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20. This research was supported in part by the Sprague Electric Company. We thank S. Esnouf for contributions to the ac conductivity measurements.

27 June 1994; accepted 8 September 1994

Precipitation Hardening in the First Aerospace Aluminum Alloy: The Wright *Flyer* Crankcase

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Aluminum has had an essential part in aerospace history from its very inception: An aluminum copper alloy (with a copper composition of 8 percent by weight) was used in the engine that powered the historic first flight of the Wright brothers in 1903. Examination of this alloy shows that it is precipitation-hardened by Guinier-Preston zones in a bimodal distribution, with larger zones (10 to 22 nanometers) originating in the casting practice and finer ones (3 nanometers) resulting from ambient aging over the last 90 years. The precipitation hardening in the Wright *Flyer* crankcase occurred earlier than the experiments of Wilm in 1909, when such hardening was first discovered, and predates the accepted first aerospace application of precipitation-hardened aluminum in 1910.

Progress in the aerospace industry, from the development of commercial airliners to the space shuttle, has been dependent on the great strength and fracture toughness provided by precipitation hardening (*1*), especially in aluminum-based alloys. In the historic first flight of 17 December 1903, Wilbur and Orville Wright used an Al–8% copper alloy (with about 1.0% iron and 0.4% silicon as impurities) (*2*) for the crankcase of their self-designed internal combustion engine because of the alloy's strength and the weight requirements of the aircraft. This alloy represented the state of the art in casting alloys at the turn of the century, primarily because of its good casting qualities (*3*). The crankcase of the original engine has recently been identified (*4*, *5*); because it was the only Al part on the Wright *Flyer*, it thus became the first aerospace Al. Our study here reports the microstructure and strengthening mechanisms operating in this crankcase alloy.

Small samples of the *Flyer* crankcase were taken from three locations in the crankcase wall (*6*), which was approximately 4 to 5 mm thick. The microstructure (Fig. 1) consists of a typical solidification structure of α-Al dendrites (*7*) [face-centered-cubic (fcc) crystal structure] with interdendritic blocky θ-Al_2Cu and needlelike ω-Al_7Cu_2Fe phases. Dendrite arm spacings ranged from 40 to 80 μm, which suggests that the local solidification time was approximately 2 min (*8*). A gradient of Cu content across the dendrites, or coring, is expected in Al-Cu solidification structures and was analyzed by electron microprobe (*9*). The concentration of Cu was about 2.25% near the dendrite centers and approximately 4.75% near the surface of the dendrites (*10*). Most of the Cu in the alloy is thus present in the interdendritic intermetallic phases Al_2Cu and Al_7Cu_2Fe.

A higher spatial resolution than that attainable with optical microscopy is required to detect precipitates formed in the solid state in Al alloys. Transmission electron microscopy (TEM) (Fig. 2) revealed a remarkably well developed Guinier-Preston (GP) zone structure (*1*, *11*, *12*). These metastable GP zones consist of disks of Cu, a single atomic layer in thickness, lying on the three equivalent {100} planes within the fcc Al matrix. GP zones are readily imaged in TEM because of the large strain field associated with the zone, resulting in images several atomic layers in apparent thickness. Two mutually perpendicular variants, viewed edge-on, are apparent in this specimen orientation, viewed down a cube orientation of the matrix, or **B** = [001]. The zones are predominantly 10 to 20 nm in diameter. An occasional precipitate of θ′-Al_2Cu with a neighboring region free of GP zones (a result of solute depletion) was also observed, but occurs with a statistically unknown number density because of the small volume examined by TEM.

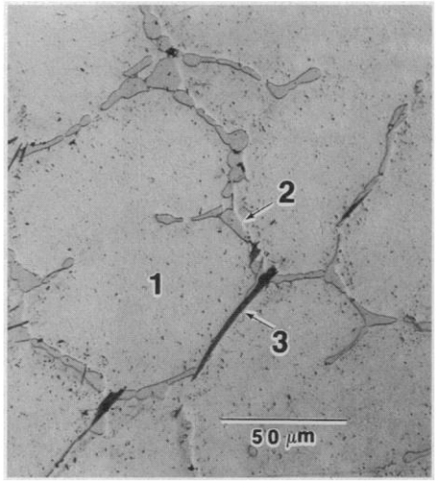

Fig. 1. Typical microstructure of the Wright *Flyer* crankcase (light optical micrograph), showing dendrites (area 1) of fcc Al(Cu) and the interdendritic second phases Al_2Cu (arrow 2) and Al_7Cu_2Fe (arrow 3). The dendrites exhibit coring wherein the center of each dendrite is approximately 2.25% Cu, increasing to 4.75% Cu at the edge of the dendrite.

