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POWDER AND PARTICULATE PRODUCTION OF METALLIC ALLOYS

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The focus of this presentation is on the more recent developments of particulate metallurgy of alloyed materials wherein the final product will be a fully dense body. These particulates are not intended for the PM press and sinter technology, although some of the powdered particulates could also serve in the PM press and sinter industry and elsewhere. Concern also is for more highly alloyed particulates in contrast to lean alloys or pure metals; the latter are capable of being produced by many additional techniques, for example, by reduction of fine oxides, grinding of cathode sheets, etc.

Particulates are defined here as powders, flakes, foils, slivers, ribbons and strip. Because rapid solidification is an important factor in particulate metallurgy as discussed here, all of the particulates must have at least one dimension which is very fine, sometimes as fine as 10 to 50 microns, but more typically up to several hundred microns, provided that that dimension permits a minimum solidification rate of at least 10^2 K/s. The maximum solidification rate may be as high as 10^9 K/s for special purposes, but more typically would be in the range 10^3 to 10^6 K/s.

The major demand for rapid solidification (RS) is based on our awareness of the new-found control that rapid solidification provides over the micro and macro structures of the resultant particulates, which structures, in turn, can be manipulated to enhance the properties of the resultant fully dense body produced from the particulates.

It has always been the primary aim of all materials scientists and engineers to control structure, because control of structure equates to control of properties. For many years, and still true but to a lesser degree today, as property requirements became more demanding, complex

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alloying provided many of the answers. Today, taking into account the high cost of many alloying elements, the need for special melting and casting technology, and the difficulty of hot converting large, coarse-grained, segregated ingot structures, alloying technology of itself has lost some of its appeal.

Look through the literature and the handbooks, how many new ingot-based high-speed tool steels have appeared in the past 15 years? The last important wrought superalloys were developed in the mid-sixties; the last cast superalloys were developed in the late sixties. The end points were reached when the highly alloyed wrought materials could not readily be hot worked on the best available equipment; the end point for cast alloys was associated with lack of toughness due to large amounts of coarse secondary phases and a very coarse grain size.

Rapid solidification technology (RST), first a curiosity for the making of glassy alloys,(1) was soon thereafter demonstrated to offer an unusual degree of structure control in microcrystalline alloys.(2) As the high potential of RST for structure control became more and more evident, the number of interested scientists and engineers who came and are coming aboard is quite remarkable.

An unexpected benefit of structure control through RST is the total reopening of alloying technology in materials developments. In microcrystalline alloys the high degree of metastability of the structure and its otherwise homogeneous nature are strong inducements to try unusual alloying combinations. With glassy alloys we hope to see the development and emergence of a Hume-Rothery of metallic glasses.

The Achievements of Rapid Solidification

To date four curves are known relating secondary dendrite arm spacing (DAS) and solidification rate. These four curves are shown in Fig. 1; they represent plots for aluminum alloys,(3,4) copper alloys,(5) an austenitic stainless steel,(6) and an iron-base Mar-Aging steel(7) Fairly significant differences are observed among these curves, which should discourage the

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hasty use of measured DAS values from aluminum alloys as a measure of the solidification rates of highly different alloy systems in the absence of at least a partial calibration curve.

As the literature has already shown, there are numerous structural changes with increasing solidification rates. Most of the structural changes are not continuous functions of the quench rate.

Changes which have been studied and recorded are the following.

1. Decreased micro and macro segregation. This would appear to be a continuous function of increasing solidification rate.

2. Increased solid solubility. On average, the increase varies from alloy to alloy and alloying types. Important changes are not observed until some minimum value of quench rate is exceeded. Extensive reviews are available in the literature. In aluminum alloys this occurs above about 10^3 K/s.(8,9) In austenitic stainless steels 10^4 K/s will suppress precipitation of TiC. More than 95% of the TiC, over a fairly wide range of Ti and C contents, can be maintained in solid supersaturation.(10)

3. Changes in size, shape and distribution of secondary phases. These changes parallel, to an important measure, the changes in DAS. There are subtle changes in chemistry as well; such changes have been poorly documented thus far but could be important enough to stimulate additional research.

4. Elimination of most segregation phases. Since segregation phases are a function of the slowness of solidifications, their chemistries should be (and are) related to the solidification rate. For solidification rates in excess of about 10^4 K/s for aluminum alloys, the equilibrium phases rather than the segregation phases are observed. The many complex segregation phases in aluminum involving Al, Cu, Fe, Ni, Mn, Zr, etc., disappear in favor of the equilibrium phases Al_3M(M = Fe, Ni, Zr), Al_6Mn, and others.(11,12,13)

5. Formation of certain metastable phases. These phases, on heating,

later decompose to other metastable phases or to stable phases. Solidification rates in excess of about 10^4 K/s are generally necessary.(14,15)

6. Formation of glassy alloys. Quench rates generally in excess of about 10^5 K/s have been shown by many investigators to be required to preserve the glassy state. There are a significant number of exceptions, but the need to exceed some minimum quench rate is clearly required. One might be reminded that the glassy state represents the condition of "zero" segregation since the liquid state is preserved to room temperature with minor changes in atomic rearrangements. This, it would seem, is the ultimate achievement of rapid solidification technology.

Referring to Fig. 1, the following solidification modes and processes are identifiable, with approximate solidification rates (K/s):

a) Ingots and large castings: from about 10^{-3} to 10^0
b) Gas atomization (subsonic): from about 10^0 to 10^2
c) Gas atomization (ultrasonic): from about 10^3 to 10^5
d) Water and steam atomization: from about 10^2 to 10^4
e) Metallic substrate particulates (coarser than about 20 microns): from about 10^4 to 10^6
f) Metallic substrate splats (finer than about 10 microns and down to sub-micron thicknesses): 10^6 to 10^{10}

All of the above particulate forming techniques have now been applied sufficiently broadly that materials research people are knowledgeable about the structures which can be produced for a wide range of alloys. Since there are two or three orders of magnitude of solidification rates to contend with for each process, the experimentalist must apply his knowledge and skills cleverly to achieve the rates necessary for his structural control.

