**Article ID:** 1003 - 6326(2000)03 - 0358 - 06

# Phase transformation and properties of quasicrystal particles/ Al matrix composites①

QI Yu-hong(齐育红)[1,2], ZHANG Zhan-ping(张占平)[1,2],
HEI Zu-kun(黑祖昆)[1,2], DONG Chuang(董 闯)[3]
1. *Institute of Materials and Technology, Dalian Maritime University, Dalian 116026, P. R. China;*
2. *State Key Laboratory of Structural Analysis of Industry Equipment, Dalian 116024, P. R. China;*
3. *Department of Material Engineering, Dalian University of Technology, Dalian 116026, P. R. China*

**Abstract:** Diffusion-controlled phase transformations and tribological properties and hardness of $Al_{65}Cu_{20}Cr_{15}$ quasicrystal particles($QC_p$)/ Al matrix composites have been studied. The mixtures of the quasicrystal particles with volume fractions of 15%, 20%, 25%, 30% and pure Al powder were hot-pressed at 600, 650, 700 ℃. During the diffusion-controlled phase transformation induced by hot-pressing, a simple cubic icosahedric quasicrystal (SIQC) phase transforms into stable $\Theta$ phase with the microstructure of monoclinic of $Al_{13}Cr_2$ through a transitional faced cubic icosahedric quasicrystal (FIQC), a decagonal quasicrystal (DQC) and an approximant of decagonal quasicrystal (DA) phases. And G. P. zones and Al-Cu precipitates, $\theta'$-$Al_2Cu$ and $\theta$-$Al_2Cu$, are separated out from the Al matrix respectively after hot-pressing. The $QC_p$/ Al composites have double-strengthening effect after hot-pressing. One is the strengthening of the particles that reinforce the matrix Al; the other is the dispersion strengthening of the precipitates in the Al matrix. The hardness of the composites increases with increasing volume fraction of quasicrystal particles. The maximum hardness reaches 1 200 MPa, being 4 times that of Al. The frictional coefficient and the wear rate of the $QC_p$/ Al are lower than those of Al. In comparison with $SiC_p$/ Al matrix composites, $QC_p$/ Al composites have higher hardness and lower frictional coefficient.

**Key words:** composites; quasicrystals; aluminium alloys; phase transformation **Document code: A**

## 1 INTRODUCTION

The formations, atomic structures, electronic structures, high temperature stability, phase transformations and physical properties of quasicrystals have been studied deeply for the last twelve years, but it is nearly impossible to use them as fundamental structural materials because of their intrinsic brittleness, thus the research work on quasicrystalline applications has rarely been carried out. However, the quasicrystalline materials have better comprehensive properties[1~6], such as high hardness, low frictional coefficient, heat-resistance, wear-resistance and corrosion-resistance so that it becomes possible to use them as surface strengthening materials or reinforcing particles of composites. In the applications of the surface strengthening materials, French scholars have successfully used quasicrystalline plating layer to non-stick cookware[7]. Tsai et al[8] have simply studied $Al_{65}Cu_{20}Fe_{15}$ quasicrystalline particles dispersed Al base composites, but they only tested the hardness of the composites. Thus the studies on quasicrystalline materials used as reinforcing particles of composites are very few.

For the above reasons and in order to explore and develop the application areas of quasicrystalline materials, making use of their properties of high hardness and low frictional coefficient, especially the characteristic of low density of Al base quasicrystalline materials and their matching with Al, we try to use Al base quasicrystal, $Al_{65}Cu_{20}Cr_{15}$, as reinforcing particles of Al matrix, and will study the phase transformation regularity and the frictional and wear properties of the composites prepared by hot-pressing technique in this paper.

## 2 EXPERIMENTAL

The $Al_{65}Cu_{20}Cr_{15}$ master alloy was prepared by means of melting high pure aluminum, electrolytic copper and metal chromium in the magnetic suspension vacuum furnace. The rapidly solidified ribbons were cast by melting-spinning in an argon atmosphere of 0.45 MPa with a single copper wheel of 345 mm radius rotating at a rate of 1 800 r/ min. A nearly 100% simple cubic icosahedral quasicrystal (SIQC) phase was obtained in the melt-spun sample.

