

The effects of process control agents on mechanical alloying mechanisms in the Ti–Al system

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Abstract

During the mechanical alloying (MA) of ductile materials, it is often found that welding becomes so dominant that a very fine layered structure or homogeneously alloyed powders cannot be obtained. It is often desired to add an appropriate amount of process control agent (PCA) to powders in order to retain the equilibrium state between welding and fracturing processes. The present work investigated the effects of PCAs on MA mechanisms in the Ti–Al system. It was found that the amount of PCA and the energy transfer from ball to powder during MA influenced the mechanism of MA. As the amount of PCA and/or energy transferred from ball to powder increased, the mechanism of MA changed from a substitutional diffusion to a penetration of metallic atoms into interstitial sites. The penetration of metallic atoms seems to play an important role in the formation of the metastable f.c.c. phase, for which the lattice parameter is about 4.2 Å in the Ti–Al system.

Keywords: PCA; Mechanical alloying; Ti–Al; Atomic penetration; Amorphization

1. Introduction

The mechanical alloying (MA) of multi-component powders [1–3] and the production of nano-crystalline powders by ball milling [4,5] have attracted much attention from researchers in recent decades owing to their several advantages [6,7]. However, some researchers [8,9] have reported problems related to the desired final chemical composition, homogeneity and grain refinement after ball milling due to severe plastic deformation and welding of very ductile f.c.c. powders. There are two methods to prevent the severe welding: one is to lower the temperature of the milling vial [1,10] and the other is to add PCA to the powders [9,11]; the latter is more favored. Organic PCAs containing atoms such as O, C, H, etc. may affect the process of MA [12,13] and sometimes the atoms exist as impurities after consolidation of mechanically alloyed powders. For example, the ductility of the intermetallic compound TiAl decreases as the amount of O and/or C increases [14]. Therefore, it is important to select an appropriate PCA and its amount in order to avoid complications.

Many researchers [15,16] have also reported the formation of the metastable f.c.c. phase during MA in

the Ti–Al system. The formation mechanism of this metastable f.c.c. phase has not been proved clearly, in spite of reports that the f.c.c. formation may be due to O and N contamination [15]. The effect and the role of PCA on the MA process or mechanism are studied here systematically in terms of the amount and species of PCA.

2. Experimental details

Horizontal ball mills with stainless steel vial (diameter $130 \times 130 \text{ mm}^2$) and balls were run at 100 rev min^{-1} and room temperature for MA in this experiment. The nominal composition was chosen as Ti–48 at.% Al and the high purity elemental powders of 99.9% Ti (No. – 325) and 99.9% Al (Nos. 150–250) were charged with PCA. To prevent contamination, the balls and inner vial were sealed with nominal composition elemental powders (Ti–48 at.% Al) and milling was performed under Ar atmosphere. In order to investigate the effects of the species of PCA on the MA mechanism, CH_3OH (methanol) and C_6H_6 (benzene) were chosen as PCAs. As much as 0.3 or 3.0 wt.% of the PCA CH_3OH was added to the total

Table 1
The number of atoms and molecules under different PCA conditions

PCA	Designation	No. of molecules ($\times 10^{21}$)	No. of C atoms ($\times 10^{21}$)	No. of O atoms ($\times 10^{21}$)	No. of H atoms ($\times 10^{21}$)
CH ₃ OH 0.3 wt.-%	A	$1/10 \times 6.1$	$1/10 \times 6.1$	$1/10 \times 6.1$	$2/5 \times 6.1$
CH ₃ OH 3.0 wt.-%	B	6.1	6.1	6.1	4×6.1
C ₂ H ₄ 3.0 ml	C	$1/3 \times 6.1$	2×6.1		2×6.1

elemental powders (108.56 g). The amount and its respective number of molecules, and the number of C, O, and H atoms in PCAs, are given in Table 1. Condition B contains the same kind of molecules and atoms but 10 times as many as condition A. In contrast, condition C contains one third of the number of molecules and no O atoms, but twice the number of C atoms as condition B; in other words, the number of C atoms in condition C is equal to the number of C atoms plus O atoms in condition B. The powders used for investigation of phase transformations during DTA analysis were encapsulated in a quartz tube with about 10^{-3} Torr pressure. DTA analysis was performed at temperatures increasing at a rate of $10^\circ\text{C min}^{-1}$ using a Stanton Redcroft STA 1500, and XRD was carried out with a Cu target using a Rigaku DMAX 2200.