Coring, or microsegregation of Cu during solidification, had a pronounced effect on GP zone size and distribution. The regions richest in Cu, near the edges of the dendrites, contained a very dense zone structure, with individual zones about 10 nm in diameter (Fig. 2A). Intermediate Cu levels resulted in a somewhat lower density of zones, although the zones were significantly larger (up to 20 nm in diameter) (Fig. 2B). The Cu-poor regions, near the dendrite centers, contained a low density of GP zones, with diameters from 18 to 22 nm. Close inspection of this region revealed a second distribution of GP zones, consisting of a large number of very fine zones, typically 3 nm in diameter (Fig. 2C).

Electron diffraction patterns for the Cu-rich and Cu-poor regions confirm the presence of GP zones. In a cube orientation, Bragg reflections from the fcc matrix planes occur as bright spots in a square array. Reflections from the GP zones appear as continuous streaks because of the very thin disk morphology of the zones (one unit cell in thickness). The continuous nature of the streaks shows that the zones are monoatomic layers of Cu atoms known as GPI zones: streaks from GPII zones, or θ″, would show intensity maxima halfway between the fcc Bragg reflections (*13*). The streaks are very pronounced in regions with dense GP zones (Fig. 2A, inset) and are only barely visible in the regions with small amounts of Cu (Fig. 2C, inset).

The appearance and bimodal distribution of GP zones in the *Flyer* crankcase can be understood in terms of the phase diagram (Fig. 3) that describes the metastable equilibrium between α-Al and GP zones as well as the equilibrium Al-θ(Al_2Cu) system. The requirements for precipitation of a phase (whether stable or metastable) are (i) sufficient supersaturation for nucleation of the precipitate or for spinodal decomposition (a thermodynamic instability whereby nucle-

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ation is not necessary) and (ii) adequate atomic diffusivity. In the Al-Cu system, GP zones are not normally observed to develop at room temperature, a fact that can be attributed to the low diffusivity of Cu in Al (*14*).

From this and the observation of a duplex size distribution of the zones in the crankcase, we conclude that the large GP zones, with diameters from 8 to 22 nm, must have precipitated during elevated temperature exposure. Because the crankcase cracked after the four flights on 17 December 1903, when a gust of wind flipped the aircraft over, this elevated temperature exposure did not occur after the first flight, but only through testing of the engine before the first flight or during the slow cooling associated with the sand casting. From the phase diagram, it is apparent that the GP zone development must have occurred at temperatures below 200°C for the 4.75% Cu regions and below 130°C for the 2.25% Cu areas, because the zones would not be stable above these temperatures.

In an Al-Cu alloy with significant supersaturation, GP zones develop by spinodal decomposition. The spacing between zones (before coarsening) is determined by the fastest growing wavelength during decomposition. The favored wavelength is inversely related to the second derivative of the free energy versus composition function, which is zero at the spinodal line (located inside but near the GP zone solvus curve) (Fig. 3) and increases (negatively) with an increase in Cu or a decrease in temperature (*15*). Thus, the favored wavelength in the region with a large amount of Cu is smaller than in the regions with small amounts of Cu, and the resulting spacing between zones is smaller. The growth of zones is ultimately limited by solute depletion in the matrix. Despite its high solute concentration, the region with a large amount of Cu is depleted of solute by the time the zones have grown to about 10 nm. With a longer optimal wavelength or spacing between zones, in the regions with smaller amounts of Cu the zones grow to about 20 nm in diameter before solute is depleted. Thus, the regions with large amounts of Cu developed a fine, dense structure of GP zones, whereas regions with smaller amounts of Cu developed a less dense structure with larger zones.