Briefly, since the topic has been well reviewed in recent literature, one strives to optimize the heat transfer coefficient. This is done primarily by control of particulate dimensions. With powders it's the particle diameter; with nonspherical particulates it's the thickness dimension. In each case the smaller the diameter or thickness of the particulate the higher the quench rate. The second important variable, in the case of atomized powders, is the velocity of the particle in its atmosphere; in the case of metallic substrates, it's the effective conductivity of the substrate. Secondary factors, but still very important, are the conductivity of the gas phase in atomization (helium will give an order of magnitude higher quench rate than either argon or nitrogen), the conductivity of the metal or alloy being solidified, and the superheat of the liquid metal. In atomization the superheat serves two tasks: it has a small effect on the solidification rate and, in the case of powders, it is important in terms of particle spherodization before solidifying.

The Economic Point of View

It takes energy to convert a metallic liquid stream into particulates of large surface area. The efficiency of the conversion is very poor, especially in atomization, and has been calculated to be of the order of 0.5% in subsonic gas atomization.(16) In similar calculations, the same source calculated an efficiency of 2% for the ultrasonic gas atomization process. This difference of 4 can account for a large difference in the volume of gas required to achieve a given atomization goal. In flat particulate production, there is also a cost associated with the achievement of thinner and thinner particulates. Since the primary aim of particulate production is to achieve a particular structure (for example, a selected value of secondary dendrite arm spacing), the aim should be to produce the coarsest particulate which will achieve that structure. In RST technology, the yield of a given particulate (size, shape, size distribution) must be secondary to the yield of material with the desired structure. Hopefully both yields will be high.

Because the degree of contamination from subsequent handling of the particulates is also sharply influenced by the surface area, the coarser particulates offer important advantages. What is being said here, is the following: if a solidification rate of 10^2 K/s provides the desired initial structure and is convertible to a product with the desired structure and properties, don't strive to attain solidification rates of 10^5 or 10^6 K/s.

Particulate Production

The proliferation of particulate production techniques is well documented in the publications of the four RQ International Conference Proceedings, and in the even larger number of smaller but equally productive conferences on the same topics.(17-20) There are nevertheless some comments and generalities to be made about each of the classes of RS techniques, without attempting to select any one type of process.

Gas Atomization (Subsonic). Clearly this is one of the oldest, best understood RS methods. The use of inert gases is an advantage in several ways. Nitrogen, the least expensive, can be used wherever there is no concern over reactions of nitrogen either with the solvent metal(s) or with reactive alloying elements. Helium can be used instead of argon with the potential for a gain approaching one order of magnitude in solidification rate. There are also subtle differences in the delivery of helium gas in contrast to argon or nitrogen; these differences have been observed both with subsonic and ultrasonic gas atomization but are otherwise poorly documented.

Where air is used, as for low alloy steel powder production, it is obviously much cheaper but can only be utilized effectively in special cases (easy reduction of the oxides, lesser concern over some retained oxides, utilization of an oxide as a structural stabilizer). Where moisture is a problem, as with aluminum atomization, subsequent treatment of the powders to break down formed hydrates may easily cancel out any benefits of the low cost of air (or combustion gases).

The extremely low efficiency of subsonic gas atomization (in terms of new surfaces generated, for example) can result in high costs of inert gases, in which case recirculation and recovery of the gases is an economic necessity.

Satellite accumulation is often a problem in gas atomization, Satellites are the fine powder particles which are attached in varying degrees to a coarser particle. Satellite buildup is very much a characteristic of each different gas atomization process. The degree of swirling or turbulence of the solidifying droplets in each production facility; the solidification rate; and the relative velocities of large and small droplets are some of the features of atomization which will determine satellite buildup. Figure 2 shows varying degrees of satellite buildup in subsonic gas atomization.

The presence of the satellites is undesirable on several counts:

a) the packing density can be decreased several percent.

b) the fine satellites are generally quenched much more rapidly than the parent particle (substrate quenching, in effect). These differences lead to important microstructural differences in the consolidated product.

The more extreme case of two larger particles colliding, with one of the particles already solid, which leads to the formation of a cap, is more serious. Again, the cap is substrate quenched and is much more finely structured, leading to microstructural variations which may present property problems. Some of the centrifugal atomization methods are known to exhibit this type of collision to a greater degree than is observed with gas atomization. Figure 3 shows the finer structure of the cap.

Gas Atomization (Ultrasonic). The ultrasonic gas atomization (USGA) process to be discussed below is that based on the invention of Nielson and Tove (Kohlsva, Sweden) which utilizes a series of modified Hartman shockwave nozzles (an annular ring has also been used) to generate a set of pulsed, ultrasonic gas jets onto a flowing liquid metal stream.(21) Two frequency ranges are indicated, a major one at about 100 kilohertz and a broader, weaker one at 20 to 30 kilohertz. Exiting gas velocities are reported to be in excess of Mach 2.(16) The combination of ultrahigh velocity gas jets, in the pulsed mode, was reported to be responsible for the generation of very fine powders in a narrow size range. Our studies tend to confirm these claims. Perhaps the most interesting aspect of the USGA process is that high-speed movies show that atomization is a single-step process, in contrast to the three-step process observed, again by high-speed movies, for the subsonic gas atomization process.(22,23)

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The high velocity, pulsed gas jets can produce very fine powders (22μm, average size, for aluminum alloys using 1000-1200 psig gas pressure), with indicated DAS values from about 0.5 to 5 microns for powders finer than 250μm. See Figs. 4 and 5.

Unlike the subsonic, three-step gas atomization process, the USGA process does not trap the atomizing gas; powders tend to be quite spherical, and satellite population tends to be small (however, satellite density is the result of other production variables, as well). Figure 6 shows typical USGA aluminum powders.

