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RAPID SOLIDIFICATION OF METALLIC PARTICULATES

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5. The centrifugal atomization processes produce the coarsest powders, associated with the poorer shear characteristics of the processes and the lower particle velocities on shearing off.

Table II summarizes the atomized powder characteristics.

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Finally, in terms of structure/property relationships, it is desirable to attain the highest possible yield of usable powder. There are cost considerations of major proportions in achieving this aim. Whereas for press and sinter operations (less than 100% density product), features such as powder flow rate and packing density are very important; for RS powders, intended for full density in the final product, narrow structural reproducibility (usually DAS) is the critical issue for optimization of properties. Accordingly, yield of powders, for example, minus 100 μ m or minus 250 μ m, is important but not controlling. Instead the DAS should determine which powder sizes are usable. As Fig. 3 illustrates, it is possible to achieve a range of powder sizes for a given atomization process by varying the delivered gas pressure, the superheat temperature, and other processing variables. Figure 4 shows the variation of DAS with powder particle size for an aluminum alloy. On the basis of DAS values, all the powders from about 1 to 250 μ m have DAS values from about 0.5 to 5 μ m, and are judged to be acceptable for powder consolidation. Thus, on the basis of structural requirements, yield of useful powders has a different meaning than powder particle size. Figure 5 is a plot of dendrite arm spacing vs. solidification rate for four alloy systems, namely Al, Cu and two austenitic alloys. Each different alloy system has a curve of its own, with the higher conductivity alloys showing steeper slopes (greater sensitivity to quench rate)

(25 26 27)

thin streams of liquid metal are delivered in the liquid state to a high conductivity metallic substrate where the droplets or streams are converted to thin foils, flakes, ribbon, in intimate contact with the substrate. For splats of 100 to 30 μm , solidification rates are typically 10^5 to 10^6 K/s. For splats as fine as 0.1 to 1 μm thick, 10^8 to 10^9 K/s quench rates have been achieved (7); the highest reported value for splat quenching is reported to be 10^{10} K/s (12).

Basically, therefore, for maximum solidification rates, one dimension of the powders or flakes (splats) must be very fine; the finer, the higher is the rate, all other variables having been appropriately controlled.

Atomization Processes

1. Subsonic Gas Atomization

Most of the common gas atomization techniques are subsonic in nature. Nozzle (die) exit gas velocities typically are 0.3 to 0.6 Mach, and the processes are three-step processes, as described by Johnston and See (13) and reviewed by others (14,15). The major function of the high velocity gas stream is to increase the velocity of the free-falling liquid metal, thereby overcoming the low shear resistance of the liquid stream, leading to atomized particles. The stream first flares then breaks down into a broad spectrum of coarse shapes, mostly irregular thin platelets and ligands, and finally into droplets (13). If sufficient superheat is provided and the atmosphere is neutral to the alloy, the final product is a sphere. The range of powder sizes is broad due to the loss of control over the atomization process from the point of impingement of the gas jets on the liquid metal stream to the zone of droplet formation. Both submicron particles and those in excess of 0.5 mm are usual.

Solidification rates of about 10^2 K/s are average values and are a function of the powder size.

2. Centrifugal Atomization Processes

There are a number of centrifugal atomization processes, some of commercial stature and others at a pilot operating stage.

a. Perforated Rotating Cup. This process is common for lower melting metals and alloys and has been used successfully to make a wide variety of atomized products in lead, for example, where the particulate aspect ratio can be changed widely by altering the hole size in the cup wall and the speed.

The Reynolds Metals Co. has produced aluminum powders in air on a continuous basis. The melt furnace is tapped continuously with liquid metal delivered to a tubular cup with holes drilled through the wall with a selected hole size. Accicular powders (rice shaped but with sharper ends) are literally extruded through the holes and are quenched in air, continuously screened, delivered to a holding bin, metered into a tall radiant tube furnace wherein on free fall the particles are preheated to 400°C (673K), and are again metered onto a travelling belt to be fed into the roll gap generally of a single roll stand for continuous production of essentially fully dense sheet (16,17). The mill has operated on a commercial basis, producing one meter wide sheet by perhaps 0.25 cm thick, capable of further reduction to other finished thickness.

