Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 21(2011) s280−s284
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Metastable phase of β-eucryptite and thermal expansion behavior of eucryptite particles reinforced aluminum matrix composite

WANG Li-dong[1], CUI Ye[1], YANG Cong-tao[2], WANG Kang-peng[1], FEI Wei-dong[1, 3]

1. School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China;
2. Harbin Dongda High-tech Materials Co., Ltd., Harbin 150060, China;
3. School of Mechanical Engineering, Qinghai University, Xi'ning 810016, China

Received 10 May 2011; accepted 25 July 2011

Abstract: The aluminum matrix composites with 15%, 35%, 55% and 75% (volume fraction) of β-eucryptite (Euc) particles were prepared by spark plasma sintering (SPS) process. To prevent the interfacial reaction between Euc and Al, ZnO was coated on the surface of Euc particles. The microstructures of Euc/Al composites were studied by optical microscope (OM) and transmission electron microscope (TEM). The phase compositions in the composite were studied by X-ray diffraction method. The thermal physical properties of Euc/Al composites were analyzed by means of thermal dilatometer. A metastable phase of Euc was discovered which may be produced by the high anisotropic residual stress in the composite. The metastable phase of Euc can transfer to normal Euc when the residual stress is relaxed by stress relief annealing process and has great influence on the CTE behavior of the Euc/Al composite.

Key words: aluminum matrix composite; β-eucryptite; metastable phase, thermal expansion; residual stress

1 Introduction

Metal matrix composites (MMCs) with low coefficient of thermal expansion (CTE) are of great value because of their broad range of use in many areas, such as electronic packaging and thermal management application [1]. Ceramics with a negative CTE, such as ZrW_2O_8 and β-eucryptite (β-$LiAlSiO_4$, denoted as Euc), are potential excellent choices as reinforcements to reduce the CTE of MMCs [2−4]. However, the CTE of the ZrW_2O_8/Cu composite was significantly larger than the theory prediction because of the allotropic transformation of ZrW_2O_8 under high mismatch stress in the composite [5]. The CTE of β-eucryptite is also negative [6−7]. Interestingly, composites containing β-eucryptite particles exhibit attractive properties. For example, an aluminum matrix composite hybride reinforced by both β-eucryptite and aluminum borate whisker (denoted as (Euc+ABO)/Al) shows both lower CTE and higher strength [8]. A copper matrix composites reinforced by β-eucryptite particle (Euc/Cu) exhibits both low CTE and good thermal conductivity [9].

However, because β-eucryptite can react with Al at elevated temperature, resulting in a distinct increase of the CTE of (Euc+ABO)/Al [10], it is difficult to produce β-eucryptite reinforced Al composite with stable properties. To obtain Euc/Al composite with stable properties, the interfacial reaction must be controlled, so some effective interfacial modification process is necessary.

In the present work, ZnO coating on β-eucryptite was used to prevent the interfacial reaction between β-eucryptite and Al. An interesting crystal structure evolution was found which may be caused by the anisotropic mismatch stress in the Euc/Al composite. The thermal expansion behaviors of Euc/Al composites with ZnO coating were studied, which suggests that the thermal expansion behaviors of the composites are closely related to the phase state.

2 Experimental

The materials used were β-eucryptite particles with a diameter of 5−10 μm produced by a method developed in Ref. [11] and pure aluminum powder with a diameter

Foundation item: Projects (50671029, 50801016) supported by the National Natural Science Foundation of China; Project (2011CB612200) supported by the National Basic Research Program of China; Project (2011RFXXG025) supported by the Harbin Science and Technology Research Funds for Innovation Talents

Corresponding author: FEI Wei-dong; Tel: +86-451-86413908; E-mail: wdfei@hit.edu.cn

of 40 μm (Northeast Light Alloy Co., Ltd. China). ZnO was coated on the surface of *β*-eucryptite using a sol–gel coating process which was used to produce ZnO coating on $Al_{18}B_4O_{33}$ whisker. The mass ratio between ZnO and *β*-eucryptite is 1:20, detailed coating process can be found in Ref. [12].

The composites with *β*-eucryptite volume fraction of 15%, 35%, 55% and 75% were fabricated by powder metallurgy method. The *β*-eucryptite and Al composite powders were mixed and then consolidated by spark plasma sintering (SPS) at 600 °C for 5 min in a vacuum level of 0.1 Pa with an applied pressure of 50 MPa. The heating rate up to the sintering temperature was about 100 °C/min. The final size of the spark plasma sintered composite was 20 mm in diameter and 5 mm in thickness.

