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Density, Young's modulus, specific heat, and stability of icosahedral $Al_{86}Mn_{14}$

H. S. Chen, C. H. Chen, A. Inoue,* and J. T. Krause
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The melt-spun icosahedral phase of $Al_{86}Mn_{14}$ exhibits a density ($=3.26\pm0.06$ g/cm^3) only slightly less dense by ~1% and a specific heat higher by ~0.20 cal/mol K compared with the stable orthorhombic phase. The room-temperature Young's modulus, however, is found to decrease drastically by ~20% from 12.60×10^{11} dyn/cm^2 for the orthorhombic phase to 10.12×10^{11} dyn/cm^2 for the icosahedral phase. The activation energy and heat of the icosahedral-orthorhombic transformation are found to be 53 kcal/mol and 560 cal/mol, respectively. The changes in these physical properties observed here are in many ways similar to those reported for many metal glasses. It is thus inferred that the icosahedral $Al_{86}Mn_{14}$ consists of a highly disordered defective structure.

It has been observed that a number of metallic solids and nonmetallic particles display fivefold symmetry in electron microscopy and diffraction patterns.[1] These particles have been often characterized by five tetrahedra which are bounded by {111} planes and twin planes related to one another.[2] If the pentagonal crystal consisted of perfect tetrahedra, a misfit angle of 7° 21′ should result. This misfit could be accommodated by lattice distortions or imperfections, and these particles would be stable energetically only for small clusters of $\sim10^3$ Å. Recently Shechtman *et al.*[3] observed long-range icosahedral orientation order and five fold symmetry in rapidly solidified $Al_{86}Mn_{14}$. Grains up to 2 μm in size were reported.

Different structural models have been proposed.[1,2,4] Bagley[1] proposed a structure which can grow continuously from a low-energy pentagonal dipyramid nucleus. It has fivefold symmetry and a packing density of 0.7236 to 0.7341 which is only slightly lower than that for close packing (0.7405) but higher than that of icosahedral packing (0.6882). Levine and Steinhardt[4] construct quasicrystals by extending the two-dimensional (2D) Penrose tiling concept.[5] The Penrose lattices exhibit the bond orientation correlation and a crystal structure with quasiperiodic, rather periodic, translational order. A 3D icosahedral quasicrystal has been generated with a pair of polyhedra which are the analog of the Penrose tiles. These polyhedra can form space-filling volumes of infinite extent with quasiperiodicity. Because of quasisymmetry, it contains confined vacant volumes throughout the structure and is believed to be less dense than a dense-random-packed solid.

We report here the density, Young's modulus, specific heat, and heat of transformation of icosahedral $Al_{86}Mn_{14}$. These physical parameters are known to be very important in constructing model structures for metallic glasses and are expected to be so for this novel icosahedral phase. We also report the kinetics of transformation and transmission electron microscopy (TEM) observations.

An $Al_{86}Mn_{14}$ alloy was made by induction melting of high-purity Al and Mn in a boron-nitride crucible under argon atmosphere. Ribbon samples of about 1 mm width and 30 μm thickness were obtained by melt spinning on a copper wheel ~20 cm in diameter rotating at 2000 rpm in an argon atmosphere. Samples were chemically thinned for TEM observations in an acid solution containing H_3PO_4, H_2SO_4, and HNO_3 at 75 °C. We found spherulites of icosahedral phase in agreement with Schechtman *et al.*[3] (see Fig. 2).

The density ρ of ribbons was determined by the Archimedean method. A Cahn balance with sensitivity of 0.001 mg was employed. Samples weighed about 10 mg and the uncertainty in the density obtained as an average of five measurements was about 1%. The Young's modulus sound velocity V_E was measured on ribbons about 20 cm length at 100 kHz and ambient temperature using a pulse-echo technique. The scatter of this measurement is about 10^{-3}. The Young's modulus was given by $E=\rho V_E^2$. The specific heat and kinetics of transformation of the icosahedral $Al_{86}Mn_{14}$ were measured with a Perkin-Elmer DSC-2 calorimeter. The measured data were better than ±0.2 cal/mol K for absolute specific-heat values and ±0.1 cal/mol K for the relative values. The samples were first scanned to 820 K to obtain data on the as-quenched state, then cooled to room temperature. The measurements were repeated *in situ* to obtain data for annealed samples. This procedure is necessary to eliminate the uncertainty in the positioning of the base line. Data were taken only when the isothermal baselines at the beginning and the end of the scans coincide with each other between the two consecutive runs. The change in apparent specific heat was monitored to examine the transformation behavior. Isothermal anneals were carried out at temperatures in the transforming regime. For these experiments the sample was heated at 80 K/min to the isothermal temperature.