The solidification rate is only about 10^2 K/s but leads to significant grain refinement and improved properties. Yield of product from melt to final sheet or strip is attractively high.

b. Rotating Electrode Process (REP). This process, which uses a pre-cast or wrought round bar electrode, achieves melting by striking an arc, for example, to melt the tip of the rotating consumable electrode. Melting may be accomplished by a water-cooled W-arc, electron guns (which require a vacuum), laser beams, plasma arc, etc. The rotational speed of the consumable electrode and the speed of melting control the powder size which tends to be relatively coarse, typically 100 to 600 μm , with solidification rates of perhaps 10^1 K/sec.

The process is fairly widely used and is especially useful for reactive metals and alloys which are contaminated by crucible melting; thus Ti, Zr, Nb, Ta, V, and their alloys are atomized by REP. Costs tend to be high because of the use of carefully prepared solid electrodes which have already been melted once, or have been fabricated into an electrode; further, the melting techniques for REP are slow and expensive in their own rights.

c. Rotating Cup and Dish. A high-speed rotating cup with a sharp inner lip over which a thin film of liquid metal flows can produce fine powders. Unfortunately, the rapid degradation of the sharp shear lip above about 1500 or 1600°C (1773-1873K) leads to progressively coarser powders and lower quench rates; the overall life of the cup presents other problems at very high centrifugal speeds. Substitution of a shallow dish and shearing the liquid off a liquid-solid interface results in more predictable atomization, however, with relatively coarser overall powder size (typically 70-80 μm average powder diameter). Augmentation of the solidification process by use of a dynamic helium gas quench permits attainment of rates of about 10^5 K/s with superalloys (18). Duplex dendritic structures in individual powder particles have been reported (19) as a result of the quench dynamics.

d. Singer Single Roll. A novel process is to pour a thin stream of metal onto a high-speed roll; the acceleration of the liquid stream, combined with its low shear resistance, leads to atomization (42). Details of powder size range, average particle size, quench rates, etc., are not well known, but the atomization conditions can be varied fairly extensively. The resultant solidification rates will depend on the powder size and particle velocity in the surrounding gas atmosphere. Vacuum can of course be used.

3. Ultrasonic Gas Atomization (USGA)

The use of a Hartman Shock Wave Device permits the acceleration of high pressure gas and imparts a high-frequency pulsed mode to the gas stream. The application of the Hartman principle to an atomization nozzle was accomplished in Sweden (20) and applied to progressively higher melting alloys in recent years (11,21). Exit gas velocities are reported to be Mach 2-2.5, with the major pulsed frequency at about 100,000 cps. Powder size range is relatively narrow (-250 μm for Al; -90 μm for Cu); average particle size is about 22 μm for Al and 20 μm for Cu. These values will vary depending on the initial gas pressure entering the atomization die and on metal superheat. Indicated solidification rates are 10^5 K/s for aluminum.

4. Osprey Process

The Osprey Co. of So. Wales, Great Britain reports a high velocity gas atomization process (near Mach 1) which is capable of producing a range of powder sizes through control of atomizing variables (22). Powder size range is considerably narrower and finer than for subsonic gas processes, and estimated solidification rates are 10^4 to 10^5 K/s.

5. Gas Solubility Process

Developed by the Homogeneous Metals Co., molten metal, in an argon atmosphere, is injected with hydrogen (23). The melt is then exposed to a vacuum chamber via an immersed tube, resulting in an "explosive" atomization of the melt as the hydrogen is rejected by the melt (similar to the hydrogen stream degassing process in steel). Very clean particulates are produced, and are a mixture of powders and flakes, depending on the actual disintegration process leading to particulate formation, and on the size of the atomization chamber. Solidification rates are low as a result of cooling in a vacuum and are at best 10^2 K/s or less. This is a production process.

A summary of the methods described above is shown in Table 1 and includes approximate powder size range, average particle size, and solidification rate.

Table I. Characterization of Atomization Processes

Method	Powder Size Range, μm	Average Particle Size, μm	Solidification Rate, K/s
Gas - subsonic	<1 to >500	50-70	10^0 - 10^2
Gas - subsonic* (Alum. Production)	-100	12-14	10^5
USGA	1 to 250	22	10^4 - 10^5
REP - Centrf.	100 to 600	200	10^1
Perforated Cup**	narrow	1-4 x 1-2 mm	10^2
Centrf. Cup/dish**†	1 to >500	70-80	10^5
Gas Solub. Proc.	1 to ~500 (some splat)	40-70	10^2
Osprey	1 to 300	40-50	10^4

* Powders sometimes show several quench zones

** Aluminum, production

† Dynamic helium quench addition

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What are some other important aspects of atomization (the results are summarized in Table II)?

