

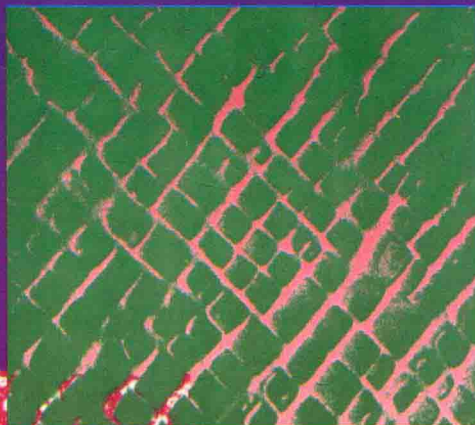
Volume 1

Microstructure *and* Properties *of* Materials

材料的显微结构和性能 第1卷

Editor

J.C.M.Li



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Volume 1

Microstructure and Properties of Materials

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PREFACE

This is an advanced text book on the microstructure and properties of materials, the first volume of a possible 3-volume set. While there are many elementary text books in materials science, there are very few advanced text books. In our graduate school courses, we rely on our own notes or some conference volumes and journal articles. One of the reasons is that there are so many different kinds of materials and each has its own microstructure property characteristics. So it is difficult for a single person to be expert in all the materials. Thus the idea of a multi-author collection appears good. I am inviting the best authoritative expert that I can find in each material area and since they are all busy people, it has taken longer than expected to finish the task. Hence this is the first volume which should be a good supplement to your microstructure course. If you are working with a certain material area in one of the chapters, you will find a rich source of design ideas and applications as well as a good understanding of how does the microstructure affect the properties.

Chapter 1 on aluminum alloys presents microstructural optimization and critical considerations in design applications. Chapter 2 on Nickel-base superalloys reviews the compositional, microstructural and processing advances in increasing their maximum use temperature. Chapter 3 on metal matrix composites discusses the strengthening mechanisms of metals dispersed with short fibers or particles. Chapter 4 on polymer matrix composites contains the details of the microstructure property relationships of high performance fibers, polymer matrix material and the advanced composites made therewith. Chapter 5 on ceramics matrix composites describes the fibers and matrix materials used, the processing techniques involved and the mechanical properties under different loading conditions. Chapter 6 on inorganic glasses describes the influence of second phases, both glassy and crystalline on their properties. Chapter 7 on superconducting materials shows the importance of twins, grain boundaries, dislocations and stacking faults. Chapter 8 on magnetic materials introduces the domain structure and its effects on the soft and hard magnetic properties.

Material problems are the bottle necks of most industries. New materials are created daily. But the principles and the relation between properties and microstructure remains the same. The more we know about these relations the easier will be to find new materials with desired properties.

James C. M. Li
Rochester, NY
October, 1995

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Chapter 1

MICROSTRUCTURE AND PROPERTIES OF ALUMINUM ALLOYS

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I. INTRODUCTION

A little over 100 years ago Charles Martin Hall, an American, and Paul Heroult, a Frenchman, independently developed a process which allowed the economical production of aluminum by electrolysis from a fused salt bath. Although aluminum was a "late comer," its versatility has resulted in it replacing many older, more established materials, so it now is consumed, on a volumetric basis, more than all other non-ferrous metals combined, including copper, lead and zinc [1]. Aluminum is light, ductile, has good electrical and thermal conductivity and can be made strong by alloying. An advantageous chemical property of aluminum is its reactivity with oxygen which leads to the formation of a dense layer of Al_2O_3 on the surface which shields the base metal from further environmental interaction. However, problems are encountered if the layer is disturbed, for example by second phases, plastic deformation which fractures the protective layer, or by friction (tribo-chemical reaction).

Aluminum alloys are classified as heat-treatable or non-heat-treatable, depending on whether or not they precipitation harden. However, the properties of both classes of alloys depend on their structural characteristics and can be associated with different levels of structure:

(A) *The atom:* The low density is due to the low atomic mass ($A_{Al} = 27$). By alloying with Mg ($A_{Mg} = 24$) or Li ($A_{Li} = 7$), for example, the density can be reduced still further. Other elements, e.g., Si ($A_{Si} = 28$), have little effect.