Specific heats (C_p) and the rate of heat evolution (ΔC_p) of the icosahedral phase are shown in Fig. 1. The scanning rate was 40 K/min. For the temperature range measured, C_p's of $Al_{86}Mn_{14}$ increase linearly with temperature with $dC_p/dT=2.5\times10^{-3}$ cal/mol K^2 [Fig. 1(a)]. The icosahedral phase shows C_p values higher by 0.2 cal/mol K than the stable phase. The icosahedral phase was stabilized by heating to 640 K prior to the measurement. For comparison C_p's of pure Al were also mea-

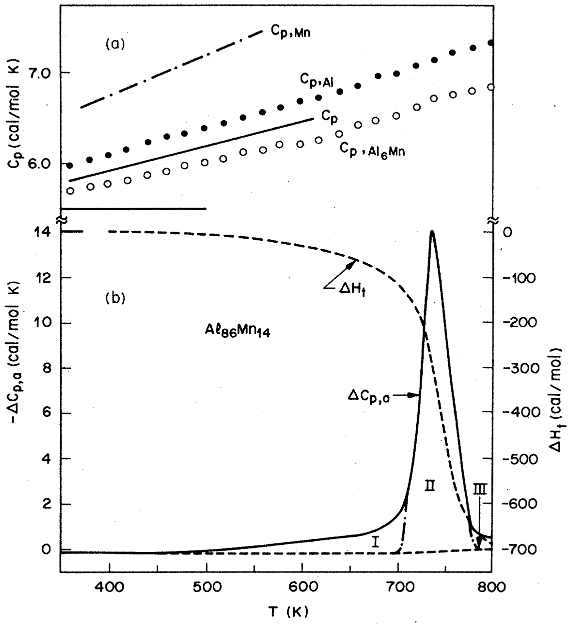

FIG. 1. The specific heat $C_p(a)$, the rate of heat evaluation $\Delta H_t/dT = \Delta C_{p,a}$, and the heat of transformation $\Delta H_t(T)$ of the icosahedral $Al_{86}Mn_{14}$. The scanning rate $dT/dt = 40$ K/min.

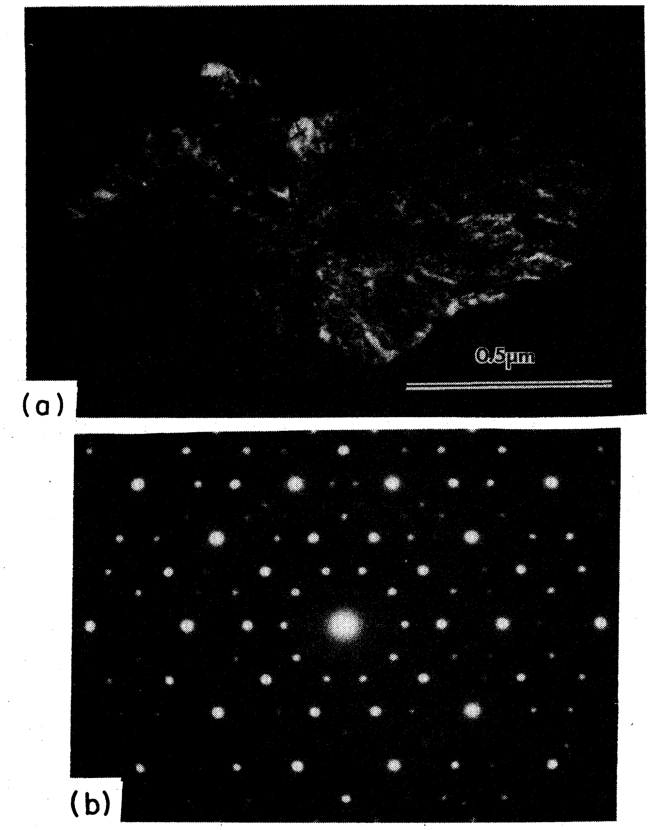

FIG. 2. (a) Dark field electron micrograph showing the morphology of the icosahedral domains, (b) selected area diffraction pattern showing fivefold symmetry.

