY_{eq} + cZ_{eq} + \dots, \quad (1)$$

where a, b, c stand for the amount of alloying of X, Y, Z elements, respectively and X_{eq} , Y_{eq} , Z_{eq} stand for ‘Al-equivalent’ of alloying elements X, Y, Z, respectively. In equation (1), the composition of Ti-47Al is taken as the standard composition since the seeding technique is successful for the composition range of Ti-46~48Al. In this equation, we assume that linear combination of the product of the amount of addition and the Al-equivalent for each alloying element is valid. This may be true even alloying elements of high solubility are included, since the value of Al-equivalent for a particular alloying element may not vary significantly in the existence of other alloying elements because the interaction between alloying elements may be sufficiently small in the melt of TiAl.

Al-equivalents for Alloying Elements

The primary solidification phase (either α or β) can be determined by examining the symmetry (either six- or four-fold, respectively) of primary dendrites in arc-melted ingots. The result of determination of the general shape of the liquidus surface near the Ti-50Al region of the Ti-Al-Nb and Ti-Al-Ta systems are shown in Figs. 2(a)-(c), where compositions for α and β primaries are plotted as closed and open circles, respectively. Although inspection up to the range of 2~3 at.% is enough for most alloying elements (such as Mo, W and Re) with a small solid-solubility, the Ti-Al-Nb and Ti-Al-Ta systems need inspection up to large amount of additions (near 10 at.%) because of their large solubility. For the former case, a straight line can be drawn to separate the α/β primary phase boundary and the inclination of the line correspond to the value of ‘Al-equivalent’, which can be used in the whole composition range for these alloying elements. The values thus determined are tabulated in Table 1. For Ta, the α/β primary boundary is fortunately almost straight up to the highest alloying level investigated. Thus the value of ‘Al-equivalent’ for Ta can be determined to be a constant value +0.35 up to 8 at.%Ta from the inclination of the α/β primary boundary. In contrast, the α/β primary boundary for the Ti-Al-Nb system has a curvature at a low concentration around 3 at.%Nb. Since the Al-

equivalent is defined as the gradient made by a straight line between the composition point of concern on the α/β primary boundary line and the corresponding point for the binary system, the Al-equivalent for Nb varies with the amount of additions. The value of Al-equivalent for Nb is +0.3 up to 3 at.%Nb but the values above 3 at.%Nb should be evaluated from the curve of Fig. 2(b), for example, +0.25 and +0.15 for 5 and 8 at.%Nb . Then, we can predict alloys compositions that may be appropriate for aligning the lamellar structure even for alloys containing large amounts of Nb and Ta with the use of the determined values of Al equivalent.

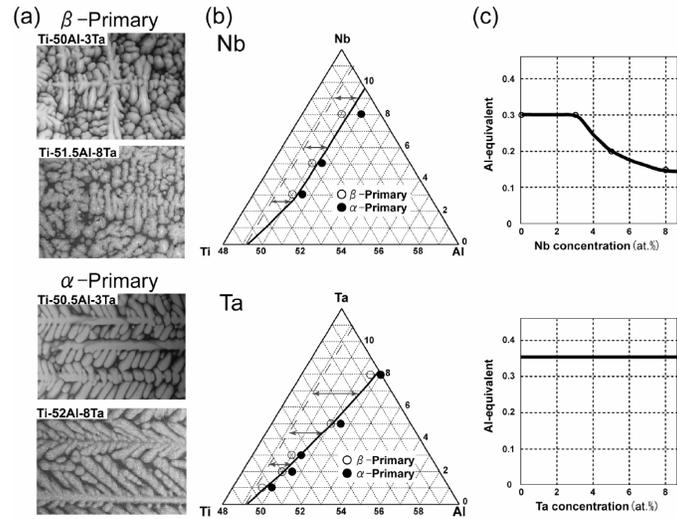


Fig. 2. (a) Microstructures of alloys from the Ti-Al-Ta system showing four- and six-fold symmetry of primary dendrites. (b) projected view of a partial liquidus surface from the Ti-Al-Nb and Ti-Al-Ta systems showing the primary α (closed circles) and β (open circles) regions. (c) Al equivalents for Nb and Ta deduced from (b) [11,12].