(B) *The phase:* The ductility and formability of aluminum is due to the high symmetry and thermodynamic stability of the fcc lattice (high stacking fault energy), Fig. 1. Other phases of interest include aluminum solid solutions, intermetallic compounds (Al_3Ti), non-metallic compounds (AlN), quasi-crystals and metallic glasses.

(C) *The microstructure:* The high strength of precipitation hardened alloys is associated with an ultra-fine dispersion of particles ($d < 10$ nm). Other microstructural features, e.g., grain boundaries, may have a beneficial effect on strength, but may have a detrimental effect on fracture resistance, Fig. 2.

There are a number of properties that distinguish aluminum and its alloys from other metallic materials and these include:

(1) An intermediate melting temperature ($T_m = 930\text{K}$) of the fcc crystal, which results in substitutional diffusion being slow but not impossible at ambient temperatures ($20^\circ\text{C} \sim 1/3 T_m[\text{K}]$).

(2) The high stacking fault energy (SFE) of the fcc crystal is not considerably lowered by solute additions: $\gamma_{\text{Al}} = 200\text{mJm}^{-2} > \gamma_{\text{Ni}} > \gamma_{\text{Fe}} > \gamma_{\text{Cu}} > \gamma_{\text{Au}}$. It follows that cross slip of dislocations is easy and crystal plasticity is high. Microscopic plasticity is similar to that of $\gamma\text{-Fe}$ above its brittle transition temperature. However, unlike Fe, aluminum stays ductile down to at least 4K. There is a low probability for the formation of twins during plastic deformation or recrystallization. This implies crystallographic textures different from low SFE alloys (Cu, Au, $\gamma\text{-Fe}$). Dislocation rings may form by condensation of vacancies during quenching or annealing. This phenomenon has not been observed to the same extent in other fcc metals.

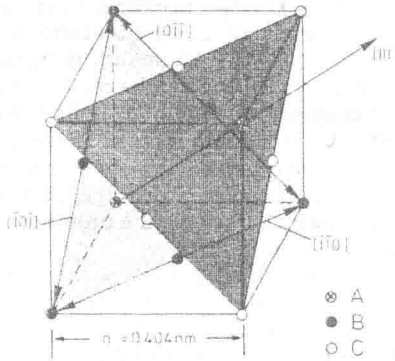


Fig. 1. The face-centered cubic (fcc) lattice with (111) slip planes and $\langle 110 \rangle$ slip directions; stacking sequence ABC....

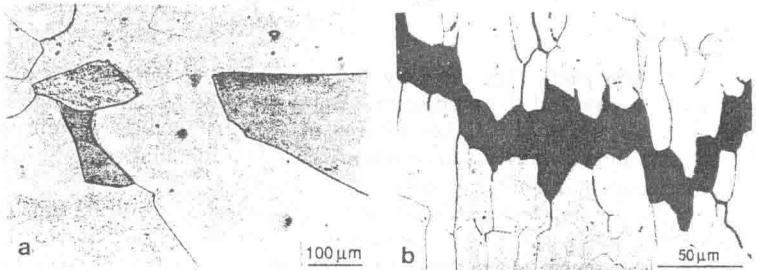


Fig. 2. Light micrographs of (a) grain structure of 99.9 Al; (b) intercrystalline stress corrosion cracking in an Al-Cu-Mg-Li alloy.

(3) Aluminum forms intermetallic compounds with most metals. Solute elements like Be, Si, Zn, Ga, Ge, etc., solidify by eutectic crystallization without forming compounds. Alkaline metals, except for Li, form no compounds and are completely insoluble in the solid state. Compounds with small atoms AlB_2 , Al_4C_3 , AlN , Al_2O_3 are ceramic phases with predominately covalent and ionic bonding. The solubility of small elements is very limited in liquid aluminum. The covalently bonded elements Si and Ge behave as metals in liquid and solid solution with aluminum, Fig. 3. There exists no case of complete miscibility in the solid state. Miscibility is largest with Zn which forms no compounds with aluminum.