3. Results and discussion

3.1. Effect of PCAs on the MA mechanism

The powders were milled for 1000 h under conditions A, B, and C in Table 1, and one without PCA as well. The X-ray diffraction patterns of each condition after various milling times, to follow the phase transformations during MA, are shown in Figs. 1–4. In the condition without PCA, as shown in Fig. 1, elemental powders were transformed to an amorphous phase after 300 h of milling and to a metastable f.c.c. phase [1,2] with a lattice parameter a of around 4.20 Å after 500 h. Under condition A, which contains less CH₃OH, the metastable disordered Ti₃Al [1,17] was formed after 300 h of milling and an amorphous phase was obtained only after 1000 h (Fig. 2). Under condition B, the intensity of the main peak of Ti, diffracted from the (011) plane, was reduced rapidly after 300 h, while the (010) peak remained obvious with relatively strong intensity even after 700 h, and the broadened (011) peak seemed to separate into two peaks after 1000 h (Fig. 3). Finally, under condition C, which contains no O atoms in PCA as shown in Fig. 4, the Ti element peaks, although shifted slightly, still remained after 700 h and a metastable f.c.c. phase

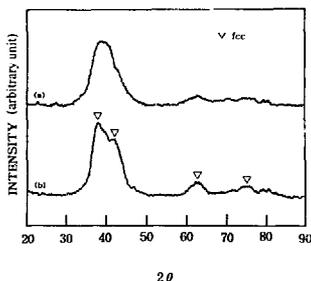


Fig. 1. X-ray diffraction patterns of the condition without PCA as a function of milling time: (a) 300, (b) 500 h.

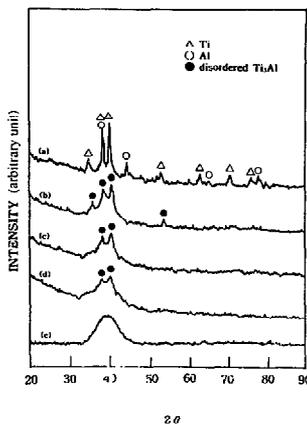


Fig. 2. X-ray diffraction patterns of the condition A as a function of milling time: (a) 100, (b) 300, (c) 500, (d) 700, (e) 1000 h.

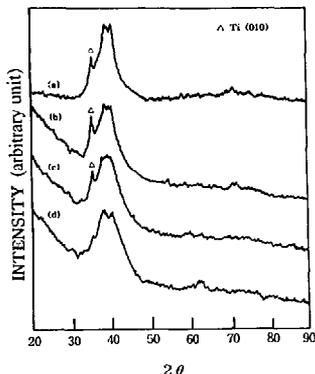


Fig. 3. X-ray diffraction patterns of the condition B as a function of milling time: (a) 300, (b) 500, (c) 700, (d) 1900 h.

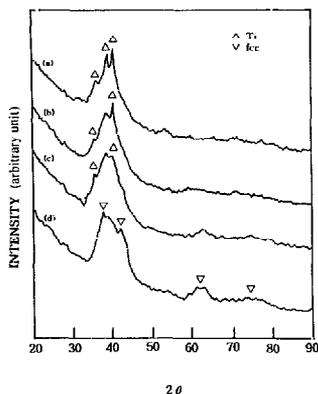


Fig. 4. X-ray diffraction patterns of the condition C as a function of milling time: (a) 300, (b) 500, (c) 700, (d) 1000 h.

appeared after 1000 h. From the above results it can be deduced that the MA mechanism depends on PCA conditions.

