Icosahedral particles of an Al-Mn alloy produced by gas evaporation

Yahachi Saito and Kazuhiro Mihama
Department of Applied Physics, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

H. S. Chen
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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Small particles of icosahedral Al-Mn alloy have been produced by evaporation of Al and Mn metals in Ar gas and studied by electron microscopy. The quasicrystalline particles were spherical in shape, with diameters ranging from 500 to 3000 Å, and showed speckled contrast in bright-field images, characteristic of strain. Dark-field images revealed granular bright and dark areas of a few hundred angstroms. This appearance is common with that of the melt-spun samples and may be attributed to misorientations between the granular domains. Elongated domains of ~50 Å in width and a few hundred angstroms in length, which are unique in the present sample and not observed in the melt-spun sample, were also found. The critical cooling rate for the quasicrystal formation of the Al-Mn alloy was found to be 10^5 °C/sec.

I. INTRODUCTION

The icosahedral quasicrystal of Al-Mn alloy was first discovered in melt-spun ribbon samples by Schechtman *et al.* in 1984.[1] Following this discovery, it was shown that the quasicrystalline phase can be formed by various methods such as annealing of glassy alloys,[2] transformation of amorphous alloys through ion-beam-assisted thermal processes,[3,4] and precipitation from solid solutions.[5] Investigations of the quasicrystals formed by various preparation techniques will add to our understanding of the stability and growth kinetics of this new phase. We reported previously[6] that Al-Mn alloy particles of icosahedral phase could be produced by a gas evaporation technique (GET), i.e., evaporation and condensation of the material in an atmosphere of a low-pressure inactive gas.[7] In the previous experiment, a piece of Al-Mn alloy was evaporated from a single source in He gas of 100 Torr, and the formation of the icosahedral phase was identified by powder electron diffraction patterns. In the present experiment, particles of Al-Mn alloys were produced by simultaneous evaporation of Al and Mn from two sources in Ar gas. The particles in the icosahedral phase were examined by selected-area diffraction and dark-field imaging in electron microscopy.

II. EXPERIMENTAL

The evaporation chamber for the sample preparation was a stainless-steel cylinder 21 cm in diameter and 25 cm in height. Two tungsten boats, which were independent evaporation sources of Al (purity 99.99%) and Mn (99.99%), were placed parallel to each other with a separation of 15 mm between their centers. The length, width, and depth of the boats are 50, 6, and 1.5 mm, respectively. The chamber was evacuated to a pressure of 1×10^{-6} Torr by an oil diffusion pump and Ar gas (99.99%) was introduced to a pressure of 30 or 100 Torr. Evaporation of Al and Mn was carried out under four different conditions as listed in Table I. The admitted Ar gas was at room temperature.

Since the heating of the sources brings about a convective flow of the gas, the metal vapor is exposed to this gas flow and cooled rapidly. A supersaturation sufficient for nucleation is attained and nuclei of the particles are formed. Eventually, a smoke cloud consisting of small particles is formed around the sources as shown in Fig. 1.

The smoke particles were collected on grids for electron microscopy from various positions at a vertical distance of 4 cm above the sources by using a collection device.[8] The particles thus obtained were studied under a 200-keV electron microscope with an energy-dispersive x-ray analyzer and a double-tilting holder.

III. RESULTS AND DISCUSSION

Quasicrystalline particles were formed most efficiently under condition No. 4 in Table I. When the Ar pressure (P_{Ar}) was low, i.e., 30 Torr, quasicrystals were not found. Figure 1 shows the smokes from the two evaporation sources, whose lengthwise directions are almost perpendicular to the photographic plate. Four dense zones (*A*, *B*, *C* and *D*) look bright due to scattering of light.

The composition of the particles varied as a function of

TABLE I. Parameters for preparation of Al-Mn alloy particles.