DS-processing to Check the Validity of the Prediction Method

Nominal alloy compositions at which aligning the lamellar microstructure by the DS seeding technique was tested are listed in Table 2. The Al concentrations calculated based on equation (1) as well as the difference between the actual (nominal) and calculated Al concentrations are listed as well. The differences in the Al concentrations in most cases are as small as less than 0.2 at.%Al and aligning the lamellar structure by the DS seeding technique is thus successful for all these ingots, as an example of microstructure of successfully produced DS ingots is shown in Fig. 3 for a Ti-46.5Al-0.5Si-3 Nb alloy [11]. In contrast, we failed to align the lamellar structure of, for example, Ti-49Al-7Nb alloys, whose composition deviates by a large amount (0.84 at.%Al) from the calculated appropriate Al composition. All these indicate the validity of our method to predict appropriate alloy compositions for aligning the lamellar microstructure by the DS seeding technique even for alloys containing alloying elements of large solubility in TiAl.

Table 1: Values of Al equivalent for various alloying elements [11,12]

element	α -stabilizer		β -stabilizer						
	C	Si	Cr	V	Nb	Ta	Mo	Re	W
Al-equivalent	-4.2	-2.8	+0.1	+0.3	+0.3	+0.3	+0.6	+0.8	+1.0

Table. 2: Nominal alloy compositions at which aligning the lamellar microstructure by the DS seeding technique were tested. The Al concentrations calculated based on eq. (1) as well as the difference between the actual (nominal) and calculated Al concentrations are listed as well. The symbols \circ and \times in the last column indicate ‘success’ and ‘failure’ in aligning the lamellar structure, respectively [11].

Composition	Calculation	Calculated Al-concentration	Difference	Result
Ti-46.5Al-0.5Si-3.0Ta	$47+(-2.8) \times 0.5+0.35 \times 3.0$	46.65	-0.15	\circ
Ti-46.5Al-0.5Si-3.0Nb	$47+(-2.8) \times 0.5+0.3 \times 3.0$	46.5	0	\circ
Ti-46.6Al-0.5Si-5.0Nb	$47+(-2.8) \times 0.5+0.2 \times 5.0$	46.6	0	\circ
Ti-47.5Al-0.5Si-6.0Nb-2.0Ta	$47+(-2.8) \times 0.5+0.184 \times 6+0.35 \times 2.0$	47.4	0.1	\circ
Ti-48.0Al-8.0Nb	$47+0.15 \times 8.0$	48.2	-0.2	\circ
Ti-49.0Al-7.0Nb	$47+0.166 \times 7.0$	48.16	0.84	\times

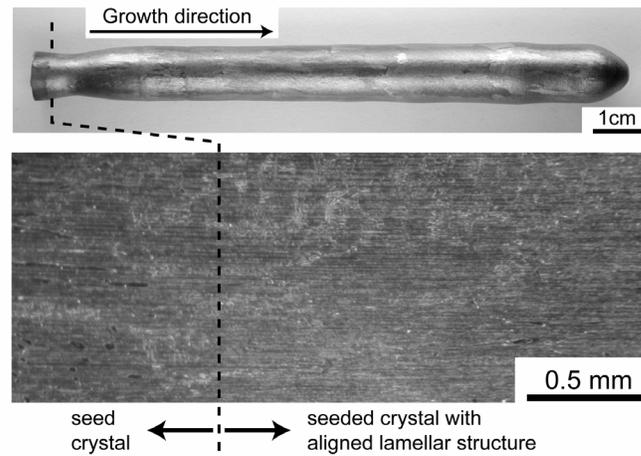


Fig. 3: (a) Microstructure of the seeded and directionally-solidified Ti-46.5Al-0.5Si-3Nb ingot showing the aligned lamellar structure parallel to the growth direction [11,12].