1. The subsonic gas atomization processes are three-step processes and lead to entrapped gases: Fig. 1.

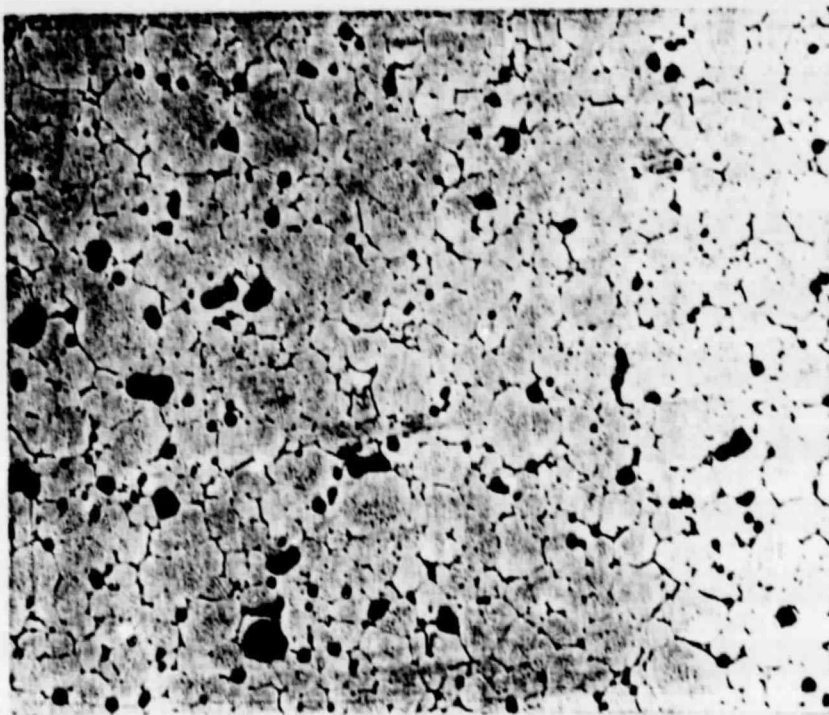


Figure 1 - Nickel-base, γ - γ' Astroloy, hot isostatically pressed at 1204°C (1477K) for 2h. Argon gas, trapped in powder particles, expands on solution heat treating at 1066°C (1339K) for 2h. x26

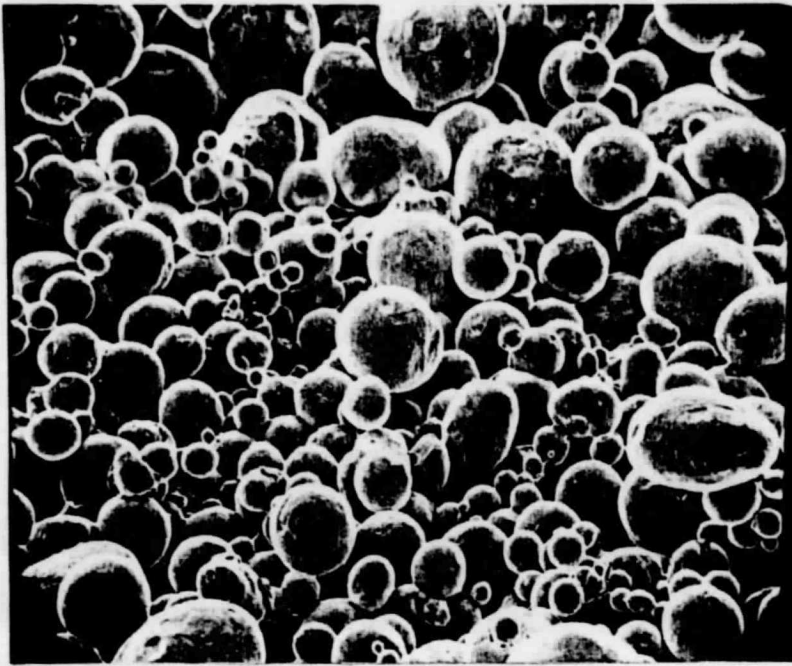
2. The ultrasonic gas atomization process is a single-step process with atomization taking place at the point of impact of the pulsed gas jets against the liquid metal stream (verified by high-speed movies) (24), and does not show any evidence of gas entrapment.

