CONSTITUTION OF Al-BASE MULTI-COMPONENT QUASI-CRYSTALLINE ALLOYS①

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ABSTRACT Based on the similarity of some of the quasi-crystalline alloy′s structures and atomic energy band factors, an empirical composition addition principle for multi-component quasi-crystal constitutions was proposed, which has been tested positively in many quasi-crystal alloy systems such as Al-Cr-Mn, Al-Cu-Fe-Cr-Mn, Al-Cu-Fe-Pd-Mn, Al-Cu-Fe-Mg. These newly constituted quasi-crystals possess various formation characteristics; they can be prepared through rapid solidfication process(RS), ingot metallurgy process(IM), annealing or high pressure, high temperature treatment of RS powders. The function of this principle was discussed.

Key words quasi-crystal Al-base alloy composition addition

1 INTRODUCTION

Since the discovery of quasi-crystalline phase in rapidly solidified Al-Mn alloy by Shechtman *et al*[1], more than 10 years have passed. During this period, the scientific community around the world paid special attention to the research of quasi-crystals. The novel quasi-periodic structure brings novel properties to the quasi-crystalline alloys, makes them potential structural or functional materials. So far, many quasi-crystals have been found, but there exist many problems about the constitution characteristics of quasi-crystalline alloys. In this paper, the authors propose a quasi-crystalline alloys composition addition principle, present the Al-base multi-component quasi-crystalline alloys constitution and formation characteristics, and analyze those results.

2 COMPOSITION ADDITION PRINCIPLE OF MULTI-COMPONENT QUASI-CRYSTALS

For known quasi-crystals, the alloys in which the *I* phase (icosahedral phase) can form can be roughly divided into three categories: (1) Al-transition metals or metalloids, (2) MT_2 alloys (M represents group ⅧA metals), (3) the Frank-Kasper topologic phase. The *T* phase (decagonal phase), on the other hand usually forms in the Al-transition metal alloys. Additionally, the *I* phase can form in alloys such as Cu_4Cd_3 with complex cubic structures. In general, the alloy systems which can form quasi-crystalline phases possess structural characteristics as follows.

These alloys can form amporphous alloys; or the equilibrium phases of these alloy systems contain a large number of icosahedral atom groups; or the equilibrium phases are similar in structure to the *T* phase. The structural similarity plays an important role in the formation of quasi-crystalline phase and it is also a criterion for searching for new quasi-crystals.

The authors thought that the addition of several quasi-crystalline alloy compositions does not change their structural similarity. The new alloys still contain icosahedral atom groups or their equilibrium phases are still similar to the *T* phase in structure. Therefore, according to this principle of structural similarity, the authors

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suggest the principle of composition addition in multi-component quasi-crystals.

Using rapid solidification or ingot casting, multi-component quasi-crytalline alloys can be obtained. This principle was tested positively by several experiments as follows.

(1) The constitution of Al-Cu-Fe-Mn, Al-Cu-Fe-Cr and Al-Cu-Fe-Cr-Mn quasi-crystals[2]. Multi-component alloys were prepared in two ways. One was by mixing known quasi-crystalline master alloys $Al_{65}Cu_{20}Fe_{15}$, $Al_{77.5}Mn_{22.5}$ and $Al_{85}Cr_{15}$ according to the ratios listed in Table 1. The other was by using elemental metals as raw materials according to the composition listed in Table 2. All these rapidly solidified alloys are basically composed of icosahedral quasi-crystalline phase. Fig. 1 shows the XRD patterns of some of these alloys. Fig. 2 demonstrates the electronic diffraction patterns of Al-Cu-Fe-Cr-Mn quasi-crystal. It is concluded that: (a) The structures of quinary Al-Cu-Fe-Cr-Mn and quaternary Al-Cu-Fe-Cr, Al-Cu-Fe-Mn quasi-crystalline powders at room temperature are icosahedral. When these powders were heated, their structures transformed to decagonal structures (T phase) at about 923 K. (b) For the quinary Al-X% (X= Cu, Fe, Cr, Mn), quaternary Al-X% (X= Cu, Fe, Cr), Al-X% (X= Cu, Fe, Mn) alloys, when the value of X changes in the range of 35~ 50, single I phase quasi-cryistals are easy to obtain.