Preparation condition No.	Ar Pressure (Torr)	Al Source temp. (°C)	Mn Source temp. (°C)
1	30	1950	1500
2	30	2100	1500
3	100	1950	1500
4	100	2100	1500

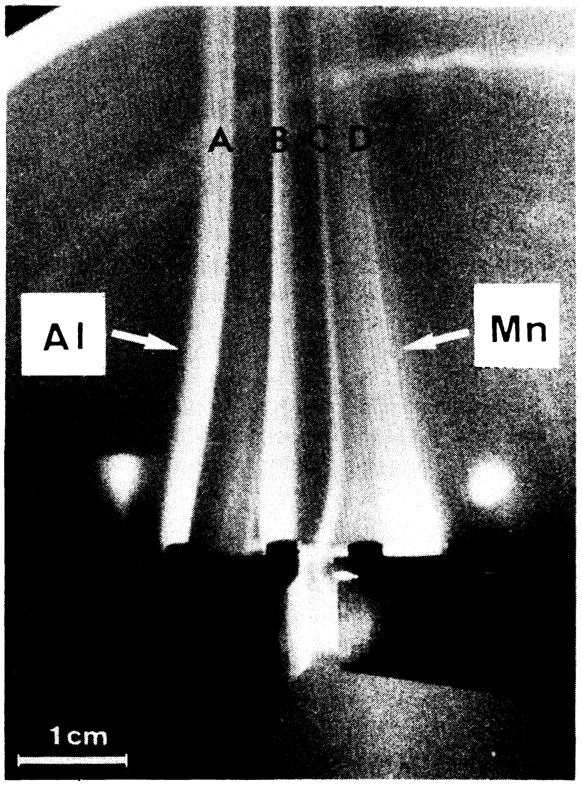


FIG. 1. Photograph of Al and Mn smokes. Al source: 2100 °C; Mn source: 1500 °C; Ar pressure: 100 Torr.

collection position on the horizontal cross section of the smokes: from pure Al at the extreme end of the Al smoke (zone *A*) to pure Mn at the other side of the Mn smoke (zone *D*). Quasicrystalline particles (500—3000 Å) were found in zone *B*, where the particle composition was appropriate for the formation of the phase. Particles in the other phases were also found in the same zone. Around 30% of the particles in zone *B* were quasicrystalline. The other particles in this zone were mainly fcc Al and orthorhombic Al_6Mn. However, α- and β-Mn particles were sometimes observed among the particles collected at the position corresponding to zone *B* due to the instability of the convective flow. X-ray energy dispersive analyses were carried out for aggregates of a few tens of particles including those in the various crystalline phases. The averaged composition of the particles in this zone was in a range of 8—32 at. % Mn. Though the composition of a single quasicrystal was not measured in the present experiment, the previous experiment showed that the Mn content for quasicrystalline particles was about 24 at. %.[6]

Figure 2 shows electron micrographs and the corresponding diffraction patterns of an Al-Mn particle in the icosahedral phase taken along three symmetry axes. Angles between the symmetry axes agree with those expected from the icosahedral point-group symmetry as shown in Fig. 3. The particle is spherical in shape, and shows speckled contrast characteristic of strain. Figure 4 shows dark-field images of the *i*—Al-Mn particle shown in Fig. 2. The dark-field images do not show uniform contrast but a granular one. The granular bright or dark areas