The Osprey Process presumably is a one-step process by virtue of observed powder characteristics.

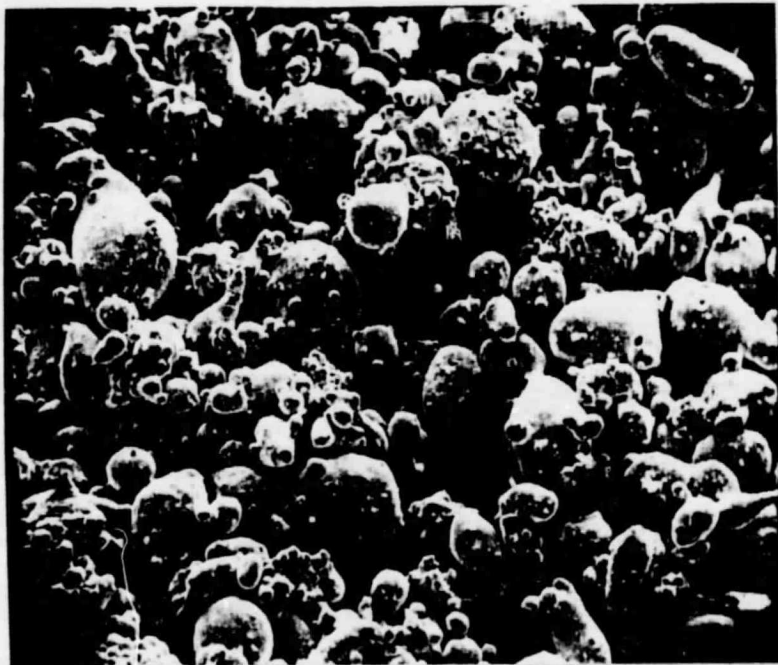
3. All of the centrifugal processes are single-step atomization methods and powders are free of trapped gas.

4. Satellite buildup (impingement of fine powder particles onto coarser particles, with each particle at different stages of solidification) is highly variable among the various processes. Such formations are highly undesirable because of poorer packing density and because of the highly different structures of the attached very fine and the coarse host particles. A fine liquid droplet impacting a coarse solidified particle is actually substrate quenched by the large particle and can have a DAS 10 to 100x finer. The large differences in dendrite arm spacings result in dissimilar structure and properties in the final alloy.

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a.



b.

Figure 2 - a) Ultrasonic gas atomization product with low satellite concentrations. x1000. b) Subsonic gas atomization product with heavy satellite concentration. x200.

Figure 2 illustrates the heavy satellite density common with many subsonic gas atomization methods, and the more acceptable single-step atomization product (USGA, also Osprey). All the centrifugal processes tend to

produce low satellite concentrations, with the REP atomization product almost always completely free of any satellites.

5. The centrifugal atomization processes produce the coarsest powders, associated with the poorer shear characteristics of the processes and the lower particle velocities on shearing off.

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Finally, in terms of structure/property relationships, it is desirable to attain the highest possible yield of usable powder. There are cost considerations of major proportions in achieving this aim. Whereas for press and sinter operations (less than 100% density product), features such as powder flow rate and packing density are very important; for RS powders, intended for full density in the final product, narrow structural reproducibility (usually DAS) is the critical issue for optimization of properties. Accordingly, yield of powders, for example, minus 100 μm or minus 250 μm , is important but not controlling. Instead the DAS should determine which powder sizes are usable. As Fig. 3 illustrates, it is possible to achieve a range of powder sizes for a given atomization process by varying the delivered gas pressure, the superheat temperature, and other processing variables. Figure 4 shows the variation of DAS with powder particle size for an aluminum alloy. On the basis of DAS values, all the powders from about 1 to 250 μm have DAS values from about 0.5 to 5 μm , and are judged to be acceptable for powder consolidation. Thus, on the basis of structural requirements, yield of useful powders has a different meaning than powder particle size. Figure 5 is a plot of dendrite arm spacing vs. solidification rate for four alloy systems, namely Al, Cu and two austenitic alloys. Each different alloy system has a curve of its own, with the higher conductivity alloys showing steeper slopes (greater sensitivity to quench rate)