Collision of balls during milling raises the temperature of the trapped powders and causes substitutional diffusion at the interface between them [18–20]. Thus, it is generally accepted that amorphization by MA is

caused by this substitutional diffusion, so-called interdiffusion, which is based on Johnson and coworker's suggestion [21] that it is necessary for amorphization that the heat of mixing between elemental powders should be a negative value and the diffusion velocity of one element should be faster than that of the other. However, collision of balls can also transfer the kinetic energy of the balls to atoms of the powders. Chakk et al. [22] recently reported that amorphization by MA is caused by the penetration of metallic atoms into interstitial sites, which is based on the fact that the energy of 6.2 eV per atom is enough to enable atoms to penetrate into interstitial sites in pure elements and many bi-elemental metallic systems [23,24]. Koch [25] also suggested the possibility of penetration of atoms into interstitial sites from his experimental results in the mechanically alloyed Nb,Sn-Fe system. Considering that an amorphous phase can be obtained even in the alloy system that has a positive enthalpy of mixing [26,27], the penetration model rather than the substitutional diffusion model can easily explain amorphization in these systems. In our device, the maximum kinetic energy of a ball with a speed of 100 rev min⁻¹ was estimated to be 3.71×10^{-3} J. Assuming that powders are coated evenly on balls, that they are compressed under the area calculated from Hertz's elastic theory [28], and that half of the kinetic energy of a ball is transferred to powders [29], the estimated maximum energy that an atom in powders experiences is about 8.9 eV. Therefore, it can be said that the penetration of atoms into interstitial sites is possible in our system.

It is generally known that an amorphous phase can be obtained in the composition range 50 at.% \leq Ti \leq 80 at.% in the Ti-Al system by MA [1,30]. Bonetti et al. [16] reported that an amorphous phase was produced only after complete dissolution of Al into Ti in the Ti₇₅Al₂₅ composition. Therefore, it can be deduced that an amorphous phase is produced in the composition range 20 at.% \leq Al \leq 50 at.% and a solid solution of Al in Ti is produced for Al < 20 at.%. As the interatomic distances Ti-Ti and Ti-Al are 2.950 [31] and 2.4799 Å [32] respectively, the substitutional diffusion of Al atoms into Ti results in a decrease in both *a*- and *c*-axis lattice parameter of Ti. However, when interstitial atoms such as O or N are dissolved in Ti, the *c*-axis of the Ti lattice increases with almost no change in the *a*-axis [33]. Therefore, when Al atoms occupy interstitial sites in Ti, a similar trend can be expected.

Under conditions B and C, X-ray diffraction patterns (Fig. 5) and interplanar distances (Table 2) of Ti after milling for 500 h were investigated in detail. A small peak appeared at about 37° under conditions B and C after milling for 500 h. Assuming that this is Ti(002), the interplanar distance of the measured

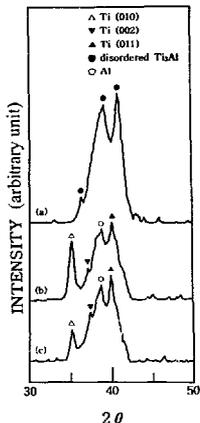


Fig. 5. X-ray diffraction patterns of milled powder under conditions: (a) A (300 h milling), (b) B (500 h milling), (c) C (500 h milling).

Ti(011) was coincident with that calculated by Ti(010) and Ti(002) (Table 2). These results indicate that the lattice parameter of the *c*-axis increases under conditions B and C during milling, while it decreases under condition A.

The variations in lattice parameter with milling time under each PCA condition are shown in Fig. 6. Under condition A, both the *a*- and *c*-axis decreased rapidly until 300 h of milling, when a metastable disordered Ti₃Al phase was formed (Fig. 2); they then remained almost constant until 700 h. This implies that MA

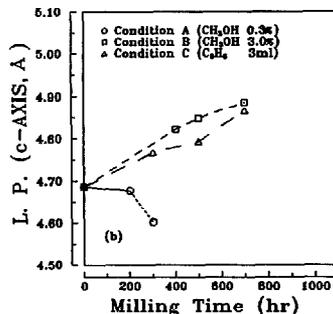
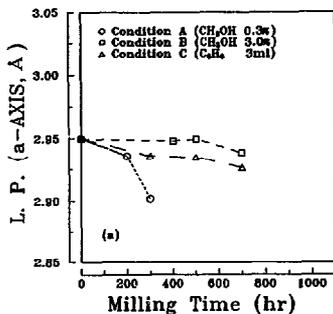


Fig. 6. Variation of Ti lattice parameters as a function of milling time under each PCA condition: (a) *a*-axis, (b) *c*-axis.