The particles of $Al_{65}Cu_{20}Cr_{15}$ alloy were prepared

① **Foundation item:** Project 970113331 supported by the National Natural Science Foundation of China and project A9707233431 supported by the Dalian Youth Science Foundation **Received date:** Mar. 12, 1999; **accepted date:** Jul. 21, 1999

by grinding the melt-spun samples for 3 h in QM-IST ball mill and screening them below the size of 50 μm. The commercial pure aluminum powder with a size of 75 μm was used as the matrix material.

The $Al_{65}Cu_{20}Cr_{15}$ particles with volume fractions of 15 %, 20 %, 25 % and 30 % and pure Al powder were mixed for 30 min in ball mill. The mixed powders were hot-pressed into samples of dimensions of $d$25 mm × 5 mm at 600, 650 and 700 ℃ under 40 MPa for 30 min.

The microstructures of the composite samples were analyzed by X-ray diffractometry ( $\lambda(CuK_\alpha)$ = 0.154 4 nm) and transmission electron microscopy (TEM), the phase compositions were obtained by electron probe microanalyser (EPMA).

The hardness of the composites was tested with a HV-120 Vicker's hardometer, and determined by averaging the hardness of six points on the up and down surfaces of each sample.

The frictional and wear properties were measured in a MM-200 wear test machine under a load of 20 N at 200 r/ min in the state of dry friction. The dimensions of the samples are 10 mm × 10 mm × 16.5 mm. 6CrW2Si steel was used as frictional counter, whose hardness is HRC 60 ~ 62. According to the variational curves of the frictional moment with frictional time, the frictional coefficient was obtained. The wear resistance was described by the width of the grinding cracks. The morphology of the grinding crack was observed by JSM-35CF Scan Electric Microscope.

## 3 RESULTS

### 3.1 Distribution of reinforcing particles

The distributions of the quasicrystal particles are shown in Fig.1. The particles are homogeneously distributed in the Al matrix for the composites of particle volume fractions of 15 % and 20 %, such as the composite of particle volume fraction 15 % at 650 ℃ for 30 min (Fig.1(a)). While the particle volume fraction exceeds 20 %, for example, 25 % and 30 %, the particles segragate progressively (Fig.1(b)).

The volume fraction of practical particles and the geometrical parameters are calculated by quantitative metallography (Tables 1 and 2). Table 1 shows that the practical volume fractions of particles are close to the original ones. Thus, after transformations in hot pressing process, it is possible to neglect the change of particle volume. Table 2 shows that $\lambda$ and $\sigma$ decrease with increasing volume fraction, and the change of $d$ is not obvious. The distribution parameter of the second phase particles is one of the important factors which determine the strength of materials.

### 3.2 Microstructures

The microstructures of $QC_p$/ Al composites depend on the parameters of hot-pressing processing, such as temperature, pressure, time and volume fraction of quasicrystal particles. This paper only studied the influence of temperature and volume fraction of the quasicrystal particles on microstructure.

It is found that the microstructures vary with hot-pressing temperature in 20 % $QC_p$/ Al composite under the conditions of 40 MPa pressure and 30 min time as follows.

(1) In hot-pressing at 600 ℃

Under this testing condition both the Al matrix and QC particles keep solid; the morphology is shown in Fig.2(a). The composition of the particles is $Al_{69}Cu_{19}Cr_{12}$, whose structure is a faced cubic icosahedric quasicrystal[9]. A small amount of $Al_2Cu$ particles is observed at the grain boundaries of Al matrix by TEM (Fig.3(a)).

(2) In hot-pressing at 650 ℃

The Al matrix and the particles still keep solid, but the temperature of the Al matrix is close to its melting point. The speed of diffusion is faster than that at 600 ℃. The back-scattered electron image of the composite is shown in Fig.3(b). The reinforced particles consist of white phase and intergrowth-like