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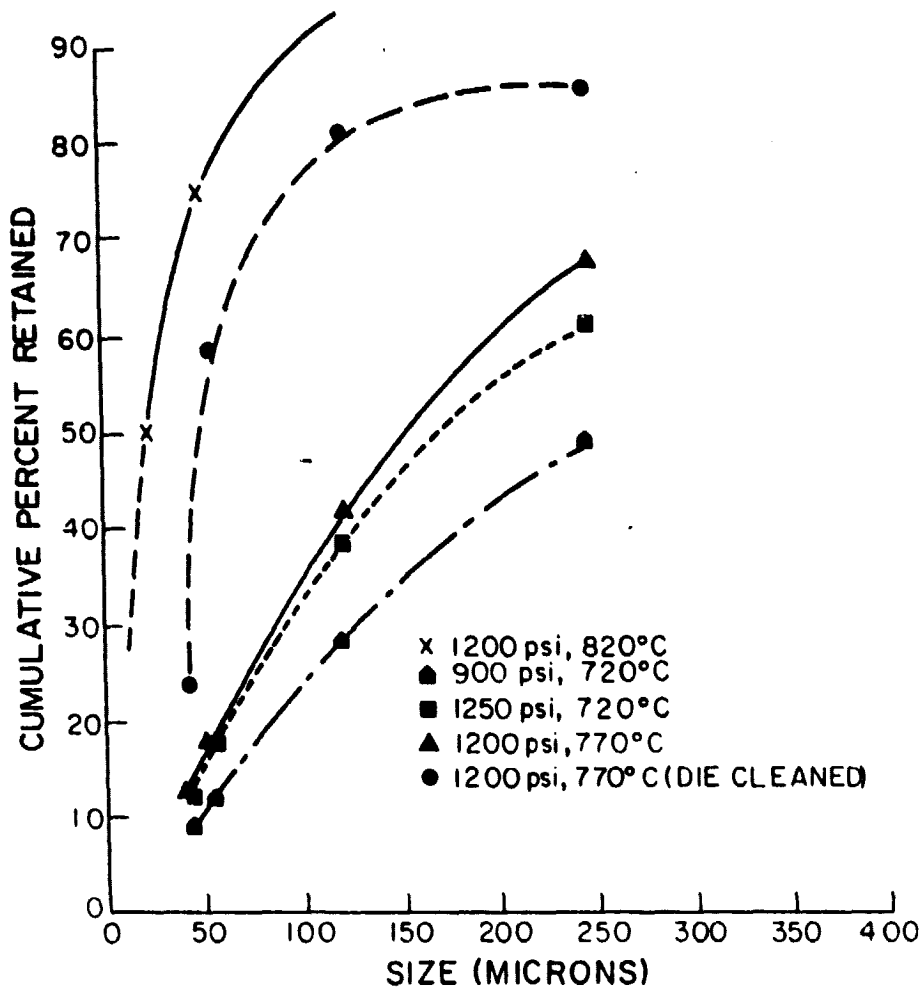


Figure 3 - Variation in powder particle size for aluminum alloys as a function of gas pressure and melt superheat: ultrasonic gas atomization.