Table 2

Lattice parameters and *d*-values of pure Ti and milled powders under each condition

	Lattice parameter		<i>d</i> -Value		
	<i>a</i>	<i>c</i>	<i>d</i> ₀₁₀	<i>d</i> ₀₀₂	<i>d</i> ₀₁₁
Pure Ti	2.95	4.686	2.557	2.342	2.244
Condition A (CH ₃ OH 0.3 wt.%, 300 h milling)	2.902	4.602	2.513	2.301	2.206
Condition B (CH ₃ OH 3.0 wt.%, 500 h milling)	2.95	4.848	2.555	2.424	2.252
Condition C (C ₂ H ₆ , 3 ml, 800 h milling)	2.938	4.793	2.545	2.396	2.260 ^a
Condition A ^b (CH ₃ OH 0.3 wt.%, 300 h milling)	2.925	4.826	2.534	2.413	2.248 ^a
					2.243 ^a

^a Calculated by *d*-values for Ti(010) and Ti(002).

^b Charged half amount of powders and PCA of condition A.

proceeds by substitutional diffusion of Al atoms in Ti, and this diffusion is completed before 300 h.

Condition B, which contains relatively many molecules and O atoms, showed a very broad main peak of Ti after 300 h of milling (Fig. 3), and only the *c*-axis increased with little change in the *a*-axis until 500 h of milling (Fig. 6). This means that interstitial penetration, instead of substitutional diffusion, prevails at the interface between powders under this condition. The interplanar spacing *d* of (*hkl*) planes in the h.c.p. structure is expressed as

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

The random penetration of Al atoms into Ti interstitial sites will cause the random dilated distortion of the lattice along the *c*-axis, resulting in an increase in *c*-axis and a decrease in intensities for the planes *l* ≠ 0, for example (011) and (002). The reason for the small change in *a*-axis lattice parameter of the peaks from planes *l* = 0, for example (010), is the offset between the decrease by substitutional diffusion and the increase by interstitial penetration, which results from a small change of *a*-axis by interstitial penetration. In contrast, the increase in *c*-axis by interstitial penetration is too large to be offset by the small decrease due to substitutional diffusion.

Under condition C, which contains one third of the number of molecules in condition B and the most C atoms but no O atoms, the Ti peaks still remained after 700 h of milling (Fig. 4) with a slight decrease in *a*-axis and a large increase in *c*-axis (Fig. 6). This result suggests that the substitutional diffusion of Al in Ti and the interstitial penetration occur simultaneously under this condition, and that interstitial penetration is relatively more prevailing in condition B. However, it is not yet clear whether the overall smaller decrease in *a*-axis under condition B compared with condition C comes from more restraint of the substitutional diffusion due to the number of molecules and/or the species, or due to O atoms in the former.

In our previous investigation [34], when 9.1 ml of C₆H₆ was added so that the number of H atoms is almost three times that in condition C, the DTA curve showed a different shape from that for condition B, similar to condition A instead. This result suggests that H atoms at least do not affect the MA mechanism. However, the role of H atoms in PCAs is not clear at present.

The above results imply that the predominant MA mechanism changes from substitutional diffusion to atomic penetration into interstitial sites as the amount of PCA increases, even though the reason for this has not been explained clearly yet. The reason for earlier formation of amorphous phase in the condition with-

out PCA compared with condition A is that the composition for amorphous phase can be obtained sooner due to higher energy transfer from balls to powders during milling. Our previous investigation [34] observed that the amount of powders recovered from the vial after milling under the condition without PCA was about one third of that under condition A. This means that the amount of powders trapped between balls will be less, and the energies that the powders experience will thus be higher in the condition without PCA. Eckert et al. [35] also reported that it took less time to obtain the amorphous phase as the intensity of the balls increased. In order to confirm this analysis in another way, half of the elemental powders and PCA under condition A was charged in the milling vial so that the powders in this condition experienced more energy than those under condition A. In this experiment, an amorphous phase was already obtained after 400 h, compared with 1000 h under condition A, and the lattice parameters of powders after 300 h of milling were *a* = 2.93 and *c* = 4.83 Å (Table 2), indicating that the *c*-axis was increased by milling in this condition, while decreased under condition A. It is clear to say from the above experimental results that the time to form the amorphous phase decreases as the energy transferred from balls to powders increases. The results also suggest that the predominant mechanism for the condition without PCA is atomic penetration into interstitial sites, and the predominant mechanism for MA changes from substitutional diffusion to atomic penetration as the energy increases.