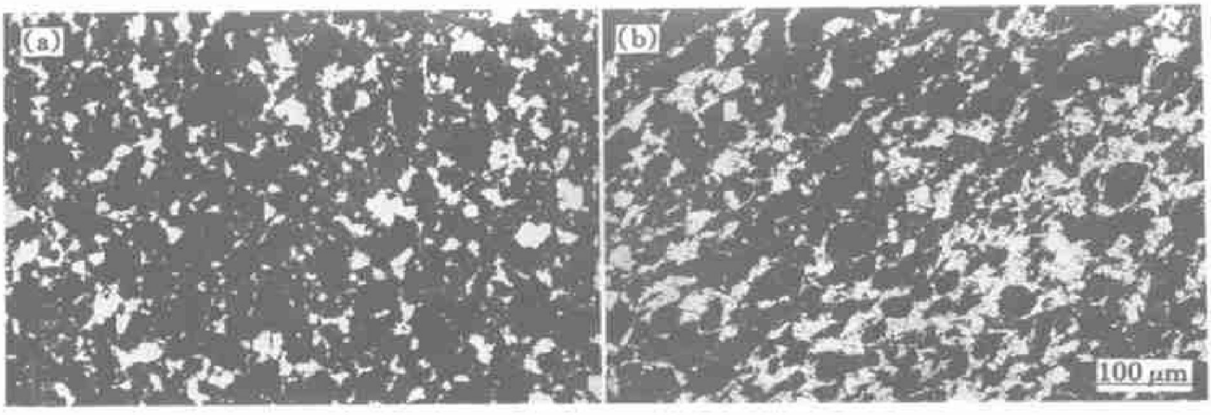


**Fig.1** Distributions of reinforced particles in composites
(a) — $\varphi_f$ = 15 %, 650 ℃, 30 min; (b) — $\varphi_f$ = 30 %, 650 ℃, 30 min

**Table 1** Volume fraction of original and practical particles (%)

| $t$/ ℃ | Original | Practical |
|---|---|---|
| 600 | 20 | 19.2 |
| 700 | 20 | 19.7 |
| 650 | 15 | 14.3 |
| 650 | 20 | 18.6 |
| 650 | 25 | 23.5 |
| 650 | 30 | 28.2 |

**Table 2** Geometrical parameters of particles

| $\varphi$/ % | $\lambda$/ mm | $\sigma$/ mm | $d$/ mm |
|---|---|---|---|
| 15 | 0.1604 | 0.1887 | 0.0283 |
| 20 | 0.1053 | 0.1316 | 0.0263 |
| 25 | 0.0816 | 0.1087 | 0.0272 |
| 30 | 0.0609 | 0.0869 | 0.0261 |

$\lambda$—average free distance; $\sigma$—average distance between particles; $d$—average diameter of particles

phases. EMPA and TEM experiments show that the white phase has a composition of $Al_{83}Cu_{4.5}Cr_{12.5}$ and a microstructure of monoclinic of $Al_{13}Cr_2$. The composition of the intergrowth-like phases can't be distinguished; the average is $Al_{78}Cu_{10}Cr_{12}$, and their microstructures are respectively decagonal quasicrystal (DQC) and an approximant of decagonal quasicrystal (DA)[9]. There are a lot of $\theta'$-$Al_2Cu$ and $\theta$-$Al_2Cu$ in the Al matrix, which precipitate both in the grains and at the grain boundaries, and the typical images are shown in Fig.3(b).

(3) In hot-press processing at 700 ℃

The particles still keep solid, but the matrix becomes liquid, the diffusion is accelerated even more, its back-scattered electron image is shown in Fig.2(c). The particles only consist of a single white phase. The analyses of EMPA and TEM show that the phase has $Al_{88}Cu_{2.5}Cr_{13}$ composition and $Al_{13}Cr_2$ structure.

In the matrix, many G.P. zones and $\theta'$-$Al_2Cu$ are observed by TEM; Fig.3(c) shows their images in typical areas.

The variations of microstructure with volume fraction of reinforcing particles after hot-pressing at 650 ℃, 40 MPa for 30 min were investigated by TEM and EMPA. The compositions and the structures of the composites with volume fractions of 15%, 20%, 25% and 30% are listed in Table 3. In the composites with volume fractions of 20%, 25% and 30%, the particles consist of $\Theta$-$Al_{13}Cr_2$ and (DQC + DA), and the amount of $\Theta$ phase increases while the amount of (DQC + DA) decreases with increasing particle volume fraction.

The precipitates in the composites are mainly $\theta'$-$Al_2Cu$ and $\theta$-$Al_2Cu$; the quantity and the size of both $\theta'$ and $\theta$ increase with increasing particle volume fractions.