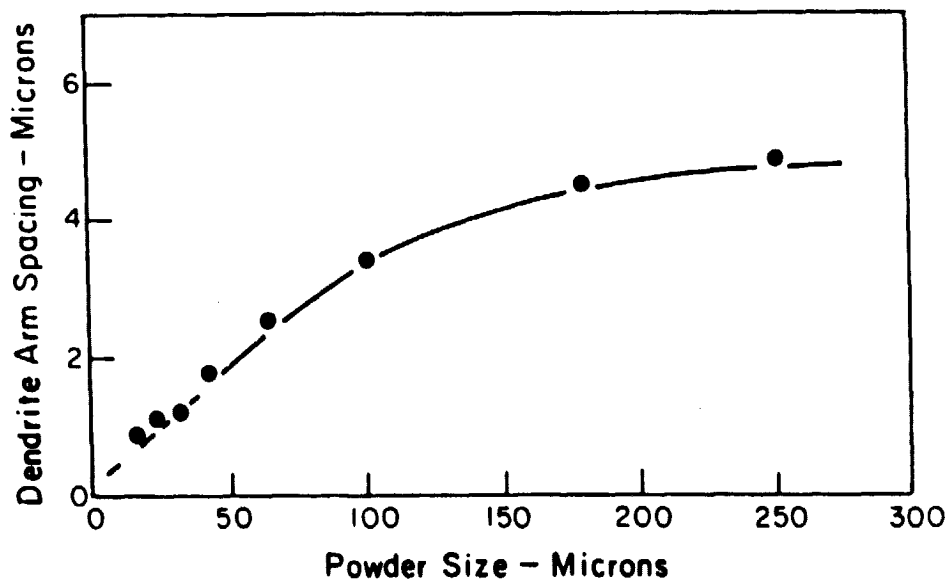


Figure 4 - Variation of dendrite arm spacing with powder size for an aluminum alloy produced by USGA.

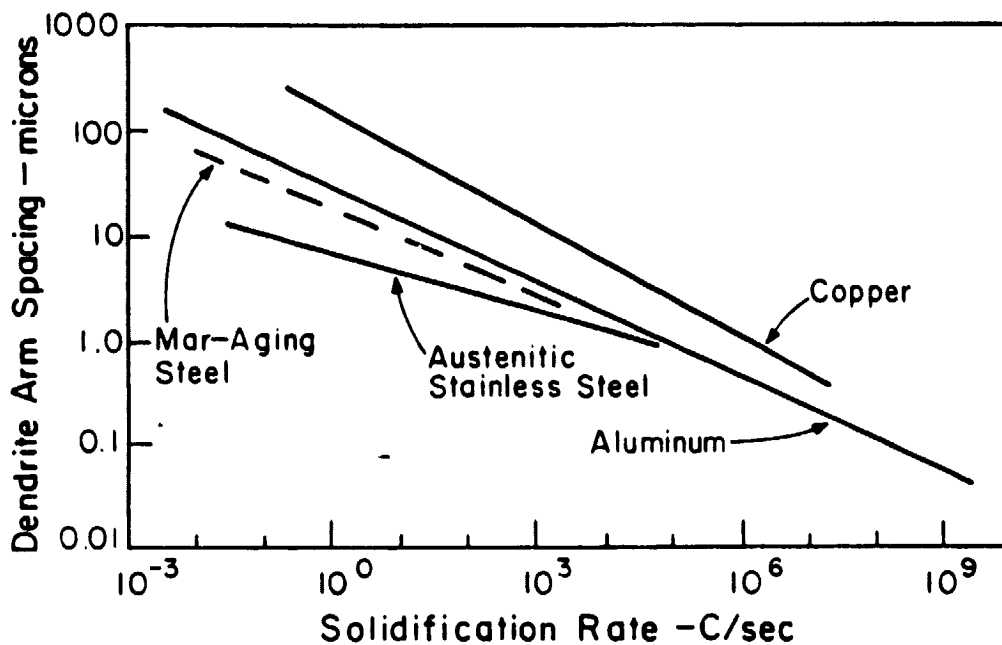


Figure 5 - Dendrite arm spacing as a function of solidification rate for aluminum alloys, copper alloys and two steels (3,26,27,28).

For solidification rates in excess of about 10^5 , metallic substrate quenching is required. Of the splat processes, in terms of Fig. 5, the highest solidification rates attainable by the several techniques are:

- Melt Spinning: 10^5 K/s at 30 to 60 μ m thickness. Primarily ribbon shapes.
- Melt Extraction: 10^5 K/s at 30 to 60 μ m thickness. Ribbon plus other particulate shapes.
- Twin Roller: 10^6 K/s at 60 to 100 μ m thickness; higher for thinner splats. Flakes and foils of irregular shape.
- Piston and Anvil: 10^6 K/s at 60 to 120 μ m thickness. One large circular flake.
- Gun: 10^6 to 10^9 K/s at 10 μ m down to 0.1 μ m thickness. Very fine flakes of irregular shape.

The first two are single-substrate methods; the next two are two-surface methods; and the last is a single-surface technique which requires flake thicknesses as fine as 0.1 to 1 μ m to achieve quench rates of 10^8 to 10^9 K/s.