3.2. Activation energy for crystallization to TiAl

The activation energy for crystallization in the Ti-Al system was obtained in order to investigate how the amount of PCA, number of impurity atoms, affects the crystallization behavior of the amorphous phase. The DTA curve of each condition displays two peaks, as shown in Fig. 7. The first peaks due to crystallization to Ti₃Al under conditions A and B are sharp, while those due to ordering of the f.c.c. phase under the condition without PCA and condition C are very broad and slowly varying. However, the second peaks due to crystallization to TiAl are very sharp under all conditions. Therefore, the second peaks in the DTA curve were used to determine the activation energy for crystallization to TiAl using Kissinger's method [36]. The result given in Fig. 8 shows the trend that, as the number of impurity atoms, especially O atoms, in PCA increases, the activation energy increases. The lowest value of 281 kJ mol⁻¹ was obtained under the condition without PCA and the highest, 411 kJ mol⁻¹, under the condition B containing most O atoms. This tendency is similar to that reported [37] for the Ni-50

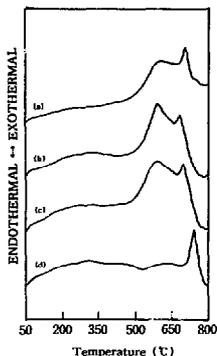


Fig. 7. DTA curves of milled powders under each condition: (a) without PCA (500 h milling), (b) A (1000 h milling), (c) B (1000 h milling), (d) C (1000 h milling).

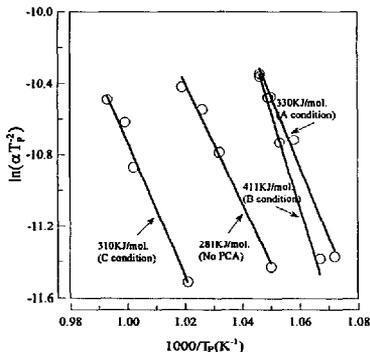


Fig. 8. Apparent activation energy of each PCA condition.

at.%Zr system, in which the activation energy for crystallization increased from 240 to 290 kJ mol⁻¹ by addition of 2.3 at.%O.

3.3. Formation of the metastable f.c.c. phase

The metastable f.c.c. phase was formed after long time milling only under the condition without PCA and condition C, in which atomic penetration was the prevailing mechanism of MA. Work on MA in the

Ti–Al system by high energy spex milling [2,16,38] also reported the formation of a metastable f.c.c. phase. It is thus thought that atomic penetration plays an important role in formation of the f.c.c. phase. However, the reason for not forming an f.c.c. phase under condition B, in which atomic penetration is also a prevailing mechanism, seems to be accounted for by O atoms.

4. Conclusions

By investigating the effects of PCA during MA of the Ti–48 at.%Al system, several conclusions were obtained.

1. As the energy transferred from balls to powders increases, it takes less time to form an amorphous phase.
2. As the intensity of the energy between balls and the amount of PCA increases, the prevailing MA mechanism changes from substitutional diffusion to atomic penetration into interstitial sites.
3. The metastable f.c.c. phase with lattice parameter a of around 4.20 Å is formed after 500 and 1000 h under the condition without PCA and condition C respectively. Atomic penetration into interstitial sites may be responsible for the formation of the metastable f.c.c. phase.
4. The activation energy for crystallization becomes larger as the number of impurity atoms, especially O atoms, in PCA increases.

References

- [1] W. Guo, S. Martelli, N. Burgio, M. Magini, F. Padella and E. Paradiso, *J. Mater. Sci.*, **26** (1990) 6190.
- [2] E. Bonetti, G. Cocco, S. Enzo and G. Valdre, *Mater. Sci. Technol.*, **6** (1990) 1258.
- [3] R.B. Schwarz and C.C. Koch, *Appl. Phys. Lett.*, **49** (1986) 1464.
- [4] J.S.C. Jang and C.C. Koch, *Scr. Metall.*, **24** (1990) 1599.
- [5] R. Bohn, T. Haubold, R. Dirringer and H. Gleiter, *Scr. Metall.*, **25** (1991) 811.
- [6] F.H. Froes, *J. Met.*, January (1989) 25.
- [7] S. Li, K. Wang, L. Sun and Z. Wang, *Scr. Metall.*, **27** (1992) 437.
- [8] H.J. Fecht, E. Hellstern, Z. Fu and W.L. Johnson, *Metall. Trans. A*, **21** (1990) 2333.
- [9] H.J. Fecht, E. Hellstern, Z. Fu and W.L. Johnson, *J. Appl. Phys.*, **67** (1990) 1744.
- [10] C. Suryanarayana and R. Sundaresan, *Mater. Sci. Eng.*, **A131** (1991) 237.
- [11] M. Zdujic, K.F. Kobayashi and P.H. Shingu, *Z. Metallkde.*, **Bd. 81** (1990) H5.
- [12] K.Y. Wang, T.D. Shen, J.T. Wang and M.X. Quan, *Scr. Metall.*, **25** (1991) 2227.
- [13] K.Y. Wang, T.D. Shen, M.X. Quan and J.T. Wang, *Scr. Metall.*, **26** (1992) 936.