### 3.3 Hardness and tribological properties

The macro-hardness of the composites with different hot-pressing process and volume fractions were measured, and the results are shown in Fig.4 and Fig.5. The hardness of 20% $QC_p$ + Al composite increases with increasing temperature and time, but when the time increases from 30 min to 90 min, the hardness increases little.

The frictional coefficients and the wear rates of the composites with volume fractions of 0% (pure Al), 15%, 20%, 25% and 30% respectively after hot pressing at 650 ℃, 40 MPa for 30 min were measured, and the results are shown in Fig.6 and Fig.7. Both the frictional coefficients and wear rate of the composites are lower than those of the pure Al. And the wear rates decrease with increasing volume

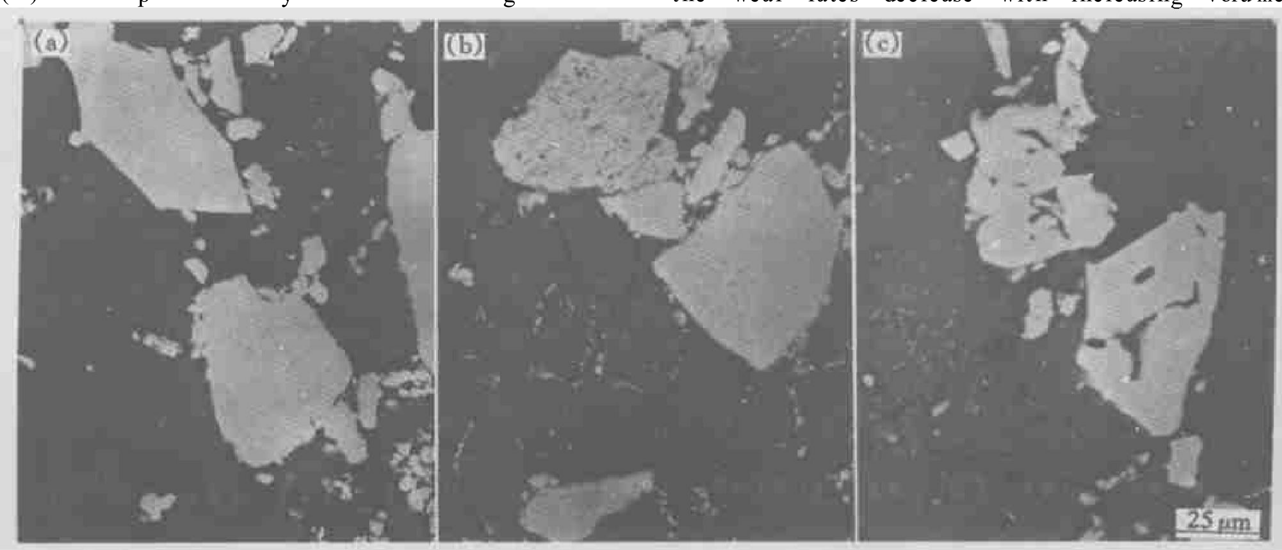


