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STRUCTURE AND PROPERTY CONTROL THROUGH RAPID QUENCHING OF LIQUID METALS AND ALLOYS

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Introduction

If we consider melting as the ultimate step in homogenization of alloys, we must also remember that solidification is a prime method of segregating the components of a solution and the separation of phases. The slower the solidification process, the greater the degree of segregation and separation: thus large ingots and castings undergo extremes of phase separation. Yet, because the pouring and handling and processing of large castings, particularly of readily malleable or plastically tolerant compositions, is cheap, this is the technique largely utilized for producing the bulk of our metals and alloys.

Solidification of ingots and large sections, for example, involves at least four identifiable stages of segregation and phase separation, namely:

1. Segregation of all solutes on an atomic or near atomic scale, a minor problem usually.
2. Segregation and separation on a dendritic pattern, the first readily detectable structural discontinuity.
3. Segregation and separation on a grain size basis, often 10 to 1000 times the size of the dendrites; this can be on a macroscopic scale.
4. Segregation and separation in proportion to the size of the ingot or casting, namely from bottom to top in the direction of the pour, and laterally in the thickness of the casting.

It is also true, unfortunately, that efforts to homogenize cast structures (ingot soaking) by heating for a number of hours at temperatures as high as 80 to 90 percent of the absolute melting temperature seldom result in significant improvements in the last three items above. Homogenization is found to be beneficial on a sub-dendrite size basis since even this represents diffusion movements over distances of 30,000 atoms or more for a fine dendrite size. In fact, in terms of the hot working response, the small amount of homogenization which is achieved may be adversely affected by grain coarsening and some excess phase coarsening (sulfides, carbides, oxide inclusions) (1).

In addition to the segregation and separation of phases, slowly cooled structures are subject to the formation of coarse excess phases (alloy phases as well as impurities such as oxides) at dendrite and grain boundaries, large pores due to gas separation, and the formation of undesired phases, such as sigma phase in high chromium and highly alloyed austenitic stainless steels.

Clearly the elimination or minimization of these structural faults would not only improve hot working capability, but could improve properties, and increase the reliability and reproducibility of alloy properties. Further, these improvements would make it possible to increase alloy content, or modify composition, or tolerate higher impurity content of current alloys.

Structure Response to Cooling Rate

As a result of recent developments in splat cooling (2, 3, 4, 5), it is now possible to show the relationship between dendrite size or grain size and cooling rate. Figure 1 shows dendrite size variation for aluminum alloys and grain size for copper alloys. Excellent straight lines appear to prevail from about 10^{-3} to 10^{9} degrees C/sec cooling rates for some alloys (6), resulting in dendrite sizes near 100 Å for cooling rates of 10^{9} degrees C/sec and increasing to 1000 microns at 10^{-3} degrees C/sec. The latter slow rates are found in large cross-section ingots, where the very coarse dendrites and grain sizes result.

What are some of the more interesting structural changes which have been observed and reported in the literature?

In examining this list of metastable or modified structures, one must keep in mind that these structures, in subsequent handling and powder consolidation, will return to a state nearer equilibrium by decomposition or other changes of the quenched material. Nevertheless, the added control over the structure and properties of the quenched or quenched and decomposed states should be a great advantage, offering benefits in hot and cold working, in ductility, in toughness and in various mechanical, physical, chemical, etc., properties.

1. Amorphous structures. An ever increasing number of alloy compositions have been reported to remain non-crystalline for cooling rates above about 10^7 degrees C/sec (7, 8, 9, 10). The preservation of an amorphous structure represents the maximum efficiency in avoiding segregation and phase separation. While it is very unlikely that the amorphous state can be preserved through consolidation and subsequent processing, nevertheless important benefits will be derived from the extremely homogeneous chemistry, such as, super-fine grain size, fine dispersions in the 50 to 1000 Å size range, etc.

Obvious immediate areas of potential benefit are the ceraming glasses and oxide ceramics, areas in which little work is so far reported. Even though conductivities are quite low, diffusivity is equally slow or slower, offering the potential of avoiding crystallization in much more highly alloyed glasses than is now possible, and offering the possibility of producing crystalline oxide ceramics in glassy form, for example, V_2O_5.

2. Micro-crystalline structures (11, 12). Such structures will essentially decompose or coarsen to structures not importantly different than decomposed amorphous materials. Perhaps it is safe to say that the number of microcrystalline structures will be large compared to the number of amorphous structures which will be found in the years ahead.