Such precipitation of GP zones—for instance, at 100°C—would deplete the Cu content of the matrix to about 1%. As seen in the phase diagram, on cooling to room temperature the equilibrium solubility of Cu is reduced to about 0.2%, and consequently the supersaturation is increased dramatically. However, room temperature diffusivity in the Al-Cu binary system is so low that zones have not previously been observed to develop in the regime with small amounts of Cu (that is, 1% Cu). Nevertheless, for compositions within the spinodal regime, the solid solution is unstable and will decompose, given enough time. This "experiment" has been underway for 3×10^9 s (90 years). The passage of this time apparently has resulted in the precipitation of the very fine GP zones (3 nm) observed in the regions with small amounts of Cu. On the other hand, the areas with large amounts of Cu do not contain a distribution of the smallest zones because the increased room temperature supersaturation can be easily depleted by growth of the finely spaced zones formed at higher temperatures.

To investigate the possibility that the GP zone–strengthened structure in the Wright alloy was a result of the casting practice, we attempted to reproduce the microstructure by casting a similar alloy. Anecdotal evidence from builders of replicas of the *Flyer* emphasizes the difficulty of obtaining a sound casting in such a complex, thin-walled design (*16*), which suggests that some degree of mold preheat was used. We cast an Al–8%Cu–1%Fe–0.4%Si alloy into sand molds to produce the same 4 to 5 mm wall thickness as the sample locations in the crankcase. The molds were either at room temperature or preheated to 100° or 170°C. Figure 4 shows the resulting microstructures: with no preheating, there was no GP zone formation, but some θ′ on grain boundaries (Fig. 4A); with preheating to 100°C (Fig. 4B), there was an abundance of GP zones; and at 170°C (Fig. 4C), θ′-Al_2Cu was quite abundant, sufficient to deplete the matrix of solute so GP zones did not form during the cooldown. For comparison, Fig. 4D shows a rare precipitate of θ′ in the Wright crankcase, which generated a small GP zone–free area only in its immediate vicinity. Thus, it appears that mold preheating or insulation equivalent to somewhat more than a 100°C preheating may have been used for the casting of the crankcase, generating the conspicuous precipitation-hardened microstructure observed in the Wright alloy. No very fine (~3 nm) GP zones were observed in the regions with small amounts of Cu of the replicated castings, which supports the interpretation that these zones in the Wright alloy resulted from ambient aging that required decades to develop.

Our finding of precipitation hardening in the Wright alloy leads to revisions of the history of technology and the history of flight. At present, it is an accepted fact that the first precipitation-hardened alloy in the

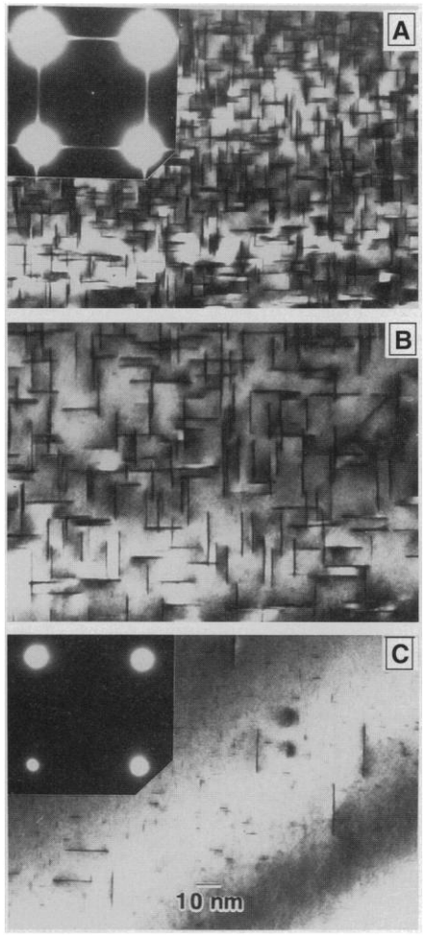

Fig. 2. Transmission electron micrographs of regions within a single cored dendrite that are (**A**) Cu-rich (~4.5% Cu), with 10-nm-diameter GP zones; (**B**) intermediate-Cu, with 20-nm GP zones; and (**C**) Cu-poor (~2.5% Cu), with 20-nm and 3-nm GP zones. GP zones are disk-shaped layers of pure Cu that are one atomic layer thick and appear as lines when viewed edge-on in this orientation. Selected area electron diffraction patterns are given in insets for (A) and (C).