(4) Quasicrystalline phases, i.e., non-periodic, ordered structures, were first found in certain Al-(transition element) alloys. Formation of metallic glasses seems to be more difficult than in some other metals, but glasses have been found in Al- T_1 - T_2 , where, for example, $T_1 = Ni$; $T_2 = Y$, Table 1, Fig. 4.

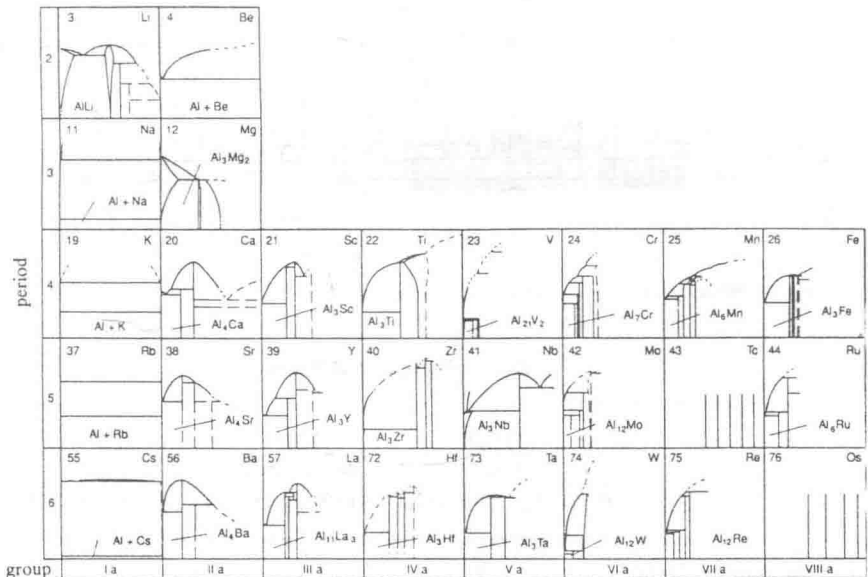


Fig. 3. Binary phase diagrams of aluminum.

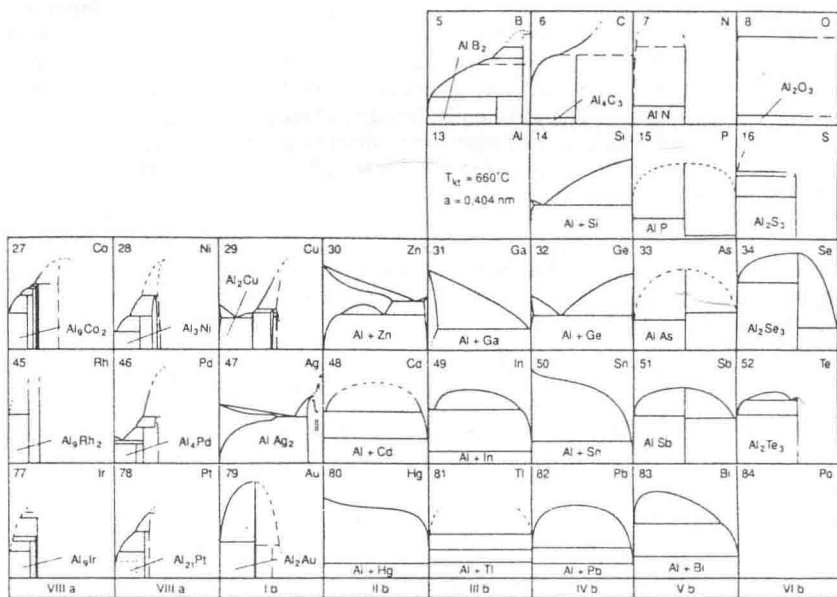


Fig. 3. Binary phase diagrams of aluminum (continued).