3. Increased solubility. This is one of the more exciting phenomena, readily achievable with many systems. It is impossible to document all the alloy systems in which important increases in solubility have been achieved, but a number will be noted and discussed.

a) The system Cu-Ag shows a classical eutectic phase diagram. Splat cooling retains a solid solution across the entire composition range (13). Both electrical and mechanical properties are of interest for the decomposed structure.

b) Alloys of aluminum. Table I shows the increase in solute solubility (at room temperature) in splat cooled binary aluminum alloys (14). The increases are quite large. In the Al-Cu system they offer a potential for increasing the volume content of $CuAl_2$ during aging by as much as 2X or 3X; in Al-Si alloys they offer a silicon dispersion strengthened system (results are shown below).

TABLE I

Maximum Metastable Solubilities Observed at Cooling Rate of $\simeq 10^8$ degrees C/sec

System	Max. Equil. Sol. (a/o)	Max. Extrap. Metastable Sol. a/o	Equil. Eutect. Comp. a/o	Solubil. Increase
Al-Pd	nil	7.5	7.5	∞
Al-Cu	2.5	18.	17.3	7X
Al-Mn	0.7	$\geq 9.$	1.0	13X
Al-Fe	0.025	$\geq 4.$	0.9	160X
Al-Co	0.02	0.5	0.45	25X
Al-Ni	0.023	1.2	2.7	50X

c) In the Cu-Zr system the solubility of Zr is increased from less than about 0.1 percent at room temperature to about 35 percent at cooling rates greater than about 10^7 degrees C/sec, offering important improvements in high strength, high conductivity copper alloys (15,16). Results with several dilute alloys are reported below.

It is not necessary to achieve cooling rates as high as 10^7 degrees C/sec to achieve important increases in solute solubility. It is, in fact, probable that more highly alloyed materials, because of slower diffusion rates, will retain solute supersaturation more readily than the more simple, purer compositions.

In the case of a commercial aluminum alloy, 2024 (4.5% Cu, 1.45% Mg, 0.57% Mn, 0.28% Fe, 0.10% Si), splat cooling against a rotating, high speed copper disc achieves significant supersaturation. Table II shows the change in lattice parameter for the alloy, comparing several cooling rates (17).

TABLE II

Changes in Lattice Parameters Versus Cooling Rate for Powders of Aluminum Alloy 2024

Alloy and Condition	Indicated Cooling Rate, degrees C/sec	2θ	a_o, Å
Pure Al (99.99%)	annealed	116.72	4.0497
2024 (ingot product)	10^{-2}	116.74	4.0494
2024 (air atomized)	10^{2}	116.83	4.0473
2024 (Cu wheel splat cooled)	10^{5}	116.92	4.0455

4. Decreased dendrite size (decreased excess phase particle size and decreased interparticle spacing). The dendrite size establishes the first important level of segregation and phase separation. The last liquid to freeze is in the dendrite interstices, enriched in impurities, especially interstitial elements, as well as with other poorly soluble elements. Thus both desired and undesired elements and phases reside in the dendrite pockets. The coarser the dendrite size, the greater the volume and concentration of separated elements and the coarser the excess phases. The coarse phases, when oxides, sulfides, carbides, or intermetallics, can destroy the hot working properties of alloys and can result in poor mechanical properties.

It is, of course, not necessary to achieve cooling rates as high as 10^{7} degrees C/sec to achieve important benefits in dendrite segregation. Figure 1 indicates, for aluminum alloys, the change in cooling rate required to decrease the dendrite size by a factor of 10; this change results in an increase of dendrite area of 100. On average, therefore, for a given volume of excess phase, that phase will be distributed over an area 100 times greater, commensurately decreasing the particle size and interparticle spacing. Major benefits are catalogued below.

5. Decreased grain size. Grain size, the next structural step above dendrite size, shows a similar but not equal response to cooling rate. Here the size of the resultant atomized powder or flake will play a larger role on grain size than on dendrite size. Nevertheless the points made in connection with dendrite size are equally valid for grain size

effects.

Of special interest is the important role played by a fine grain size on superplasticity. Data plots such as that shown for Cu-Zr alloys in Figure 1 indicate the required cooling rate to achieve grain sizes finer than about 5 microns. These are readily achievable.

6. Metastable intermetallic phases. A vast number of metastable phases have been reported in numerous systems for splat cooled materials. B. C. Giessen has provided an excellent review (18, 19). Retention of such metastable phases is a doubtful possibility; however, decomposition of the phase will result in mixed crystal structures which cannot be achieved by conventional casting, hot working, or thermo-mechanical techniques. Little or no exploitation of this potential is known.