The use of still higher gas pressures than 1000-1200 psig is known to result in still finer powder sizes, with higher solidification rates, should such finer powders or higher quench rates be desired or necessary.

In the gas atomization processes there are a rather significant number of operating variables, which apply whether the processes are sub or ultrasonic. Important variables are:

1. Metal stream diameter. For ultrasonic gas atomization this value is about 5mm or finer to allow for total interactions between the impinging gas jets and the free-falling liquid metal stream.

2. The diameter and length of the gas nozzles or ports. These dimensions determine the length of the laminar flow of gas, for maximum efficiency, as well as the velocity of the gas jets.

3. Gas velocity. Whereas one generally measures pressure, the correct variable is the gas velocity. In subsonic gas atomization the primary role of the gas stream is to increase the velocity of the liquid metal stream; the low shear resistance of the liquid metal then leads to disintegration of the liquid stream at high velocity.(23)

4. Included angle between the gas jet and the metallic stream. For maximum gas efficiency one would prefer a large angle; however, this results in lateral spray formation requiring much larger tank diameters. Further, high levels of gas back pressure are generated which usually

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prevent metal pouring and can in fact lead to gas bubbling up through the crucible or tun dish. A shallow angle of impingement leads to a large component of gas reflection off the liquid stream surface; results in turbulent gas flow (as the distance of travel increases); and generally results in very coarse powders. The total included angle between the opposing gas jets is typically 40 to 60°, being on the smaller side for greater efficiency for the USGA process.

5. Liquid metal superheat. Superheat is very important. With pure metals, which are characterized by a freezing point, sufficient superheat is especially important. The formation of refractory surface oxides by any of the components of an alloy can, in the absence of adequate superheat, lead to highly irregular powder shapes. Aluminum oxides are among the worst. In the three-step subsonic gas atomization process, high levels of superheat are essential since the powder-forming step will be well removed from the gas-metal interaction zone, and a variety of intermediate shapes are formed. See Fig. 4 for indication of the role of superheat.

Water and Steam Atomization. The much higher quench capacity of water and steam is a plus feature for these fluids, and typically solidification rates are greater by 10 to 100x compared to gas atomization (10^4 compared to about 10^2 K/s). The oxidation which can result with water and steam is somewhat more severe than with air. Accordingly, steam and water are used for atomization and quenching only where the oxide of the alloy being atomized can be reduced relatively inexpensively. Low alloy steels and cast irons are the best candidates for these processes. In the latter case, the oxides which are formed are used for reaction with the carbon of the high carbon steels or cast irons to produce a decarburized iron of suitable purity for powder processing.

Centrifugal Atomizing Processes. There are a number of centrifugal processes in operation, several of which may be classified as commercial (small-scale) ventures.

A. Rotating Electrode Process (REP). Several features characterize this process, which has a number of points of merit, as well as several which present important disadvantages.

The process utilizes rotating electrodes which can be prepared by casting, by rolling or drawing, or by sintering (with an aim for maximum practical density). Opposing electrodes can be used to strike an arc, or one can use a plasma source, electron beam(s), a water-cooled tungsten arc, lasers, etc. The aim is to melt a thin layer of liquid metal or alloy at the tip of the electrode; the centrifugal force, controlled by the rotational speed, overcomes the shear resistance of the liquid film and results in droplets of liquid metal being cast from the electrode surface.

Since no crucible is required either for melting or pouring, there is no crucible contamination. Since an inert gas atmosphere (or sometimes a vacuum) is used, purity levels are kept high. Highly reactive metals and alloys are especially well suited for REP; thus Ti, Zr, Hf, V and their alloys are powder processed by REP.

Disadvantages are:

a) Cost of electrode preparation, which includes the melting and rolling or casting or sintering of the alloy prior to machining and re-melting by the REP.

b) Coarseness of powders (typically greater than 200µm). The speed of rotation and the melting rate or thickness of the liquid metal film are important control factors; the former is a function of electrode uniformity and melting uniformity.

c) Segregation of alloying elements. The segregation state and excess phase coarseness of the prepared electrode will be felt in the final powder product, clearly not on a one-to-one basis, but present nevertheless.

d) Lower solidification rates than other atomization processes. The coarseness of the powders is the single most significant factor here. Use of preferred gases can improve the situation (helium in preference to argon, in preference to vacuum).

In addition, tungsten electrodes are known to cause W contamination;

electron beam systems require a vacuum, which is poor for high quench rates: and laser beams are expensive and too localized in their melting action.

B. Perforated Rotating Cups. The use of high-speed, rotating, perforated cups is an easy way to meter liquid metal for atomization. A search of the literature will reveal a capability to produce a wide range of particulate shapes and sizes. Spherical, tear-drop, rice-shaped (acicular), and ribbon-shaped (large aspect ratio) particulates have been produced. Most of the successes have been with the lower melting metals and alloys, less than about 900°C (1173K) atomization temperature, due to the limitations of strength and erosion or alloying resistance of the cup material. Steels, heat-resistant alloys and superalloys are preferred cups, especially at the higher end of the temperature range: 700 to 900°C (973 to 1173K).

The Reynolds Metals Co. has produced centrifugally atomized aluminum alloys commercially for a number of years, using a rotating, perforated steel cup. The powders, which are atomized in air, indicate solidification rates of about 10^3 K/s; yields of useful rice-shaped powders are high (95%); and the powders are continuously moved, heated, and hot rolled in a single-roll stand to essentially full density.(24)

C. Shear Lip Centrifugal Atomization. Originally scaled up to pilot-scale operation in England, the process of pouring liquid metal into a high-speed rotating cup, with a thin layer of liquid metal climbing up the cup wall to be atomized as it passed over the sharp lip of the cup, has a number of apparent advantages as well as some disadvantages.