In order to investigate the coating effect on the interface state, the samples of as-sintered composite were heated at 500 °C for 3 h. To study the reason for the phase evolution of *β*-eucryptite, stress relief annealing was also taken at 190 °C for 3−9 h.

Microstructures were investigated with an OLYMPAS PMG3 type optical microscope (OM) and a Philips CM−12 type transmission electron microscope (TEM). Specimens for TEM observation were thinned by ion milling. The phase compositions of the composites were analyzed using X-ray diffraction (XRD) on a Philips X'Pert X-ray diffractometer with Cu K_α radiation. Thermal expansion experiments were performed on a Netzsch DIL 402C dilatometer with a heating rate of 2 °C/min. The dimensions of the specimens for thermal expansion measurement were *d*6 mm×15 mm.

3 Results

3.1 Microstructure of composites

The OM micrograph of 35% Euc/Al composite is shown in Fig. 1. It can be found that the distribution of *β*-eucryptite particles in the composite is homogeneous. No cracks or pores can be seen in the OM micrograph.

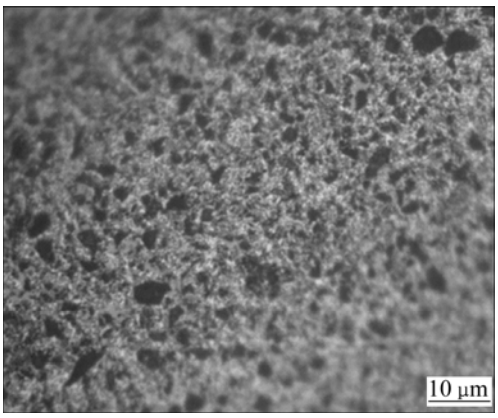

Fig. 1 OM micrograph of 35% Euc/Al composite

TEM images of the Euc/Al composite as-sintered and heat-treated at 500 °C for 3 h are shown in Fig. 2. It can be found that a layer of coating exists on the surface of *β*-eucryptite particles. Comparing the two images in Fig. 2, it is obvious that the thickness and the state of coating do not change after heat treatment, which indicates that the coating can effectively prevent the interfacial reaction between *β*-eucryptite and Al at elevated temperature, which also suggests that the properties concerning to the state of interface may be steady with the introduction of the coating.

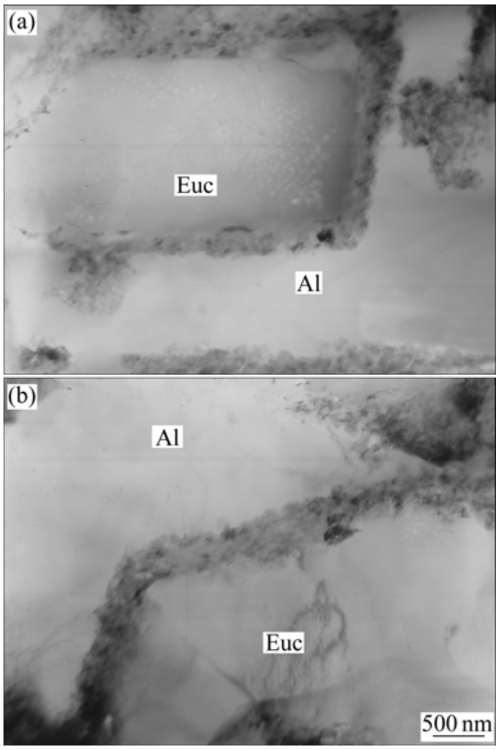

Fig. 2 TEM images of Euc/Al composites: (a) As-sintered composite; (b) Composite heated at 500 °C for 3 h

3.2 Phase compositions of composites

Figure 3 depicts the XRD patterns of the as-sintered composites. The main phases in the composite are Al and *β*-eucryptite. However, according to PDF card No.732328, the intensity of the peak at 19.5° should be two times higher than those of the peaks at 34.0° and 39.6°. Therefore, it is surprising to see that the peak of (200) plane for *β*-eucryptite at 19.5° is not visible for composites with 15%, 35% and 55% *β*-eucryptite, except for 75% Euc/Al.

The XRD patterns of the 55% Euc/Al composites with different stress relief annealing time at 190 °C are shown in Fig. 4. It can be found that the intensities of the peaks at 19.5° for specimens annealed for 0 and 3 h are near zero, but they are clear for specimens annealed for 6 and 9 h, and the longer the annealing time is, the stronger the intensities of the peaks are.