Table 1. Types of Solid Phases

	1920 crystal	1984 quasi-crystal	1988 glass
	α -Al (Mg), Θ -Al ₂ Cu	Al-Mn, Al-Cu-Fe	Al-Ni-Y
transitional lattice	+	-	-
long-range order	+	+	-

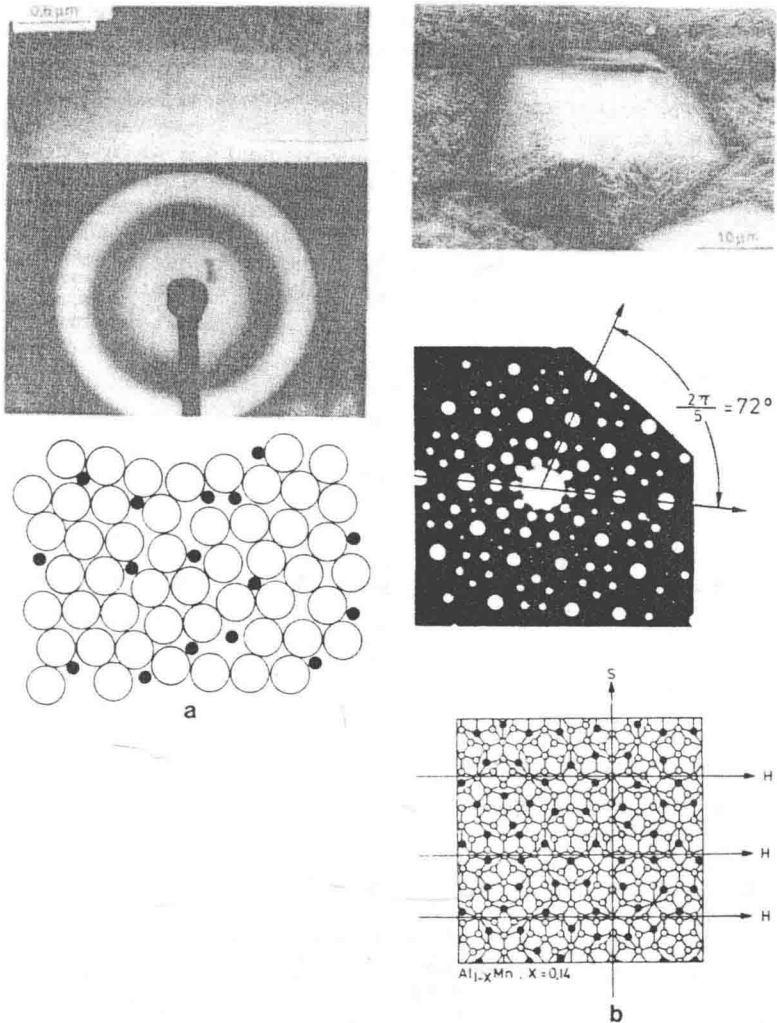


Fig. 4. Non-equilibrium structures:

(a) TEM of AlYNi-glass, electron diffraction, planar structure model; (b) SEM of icosahedral quasi-crystal of an AlFeCu alloy, electron diffraction showing five-fold symmetry, and planar structure model for Al-14at.%Mn.

(5) Diffusion of transition elements (Cr, V, Fe, Co, Ni) in aluminum is anomalously slow, which originates from electronic interactions between aluminum and these elements. Low solubilities of the transition elements (except for Mn) most likely have the same origin as the low diffusion coefficients, Table 2.

(6) The ratio of E/ρ is almost equal for Al, Mg, Fe and Ti but less than Cu, Pb and Zn.

(7) The most important non-metallic compound is Al_2O_3 which is useful as a protective surface layer, fiber and ceramic material.

(8) No polymorphous phase transformations or martensitic transformations of Al-solid solutions or Al-rich intermetallic compounds are known. Consequently, microstructures such as pearlite, bainite or martensite which are known in steels, titanium and copper alloys are absent.

Table 2. Diffusion and Solubility Data for Transition Metal Additions in Aluminum [73,74]

Element	D_0 (cm^2/s)	Q (KJ/mole)	Max Solubility (wt%)
Co	250	175	~0
Cr	1850	253	0.77
Fe	135	193	0.052
Mn	104	211	1.82
Ni	4	146	0.05

Alloy Designation System

The Aluminum Association uses a four digit numerical system to identify aluminum alloys [2]. The system used for wrought alloys is slightly different from that used for cast alloys and both are described in Table 3. For wrought alloys the first digit indicates the alloy group and the last two digits identify the aluminum alloy or indicate the aluminum purity. The second digit indicates modifications of the original alloy or impurity limits. Experimental alloys are also identified in accordance with this system, but they are indicated as experimental by the prefix X. The first digit used for casting alloys and foundry ingots also identifies the alloy group. However, the second two digits identify the aluminum alloy or aluminum purity. The last digit, which is preceded by a decimal point, indicates the product form (i.e., .0 for casting and .1 for ingot). A serial letter before the numerical

designation indicates a modification of the original alloy or impurity limits. The serial letters are assigned alphabetically, but omitting I, O, Q and X. The X is reserved for experimental alloys.