**Fig.2** Back-scattered electron images of reinforcing particles
(a) —600 ℃; (b) —650 ℃; (b) —700 ℃

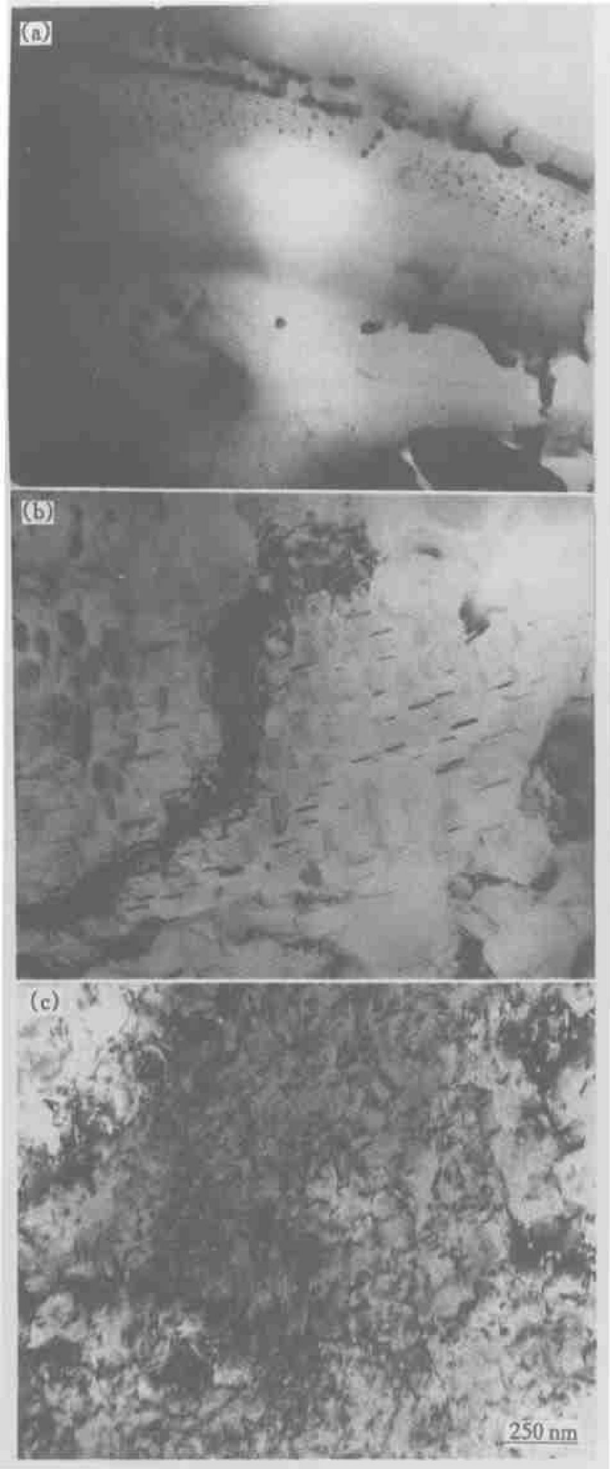


**Fig. 3** Images of precipitates in matrix
(a) —600 ℃; (b) —650 ℃; (b) —700 ℃

**Table 3** Compositions and structures of phases in particles of composites with different volume fractions

| Alloy | Features | Composition | Structure |
|---|---|---|---|
| 15 %$QC_p$ + Al | White | $Al_{69}Cu_{20}Cr_{11}$ | FIQC |
| | Gray | $Al_{78}Cu_{10}Cr_{12}$ | DQC |
| 20 %$QC_p$ + Al | Gray | $Al_{83}Cu_{14}Cr_{13}$ | θ-$Al_{13}Cr_2$ |
| | Intergrowth-like | $Al_{78}Cu_{10}Cr_{12}$ | DQC + DA |
| 25 %$QC_p$ + Al | Gray | $Al_{83}Cu_{5.5}Cr_{11.5}$ | θ-$Al_{13}Cr_2$ |
| | Intergrowth-like | $Al_{77.2}Cu_{12}Cr_{10.8}$ | DQC + DA |
| 30 %$QC_p$ + Al | Gray | $Al_{81.9}Cu_{4.8}Cr_{13.3}$ | θ-$Al_{13}Cr_2$ |
| | Intergrowth-like | $Al_{77.5}Cu_{11}Cr_{11.5}$ | DQC + DA |