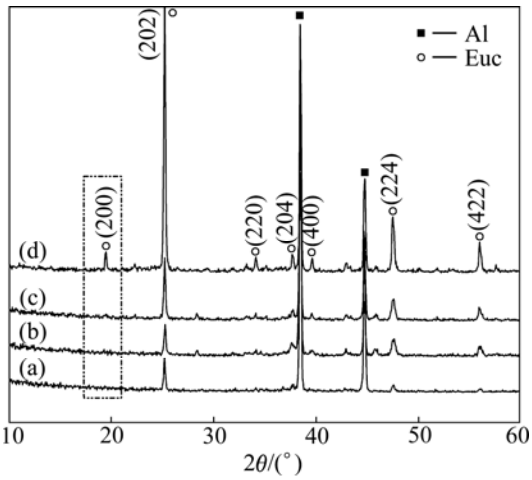

Fig. 3 XRD patterns of Euc/Al composites with different volume fractions of β-eucyrptite: (a) 15% Euc/Al; (b) 35% Euc/Al; (c) 55% Euc/Al; (d) 75% Euc/Al

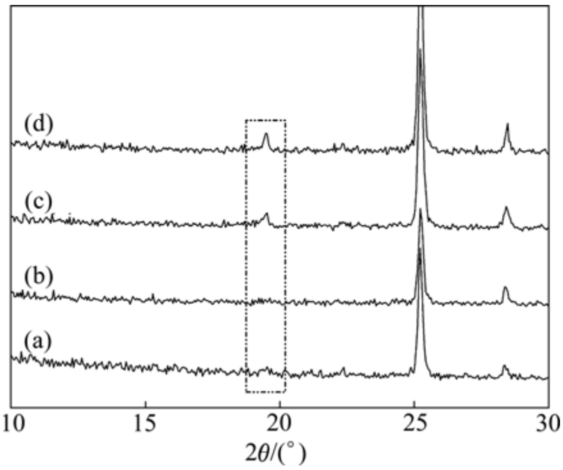

Fig. 4 XRD patterns of 55% Euc/Al composites with different stress relief annealing time at 190 °C: (a) 0 h; (b) 3 h; (c) 6 h; (d) 9 h

3.3 CTE behaviors of composites

Figure 5 shows the CTE curves of the 55% Euc/Al composite with different stress relief annealing time at 190 °C. Great difference appears for specimens with different annealing time. Firstly, it can be found that, at the initial stage, for each curve the CTE increases with the temperature rising, but the initial CTE values are different. The longer the annealing time is, the lower the initial CTEs are, from 60 to 80 °C. The CTE of the specimen annealed for 9 h is the lowest and lower than the line calculated by the mixture rule. Secondly, each CTE curve shows a decreasing trend after the initial increasing step, but the decreasing amounts are different for the specimens with different annealing time. The decreasing amount for the specimen annealed for 9 h is far less than those of the other two specimens.

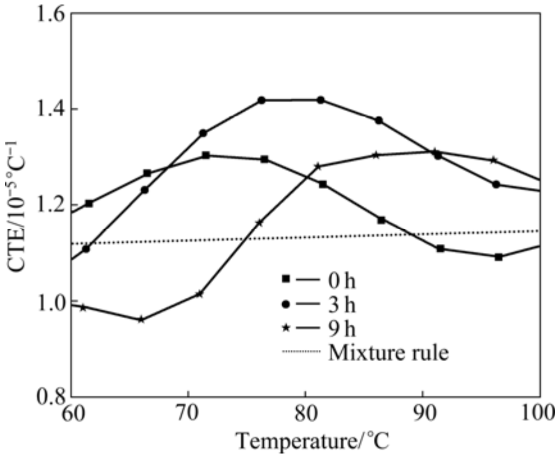

Fig. 5 CTE curves of 55% Euc/Al composites with different stress relief annealing time at 190 °C

4 Discussion

It has been reported that phase transition of β-eucryptite could be induced by hydrostatic pressure [13]. However, the reflections in Figs. 3(a)−(c) are different with the reflections of the high pressure phase in Ref. [13], which reveals that for high pressure phase the main reflections belong to the planes of h, $k = 3n$ and l=2n; while the results in the present work show that the main reflections belong to the planes h, k, l=2n, but just without the reflection of (200) plane. These facts suggest two points: firstly, the present result is a new phenomenon; secondly, the new phenomenon indicates a new phase of β-eucryptite which may be a metastable phase of β-eucryptite since the reflections are different from both the normal and the high pressure phase of β-eucryptite.