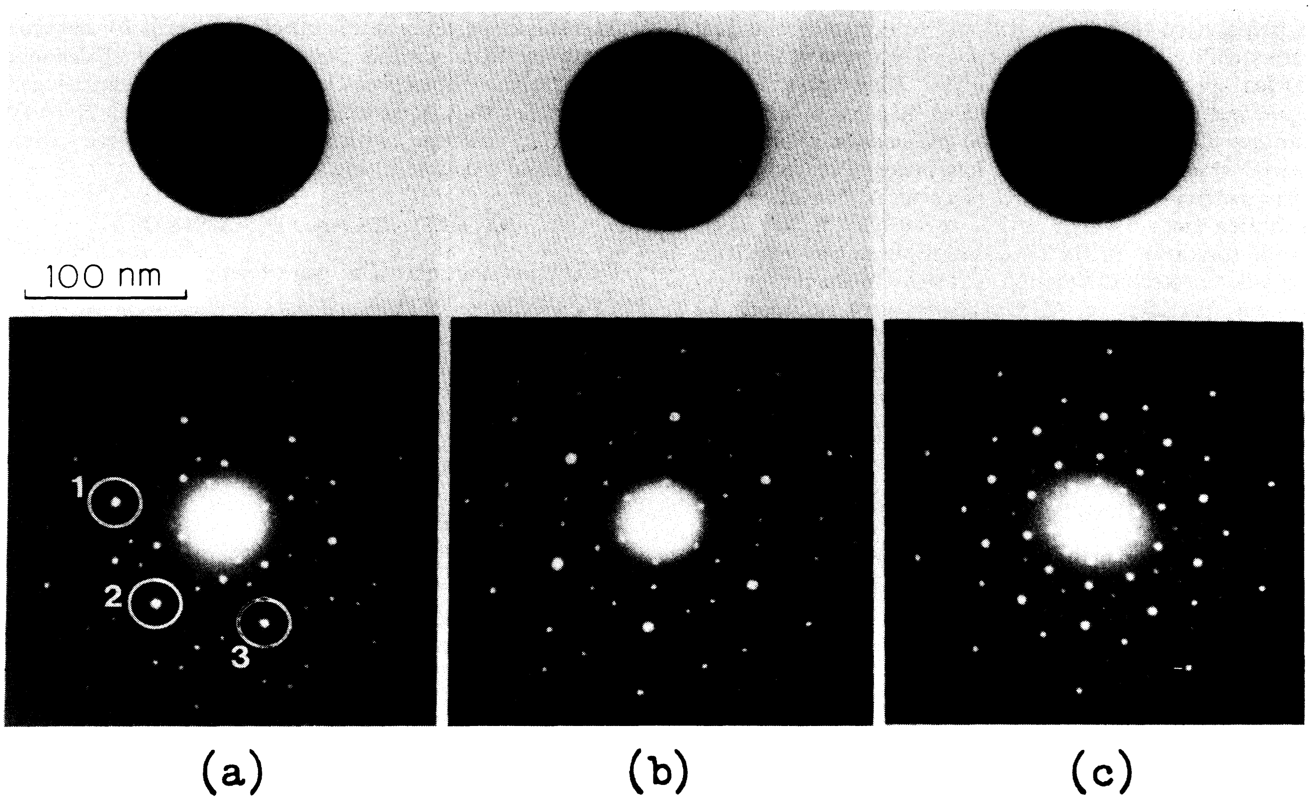


FIG. 2. Electron micrographs and the corresponding diffraction patterns taken from an *i*—Al-Mn particle. (a) Twofold axis; (b) threefold axis; (c) fivefold axis.

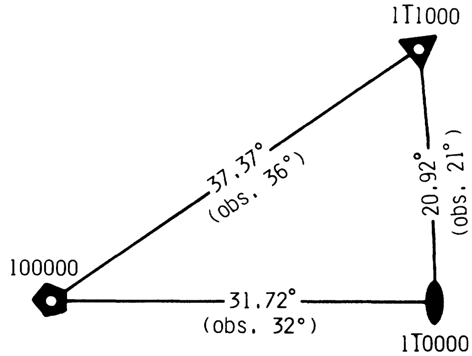


FIG. 3. Unit triangle of stereographic projection for the icosahedral symmetry. Angles between the symmetry axes are shown together with measured ones in parentheses.

change with the reflection used for dark-field imaging. Though the particle as a whole shows diffraction patterns like those of a single quasicrystal, the dark-field images show that this particle consists of domains with sizes of a few hundred angstroms. This characteristic is also found in the melt-spun samples.[4,9] Electron-energy-loss spectroscopy (EELS) work[9] with a small probe of 10 Å indeed indicates the presence of spatial chemical inhomogeneity on a 100-Å scale within icosahedral grains.

Figure 4 (DF2) shows that the central region of the particle has elongated domains of about 50 Å in width and a few hundred angstroms in length.

A study is now in progress to clarify the texture of the quasicrystals produced by GET. The reason why the diffraction patterns in Fig. 2 do not show deviations of spot position is presumably an averaging effect over many domains. Some quasicrystalline particles showed the splitting of diffraction spots.