(2) The constitution of Al-Cu-Fe-Pd-Mn multi-component quasi-crystals[3]. Thermally stable $Al_{65}Cu_{20}Fe_{15}$ and $Al_{70}Pd_{20}Mn_{10}$ quasi-crystalline alloys were used to formulate new alloys according to the ratios listed in Table 3. Results show that the alloys obtained by means of ingot process, contain icosahedral quasi-crystals, and the rapidly solidified alloys consist of almost single phase icosahedral quasi-crystals, which are also thermally stable. Extended composition searching indicated that at almost every ratio, $Al_{70}Pd_{20}Mn_{10}$ and $Al_{65}Cu_{20}Fe_{15}$ can be formulated to form quasi-crystals $(Al_{65}Cu_{20}Fe_{15})_x + (Al_{70}Pd_{20}Mn_{10})_{1-x}$ (x = 0~ 1). Figs. 3 and 4 show the XRD patterns and electronic diffration patterns of IM and RS Al-Cu-Fe-Pd-Mn alloys respectively.

Guided by this addition principle, many other multi-component quasi-crystalline alloys have been obtained too, such as

Al-Mn+ Al-Cr → Al-Mn-Cr[4]
Al-Mn+ Ni-Ti → Al-Mn-Ni-Ti[5]
Al-Mn+ Fe-Ti → Al-Mn-Fe-Ti[5]
Al-Cu-Fe+ Ni-Ti → Al-Cu-Fe-Ni-Ti[5]
Al-Cu-Fe+ Fe-Ti → Al-Cu-Fe-Ti[5]
Al-Cu-Fe+ Al-Cu-Mg → Al-Cu-Fe-Mg[6]
Al-Cu-Fe+ Al-Zn-Mg → Al-Cu-Fe-Mg-Zn[6]

Table 1 Mass ratios of master alloys for new quasi-crystalline alloys

Al-Cu-Fe-Cr-Mn		Al-Cu-Fe-Mn		Al-Cu-Fe-Cr	
Sample No.	$Al_{65}Cu_{20}Fe_{15}$: $Al_{77.5}Mn_{22.5}$: $Al_{85}Cr_{15}$	Sample No.	$Al_{65}Cu_{20}Fe_{15}$: $Al_{77.5}Mn_{22.5}$	Sample No.	$Al_{65}Cu_{20}Fe_{15}$: $Al_{85}Cr_{15}$
1	1∶1∶1	5	1∶1	8	1∶1
2	2∶1∶1	6	2∶1	9	2∶1
3	1∶2∶1	7	1∶2	10	1∶2
4	1∶1∶2				

Table 2 Chemical compositions of new quasi-crystalline alloys with elemental metals as starting materials

Sample No.	Composition/ % Al	Cu	Fe	Cr	Mn	Sample No.	Composition/ % Al	Cu	Fe	CR	Mn
11	50.0	23.4	9.5	8.6	8.5	16	65.2	8.6	9.2	7.1	9.9
12	50.5	8.0	26.4	8.0	7.1	17	50.0	24.0	19.1	–	6.9
13	55.0	11.5	12.0	13.1	8.4	18	54.3	9.3	10.6	–	25.8
14	55.0	16.9	11.9	7.3	8.9	19	51.6	23.1	17.8	7.5	–
15	60.0	10.0	11.5	8.5	10.0	20	63.1	11.0	9.8	16.1	–

Al-Cr + Al-Pd-Mn → Al-Cr-Pd-Mn[3]
Al-Cu-Fe + Al-Li-Cu → Al-Cu-Fe-Li[7]
Al-Mn + Al-Li-Cu → Al-Mn-Li-Cu[7]
Al-Cu-Fe + Al-Cu-Co → Al-Cu-Fe-Co[8]
Al-Cu-Fe + Al-Mo → Al-Cu-Fe-Mo[8]
Al-Cu-Fe + Al-W → Al-Cu-Fe-W[8]

Table 3 Formulation of Al-Cu-Fe-Pd-Mn quasi-crystals

Sample No.	Ratio	Composition/ mole fraction				
	$Al_{65}Cu_{20}Fe_{15}$: $Al_{70}Pd_{20}Mn_{10}$	Al	Cu	Fe	Cr	Mn
21	1:1	67.5	10.0	7.5	10.0	5.0
22	1:2	68.3	6.7	5.0	13.3	6.7
23	2:1	66.7	13.3	10.0	6.7	3.3

3 FORMATION CHARACTERISTICS OF MULTI-COMPONENT QUASI-CRYSTALS

So far, most of the known quasi-crystals are metastable; they can be prepared through mechanical alloying, sputtering, ion beam, or evaporation-condensation techniques, besides rapid solidification technique; only a few of Al-Cu-Fe, Al-Pd-Mn quasi-crystals can be made through ingot process.