Results of Recent Experiments

In this very young scientific-engineering development, it should be very interesting to examine a number of the early programs to gauge the potential for utilization of rapidly quenched alloy powders for the production of useful, even superior, structures.

1. Aluminum alloy 2024. As a major defect, this composition of alloy due to its permissible high level of impurities, for example 0.5 percent Mn plus 0.30 percent Fe plus 0.10 percent Si, frequently has dispersed in its microstructure, constituent particles which are 10 to 20 microns in length, and are often cracked in the as-rolled condition (see Figure 2). These very coarse constituent phases result in decreased fatigue life.

By utilizing a rotating copper disc, alloy 2024 was splat cooled, achieving cooling rates of about 10^5 degrees C/sec (see Figure 3). The resultant dendrite size was 1 - 5 microns and the associated constituent intermetallic phases were about 1 micron diameter (see Figure 3). Table III compares structure and properties of these two 2024 products.

TABLE III

Structure and Properties of Al Alloy 2024 (T4) From Ingot Bar and as a Splat Cooled Powder

Product	Y.S. (0.2%) psi	U.T.S. psi	Elon. %	R. A. %	Fatigue Life, 20 degrees C and 30,000 psi	Constituent particle size, microns
Ingot bar	40,200	67,200	23	37	100,000	10 - 20
Splat	45,300	73,200	22	34	700,000	0.5 - 1

Not only are the constituent particles not damaging to the properties of the splat cooled alloy, but in fact appear to enhance the tension properties by about 10 to 15 percent and increase the fatigue life by a factor of 7.

2. Aluminum-Silicon Alloys. The earlier work of Itagaki et al and Matyja et al (6, 20) indicated a potential to increase the solubility of silicon in aluminum to at least 11 percent by splat cooling. This suggested a potential for producing a silicon dispersion strengthened alloy in which the silicon particles could be controlled fairly readily in the 0.01 to 1 micron size range on subsequent decomposition. Using a cooling rate of only 10^3 degrees C/sec, an air atomized 7 percent silicon-aluminum alloy (as-extruded) showed significant improvement over commercial alloy No. 43 (containing 5 percent silicon) in several test conditions: see Table IV.

TABLE IV

Al-Si Alloys Tested at 20 degrees C

Alloy	Condition	0.2% Y.S. psi	U.T.S. psi	Elong. %	R. A. %
Al-7% Si	Air atomized, as-extruded	17,300	27,600	26	41
Alloy 43 (5%Si)	Die cast	16,000	33,000	9	-
	Sand cast	8,000	19,000	8	-
	Perm. mold	9,000	23,000	10	-

3. Copper-Zirconium Alloys. The commercial high strength, high conductivity copper-zirconium alloy normally contains 0.15 to 0.20 percent Zr when made by ingot techniques. The improvement in alloy stability due to the fine Cu_3Zr precipitate permits cold working to 90 percent with excellent improvement of tension properties at 20 degrees C and improved stability of structure and properties to at least 400 degrees C.

Even with inert gas atomization (quench rate of about 10^3 degrees C/sec for the -100 micron powders) the resultant structure is very fine, see Figures 4 and 1 (16). The ability to retain the fine structure allows an addition of at least 1 percent Zr to the copper without loss of plasticity (versus 0.2%), with important improvements in properties: see Table V.

TABLE V

Alloy	Condition	Y. S. (0.2%) psi	U.T.S. psi	U.T.S. at 20 degrees C after 1 hr. exposure	
				400 C	600C
Commer. Cu-0.2% Zr	70% cold work; sol. treated and aged	61,000	70,000	-	-
Splat; 0.2% Zr	As-extruded	27,000	37,000	-	-
Splat; 0.2% Zr	90% cold work	53,000	53,000	45,000	44,000
Splat; 0.9% Zr	As-extruded	29,500	44,000	-	-
Splat; 0.9% Zr	90% cold work	69,200	75,000	-	-

4. High Sulfur Stainless Steels. It is usual in ingot casting practice with austenitic stainless steels to restrict sulfur content to less than 0.3 percent and more frequently to 0.2 percent in order to avoid extensive cracking, poor surfaces, and low yield of product.