Mechanical Properties of DS Ingots with Aligned Lamellar Structures

Creep and Oxidation Properties

Tensile creep curves obtained at 750°C under a constant load of 240 MPa are shown in Fig. 4 for the seeded and directionally-solidified Ti-46Al-0.5Si-3Ta, Ti-46Al-0.5Si-3Nb and Ti-46Al-0.5Si-8Nb ingots with the tensile axis parallel to the growth direction. Tensile creep curves obtained for the directionally-solidified Ti-47Al and Ti-46.5Al-0.5Si alloys under the same creep conditions [10] are also shown in Fig. 4 for comparison. The creep strain rate for the Ti-46.5Al-0.5Si alloy is significantly reduced (by an order of magnitude) when compared to that

for the binary Ti-47Al alloy, indicating that small amounts of Si additions are beneficial to improvement in creep strength. All the quaternary alloys exhibit by far better creep properties than the binary Ti-47Al and Ti-46.5Al-0.5Si alloys, when their creep strain rates are compared. The creep strain rate for the Ti-46.5Al-0.5Si-3Ta alloy is lower than that for the Ti-46.5Al-0.5Si-3Nb alloy, indicating that Ta is more effective than Nb in improving the creep strength of TiAl alloys. However, when the amount of Nb additions is increased from 3 to 8 at.%, the creep strain rate is further decreased (by half an order of magnitude). Of importance to note here is that upon alloying with such a large amount of Nb additions, the oxidation resistance is significantly improved; while the oxide scale noted on the Ti-46.5Al-0.5Si-3Nb after the creep test is yellow in color as the Ti-47Al alloy with some evidence of spallation, that of the Ti-48Al-0.5Si-8Nb alloy is dark in color without any evidence of spallation, as shown in Fig. 5. Thus, large amounts of Nb additions are beneficial to simultaneously improving creep strength and oxidation resistance.

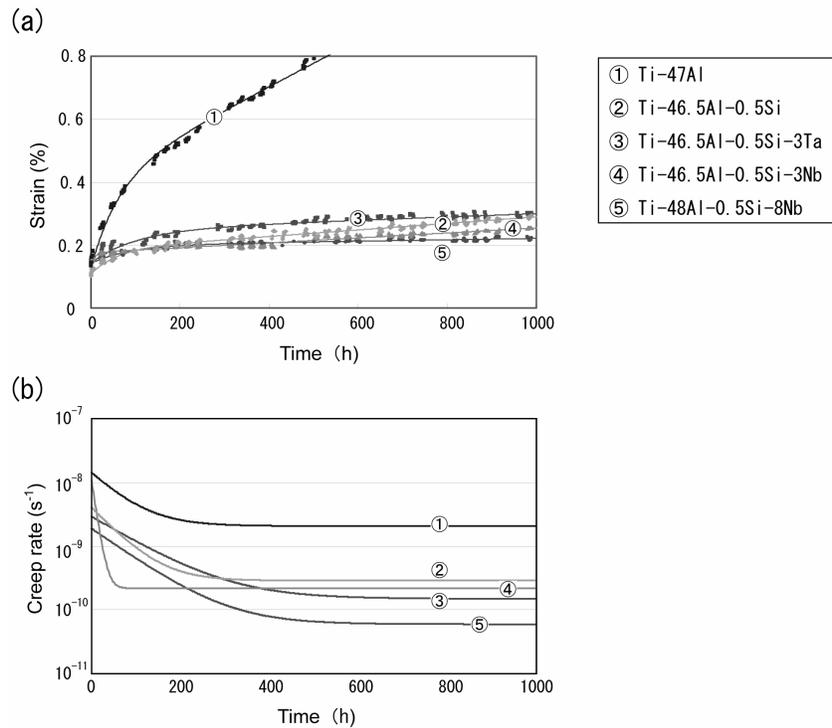


Fig. 4: Tensile creep curves obtained at 750°C under a constant load of 240 MPa for the seeded and directionally-solidified TiAl ingots with the loading axis parallel to the growth direction [11,12].