The thinner the moving metallic layer, the sharper the lip of the rotating cup, and the higher its centrifugal speed, the finer the resultant powder size and the greater the solidification rates. Rotational speeds are limited both by the strength and temperature of the cup material, as well as by the nonuniform spreading of the liquid metal layer within the cup. With alloys poured significantly above about 1300°C (1573K), most cup materials will not retain the original sharp lip required for [illegible] thinning and shearing of the moving liquid metal film. Progressively this leads to coarser powder particles with lower solidification rates.

An alternative, which eliminates the variable performance of the cup lip, is to shear the liquid metal off a liquid-solid skull. The skull is achieved by letting a layer of the alloy solidify on a rotating, internally cooled dish. With excellent temperature control and pouring rate, a uniform powder product is formed which tends to be relatively coarse. To increase the solidification rate of these coarse liquid droplets, the droplets are blasted by helium gas jets as they fly by to achieve quench rates indicated to be about 10^5 K/s.(25)

Of importance, all of the centrifugally atomized powders are free of entrapped gas, confirming a one-step atomization process in general. The biggest single problem with all of the centrifugal methods now in use or in development is the relatively coarse powder size produced, which leads to slow solidification rates unless augmented by additional quenching devices.

Hydrogen Solubility Process. One of the unusual atomization processes uses dissolved hydrogen which is introduced into the melt; the melt is then exposed to vacuum via a delivery tube. As the liquid metal rises in the tube, the hydrogen, being very poorly bound in the melt, is rapidly released, literally disintegrating into an atomized spray. Both spherical powders and flake (splatted) product are produced (a function of the container vessel size). Powder size is probably not easy to control within narrow limits; however, the product is extremely clean. Powders tend to be of intermediate size with indicated quench rates near 10^2 K/s (in part due to the fact that atomization takes place into a vacuum chamber). The technique is perhaps best characterized as an inverted stream degassing process such as has been applied to hydrogen removal during liquid pouring of hydrogen sensitive steel alloys into ingot molds through a vacuum. The "soluble gas atomization process" is a production process.(26)

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Metallic Substrate Splat Quenching Techniques. When solidification rates greater than about 10^{4} to 10[illegible] K/s are desired or required, one turns to the various splat quenching techniques which have developed since Duwez and his co-workers first demonstrated the unusual structures which could be produced using his gun-splat technique.(1,27,28,[illegible]) The quench rates were shown to be between 10^{7} and 10[illegible] K/s by Predecki and Grant([illegible]) and were then confirmed through extrapolations of prior experimental data([illegible],4) and calculations.(30,31) The use of copper substrates was extended from the gun technique to piston and anvil, then to melt spinning, to melt extraction, to twin-roller techniques and many others. The highest indicated solidification rate of 10^{10} K/s was suggested by Ramachandrarao et al.(32) The resultant particulates were generally less than 100μm thick and, if producing glassy alloys, were less than 50μm thick to maintain high quench rates and uniform through-thickness structures. For most glassy alloys, quench rates in excess of about 10^{5} K/s were found necessary, although there are significant exceptions.

The products from all these substrate quenching processes are definable as flakes, foils, ribbons, strip, and with special processing variables could be powders.

One seeks and expects solidification rates and quench rates (for the glassy alloys) of at least 10^{4}, which can be further increased to 10^{6} or 10^{7} K/s by producing thinner particulates (about 10 to 60μm).

Production Rates

An obvious question has to do with the relative merits of atomization vs. substrate quenching techniques for alloy development or production. Differences (aside from quench rates) which are important between these processes include the following.

1. Surface area of fine powders is significantly greater than for flat particulates of equal thickness; this will play a role in the oxygen or other surface contamination.

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2. Packing density of powders at best is about 65%; for sheared flat particulates it can be as high as 80 to 95%. The efficiency of heating and the HIP or extrusion efficiency favor the flat particulates.

3. Flat particulates rarely present trapped gas problems; some of the atomizing processes produce significant amounts of hollow powders which present major problems.

4. The structural uniformity of flat particulates (if thin enough) tends to be importantly greater than that for powders where the size range may vary from less than one to over 250μm.

5. For production by substrate quenching versus the several atomization techniques, for now the powder processes appear to enjoy an advantage.

Most substrate quenching techniques (not including production of wide strip as a finished or semi-finished product, but as an intermediate raw material) utilize small diameter (width) metal delivery nozzles to provide a thin particulate.(9) Multiple pouring nozzles clearly can be used to increase liquid metal delivery rates. Melt extraction can not only provide a wider particulate but could also use a series of parallel wheels. The volume of loosely packed, continuous particulates can quickly be very large and must then be consolidated into more densely packed material. More convenient shapes than continuous ribbon are also produced, such as semi-powder shapes which are not spherical. In fact such shaped products can be tailored to specific dimensions for use as finished particles (high aspect ratio rod shapes for concrete reinforcement, for example).(33)

But for more continuous, larger scale operation, using about 5mm diameter liquid pouring streams, which can also be produced through several pouring nozzles, powder production provides a much easier product to handle for subsequent HIP, hot mechanical pressing, hot extrusion, etc., into semi-finished, fully dense materials. Perhaps the most important variable is the greater specific density of the powders compared to continuously produced long ribbon shapes, which must then be sheared or fractured (if sufficiently brittle) into an intermediate shape which can be handled similarly to powders.

Nevertheless the easy achievement of solidification rates which can be 10 to 100 times greater than for most atomized powders is not to be overlooked for structure and property requirements. Excellent properties have been reported for alloys produced by substrate quenching (splatting);(34,10) further innovations in substrate quenching to produce a more controlled, discontinuous splat which can be consolidated with a minimum of handling and intermediate processing would be welcome.

The Glassy Alloy Route to Ductile Microcrystalline Alloys

If one checks the literature it becomes clear that up to the present, the bulk of all RS powder production has been concerned with microcrystalline alloys, whereas a majority of the RS substrate quenching has been concerned with glassy alloys. The latter would certainly be true of rapid solidification by melt spinning methods.