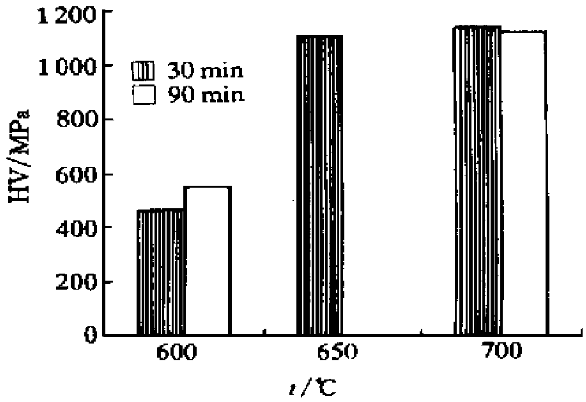


**Fig. 4** Variation of hardness of 20 %$QC_p$ + Al composite with hot pressing temperature and time

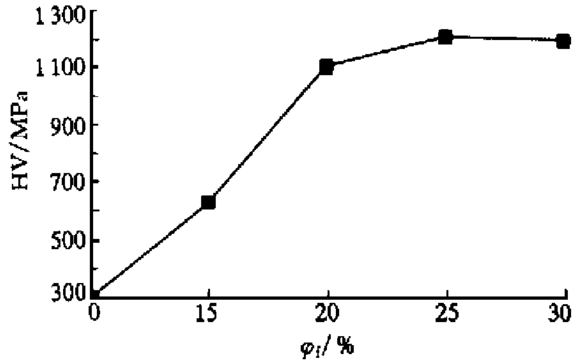


**Fig. 5** Variation of hardness of composites with volume fraction of reinforcing particles

fraction in the composites of 15 %$QC_p$ + Al and 20 %$QC_p$ + Al. When the volume fraction exceeds 20 %, both the frictional coefficient and the wear rate begin to increase, but when the volume fraction exceeds 25 %, they do not have obvious change.

## 4 DISCUSSION

It is known that the properties of composites depend mainly on the nature, distribution, size and the quantity of the reinforcing particles. The experiments showed that the size of particles keeps constant, the quantity is about the volume fraction, both of them can be controlled by man-made design in these composites. The distribution of the particles is related to the hot-pressing process and the volume fraction. When the volume fraction exceeds 25 %, the particle distribution becomes inhomogeneous in the composites prepared by hot-pressing at 650 ℃, 40 MPa for 30 min.

The nature of the particles depends on the

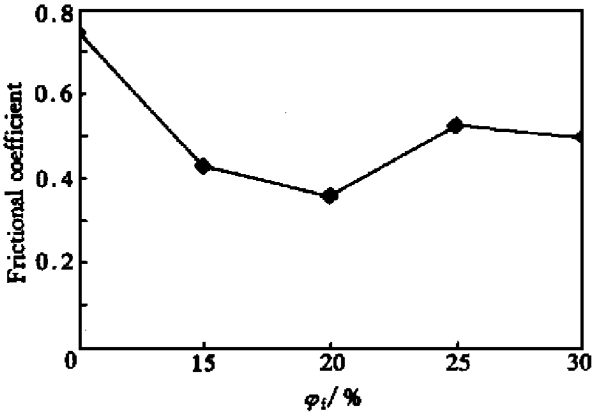


**Fig.6** Variation of frictional coefficient with volume fraction of reinforcing particles

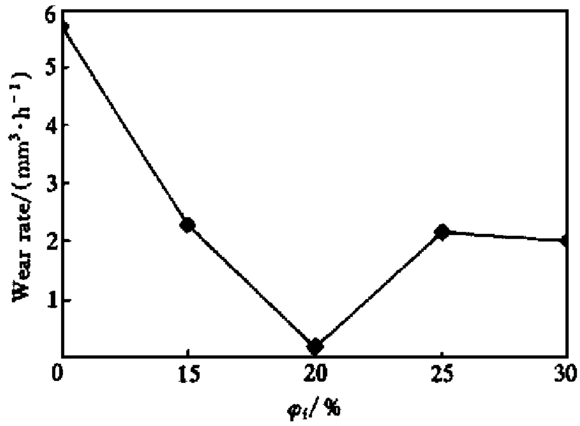


**Fig.7** Variation of wear rate of composite with volume fraction of reinforcing particles

microstructures, and at last on the hot-pressing technology and the volume fraction. So, the studies on the transformational regulation of the particles are regarded to be important for the composites.

According to the Al-Cr and Al-Cu binary diagrams, the phases that can maintain equilibrium with Al are $\Theta$-$Al_{13}Cr_2$ and $\theta$-$Al_2Cu$ in thermodynamics, but $\theta$-$Al_2Cu$ was only observed in the Al matrix, not in the particles, and $\Theta$-$Al_{13}Cr_2$ was only observed in the particle, not in the Al matrix. Although both Cu and Cr atoms can diffuse from the particles to the matrix Al, the experiments showed that Cr atoms exist mostly in the particles, there is only an insufficient quantity of Cr atoms in the matrix Al, maybe because the Cr content in the particles approaches to the Cr content in the equilibrium phase of $\Theta$-$Al_{13}Cr_2$ ($Al_{86.7}Cr_{13.3}$). Cu atoms tend to solve into the matrix, then G.P. zones and the transitional phases, $\theta'$-$Al_2Cu$ and the stable phase $\theta$-$Al_2Cu$ are precipitated from the Al matrix, and the decrease of Cu in the particles induces the phase transformations from the original SIQC to a series of transitional phases, at last, to the equilibrium phase $\Theta$-$Al_{13}Cr_2$ in which there is a few Cu atoms. As shown above, the phase transformations of the particles could take place during hot-pressing as follows:

$$\text{SIQC}(Al_{65}Cu_{24}Cr_{11}) \xrightarrow{600\ ℃} \text{FIQC}(Al_{69}Cu_{21}Cr_{10}) \xrightarrow{650\ ℃} \text{DQC}(Al_{78}Cu_{10}Cr_{12}) \xrightarrow{650\ ℃} \text{DA}(Al_{78}Cu_{10}Cr_{12}) \xrightarrow{700\ ℃} \Theta(Al_{84}Cu_{2.5}Cr_{13.5})$$

The SIQC transformations depend fully on the diffusion ability in the system, and the diffusion ability of the system depends mainly on the hot-pressing temperature. The results of transformations are closely related to the composition of the particles and the compositions depend on the diffusing ability too, that is, depend on the hot-pressing temperature. SIQC transferred into FIQC by atom ordering at 600 ℃. There is a coherent orientation relationship between the two phases. When being hot-pressed at 650 ℃, the SIQC finally transferred into DQC and DA. The approximant of the decagonal quasicrystal DA is practically the result of the ordering transformation of the DQC, and the decagonal DQC is a result of the ordering of the FIQC. With increasing hot-pressing temperature, only a single phase of $\Theta$-$Al_{13}Cr_2$ in the particles can reach equilibrium with the Al matrix. All the transformations above are caused by the change of the composition diffusion-controlled, so the microstructure of the particles can be controlled by the hot-pressing techniques.

The precipitates in the matrix Al are formed as follows.

700 ℃: $\theta'$-$Al_2Cu$ (at the boundaries); 650 ℃: $\theta'$-$Al_2Cu$ + $\theta$-$Al_2Cu$; 600 ℃: G.P. zones + $\theta'$-$Al_2Cu$.

The strengthening of the $QC_p$/Al composite is contributed to two sides: one is the strengthening of the particles that reinforce the Al matrix, the other is the dispersion strengthening of the precipitates from the matrix Al. The hardness of composites with the same volume fraction is dependent on the microstructure of the particles and the precipitates. According to Fig.7, when the particles have the microstructure of monoclinic of $\Theta$-$Al_{13}Cr_2$, and the precipitates from the matrix Al are G.P. zones and $\Theta'$-$Al_2Cu$, the hardness of $QC_p$/Al reaches the maximum. Under the same conditions of hot-pressing the hardness of $QC_p$/Al reaches the maximum at 25 % particle volume fraction. Although there are nearly similar microstructures in the composites of 20 %, 25 % and 30 % particles, the distribution of the particles become inhomogeneous in the 25 %$QC_p$ + Al composite. So, it is not significant to strengthen the $QC_p$/Al composite by adding particles when the volume fraction exceeds 25 %.

The reduction of the frictional coefficient is mainly caused by the particles. According to Fig.6, there occurs the lowest frictional coefficient in 20 % $QC_p$ + Al which has more (DQC + DA) phases in the