sured which were found to be consistently higher by ~0.4 cal/mol K than the stable $Al_{86}Mn_{14}$. As shown in Fig. 1(b), the as-quenched samples transform to more stable phases in three distinctive stages: (1) a gradual transformation beginning at 450 K, (2) the main transition in the region between 680 K and 780 K, and (3) a continuing stabilization above 780 K. The heats (ΔH_t) evolved at each stage are ~90, 560, and 40 cal/mol, respectively.

Examination of the as-quenched sample in TEM reveals domains characterized by elongated branches stemming from a central nodule within the domain [Fig. 2(a)]. Typical domain sizes are of the order of ~1 μm. Selected areas of electron-diffraction patterns obtained from a single domain show fivefold symmetry [Fig. 2(b)] and are consistent with a point group $m\,\bar{3}\,\bar{5}$ (icosahedral) as previously reported.[3] Under favorable diffraction conditions the domains are found to be heavily speckled with sizes ~150 Å which may be related to the translational coherence in the icosahedral phase.

We have also studied the transformation from the metastable icosahedral phase to the stable orthorhombic phase *in situ* under vacuum inside an electron microscope. Figure 3(a) shows the icosahedral domains at room temperature before annealing. Annealing at 600 K for 15 min exhibits no significant changes in the domain structure except for some slight contrast enhancement near the domain boundaries which indicate that some relaxation of the existing strains in the icosahedral phase has occurred [Fig. 3(b)]. Upon further annealing at 650 K for 10 min, we found that most areas under examination have transformed into the stable Al_6Mn orthorhombic phase with a typical grain size ~2000 Å [Fig. 3(c)]. Many crystalline defects can be seen within the grains at this stage, which disappear with further annealing at this temperature for 30 min. The nucleation of the stable orthorhombic Al_6Mn phase was found to be inhomogeneous. Some metastable icosahedral domains remain intact whereas other domains have transformed completely into the stable phase. We did not notice any preferential nucleation sites either within the domains or at the domain boundaries. Annealing at even higher temperatures results in coarsening of the grains and the entire sample has transformed to the stable phase after annealing at 700 K for 20 min [Fig. 3(d)]. Electron diffraction shows a polycrystalline ring pattern characteristic of the stable phase. We have also examined samples annealed at elevated temperatures in an argon atmosphere before thinning for TEM studies, and they show essentially the same results.

The icosahedral heat evolution $\Delta H_t(t)$ of the main transition displays a familiar sigmoidal form. The kinetics of transformation were analyzed in terms of generalized theory of phase transformation. The fraction transformed x in time t is given by[6]