Table 3. Aluminum Alloy Designation Systems

<i>Alloy type*</i>	<i>Four-digit designation</i>
Wrought alloys	
99.00% (min) aluminum	1XXX
Copper	2XXX
Manganese	3XXX
Silicon	4XXX
Magnesium	5XXX
Magnesium and silicon	6XXX
Zinc	7XXX
Others	8XXX
Casting alloys	
99.00% (min) aluminum	1XX.X
Copper	2XX.X
Silicon with added copper and/or magnesium	3XX.X
Silicon	4XX.X
Magnesium	5XX.X
Zinc	7XX.X
Tin	8XX.X
Others	9XX.X

*Designations are based on aluminum content or main alloying elements

II. STRENGTHENING MECHANISMS

The strength of pure aluminum limits its commercial usefulness, and a major function of alloying is to improve this property. For structural use, the strongest alloy which meets minimum requirements for other properties such as corrosion resistance, ductility, toughness, etc., is usually selected if it is cost effective. Consequently, composition is first selected for strength.

Structural alloys are rarely strengthened by one hardening mechanism alone, Table 4. There are six mechanisms which are relevant to Al-alloys: (i) solid solution hardening, (ii) work hardening and substructure hardening, (iii) grain size hardening, (iv) precipitation and particle hardening, (v) texture hardening, and (vi) fiber reinforcement. Magnesium is the only element that offers significant solid solution hardening in aluminum. Texture hardening and fiber reinforcement will not be discussed in detail in this chapter. However, sharp textures which result in slip systems of low resolved shear stress also result in high yield strengths and fiber reinforcement may be

described, in the simplest case, by the law of mixtures. The four major strengthening mechanisms are listed according to the geometric dimension ($i = 0, 1, 2, 3$) of the obstacles which impede gliding (and/or climbing) of dislocations [3].

$$\sigma_y = \sigma_{\perp} + \sum \Delta\sigma_i = \sigma_{\perp} + \Delta\sigma_0 + \Delta\sigma_1 + \Delta\sigma_2 + \Delta\sigma_3 \quad [1a]$$

There is, however, not a simple additivity of the contributions $\Delta\sigma_i$ from the individual mechanisms to the yield stress σ_y . σ_{\perp} , the yield stress of pure (99.99) Al, amounts to 16 MPa at ambient temperature and 60 MPa at -200°C .

Table 4. Elementary Hardening Mechanisms in Al

	<i>Geometric dimensions</i>	<i>Obstacle</i>	<i>Density</i>	<i>Designation</i>		
1	$\Delta\sigma_0 = \Delta\sigma_{ss}$	0	solute atom	m^{-3}	C	solid solution hardening
2	$\Delta\sigma_1 = \Delta\sigma_D$	1	dislocation	m^{-2}	ρ_D	work hardening, substructure hardening
3	$\Delta\sigma_2 = \Delta\sigma_B$	2	grain boundary	m^{-1}	S_B^{-1}	grain size hardening
4	$\Delta\sigma_3 = \Delta\sigma_p$	3	particle, pore	m^0	f_p	precipitation hardening
5	$\Delta\sigma_c$	-	crystal anisotropy	-	-	texture hardening
6	$\Delta\sigma_M$	-	discontinuous and continuous fibers	-	-	fiber reinforcement