Structural Refinements Through Rapid Solidification

Because a significant number of previous review articles have dealt with the specifics of the contributions of rapid solidification processes, it may be more valuable to look at the shortcomings of prior research on the benefits of structural refinements achieved through rapid solidification; a few specific problems are mentioned, among many, for illustration.

a. Decreased Segregation. We still do not have anything approaching an understanding of the benefits of gradual elimination of segregation with increasing solidification rates. We understand a bit better the special instance of total elimination of segregation through retention of the glassy state; however retention of the glassy state is restricted to special compositional conditions, for example, the presence of a deep eutectic in the alloy system, or the use of large amounts of nonmetallic elements.

If 10^5 K/s eliminates segregation of carbon at the grain boundary of an austenitic stainless steel and guarantees the absence of subsequent carbides on the boundary (28), what are the benefits of solidification rates of 10^2 or 10 K/s? And what are the relative corrosion rates of the resultant 304 or 316 stainless steels for these several quench states?

b. Refined Grain Size. We have become quite accustomed to producing a broad range of alloys with grain sizes down often to about one micron, and routinely down to 1 to 20 μm . This is often accomplished by using particulates which have experienced solidification rates of 10^4 to 10^6 K/s and then using a hot consolidation temperature several hundred degrees lower than would have been used for the same composition prepared by ingot technology. But we are still only flirting with the production of grain sizes down to 0.1 μm , where further significant property improvements will undoubtedly be achieved.

In this respect there is today greater interest in finer grain size control by starting from the glassy state (completely homogeneous) and crystallizing to highly refined structures (29). This is obviously a highly rewarding approach, but has limitations in terms of the compositions which can be used.

Recrystallization of the initial dendritic structure deserves much greater study. Can the use of second-phase precipitates from an initial quenched structure, or from a supersaturated condition, enhance grain refinement? What modifications of the hot consolidation processes can be made to enhance grain size control, and what are the specific effects on strength, fracture toughness, ductility, corrosion? For an "unsegregated" RS alloy, what are the benefits, if any, of a one-micron grain size versus 10 μm or 0.1 μm on a specific corrosion situation?

The achievement of superplasticity in many RS alloys of appropriate fine grain structure is a particularly exciting discovery, but what about strength properties at intermediate and high temperatures, in creep, or what is needed in lower deformational energies at various strain rates?

For example, in comparing a 316 stainless steel prepared from a conventional ingot, and as an RS twin-roller flake extrusion (10^5 K/s), at 650°C (923K), in creep rupture, the much coarser ingot product (65 μm grain size versus 5 μm for the RS alloy) is importantly stronger in long time tests (30). A similar 316 alloy modified with a small addition of Ti (0.3% Ti and 0.05% C) and processed to produce a very fine dispersion of TiC (average size about 160 Å), is significantly stronger at the same temperature of 650°C (923K) in the 5-micron RS condition than in the 60 μm ingot condition. Is the benefit due to fine carbide dispersion strengthening, or is the benefit due to grain-boundary stabilization?

c. Increased Solid Solubility. This is and should be an area of extreme interest. Important benefits have been reported quite broadly for numerous alloy systems which cannot be adequately documented here. The use of increasing amounts of lithium in aluminum alloys (31,32,33); the use of

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large amounts of Fe, Co, Ni, Zr, Ce, etc. for high strength and for high temperature improvements in aluminum alloys (34,35,36); the use of increasing amounts of Zr, Cr and other "insoluble" elements in copper (37,38); the benefits to low and high temperature strength due to significant increases in carbon content in alloys such as Mar M-509 (39) while retaining hot plasticity: these are but a few examples of the exciting potential offered by achieving some measure of supersaturation of otherwise insoluble or poorly soluble alloying elements, and then controlling the subsequent size, shape and distribution of the excess phases.

There are, however, problems associated with such supersaturation. In uncontrolled heating for hot consolidation, the excess phases will precipitate at some higher temperature range, probably not ideally. There is need for more detailed studies of the control of the precipitation processes from supersaturation. Once such precipitates are formed, they are not generally resolvable on reheat treatment. T-T-t curves of essentially classically transformations are required. How might one benefit from prior cold work of the particulates? Atomized powders have been cold deformed, as have foils, flakes and ribbons, with beneficial effects on the resultant precipitation from the supersaturated solutions achieved in the RS state.

d. Elimination of Segregation Phases. Here too enough background work has been reported to stimulate much additional interest, for example, the elimination of coarse segregation phases in 2024 (40) and 7075 (41) by achieving quench rates in excess of about 10^4 K/s. Domalavage (39) reports (for twin roll splat) that in modified Mar M-509 alloys containing stoichiometric amounts of Hf and C only HfC forms; no chromium carbide or M_6C was formed, both of which are found regularly in the slow cooled precision cast alloy. The absence of chromium carbides (usually at grain boundaries) results in an increase of 75K in the melting temperature of the alloy, plus large improvements in both low- and high-temperature strength properties and ductility.