$$x = 1 - \exp(-bt^n)$$

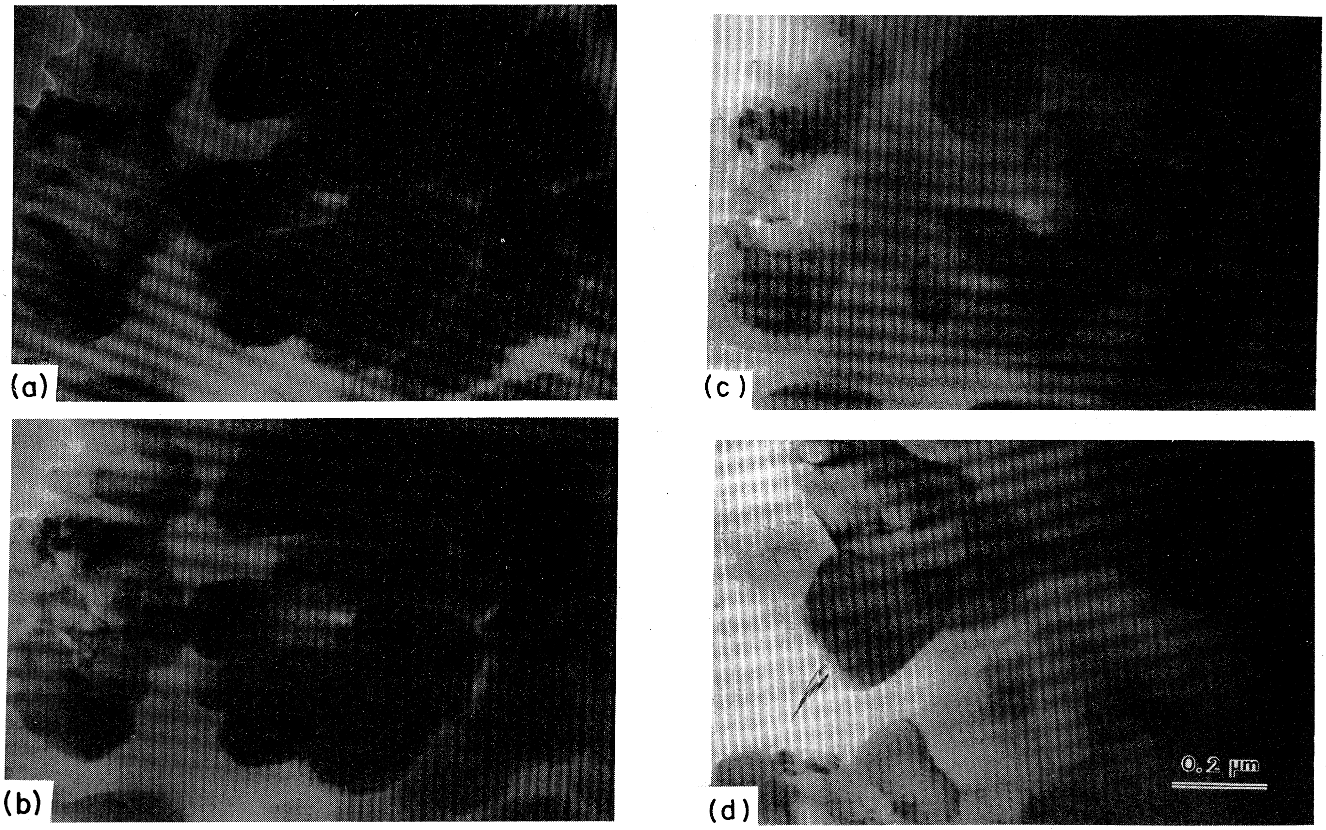

FIG. 3. (a) Electron micrograph of icosahedral domains at room temperature before thermal annealing, (b) same area after annealing at 600 K for 15 min, (c) same area after annealing at 650 K for 10 min, (d) same area after annealing at 700 K for 20 min.

or

$$\log_{10}[-\ln(1-x)]=\log_{10}b+n\log_{10}t\ , \qquad (1)$$

where b is a rate constant and n is an exponent depending on the mode of transformation. These plots are shown in Fig. 4. For $x \leq 0.8$ they fit straight lines with slope $n=2.1\pm0.1$. The activation energy for the transformation was deducted from $t(T)|_{x=0.5}$ data and found to be 53 kcal/mol.

The measured densities are 3.26 ± 0.06 g/cm^3 and 3.31 ± 0.07 g/cm^3, respectively, for the icosahedral and the stable $Al_{86}Mn_{14}$. The latter value agrees fairly well with the estimated density (3.306 g/cm^3) of the stable Al_6Mn from the measured lattice parameters.[7] The metastable icosahedral phase is only ($\sim 1\%$) slightly less than the stable phase, as has been commonly observed for glassy metals.