In the addition constituted multi-component alloys, the way of forming quasi-crystalline phase can be different: (1) In most cases, quasi-crystals can be obtained through rapid solidification process, sush as in Al-Cr-Mn, Al-Cu-Fe-Cr-Mn, Al-Cr-Pd-Mn. (2) In some RS alloys, quasi-crystals can be formed when annealed, for example, RS Al-Cu-Fe-Mg alloy is crystalline, through annealing, icosahedral quasi-crystalline phase can be obtained[6]; in systems such as RS Al-Cu-Fe-Cr-Mn, decagonal phase (*T* phase) forms after annealing treatment[2]. (3) In Al-Cu-Fe-Li, Al-Cu-Fe systems, high pressure and high temperture (5~ 7 GPa, 500~ 800 ℃, 5~ 10 min) treatment can result in an increase in the fraction of icosahedral quasi-crystalline phase[7, 9]. (4) Quasi-crystals form during the slow cooling of Al-Cu-Fe-Pd-Mn alloys.

The variety of the ways of forming quasi-crystals indicated that for various alloys the formation of the quasi-periodic structures is probably related to different thermodynamic and kinetic conditions, as in the case that a special amorphous alloy formation needs a critical melt cooling rate. For those quasi-crystals whose stability lies between amorphous phase and crystalline phase, the necessary formation condition

Fig. 1 XRD patterns of three quasi-crystalline alloy powders
(a) —Al-Cu-Fe-Cr-Mn (sample No. 1);
(b) —Al-Cu-Fe-Mn (sample No. 5);
(c) —Al-Cu-Fe-Cr (sample No. 8)

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Fig. 2 Electron diffraction patterns of Al-Cu-Fe-Cr-Mn quasi-crystal (sample No. 15)

Fig. 3 XRD patterns of IM and RS Al-Cu-Fe-Pd-Mn alloys
RS sample:
(a) —No. 21; (b) —No. 22; (c) —No. 23;
IM sample:
(a′) —No. 21; (b′) —No. 22; (c′) —No. 23

is difficult to obtain and control. Thus many alloy systems or certain composition alloys in which quasi-crystals are still not found till now, will probably be proved to be quasi-crystalline alloys with the improvement of experimental technique in the future.

4 ANALYSIS OF Al-BASE MULTI-COMPONENT QUASI-CRYSTAL CONSTITUTION CHARACTERISTICS

In the known quasi-crystals, Al-base alloys are the majority, they can be roughly divided into categories as follows:

(1) Al-TM;

(2) Al-TM_1-TM_2;

(3) Al-TM-X (TM represents transition metal, X represent Li, Mg, Si, B ……).

Al-TM (TM metals are VA ~ ⅧA elements.) quasi-crystals are the basic quasi-crystals. So far, many binary quasi-crystals have been found, which are Al-Mn[1], Al-Co[10], Al-Fe[11], Al-Cr[12], Al-Mo[13], Al-W[13], Al-Pd[14], Al-Pt[15], Al-Re[13], Al-Ru[13], Al-V[16], Al-Ni[16] …….

Al-TM_1-TM_2 quasi-crystals can be considered to be constituted by adding two basic quasi-crystals in certain composition scope; the following quasi-crystals constituent elements are in accordance with the principle:

Al-Co-Ni[17], Al-Cr-Co[18], Al-Cr-Fe[18], Al-Cr-Ni[19], Al-Cr-Ru[13], Al-Fe-Mo[20], Al-Fe-Ni[17], Al-Mn-Cr[4], Al-Fe-Mn[21], Al-Mn-Ni[19], Al-Mn-Ru[13], Al-Pd-Mn[22], Al-Pd-Re[22], Al-V-Co[18], Al-V-Fe[18].

Similar to the case in Al - TM quasi - crystals, these TM_1, TM_2 metals are VA~ ⅧA elements.