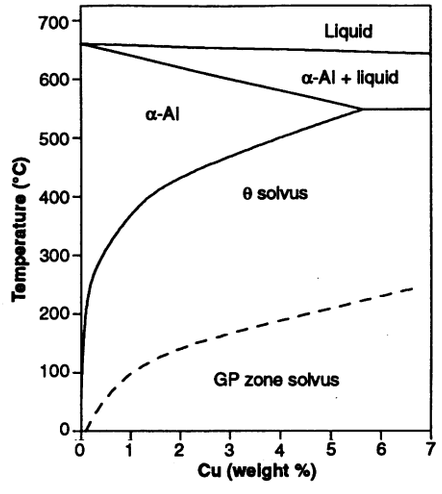

Fig. 3. Phase diagram showing the Al-Al_2Cu equilibrium system [after (*21*)]. Also shown is the metastable equilibrium between fcc Al and GP zones [data from (*22*)].

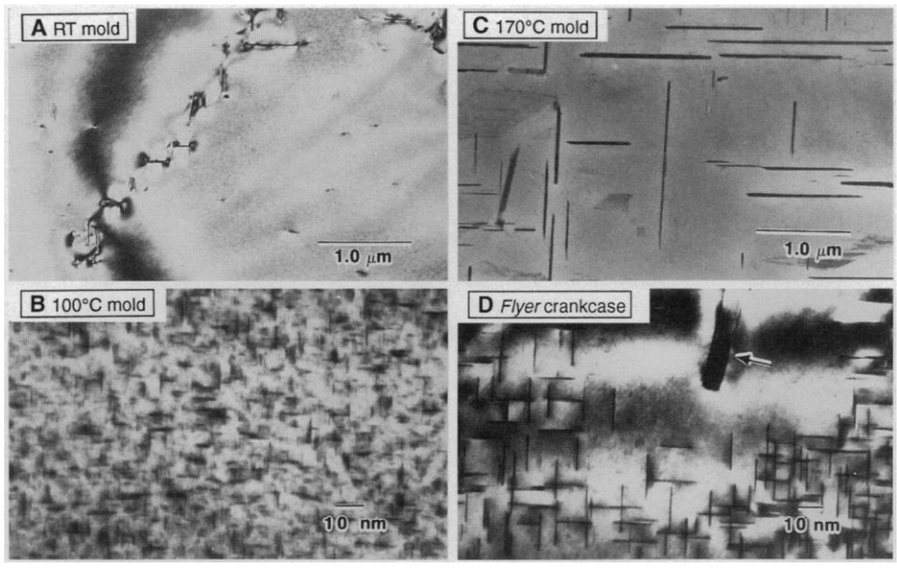

Fig. 4. TEM micrographs of an Al–8%Cu–1%Fe–0.4%Si alloy cast into (**A**) a sand mold at room temperature (RT) (showing some θ′ on grain boundaries); (**B**) a 100°C mold (showing GP zones); and (**C**) a 170°C mold (showing abundant θ′-Al_2Cu precipitates with no GP zones). (**D**) Area of the *Flyer* crankcase containing GP zones and a θ′ precipitate (arrow) with a surrounding GP zone–free area; this represents a microstructure intermediate between that shown in (B) and (C).

history of technology (*18*) and the history of flight was an Al-Cu-Mg-Mn alloy called "duralumin." The development of duralumin was an outcome of the observations by Alfred Wilm in 1909 (published in 1911) of an Al-Cu-Mg alloy that increased in strength with time when held at room temperature after a high-temperature thermal treatment (*17*, *18*). Commercial production of this alloy began in 1909 in Germany and found immediate application in the structure of airships. The first such airship crashed in 1911, but a total of 97 zeppelins were subsequently produced in Germany for use during World War I, each requiring up to 8 metric tons of duralumin.