- [14] T. Kwabata, M. Tadano and O. Izumi, *Ser. Metall.*, **22** (1988) 1725.
- [15] W. Guo, S. Martelli, F. Padella, M. Margini, N. Burgio, E. Paradiso and U. Franzoni, in P.H. Shingu (ed.), *Proc. Int. Symp. on Mechanical Alloying, Kyoto, Japan, 1991*, p. 139.
- [16] E. Bennetti, G. Valdre, S. Enzo and G. Cocco, *J. Alloys Comp.*, **194** (1993) 331.
- [17] N. Burgio, W. Gue, M. Magini, F. Padella, S. Martelli and I. Soletta, in F.H. Froes and J.J. deBarbadillo (eds.), *Proc. ASM Int. Conf. on Structural Applications of Mechanical Alloying, Myrtle Beach, SC, 1990*, p. 175.
- [18] J.S. Cho and S.I. Kwan, *Ser. Metall.*, **27** (1992) 1813.
- [19] R.B. Schwarz and C.C. Koch, *Appl. Phys. Lett.*, **49** (1986) 146.
- [20] R.M. Davis and C.C. Koch, *Ser. Metall.*, **21** (1987) 305.
- [21] R.B. Schwarz and W.L. Johnson, *Phys. Rev. Lett.*, **51** (1983) 415.
- [22] Y. Chakk, S. Berger, B.-Z. Weiss and E. Brook-Levinson, *Acta Metall. Mater.*, **42** (1994) 3679.
- [23] D.E. Luzzi and M. Neshii, *J. Less-Common Met.*, **140** (1988) 193.
- [24] J.R. Shoemaker, D. Wesley, W.R. Wharton, M.L. Oehrl, M.J. Sabochick and N.Q. Lam, *Mater. Res. Soc. Symp. Proc.*, **193** (1990) 339.
- [25] C.C. Koch, *Proc. TMS Fall Meet. on Solid State Powder Processing, Indianapolis, October, 1989*, p. 35.
- [26] E. Galfet, C. Louison, M. Harmeline and F. Faudot, *Mater. Sci. Eng., A134* (1991) 1380.
- [27] T. Fukuda, K. Nacamura, K. Suzuki and U. Mizutani, *J. Non-Cryst. Solids*, **117/118** (1990) 700.
- [28] S.P. Timoshenko and J.N. Goodier, *Theory of Elasticity*, McGraw-Hill, New York, 1970.
- [29] M. Magini, *Mater. Sci. Forum*, **88–90** (1992) 121.
- [30] N. Inoue, K.N. Ishihara and P.H. Shingu, *Proc. First Japan Int. SAMPE Symp., November, 1989*, p. 13.
- [31] *JCPDS card 5-0682*.
- [32] *JCPDS card 5-0678*.
- [33] H.T. Clark, Jr., *Metal. Trans.*, **185** (1949) 588.
- [34] W.S. Lee and S.I. Kwan, *J. Korean Inst. Met. Mater.*, **31** (1993) 1601.
- [35] J. Eckert, L. Schultz and K. Urban, *J. Mater. Sci.*, **26** (1991) 441.
- [36] H.E. Kissinger, *Anal. Chem.*, **29** (1957) 1702.
- [37] P.Y. Lee and C.C. Koch, *J. Mater. Sci.*, **23** (1988) 2837.
- [38] G. Cocco, I. Soletta, L. Baltezzati, M. Barocco and S. Enzo, *Philos. Mag. B*, **61** (1990).