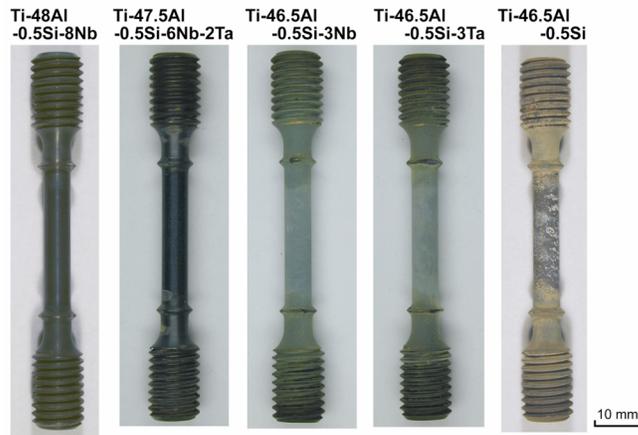


Fig. 5: Appearance of TiAl ingots after a creep test 750°C for 1000 h.

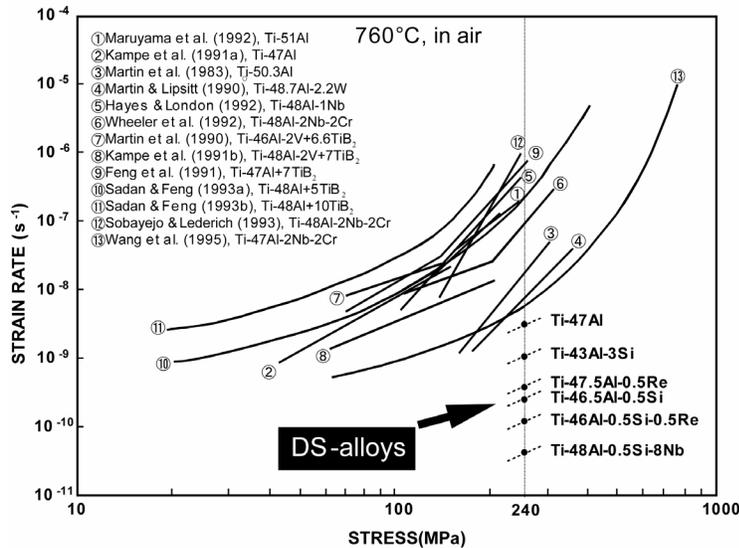


Fig. 6: Summary of creep strain rate at 750°C for our DS TiAl ingots and conventionally processed TiAl alloys [13,14].

Fig. 6 compares the creep strain rates at 750°C of our TiAl DS ingots with the lamellar structure aligned parallel to the tensile axis with those of TiAl alloys produced by conventional (ingot metallurgy and powder metallurgy) methods summarized in refs. [13] and [14]. The creep strain rates for DS TiAl ingots are significantly smaller than those for conventional TiAl alloys, indicating the advantage of DS processing in improving creep strength. The creep rates for these DS TiAl alloys can be further improved by alloying so that the creep rate achieved by the DS Ti-48Al-0.5Si-8Nb alloy is two orders of magnitude lower than the best value of conventionally processed TiAl alloys.

Balanced Mechanical Properties

All these DS ingots of TiAl alloys containing Nb and Ta usually exhibit room temperature yield strength greater than 500 MPa, tensile elongation greater than 10% and creep strain rate

smaller than 10^{-9} s^{-1} at 750°C at 240 MPa. Since they show such nice balanced mechanical properties and oxidation resistance can be given to these alloys by adding a large amount of Nb with keeping the lamellar structure all aligned parallel to the loading axis, DS processing can provide a way of making alloy design of high property levels, which cannot be achieved by conventional processing routes.