The reason for the new phenomenon may be connected with the anisotropic residual stress in the β-eucryptite particles. As β-eucryptite is a highly anisotropic material with CTE values along the crystallographic a- and c-axes of 7.8×10^{-6} °C^{-1} and -17.5×10^{-6} °C^{-1} [7], respectively. Furthermore, a great difference of the CTE between β-eucryptite and Al exists. As a result, for Euc/Al composite, when the composite is cooled from higher temperature to room temperature in the fabricating process, large and anisotropic residual compressive stress can be generated in the β-eucryptite particles at room temperature, at the same time tensile stress exists in the Al matrix [14]. The anisotropic residual stress is unlike the hydrostatic pressure in Ref. [13], which may cause the special metastable phase of β-eucryptite.

The stress relief annealing experiment can act as a confirmatory experiment to prove the speculation regarding the relationship between the compressive residual stress and the metastable phase of β-eucryptite.

The experiment is based on the fact that the residual stress in MMCs can be relieved by annealing. If the metastable phase of β-eucryptite is caused by a higher residual stress on β-eucryptite and assuming that the metastable phase could recover to β-eucryptite when the residual stress is relaxed to be low enough, then the disappeared peak of (200) plane of β-eucryptite would reappear.

The results in Fig. 4 prove that the speculation above-mentioned is correct. Since during stress relief annealing process, the stress in the composite will be relaxed gradually with the annealing time increasing. The longer the annealing time, the lower the stress between β-eucryptite and Al matrix. Consequently, the appearance of the peaks at 19.5° for specimens annealed for 6 h and 9 h obviously indicates that the residual stress is the main reason for the emergence of the metastable phase of β-eucryptite in the Euc/Al composite. It suggests that when the residual stress is high enough, β-eucryptite transfers to a new phase, which is not found in other high pressure tests and may be a metastable phase having structure close to β-eucryptite and can recover to β-eucryptite when the stress is relaxed.

The relationship between CTE behavior and residual stress in MMCs composite has been studied and established in Refs. [14−15]. From the conclusions in Refs. [14−15], for MMCs composite, compressive stress exists in the ceramic reinforcements and tensile stress exists in the metal matrix at room temperature. When the temperature is increased from room temperature, the relaxation of compressive stress in ceramic reinforcements makes the CTE of the composite lower than the value calculated by mixture rule. The higher the relaxation rate, the lower the CTE of the composite.

If the metastable phase of β-eucryptite is produced by a higher residual stress in the composite, specimens of the 55% Euc/Al composite with different stress relief annealing time would exhibit different CTE behaviors. In other words, the CTE behavior can act as another evidence for the existence of the metastable phase of β-eucryptite. Figure 5 evidently shows the different CTE behaviors for the same composite with different stress relief annealing time. These phenomena can be explained as follows.

Firstly, with the annealing time prolonging, the stress in the metastable phase of β-eucryptite decreases, and more metastable phases can transfer to normal β-eucryptite. As a result, the volume fraction of β-eucryptite in the composite increases. Because of the negative expansion of β-eucryptite, the higher volume fraction of β-eucryptite can cause a lower CTE of the composite according to the mixture rule. Therefore, at the intial stage, the longer the annealing time is, the lower the initial CTEs are, and for the specimen annealed for 9 h with the least stress and the highest volume fraction of recovered β-eucryptite, the CTE is the lowest and lower than the value calculated by the mixture rule.

Secondly, for the specimens annealed for 0 and 3 h, more metastable phases of β-eucryptite exist in the composite caused by the larger residual stress. During the temperature increasing, the compressive stress in particles decreases because of the expansion of Al matrix. When the compressive stress is low enough, the metastable phase of β-eucryptite will transfer to normal negative expansion β-eucryptite. Therefore, the volume fraction of β-eucryptite increases, which causes the decrease of CTE of the composite after 80 °C, and the higher the temperature is, the less the stress is, and the more the β-eucryptite emerges, which causes the lower CTE of the composite. For the specimen annealed for 9 h, most of the metastable phases has been transferred to β-eucryptite, so the decrease of CTE is very small at the temperature range.

Since these phenomena are well explained by the existence of the metastable phase of β-eucryptite, it is no doubt that the CTE behaviors of composite with different stress relief annealing time offer another evidence for the existence of the metastable phase of β-eucryptite.

5 Conclusions

1) A metastable phase of β-eucryptite is discovered, which shows the reflections different from both the normal and the high pressure phase of β-eucryptite. The high anisotropic residual stress in the composite may be the main reason for the emergence of the metastable phase.

2) The metastable phase of β-eucryptite can transfer to normal β-eucryptite when the residual stress is relaxed by stress relief annealing process.