Clearly those atomization processes which can reach or exceed about 10^5 K/s will allow glassy alloys to be produced.(35,36) Also, since there are no real barriers to producing microcrystalline ribbons, strip and flake by substrate quenching the subsequent processing steps should determine which of the several rapid solidification processes to use for particulate production.

If an alloy is a responsive glass former; and if its compositions can be modified to minimize the volume fraction of the resultant hard or brittle phase on crystallization (typically below about 50 vol. pct. and preferably less than about 35 vol. pct.), the production of extremely fine-grained, ductile alloys becomes an attractive potential.(37) The more attractive basic alloy systems are the glass-forming Transition Metal_{80}-NonMetal_{20} alloys. A number of T_{M1}-T_{M2} compositions in the range from 85-15 to 75-25 atomic percent look attractive for crystallization from the glassy state. The major (initial) attraction of starting from the glass state is the potentially, extremely uniform, fine grain size which can be produced. In contrast, a much more variable grain size will result when attempting to quench to a selected fine DAS which can be converted to a desired, uniform, fine grain size through hot work. Grain sizes well below one micron have been reported,(38,39,40) including some fine-grained ductile alloys crystallized from the glassy state;(37) see Fig. 7. In fact careful work should be capable of producing grain sizes between 0.01 and 0.1µm on crystallization. Retention of these structures during hot consolidation will probably be much more difficult. These extremely fine-grained alloys should be of unusual interest in terms of many properties.

Defects in RS Particulates

A number of defects have already been mentioned above, but are worth repeating and elaborating upon.

1. Alloy Reactivity, Surface Area, and Surface Defects.

The finer any powder or particulate, the greater its reactivity with the various atmospheres it will encounter in subsequent processing to a fully dense structure. The purity and type of gas used for atomization or the working atmosphere is therefore very important. Clearly inert gases would be preferred, realizing that the specific gas will also play a role in determining the solidification and cooling rate of the particulates.

The probability is that the gases to be used will not be of ultra-high purity both because of cost and because of difficulties in purging the tank or container in which the particulates will be formed. Further, the probability is extremely great that the particulates will be exposed to air for a significant time for processing reasons. With powders, this suggests a preference for spherical shapes with a minimum of satellites and an absence of submicron particles to achieve minimum reactivity.

Alloys based on or rich in elements which oxidize readily must be [illegible] and so as to limit contamination, which [illegible] significant surface area for a given powder lot size. In the case of aluminum powders, there is danger of formation of hydrates on the surface, which, if formed, must be treated in the powder state at or above about 500°C (773K) to decompose the hydrate. If the hydrate is incorporated into the hot consolidated product, swelling will occur on subsequent solution heat treating at temperatures near to or above 500°C (773 K).

Oxide contents at levels of several tenths of a percent (in aluminum) are not unknown for a significant number of powder based alloys produced in air or in an oxidizing gas.

2. Gas Porosity. Reiterating what was said above, gas porosity (hollow powder) can be extremely detrimental to properties. All of the subsonic gas atomization processes tend to produce gas-entrapped powder particles; this is characteristic of the three-step atomization processes (see Fig. 8). In the as-hot-extruded or as-HIP'ed structures of gas containing particulates, one generally does not see the presence of trapped gases, but subsequent temperature exposure for solution heat treatment, or for welding, will cause swelling when the internal gas pressure exceeds the creep resistance of the alloy at the appropriate temperature (see Fig. 9).

3. Refractory Oxide Films. The nickel-base superalloys in particular, containing large amounts of Al, Ti and Cr, plus perhaps Ta or Cb, form thin, highly refractory oxide films on powders and particulates; these oxides will not dissolve and may not spheroidize to an important extent in hot working. As with the thin, continuous refractory oxide films on aluminum particulates, the superalloys will show good to excellent mechanical behavior if hot extruded or hot worked extensively. In the hot isostatically or hot mechanically pressed conditions, problems can be encountered by the above superalloys. The degree of oxidation, the amount of relative movement of the powder mass, and the degree of oxide spheroidization will determine the resultant mechanical properties. With aluminum, because of the very low temperatures used, the oxide films tend

to remain continuous, so that hot pressed particulate bodies rarely show optimum properties, and the product must be hot worked.

The whole subject of oxide films, their stability, methods of promoting breakdown or spheroidization, and their subsequent role on properties remains a critical issue, especially in pressed to shape RS particulate structures where excellent properties are being sought.

Figure 9 shows the role of such stable oxides in HIP'ed fully dense materials. Figure 9a shows the sharp retention of particle shape, with new recrystallized grains staying within particle boundaries; note in particular the resultant large grain size variation from point to point due to the use of a wide range of powder sizes.(41) Figure 9b shows a not-untypical fracture of an alloy such as that shown in Fig. 9a. The fracture is an interparticle failure, therefore, in this case, also an intergranular failure. The alloy is not actually brittle since as much as 10% elongation can be realized in short time stress-rupture tests; however, both the rupture strength and the ductility at fracture are considerably less than for the same powder material after hot extrusion.(41)

4. Refractory Carbides. During rapid solidification, it is not unexpected that all or a significant amount of the carbon present in, say, superalloys or stainless steels will be there in supersaturated solid solutions.(36,41) Uncontrolled heating to the HIP temperature or to the hot extrusion temperature can result in the precipitation of coarse refractory carbides (TiC, TaC, HfC). Once formed, generally near prior particle surfaces, these carbides cannot be readily (if at all) dissolved. One can of course work with much lower carbon contents where chemistry so permits. Preferably, one should temperature and/or mechanically pretreat the particulates before hot consolidation to induce precipitation of the carbides into finer particles and thus avoid subsequent severe coarsening at the HIP or extrusion temperature.(41)

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SUMMARY

While there are numerous problems and faults with RS particulates and particulate production, the resultant structures and properties are of such excellence that major studies should be continued to learn how to eliminate some of the problems and faults, how to optimize processing variables, and how to take advantage of the unique structural control made available by RST. The potential for highly improved alloys remains high and essentially is a near term proposition.