Utilizing steam atomization plus a cold water quench, an 18 Cr-8 Ni stainless steel containing 0.65 percent sulfur was prepared as coarse powders. The resultant structure showed a fine dispersion of approximately 1 micron sulfide particles which were identified as chromium sulfides. The powder was readily hot extruded at 1000 degrees C with no cracking what-so-ever. The extruded bar was subsequently cold rolled 70 percent without intermediate anneals and without the formation of any cracks. The properties were:

TABLE VI

Room Temperature Properties of Atomized 18-8-0.65 % S Stainless Steel

Condition	0.2% Y.S. psi	U.T.S. psi	Elon. %	R. A. %
18-8, 0.03% S, as-annealed	35,000	80,000	65	70
18-8, 0.65%S, as-extruded	80,000	120,000	55	60
18-8, 0.65%S 70% cold worked	180,000	190,000	15	40

The result is a sulfide dispersion strengthened alloy with excellent hot and cold plasticity and strength properties. In annealing studies, measurable grain coarsening was not observed until a temperature of 1200 degrees C was exceeded.

5. Nickel and Cobalt Base Superalloys. The benefits of rapidly quenched powders as the basis for alloy production are most apparent as the total alloy content increases, as the volume of second phase increases (to 40 and 50 percent), as the forgeability and plasticity decrease, and as the yield of product from ingot to bar or sheet decreases. In fact, there are numerous cases now reported which demonstrate that alloys listed

as "castable only" or "non-forgeable", can be readily hot worked, and even cold worked, when prepared from rapidly cooled powders and densified by hot extrusion, sintering, hot mechanical pressing, or hot isostatic pressing. Examples such alloys are Inco 713C, Stellite X-45, IN-100, a number of high speed tool steels, and others.

	C	Cr	Co	Ni	Mo	W	Al	Ti	Zr	B	Others
IN-100	.18	10	15	bal	3	-	5.50	4.70	.06	.014	.9 V
Stellite X-45	.25	23	bal	10	7	-	-	-	-	-	
Inco-713C	.06	12	-	bal		4.4	6.02	.73	.08	.009	

The attained ultra-fine dendritic and grain structure, carbide dispersion and general lack of severe segregation result in superior low and intermediate temperature mechanical properties. The same fine structure is usually not ideal for high temperature creep resistance. The hot plasticity is remarkable when one recalls that these are "non-forgeable" compositions. In fact, superplastic behavior is observed in creep tests at 1000 to 1200 degrees C.

TABLE VII

Room Temperature Properties of Hot Isostatically Pressed Coarse X-45 Powder Alloy

Condition	Oxygen content ppm	0.2% Y.S. psi	Y.T.S. psi	Elong. %	R. A. %
Precision cast		119,000	66,000	17	14.4
As HIP, sol. treated	235	163,000	000	28	24
As HIP, sol. treated	195	158,000	81,000	19	17

Summary

It has been demonstrated that the potential for control of structure via rapid quenching of the liquid melt is an ideal way of minimizing segregation, elimination formation of coarse secondary phases (both desired and undesired phases), and achieving fine grain size. There is an immediate major improvement in hot and cold plasticity which permits forging and rolling of otherwise non-forgeable alloys, or increases forgeability by an order of magnitude. Low and intermediate temperature properties are increased by large proportions, and large fatigue life benefits are achieved. If high temperature properties are desired, the fine grain structure must be coarsened; however, this usually occurs without the simultaneous coarsening of most of the excess phase particles. To accomplish grain coarsening, the oxygen content must be reasonably low, for example, 200 ppm in nickel or cobalt base superalloys.

The use of both fine and coarse powders, provided the quench rates are adequately high, will show the desired degree of structural refinement. A number of techniques are available for consolidation of the powders into ingot compacts, bloom, billets, slabs, and perhaps preforms for direct conversion to finished shapes.

In a number of alloy systems totally new compositions will result, with unusual combinations of alloying elements and phases which cannot possibly be combined in metal processes where slow solidification takes place.

Perhaps for the first time in the operations of metallurgists and materials people, major control of structure and properties is now possible, with exciting promise for future developments.