3) The transformation of the metastable phase has great influence on the CTE behavior of the Euc/Al composite.

References

[1] CLYNE T W, WITHERS P J. An introduction to metal matrix composites [M]. Cambridge: Cambridge University Press, 1993: 7−8.

[2] YAN X H, QIU J, WANG C S, ZHANG C H, CHENG X N. Preparation of Cu coated ZrW_2O_8 composite powders via heterogeneous precipitation process [J]. Key Engineering Materials, 2008, 368−372: 1377−1379.

[3] YAN X, CHENG X, XU G, WANG C, SUN S, RIEDEL R. Preparation and thermal properties of zirconium tungstate/copper composites [J]. Material Science and Engineering Technology, 2008, 39(9): 649−654.

[4] SHIMADA T, MIZUNO M, NURISHI Y. Simultaneous fabrication of a composite with low thermal expansion and high strength in the eucryptite-yttria-stabilized PSZ system [J]. Journal of Materials Science, 1996, 31(14): 3691−3695.

[5] HOLZER H, DUNAND D C. Phase transformation and thermal expansion of Cu/ZrW_2O_8 metal composite [J]. Journal of Materials Research, 1999, 14(3): 780−789.
[6] SCHULTZ H. Thermal expansion of beta eucryptite [J]. Journal of the American Ceramic Society, 1974, 57(7): 313−318.
[7] XU H W, HEANEY P J, YATES D M. Structural mechanisms underlying near-zero thermal expansion in β-eucryptite: A combined synchrotron X-ray and neutron rietveld analysis [J]. Journal of Materials Research, 1999, 14(7): 3138−3151.
[8] WANG L D, FEI W D, HU M, YAO C K. A study on an aluminum matrix composite reinforced by both β-eucryptite particle and aluminum borate whisker [J]. Materials Letters, 2002, 53(1−2): 20−24.
[9] XUE Z W, LIU Z, WANG L D, FEI W D. Thermal properties of new copper matrix composite reinforced by β-eucryptite particulates [J]. Materials Science and Technology, 2010, 26(12): 1521−1524.
[10] WANG L D, FEI W D. Microstructure and interfacial reactions of β-eucryptite particles in aluminum matrix composites [J]. Materials Science and Engineering A, 2006, 433(1−2): 291−297.
[11] WANG L D, FEI W D. The method of β-eucryptite's production: Chinese, 200610009821 [P]. 2006−09−13.
[12] YUE H Y, FEI W D, WANG L D, LI Z J. An aluminum borate whisker-reinforced aluminum matrix composite with high plasticity [J]. Materials Science and Engineering A, 2006, 430(1−2): 260−265.
[13] MOROSIN B, PEERCY P S. Pressure-induced phase transition in β-eucryptite ($LiA1SiO_4$) [J]. Physics Letters A, 1975, 53: 147−148.
[14] HU M, FEI W D, YAO C K. A study on correlation of thermal mismatch stress of SiCw/Al composite through curves of thermal expansion coefficient [J]. Scripta Materialia, 2002, 46(8): 563−567.
[15] FEI W D, WANG L D. Thermal expansion behavior and thermal mismatch stress of aluminum matrix composite reinforced by β-eucryptite particle and aluminum borate whisker [J]. Materials Chemistry and Physics, 2004, 85(2−3): 450−457.

β-锂霞石/Al 复合材料中β-锂霞石亚稳相和热膨胀行为

王黎东[1]，崔　烨[1]，杨丛涛[2]，王康鹏[1]，费维栋[1,3]

1. 哈尔滨工业大学 材料科学与工程学院，哈尔滨 150001；
2. 哈尔滨东大高新技术材料有限公司，哈尔滨 150060；
3. 青海大学 机械工程学院, 西宁 810016

摘　要： 采用放电等离子体烧结工艺制备体积分数分别为 15%、35%、55%和 75%的β-锂霞石/Al 复合材料(Euc/Al)。为防止 Euc 颗粒和 Al 基体之间的界面反应，将 Euc 颗粒表面进行 ZnO 涂覆处理。采用光学显微镜、透射电镜、X 射线衍射和热膨胀仪对 Euc/Al 复合材料的微观组织、相成分和热膨胀性能进行测试和分析。在复合材料中，由于大的各向异性残余应力的作用，形成 Euc 颗粒的亚稳相。对复合材料进行去应力退火处理后，复合材料中的 Euc 亚稳相发生逆转变，其对复合材料的热膨胀行为产生显著影响。

关键词： Al 基复合材料；β-锂霞石；亚稳相；热膨胀；残余应力

(Edited by HE Yun-bin)