It is worthwhile to note that the quasicrystalline particles formed by the present method are in a single phase. Quasicrystals obtained by melt spinning of Al_6Mn are often surrounded by rejecting Al, however a nearly single icosahedral phase can be formed in melt-spun Al-Mn alloys containing more than 20% Mn and $Al_{74}Si_6Mn_{20}$.[10] Recently, Bendersky and Ridder,[11] in their study on the cooling-rate dependence of quasicrystal formation during electrohydrodynamic atomization, have shown that, when particles are small ($\sim$3000 Å), solidification is massive without rejection of Al and the critical cooling rate is estimated to be $\sim 10^5$ °C/sec.

In the present experiment, quasicrystals were formed at $P_{\rm Ar}=100$ Torr, but not at $P_{\rm Ar}=30$ Torr. This may be attributed to the difference in the cooling rate of the particles during their flow along the convection. The external shape of the quasicrystalline particles suggests that they are formed in the process of rapid solidification of liquid alloy particles, because the spherical shape is characteristic of particles quenched from the liquid phase. The melting temperature of the Al-Mn alloy with the composition of 24 at.% Mn is about 1000 °C. The flow velocity of inactive gases and temperature distributions around the evaporation source have been measured by Yatsuya *et al.*,[12] and they also argued that the temperature of an Al particle with 1000 Å in diameter intimately follows the ambient gas temperature with a time constant of 10^{-6} sec. The temperature distributions around the double sources have also been measured by Kaito *et al.*[13] According to their measurements, for $P_{\rm Ar}=100$ Torr the flow velocity is about 100 cm/sec and the temperature gradient at the positions of temperature of 1000 °C is roughly 1000 °C/cm. Therefore, the cooling rate of the particles at

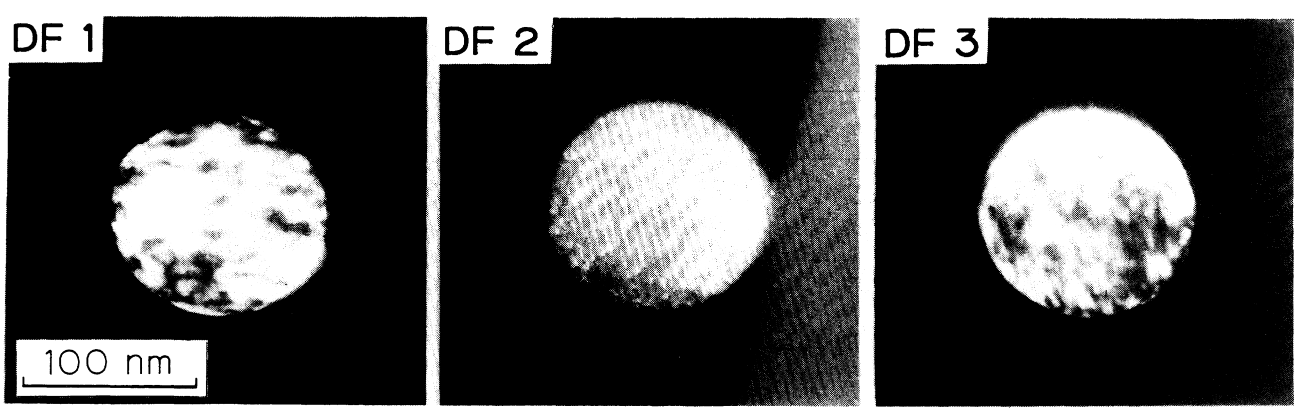


FIG. 4. Dark-field images of the particle shown in Fig. 2(a). DF1, DF2, and DF3 were taken with reflections 1, 2, and 3 in Fig. 2(a), respectively.

10^5 °C/sec. When the Ar pressure is lowered to 30 Torr, on the other hand, the flow velocity becomes about 50 cm/sec, and the temperature gradient at the position of 1000 °C is reduced to about 400 °C/cm, resulting in a cooling rate of 2×10^4 °C/sec. This value is one order of magnitude lower than that for $P_{Ar}=100$ Torr. This shows that the cooling rate of at least 10^5 °C/sec is required to form the quasicrystalline particles.

[1]D. Schechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2]S. J. Poon, A. J. Drehman, and K. R. Lawless, Phys. Rev. Lett. **55**, 2324 (1985).

[3]D. A. Lilienfeld, M. Nastasi, H. H. Johnson, D. G. Ast, and J. W. Mayer, Phys. Rev. Lett. **55**, 1587 (1985).