At present, some Al-TM_1-TM_2 quasi-

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Fig. 4 Electron diffraction patterns of Al-Cu-Fe-Pd-Mn quasi-crystal (sample No. 21)

Fig. 5 XRD patterns of RS Al-Cu-Fe-Li alloys treated at different conditions
(formulation: $Al_{65}Cu_{20}Fe_{15}$: Al_6Li_3Cu = 2∶1)
(a) —RS powders; (b) —sample treated at 6GPA, 650 ℃ for 10min

5- fold 3- fold

Fig. 6 Electron diffraction patterns of Al-Cu-Fe-Li quasi-crystal

crystals can not be constituted by two known Al-TM quasi-crystals, such as Al-Cr-Er[23], Al-Fe-Ta[24], Al-Mn-Ti[25], Al-Rh-Ni[17], Al-Cu-Rh[17], Al-Cu-Fe[26], Al-Cu-Cr[26], Al-Cu-Mn[27], Al-Cu-Ni[28], Al-Cu-Os[29], Al-Cu-Ru[29], Al-Cu-V[30]. For these quasi-crystals, even though in some Al-TM alloys, quasi-crystalline phase have not been found so far, but it is posssible that under certain condition, quasi-crystalline phase can be formed. For instance, Al-Mn-Ti quasi-crystal can be considered to be constituted with Al-Mn and Al-Ti quasi-crystals (of course, Al-Ti is a predicted quasi-crystal). On the other hand, Al-Mn-Ti is probably constituted with Al-Mn and Mn-Ti[31] quasi-crystals. For Al-Cu-Fe quasi-crystal, we can take it as an additive quasi-crystal of Al-Fe quasi-crystal and predicted Al-Cu quasi-crystal; also we can look on it as the adding quasi-crystal of Al-Fe and Cu-Fe quasi-crystals[32].

For Al-TM-X quasi-crystals, Al-Ni-Mg[33], Al-Cr-Mg[34], Al-Pt-Mg[33], Al-Mn-Ge[35], Al-Mn-Si[36], Al-Ni-Si[37], Al-Cr-Si[35], Al-V-Si[38], Al-Cu-Li[39], Al-Zn-Li[40], Al-Ag-Mg[33], Al-Au-Mg[33] quasi-crystals have been found. They can be considered to be constituted with Al-TM and Al-X quasi-crystals or Al-TM and X-TM quasi-crystals. For instance, Al-Mn-Si quasi-crystals, also can be the additivity of Al-Mn and Mn-Si[41] quasi-crystals.

This empirical principle also agrees with some other quasi-crytals, the following are some examples:

Mn-Ti + Mn-Si → Mn-Ti-Si[31],

V-Ni + Ti-Ni → Ti-Ni-V[42].

In summary, the function of this addition principle of quasi-crystal constitution is in two aspects:

(1) To predict multi-component quasi-crytals on the base of known basic quasi-crystals.

(2) To predict basic quasi-crystals on the base of already discovered multi-component quasi-crystals. At present, the constitution rule of quasi-crystals is not very clear yet, therefore this principle is useful. However, it is necessary to point out that perhaps this principle is only suitable for some certain quasi-crystalline alloys.

5 DISCUSSION

A lot of research work reveals that some quasi-crystal constitutions exhibit additivity; the cause for this characteristics may be in two aspects.

(1) Valence electron concentration and energy band factor. Quasi-crystals can be considered to be a sort of intermetallic compounds, the quasi-periodic structure formation is certainly related to the atomic size difference of the constituent atoms, the valence electron concentration and energy band structure of these alloys,

despite that we have not worked out in which way these factors work[43, 44].

As a basic Al-TM quasi-crystal, its valence electron concentration (e/a) and energy band structure are determined and approximately keep constant. The addition constituted new alloys may possess simliar e/a level and energy band structures, therefore, quasi-periodic structure may form in these new alloys.

(2) Lattice structural similarity. For icosahedral quasi-crystals, some structure factors promote the formation of icosahedral phase in newly constituted alloys: (a) Transition metals added in basic quasi-crystals have similar atomic radii. (b) The adding of basic quasi-crystals keeps the Al content at a roughly constant level; multi-component increases quasi-crystal formation ability. (c) Analogous to metallic solid solution, two or more quasi-crystals which have the same icosahedral structure can form a new icosahedral alloy phase, TM_1 can be partly substituted by TM_2.

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