The Young's modulus sound velocities (V_E) are 5.572 km/s and 6.170 km/s, respectively, for the icosahedral and orthorhombic $Al_{86}Mn_{14}$. The Young's modulus $E=(\rho V_E^2)$ are calculated to be $(10.12\pm0.18)\times10^{11}$ dyn/cm^2 and $(12.6\pm0.27)\times10^{11}$ dyn/cm^2, respectively. These values are considerably higher than the mean value $\bar{E}=9.05\times10^{11}$ dyn/cm^2 estimated from values for the

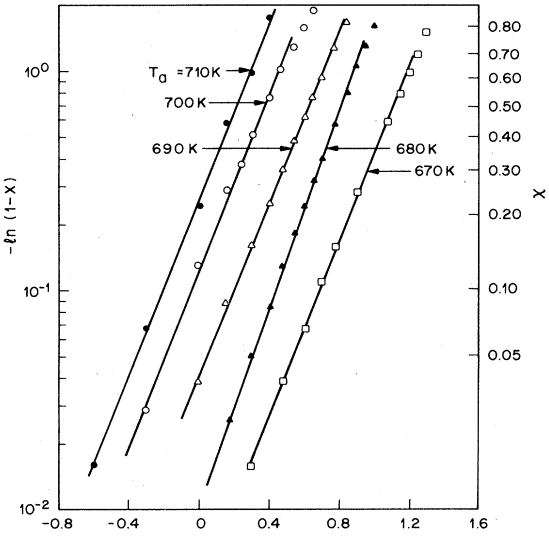

FIG 4. Avrami plots for various temperatures T_a.

TABLE I. The density ρ (g/cm^2), Young's modulus E (10^{11} dyn/cm^2), the specific heat at 300 K, $C_{p,300\ \mathrm{K}}$ (cal/mol K), the heat of transformation into stable phase, ΔH_t (cal/mol), and the activation energy Q (kcal/mol). The changes (%) in ρ and E refer to mean values. q, a, and m denote the as-quenched, annealed, and mixed states.

		ρ	E	$\Delta\rho/\bar{\rho}$	$\Delta E/\bar{E}$	$C_{p,300\ \mathrm{K}}$	Q	ΔH_t	T_t	T_m	$\Delta H_t/kT_m$
$Al_{86}Mn_{14}$	(q)	3.26	10.12	1.24	11.8	5.70	53	560	730	1190	23.8
	(a)	3.31	12.60	2.80	39.2	5.54					
	(m)	3.22	9.05			5.87					
$Pd_{77}Cu_6Si_{17}$	(q)	10.46	8.80	2.05	−17.7	6.75	110	924	670	1010	46.2
	(a)	10.51	11.64	2.54	9.8	6.50					
	(m)	10.25	10.69			5.92					

pure elements.[8]

Present results are summarized in Table I and compared with data reported for the $Pd_{77}Cu_6Si_{17}$ glassy alloy.[9] The icosahedral $Al_{86}Mn_{14}$ and the Pd-Cu-Si alloy glass show similar temperatures of transformation and melting. It should be noted that (1) both alloys in the stable phase show a higher density ($\Delta\rho/\bar{\rho}\sim 2\%$) and Young's modulus ($\Delta E/\bar{E}\simeq 10$—$30\%$) than the mean value of the constituting elements, (2) the metastable (i.e., the icosahedral and glassy) phases exhibit a lower density and Young's modulus as compared with the stable ones. The change in Young's modulus ($\Delta E/\bar{E}$) for the Al-Mn alloy is about two-thirds of that for the Pd-Cu-Si. This ratio is comparable to the relative change in the heat of transformation $\Delta H_t/RT_m$ (24% for the Al-Mn versus 46% for the Pd-Cu-Si), (3) the metastable phases as compared to the stable phases show densities slightly less ($\sim 1\%$) and specific heats higher (~ 0.20 cal/mol K), and (4) the activation energy of 53 kcal/mol for $Al_{86}Mn_{14}$ is close to the activation energies of self-diffusion in crystalline transition metals; Cu, Ni, Co, and Fe ($Q_D = 50$—60 kcal/mol).[10] The large Q value of Pd-Cu-Si is characteristic of stable glassy alloys.