[4]K. Urban, N. Moser, and H. Kronmüller, Phys. Status Solidi A **91**, 411 (1985).

[5]J. D. Budai and M. J. Aziz, Phys. Rev. **33**, 2876 (1986).

[6]Y. Saito, H. S. Chen, and K. Mihama, Appl. Phys. Lett. **48**, 581 (1986).

[7]R. Uyeda, J. Cryst. Growth **45**, 485 (1978).

[8]S. Yatsuya, S. Kasukabe, and R. Uyeda, Jpn. J. Appl. Phys. **12**, 1675 (1973).

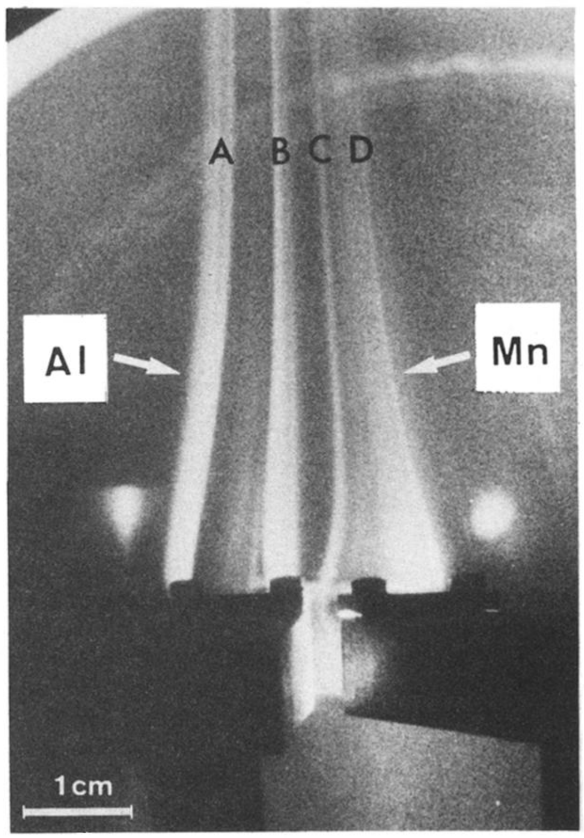
[9]C. H. Chen, D. C. Joy, H. S. Chen, and J. J. Hauser, Phys. Rev. Lett. **57**, 734 (1986).

[10]C. H. Chen and H. S. Chen, Phys. Rev. B **33**, 2814 (1986).

[11]L. A. Bendersky and S. D. Ridder, J. Mater. Res. **1**, 405 (1986).

[12]S. Yatsuya, A. Yanagida, K. Yamauchi, and K. Mihama, J. Cryst. Growth **70**, 536 (1984).

[13]C. Kaito and M. Shiojiri, Jpn. J. Appl. Phys. **21**, L421 (1982).