This is an important area of study. The potential for much higher alloy content, often using unconventional alloying elements, could lead to the formation of brittle, often fragile, intermetallic compounds unless solidification rates are maintained at a sufficiently high level to minimize or avoid formation of such segregated compounds.

Among aluminum alloys, it's interesting to see the formation of the equilibrium phases Al_3M , Al_6M , Al_9M_2 , especially for significant additions of Fe, Zr, Ti, Ni, Mn, Co and other elements. In addition to the extensively reported excellent structures and properties of KS X7091 by Alcoa, recent data for a modified 7075 alloy containing 0.7% Zr plus 1% Ni are presented in Table III showing similar improvements in mechanical properties (36). Both the Zr and Ni appear as Al_3M compounds.

Future Alloying Trends

Through rapid solidification, the combination of structure control and its direct effect on many types of properties plus the ability to retain or even gain in hot and cold workability has opened the field of alloy development once more. Alloy development has truly been a dead issue for many years in practically all of the mature alloy systems.

The emergence of new alloys is particularly evident in aluminum, where RST has encouraged additions of up to 4% Li (X2020, 2024 + Li, Al-Mg-Li, etc); up to 12% Mn; up to 5% Co in combination with several transition

Table III. Mechanical Properties of RS 7075 with 0.7% Zr + 1% Ni*

Solution	Aging	YS	UTS	Elong	$\frac{N_{UTS}}{YS}$ **	
°C	°C - h	ksi	ksi	%	YS	
460	120° - 24h	91.4	98.3	9.0	1.23	
490	" "	90.8	98.6	10.0	1.23	
490	" "	83.6	88.4	5.7	----	transverse
490	" "	95.9	100.6	7.2	----	3.8% stretch
490	120° - 66h	94.8	101.4	7.3	1.19	"
490	140° - 24h	78.2	87.8	9.5	1.32	"
490	140° - 48h	75.0	85.1	10.5	1.24	"

* All tests based on use of -250 μ m powders.
Solidification rates indicated to be $10^4 - 10^5$ K/s.
140°C (413K) represents the overaged condition, whereas 120°C is the peak hardness temperature.

** Notched UTS/smooth bar YS ratio.

metals; up to 8 or more percent of combinations of transition metals; etc. Significant benefits are reported for smaller alloying additions to conventional alloys (Co in X7091, Zr + Ni in 7075 (Table III), 1 to 3% Li in X2020 and 2024). Major improvements in strength, in elastic properties, in high-temperature strength, in corrosion, etc., are also reported. Not all of the improvements are adequately understood and much background structural analysis will be required.

The improvement in fatigue performance of a 2024 + 3% Li RS alloy, which showed 42,000 psi (290 MPa) for 10^7 cycles versus 25,000 psi (175 MPa) for IM 2024 is perhaps less exciting than the ratio of

$$\frac{\text{stress for } 10^7 \text{ cycles}}{\text{UTS}} \geq 0.5$$

versus the more usual values of 0.30 to 0.35 for Al ingot alloys. Yet this RS alloy is notch weakened. Its high fatigue strength is due to its high resistance to crack initiation. Clearly there are structural and alloying deficiencies which should be studied to permit application of such alloys.

In addition to considerations of the possible negative roles of Na, K, and H, studies of the effect of oxide content (and types of oxides) in RS alloys must be intensified, particularly in the more highly alloyed materials.

The progress shown in RS aluminum R & D should be extended to other alloy systems where much less progress is reportable.

RST is still a very young field. Many discrete and interesting

structures and properties have been reported. Work is still highly fragmented, spotty, not at all well organized, but the exciting developments which have already emerged will stimulate continued efforts among us. I am personally convinced that the rate and quality of progress ahead of us will be both stimulating and rewarding.

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