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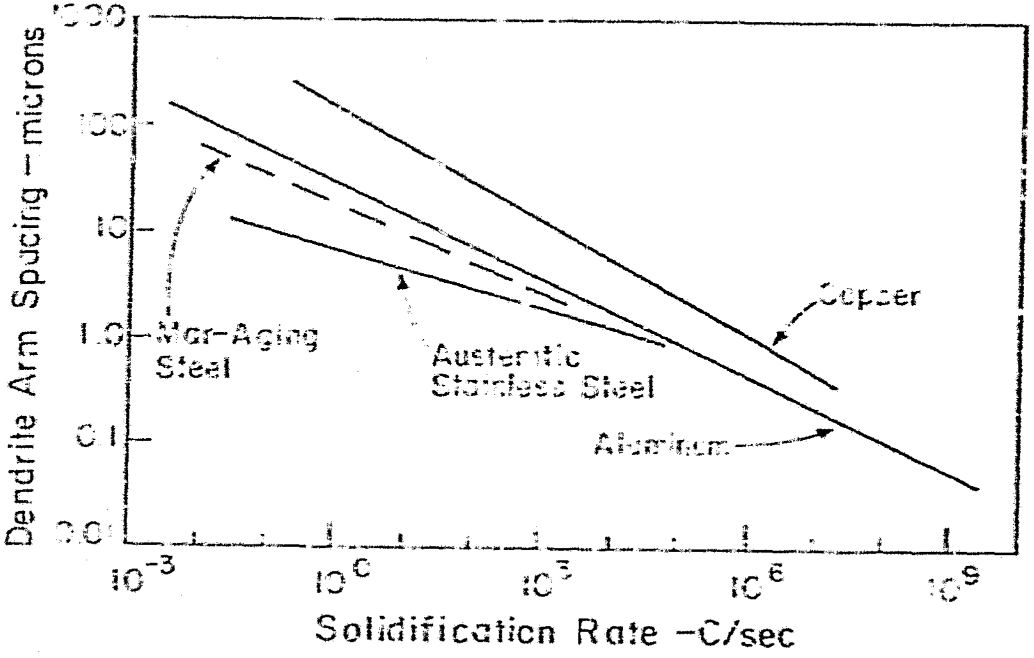
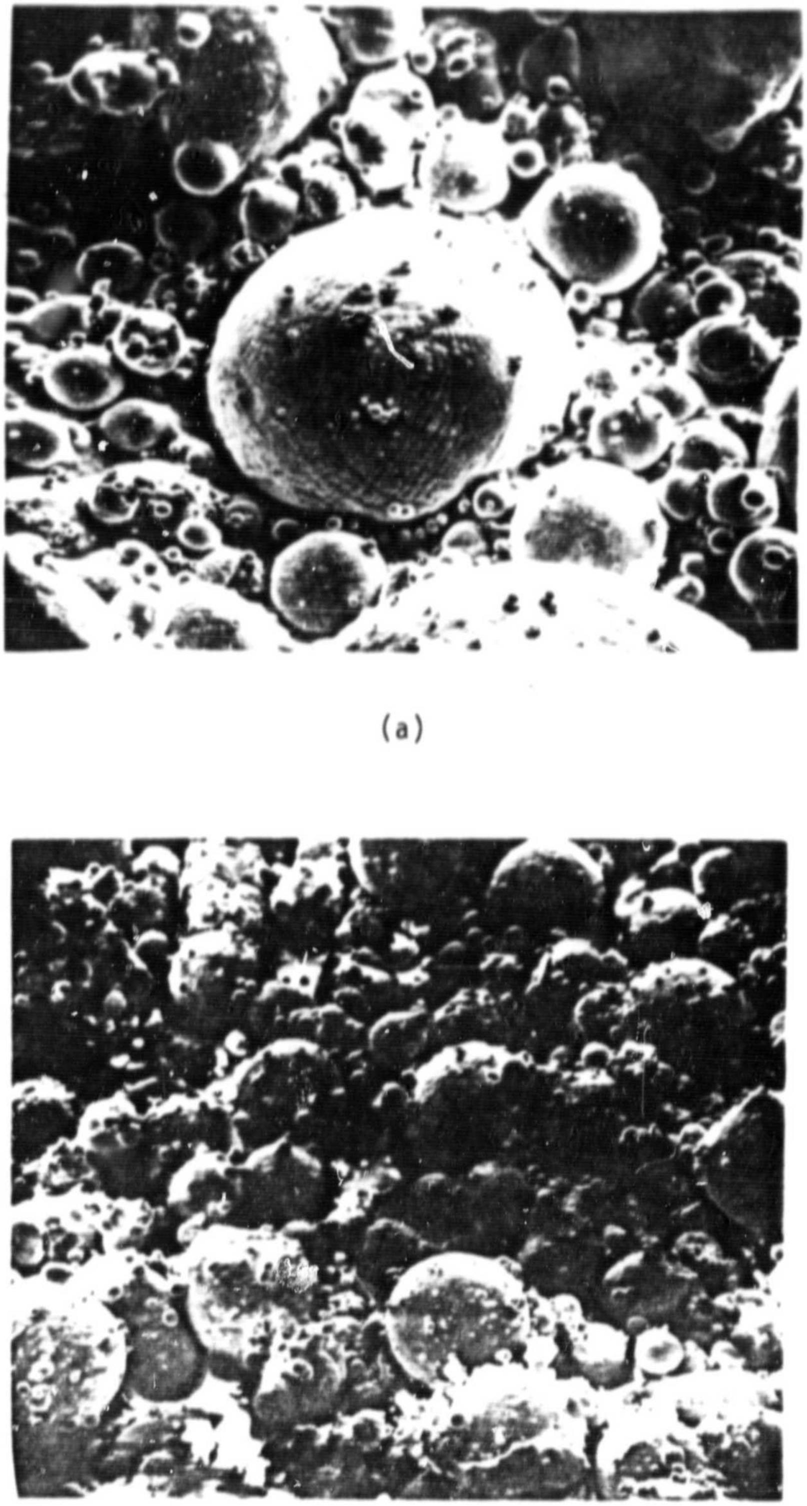


Figure 1. Dendrite arm spacing as a function of solidification rate for aluminum alloys, copper alloys and [illegible] steels. [illegible]



(a)

(b)

Fig. 2. Variations in satellite particle attachment to powders of IN-100 for two subsonic gas atomization sources. (a) 138x, (b) 200x.