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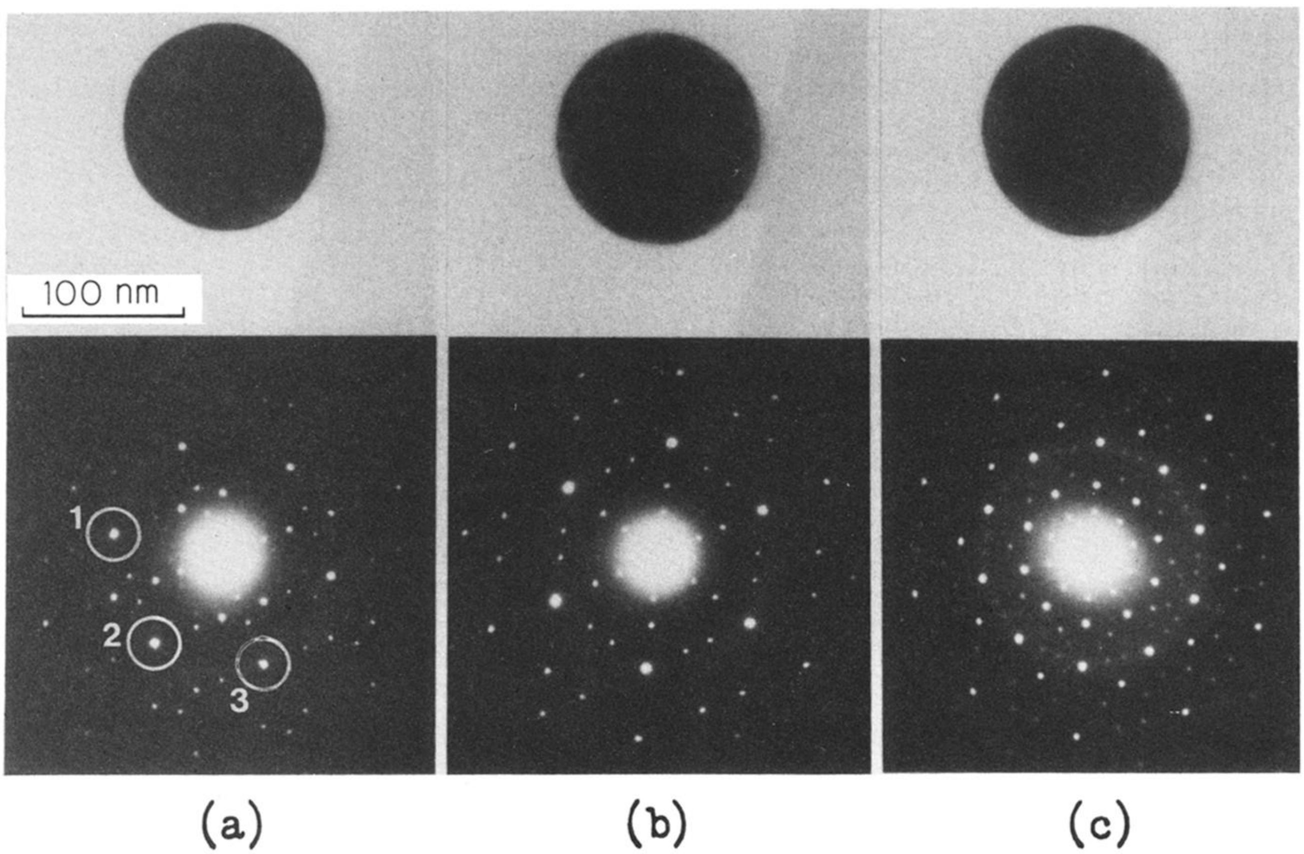

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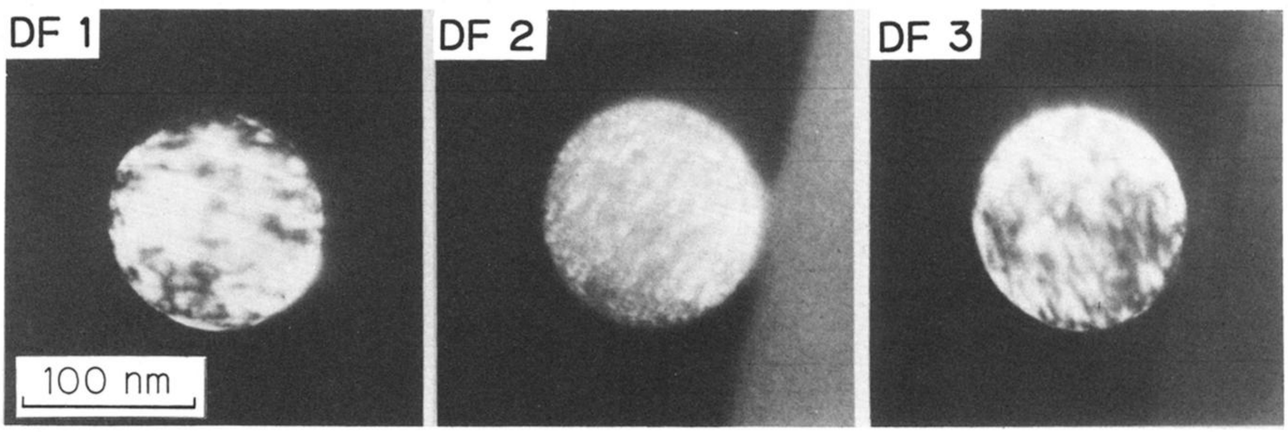

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