From these observations, probable structural features of the icosahedral $Al_{86}Mn_{14}$ may be suggested as follows: Nicol[7] described the structure of the stable $Al_{86}Mn_{14}$ as consisting of a unit cell in which a manganese atom lies inside a polyhedron formed by the ten nearest Al atoms, eight of which are shared between neighboring polyhedra. The interatomic distance between the Mn atom and the unshared Al atoms $=2.435$ Å is much shorter as compared with Goldschmidt's radius of 2.68 Å deduced from the interatomic distances in pure metals. The average MnAl distance $=2.56$ Å is also considerably smaller by 0.12 Å, while the average Al-Al distance equal to 2.78 Å is about 0.08 Å shorter than the Goldschmidt radius. Electron charge transfer from Al atoms to Mn atoms has been suggested. These features reflect in a large negative heat of mixing (~ -3.6 kcal/mol) and volume contraction $\sim 2.8\%$ upon alloying. The closer contact between unlike atom elements is also characteristic of metal-metalloid glasses. For example, the glassy $Pd_{80}Si_{20}$ alloy exhibits Pd-Si distance equal to 2.42 Å which is significantly shorter than the sum of Pd and Si Goldschmidt radii ($=2.69$ Å), and negligibly close contact of Si atoms as found in the intermetallic crystalline structure.[11] Considering such similarities between the Al_6Mn and Pd-Cu-Si it is conceivable that similar short-range order existing in the crystalline Al_6Mn may also prevail in the melt and in the icosahedral phase.[12]

In view of the relative changes in Young's modulus and the heat of transformation between the icosahedral Al_6Mn and the Pd-Cu-Si glass as described above, the structure and thermal stability of the icosahedral phase should fall intermediate between the stable Al_6Mn and "glassy" $Al_{86}Mn_{14}$. The large decrease in Young's modulus in the glassy metals is an inherent character and has been attributed to the interatomic displacements (i.e., shear displacements) at regions of "defects" in a disordered structure, the defects being dislocation or disclinationlike. The icosahedral phase thus may consist of a highly defective disordered structure. A slightly lower density $\sim 1\%$ and higher specific heat ~ 0.20 cal/mol K in the metastable and glassy state than that in the stable state may be attributed to an enhanced anharmonicity associated with structural disorder.

The activation energy of the icosahedral-stable phase transition of Al_6Mn being the order of that of self-diffusion in crystalline transition metals would exclude an interstitional diffusion mechanism. The exponent $n=2$ found is rather small compared with $n=4$ and 5 commonly found for glassy metals. The identification of the modes of transformation has to await further TEM study.

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*Present address: The Research Institute for Iron, Steel and other Metals, Tohoku University, Sendai 980, Japan.

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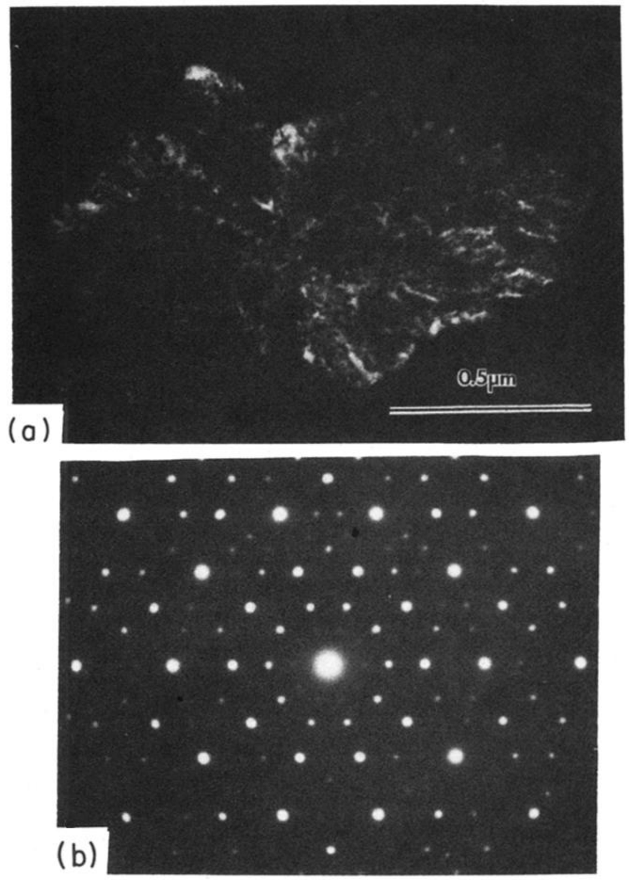