A quantitative approach to the understanding of a high yield strength σ_y of Al-alloys requires a differentiation between "hard" and "soft" obstacles, Table 5. This classification depends on whether glissile dislocations are bent to semicircles or not. Dislocations are not bent in semicircles in pure aluminum, aluminum solid solutions, or alloys containing only shearable precipitates. The addition of "hard" obstacles causes dislocations to loop and bypass the nonshearable particles. This behavior can be described by the following expression:

$$\sigma_y = \sigma_{\perp} + \Delta\sigma_s + \Delta\sigma_H \quad (1b)$$

which describes a solid solution matrix containing shearable particles and a dispersion of small non-shearable particles. Whether a certain type of particle

is sheared or looped, depends on the size of the particle and the nature of the hardening mechanism. The critical particle diameter, d_c , for the transition from shearing to looping or bypassing can be estimated by examining F , the force a single particle is able to exert on a single dislocation [4]. For $F < Gb^2$, shearing occurs, and for $F \geq Gb^2$ bypassing occurs.

Table 5. Examples of Hard and Soft Obstacles in Al

<i>Hard obstacles (H)</i>	<i>Soft obstacles (S)</i>
particles $d > d_c$ pores sessile dislocations	particles $d < d_c$ solute atoms, vacancies short range order, clusters, antiphase domain boundaries (APB)

Particle-strengthened aluminum alloys may contain ordered or disordered particles that may be coherent, partially coherent, or incoherent with the matrix. For ordered, coherent particles, $F = \gamma d$ where γ is the antiphase boundary energy, and d is the particle diameter. The critical diameter may be expressed

$$d_c = G_\alpha b^2 C / \gamma \quad (2a)$$

where G_α is the shear modulus of the solid solution and b the Burgers Vector of a matrix dislocation. For disordered, coherent particles which have a critical resolved shear stress, τ_β , that is different from the matrix, τ_α ,

$$d_c = G_\alpha b C / |\tau_\alpha - \tau_\beta| \quad (2b)$$

For particles which have a different crystal structure from the matrix,

$$d_c = 4\pi G_\alpha b C / G_\beta \quad (2c)$$

C in the above equations is a dimensionless factor determined by the shape of the particle and is close to unity for spherical particles. These expressions do not consider that dislocations may, in some cases, travel in pairs or pile up at a particle if planar slip occurs. For the latter solution, the right side of Eqs. 2a-c should be multiplied by N , the number of dislocations in the pile up.

A mixture of two "hard" species H_1 and H_2 introduces a new smaller effective spacing S_{eff} : $1/\sqrt{S_{\text{eff}}} = 1/\sqrt{S_1} + 1/\sqrt{S_2}$ and the following addition of the individual contributions $\Delta\sigma_i$:

$$\sigma_y = \sigma_{\perp} + \Delta\sigma_s + (\Delta\sigma_{H_1}^2 + \Delta\sigma_{H_2}^2)^{1/2} \quad (3a)$$

The contribution from dislocation density, ρ_D , is defined as:

$$\Delta\sigma_{H_1} = \Delta\sigma_D = G\alpha b\rho_D^{1/2} \quad (3b)$$

The contribution from particles that are bypassed by dislocations can be described by the modified Orowan equation:

$$\Delta\sigma_p = Gb/S_p \approx Gb\sqrt{f_p}/d \quad (3c)$$

for $S_p \gg d$. S_p is the spacing of the particle centers, and f_p is the volume fraction of particles.

Interaction with several dislocations (pile-up, cell structure formation) is required to derive the grain size dependence of the yield stress:

$$\Delta\sigma_B = k_y/\sqrt{S_B} \quad (3d)$$

where k_y is the Petch factor, i.e., a parameter associated with the relative hardening contribution of the grain boundaries, and S_B is the grain diameter. The pile-up model is only applicable when the aluminum alloy contains shearable particles because the high stacking fault energy of Al prohibits localized slip.

A comprehensive equation can be established for the different contributions to the yield strength of Al-alloys for the first four elementary hardening mechanisms listed in Table 4:

$$\sigma_y = \sigma_{\perp} + \Delta\sigma_s + (\Delta\sigma_D^2 + \Delta\sigma_p^2)^{1/2} + k_y/\sqrt{S_B} \quad (4)$$

where

- σ_{\perp} = pure aluminum
- $\Delta\sigma_s$ = solid solution, shearable particles
- $\Delta\sigma_D$ = dislocations, subboundaries
- $\Delta\sigma_p$ = hard, nonshearable, particles
- k_y/S_B = grain boundaries.