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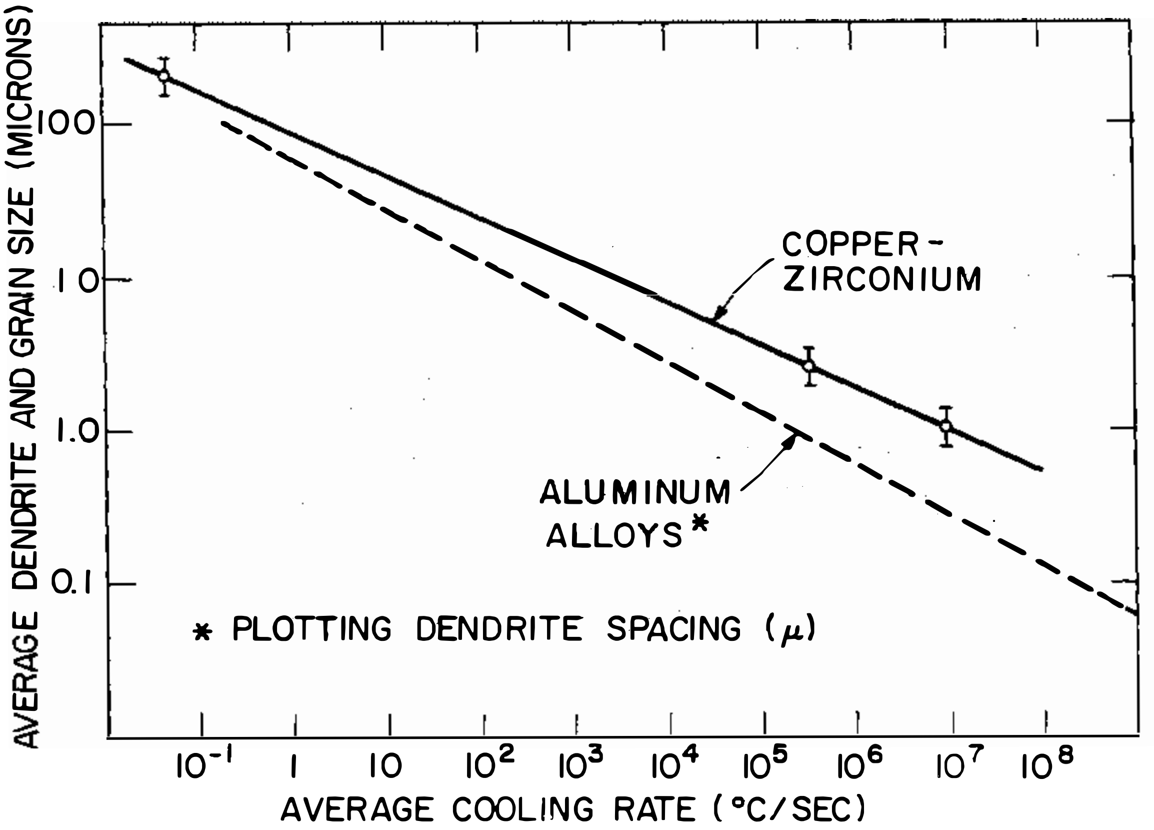

FIG. I AN APPROXIMATE CURVE OF DENDRITE AND GRAIN SIZE VERSUS COOLING RATE OF ALUMINUM AND COPPER ZIRCONINUM ALLOY

Fig. 2

Commercial 2024 aluminum alloy, rolled bar, longitudinal section
1500 X

Fig. 3

Aluminum alloy 2024, extruded from splat cooled flake powders; solution treated and aged. Longitudinal section. 1500 X

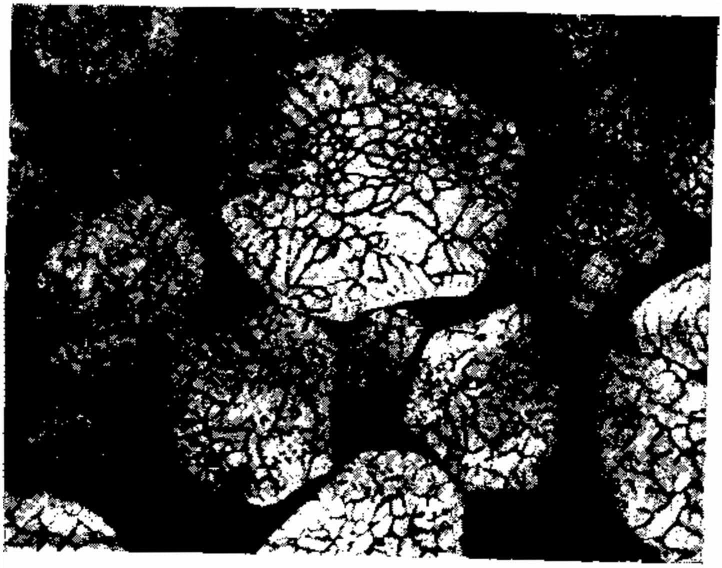

Fig. 4

Microstructure of inert gas atomized Cu-0.2% Zr alloy. Etched in $FeCl_3$.