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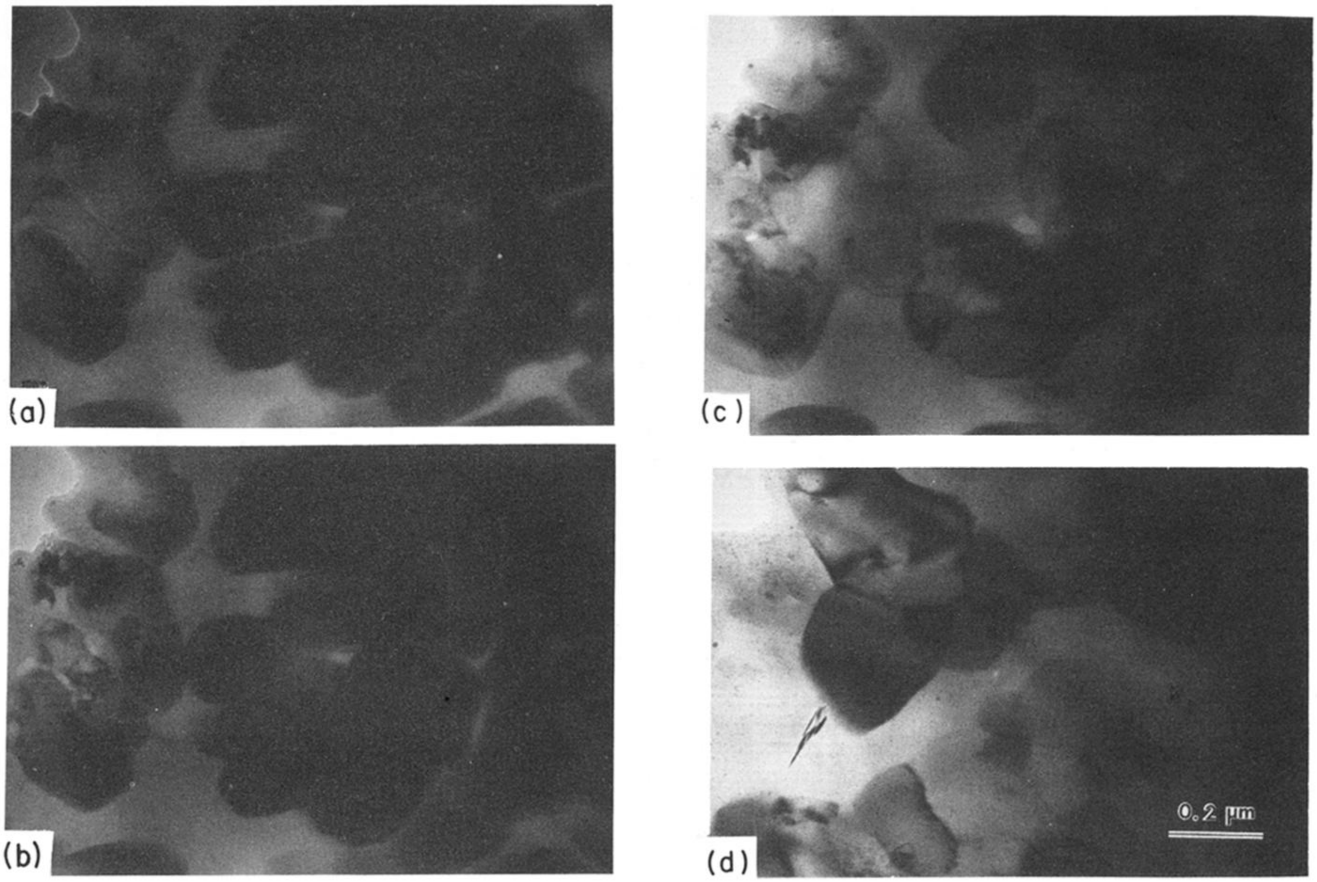

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