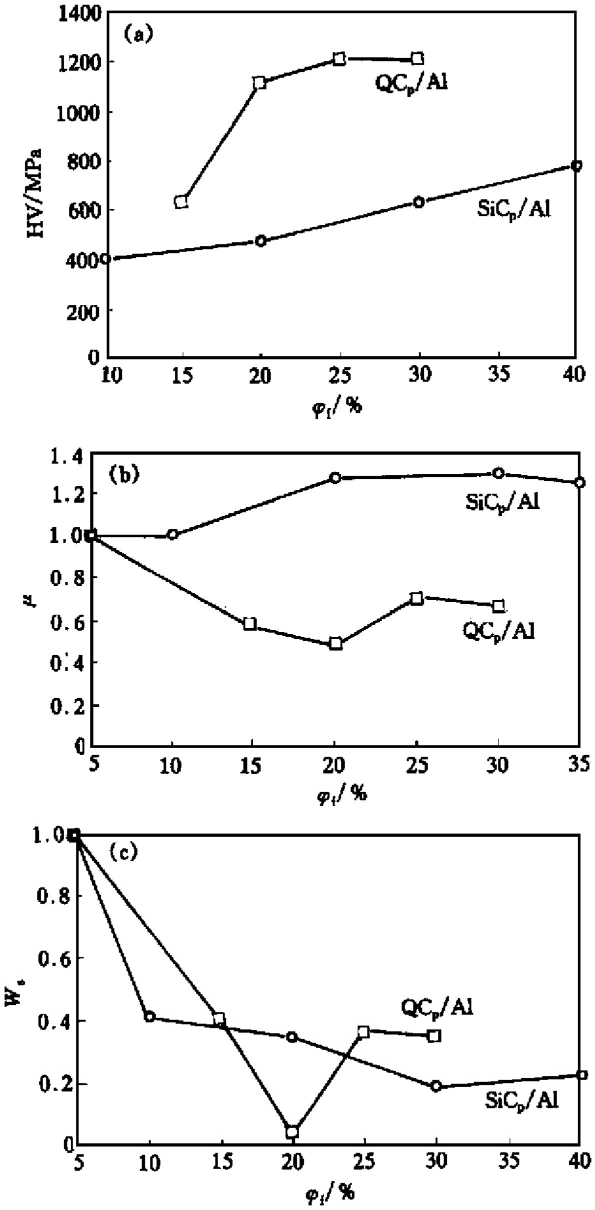


**Fig.8** Comparisons of properties of $QC_p$/ Al with corresponding properties of $SiC_p$/ Al
(a) —HV vs $\varphi_f$; (b) —μ vs $\varphi_f$ (c) — $W_s$ vs $\varphi_f$

particles. (DQC + DA) phases in the particles decrease with increasing particle volume fraction in 20 % $QC_p$ + Al, 25 %$QC_p$ + Al and 30 %$QC_p$ + Al, so the lower frictional coefficient of $QC_p$/ Al should be contributed to quasicrystals and its approximants of the particles, because the low frictional coefficient characterize the quasicrystalline alloys.

The experimental results on the properties of $QC_p$/ Al have been compared with the corresponding properties of $SiC_p$/ Al[10] in Fig.8. Fig.8(a) shows the diagram of the contrast of hardness, which shows the hardness of $QC_p$/ Al is higher than that of $SiC_p$/ Al. According to Fig.8(b), the variations of the frictional coefficient with volume fraction of particles are fully contrast to $SiC_p$/ Al. This is resulted from the specific properties of the quasicrystalline material. Fig.8(c) shows that the wear resistance of both composites have no obvious difference.

## REFERENCES

[1] Kang S S and Dubois J M. Compression testing of quasicrystalline materials [J]. Phil Mag A, 1992, 66:151.
[2] Massiani Y, Yaazza Ait and Crousier J P. Electrochemical behaviour of quasicrystalline alloys in corrosive solutions [J]. J Non-Crystal Sol, 1993, 159: 92.
[3] Wittmann R, Urban K, Schandl M, et al. Mechamical properties of single-quasicrystalline AlCuCoSi [J]. J Mater Res, 1991, 6:1165.
[4] Bresson L and Gratias D J. Plastic deformation in AlCuFe icosahedral phase [J]. J Non-Cryst Solids, 1993, 153 ~ 154: 468.
[5] Kang S S, Dubois J M and von Stebut J. Tribological properties of quasicrystalline coatings [J]. J Mater Res, 1993, 10: 2471.
[6] DONG C. Application, properties and formation mechanism of quasicrystalline materials [J]. Chinese Journal of Materials Research, 1994, 8(6):481.
[7] Dubois J M and Weinland P. Demande de brevet d'invention [P]. French Patent No.8810559,1988.
[8] Tsai A P, Aoki K, Inove A, et al. Synthesis of stable quasicrystalline particle-dispersed Al base composite alloys [J]. J Mater Res, 1993, 8: 5.
[9] QI Yu-hong, ZHANG Zhan-ping, HEI Zu-kun, et al. The microstructure analysis of Al-Cu-Cr phases $Al_{65}Cu_{20}Cr_{15}$ particles/ Al base composites [J]. Journal of Alloys and Compounds, 1999, 285(1 ~ 2): 221 ~ 228.
[10] Venkataraman B and Sundararajan G. The sliding wear behaviour of Al-SiC particulate composites- I macrobehaviour [J]. Acta Mater, 1996, 44: 451.

**(Edited by PENG Chao-qun)**