The conditions under which precipitation hardening occurred, however, were not understood until 1919, when seminal works on the theory and practice of precipitation hardening in alloys were published by Merica and his colleagues (*19*) at the U.S. National Bureau of Standards (now the National Institute of Standards and Technology). This opened an era of phase diagram and alloy development (*20*) and the commercial application of many age-hardened alloys. The practical application of precipitation hardening, especially in Al-based alloys, with the resulting improvements in important properties such as strength and fracture toughness, has been essential to the development of the aerospace industry. We have shown here that the use of a precipitation-hardened alloy in the first aerospace application occurred 16 years before the theory of precipitation hardening was proposed, and several years before the first report of a precipitation-hardened alloy and the use of such an alloy (duralumin) in airships. The Wright *Flyer*, the first powered heavier-than-air aircraft, can now be recognized as the first application in the aerospace world of technologically vital precipitation-hardened alloys.

REFERENCES AND NOTES

1. Precipitation hardening results from the nucleation and growth of a fine distribution of second-phase particles in a solid matrix that is supersaturated with respect to one or more elements. This supersaturation often occurs after quenching from a high temperature (where the solid solubility is large) to a low temperature (where the solubility is much lower). GP zones are a special class of precipitate where the structure of the phase is identical to that of the matrix but the precipitate has a different composition than the matrix. Fine precipitates cause an increase in hardness and strength of the alloy by impeding dislocation motion during deformation.
2. All percentages herein are by weight.
3. W. E. Sicha, in *Aluminum*, K. R. Van Horn, Ed. (American Society for Metals, Metals Park, OH, 1967), vol. 1, pp. 277–302. The crankcase, which included a water jacket to cool the engine and four legs for mounting to the airframe, was cast in a commercial cast shop. Aluminum at that time was no longer a precious metal, costing about a dollar a pound. The Wrights requested the strongest Al alloy available, which contained 8% Cu. Iron and Si, at less than about 1% each, were typical impurities found in Al of the period. Aluminum was chosen not only for its good strength-to-weight ratio, but also because it could be cast to near net shape.
4. R. Leyes, "The Wright *Flyer* engine: A summary of research," *National Air and Space Museum Report 1986* (Washington, DC, 1986), pp. 186–197.
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6. The samples were taken from three locations near a fracture in the crankcase. The crankcase was broken when the *Flyer*, which was not tied down, overturned in a gust of wind after the fourth and final flight of 17 December 1903. The crankcase is in the collection of the U.S. National Park Service and is on display at Kitty Hawk, NC. See (*5*) for figures of the crankcase showing the sampling locations.
7. As is common in cast Al alloys, coarsening during solidification has modified the classical treelike dendrites, such that the observed structure shows rounded dendrites.
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9. Compositional analysis by energy dispersive spectroscopy (EDS) was conducted at 15 keV and 1 nA beam current with pure Al, Cu, Fe, and Si standards to model EDS spectra. The mass concentration ratios were calculated as $I_{unknown}/I_{standard}$, where I is the x-ray intensity. Corrections were made for absorption and fluorescence. Measured weight percent composition totals were 96 to 101% before normalization. The probe excitation volume is about 1 μm in diameter, thus encompassing large numbers of GP zones, if present, and ruling out effects of underlying substructure.
10. Note that in the Al-Cu binary system, where the value of the partition coefficient, k, is 0.15, the minimum possible Cu concentration at the dendrite center is 1.2%, but higher values may result from diffusion. The maximum Cu content expected in an Al solid solution with normal casting practices is 5.65%, but this amount may be reduced because of subsequent precipitation reactions.
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12. Specimens for TEM were prepared by electrochemical jet polishing at −20°C to ensure that no precipitation was induced during specimen preparation. TEM examination was carried out at 120 keV accelerating voltage, with a point resolution of approximately 2.8 Å.
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23. We thank T. L. Hartman of the National Park Service for permission to sample the crankcase; F. S. Biancaniello at the National Institute of Standards and Technology for producing the experimental Al-Cu-Si-Fe castings; M. Williams for TEM specimen preparation and scanning electron microscope–EDS analysis; L. Smith for the optical metallography; M. Vaudin for a critical review of the manuscript; D. Smith for assistance in the Wright Archives at Wright State University; and K. Henson for assistance in the archives at ALCOA.

16 May 1994; accepted 15 September 1994