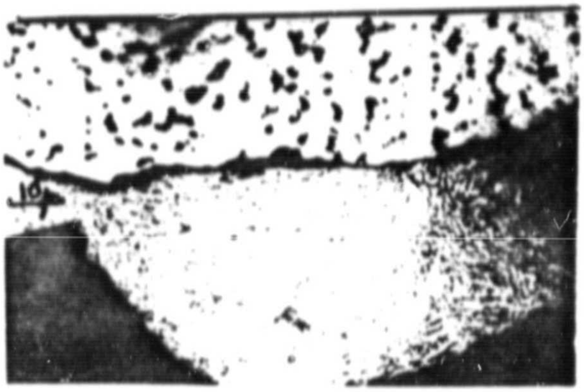


Fig. 3. Finely structured cap which splatted onto a larger, solidified, coarsely structured particle.

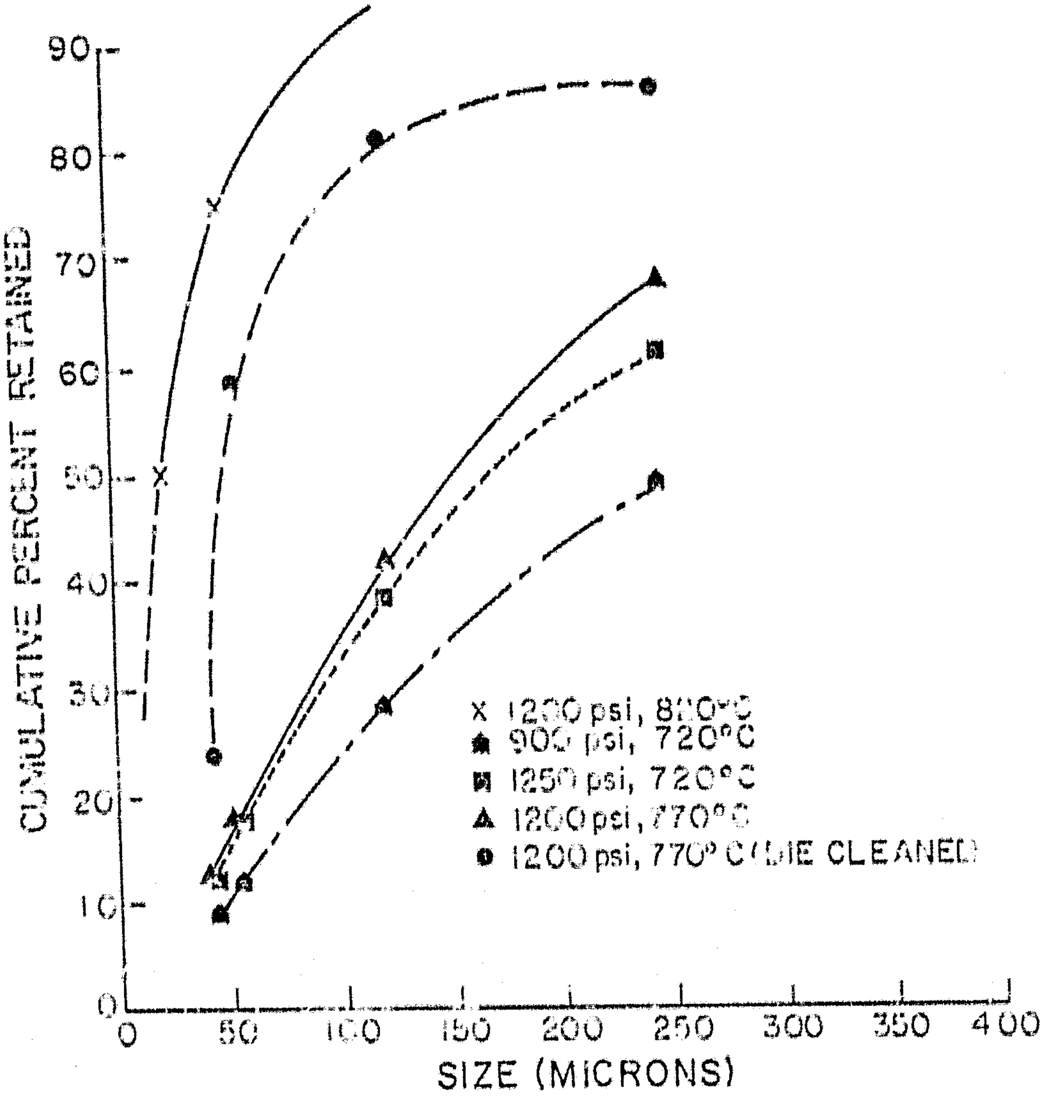


Figure 4. Powder size ranges for [illegible] aluminum as a function of superheat temperature and gas pressure (velocity).