Conclusions

- (1) Alignment of the lamellar structure of two-phase TiAl alloys is possible by directional solidification using an appropriate seed crystal (Ti-43Al-3Si) for appropriate alloy compositions that can be predicted with the concept of 'Al-equivalent'. This can be extended to TiAl alloys with high Nb and Ta concentrations (up to 8-10 at.%) by evaluating the value of Al-equivalent for these elements of high concentrations.
-
- (2) The value of Al-equivalent for Ta is constant (+0.35) up to 8 at.%Ta, since the α/β primary phase boundary is almost straight up to the highest alloying level investigated. On the other hand, the α/β primary phase boundary for the Ti-Al-Nb system has a curvature at a low concentration around 3 at.%Nb. Thus, while the value of Al-equivalent is +0.3 up to 3 at.%Nb, it varies with Nb content above 3 at.%Nb. For example, it is +0.25 for 5 at.%Nb and +0.15 for 8 at.%Nb .
- (3) The seeded and directionally solidified TiAl alloys with lamellar structures aligned parallel to the growth direction exhibit improved creep resistance when compared to conventionally processed TiAl alloys. In particular, the creep rates for these DS TiAl alloys can be further improved by alloying so that the creep rate achieved by the DS Ti-48Al-0.5Si-8Nb alloy is by two orders of magnitude lower than the best value of conventionally processed TiAl alloys.
- (4) Since DS ingots of TiAl containing high Nb concentrations exhibit nice balance of mechanical properties as well as nice oxidation properties, DS processing can provide a way of making alloy design of high property levels, which cannot be achieved by conventional processing routes.

Acknowledgments

This work was supported by Grant-in-Aid for Scientific Research (a) from the Ministry of Education, Science and Culture (No. 10355026).

References

- [1] M. Yamaguchi and H. Inui, *Structural Intermetallics*, edited by R. Darolia et al. (Warrendale, PA: TMS, 1995), 127.
- [2] Y-W. Kim, *J. Metals*, 46 (1994), 30.
- [3] F. Appel and R. Wagner, *Mater. Sci. Eng.*, R22 (1998), 187.
- [4] M. Yamaguchi, H. Inui and K. Ito, *Acta Mater.*, 48 (2000), 307.
- [5] T. Fujiwara, A. Nakamura, M. Hosomi, S.R. Nishitani, Y. Shirai and M. Yamaguchi, *Phil. Mag. A*, 61 (1990), 591.
- [6] H. Inui, A. Nakamura, M.H. Oh and M. Yamaguchi, *Acta Mater.*, 40 (1992), 3059.
- [7] D.R. Johnson, H. Inui and M. Yamaguchi, *Acta Mater.*, 44 (1996), 2523.

- [8] D.R. Johnson, Y. Masuda, H. Inui and M. Yamaguchi, *Acta Mater.*, 44 (1996), 2523.
- [9] T. Yamanaka, D.R. Johnson, H. Inui and M. Yamaguchi, *Intermetallics*, 7 (1999), 779.
- [10] S. Muto, T. Yamanaka, D.R. Johnson, H. Inui and M. Yamaguchi, *Mater. Sci. Eng.*, A329-331 (2002), 424.
- [11] Y. Omiya, S. Muto, T. Yamanaka, D.R. Johnson, H. Inui and M. Yamaguchi, *Defect Properties and Related Phenomena in Intermetallic Alloys*, edired by E.P George et al. (Pittsburgh, PA: MRS, 2003), 237.
- [12] H. Inui, D.R. Johnson and M. Yamaguchi, *Mater. Sci. Forum*, 426 (2003), 1733.
- [13] J. Beddoes, W. Wallance and L. Zhao, *Int. Mater. Rev.*, 40 (1995), 197.
- [14] T.A. Parthasarathy, M.G. Mendiratta and D.M. Dimiduk, *Scripta Mater.*, 37 (1997), 315.