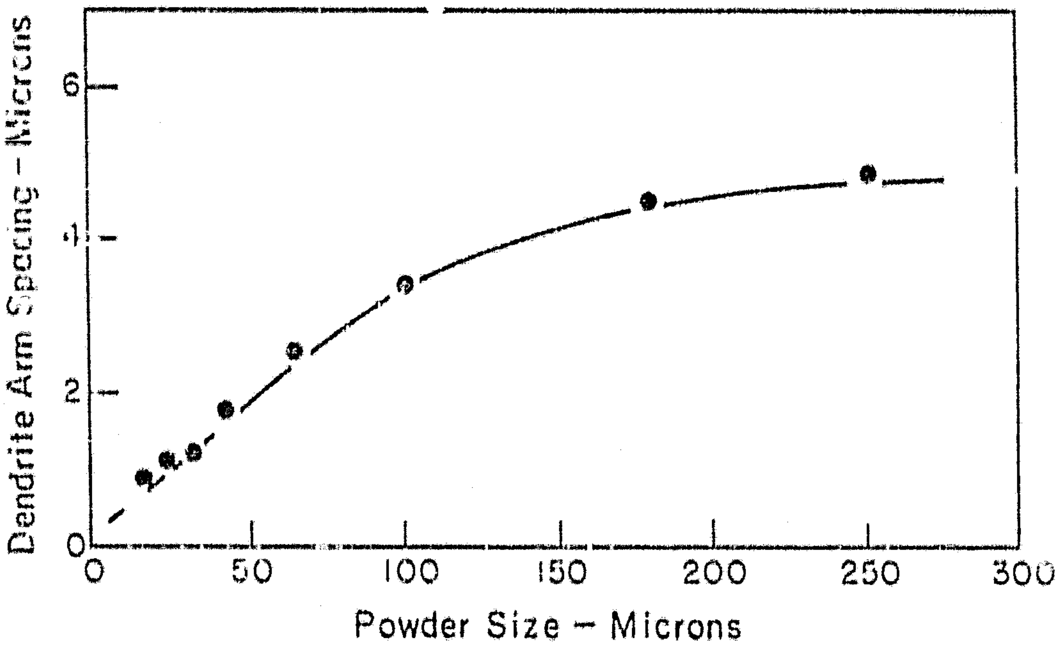


Figure 6. Variations of dendrite arm spacing with powder size for 2024 + Li [illegible] aluminum alloy.

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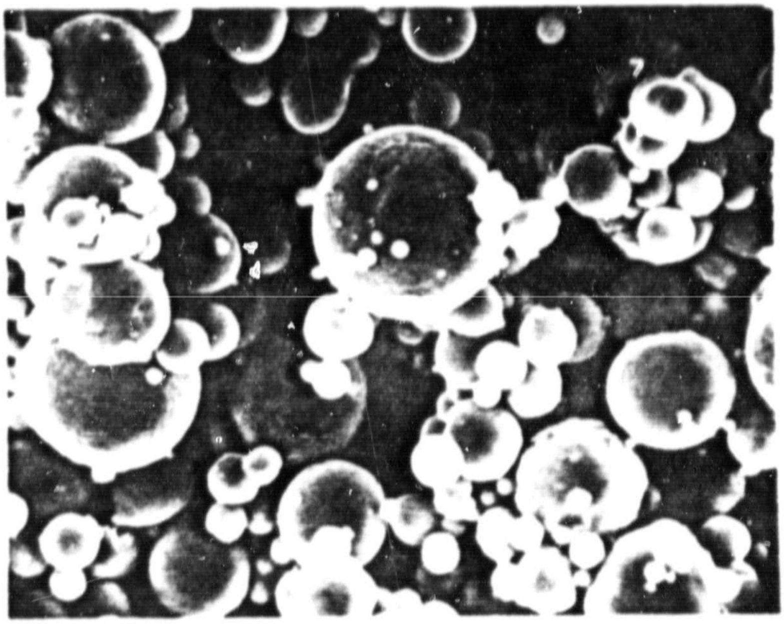


Fig. 6. SEM view of USGA aluminum alloy 2024 + Li. 1000x.

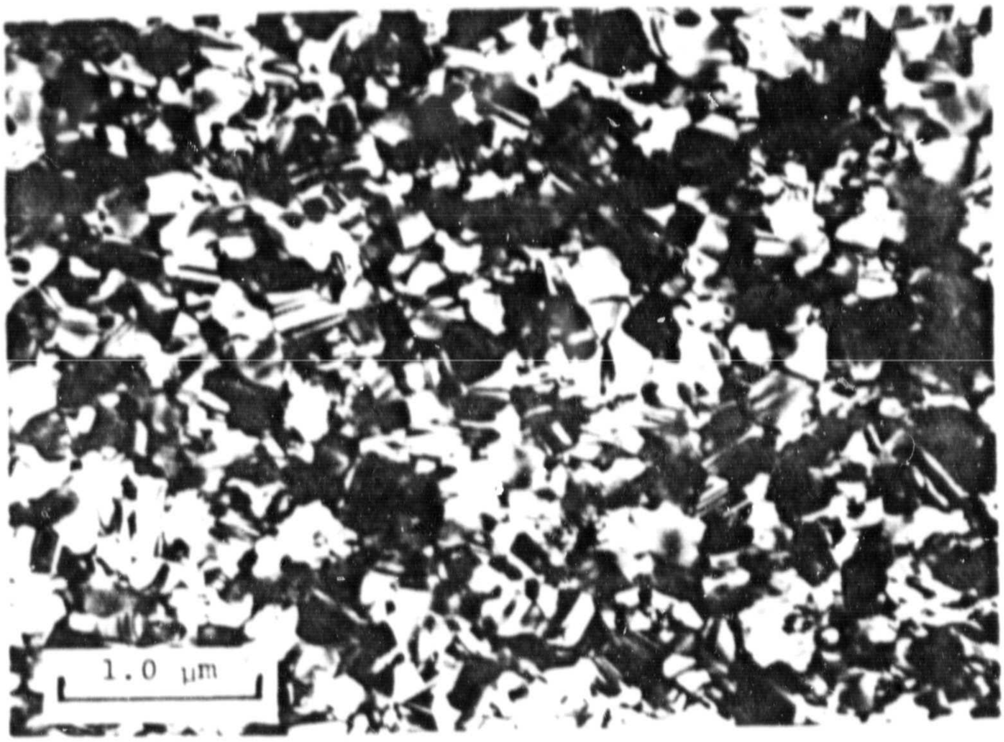


Fig. 7. Fine-grained crystallized glass showing uniform grain structure.

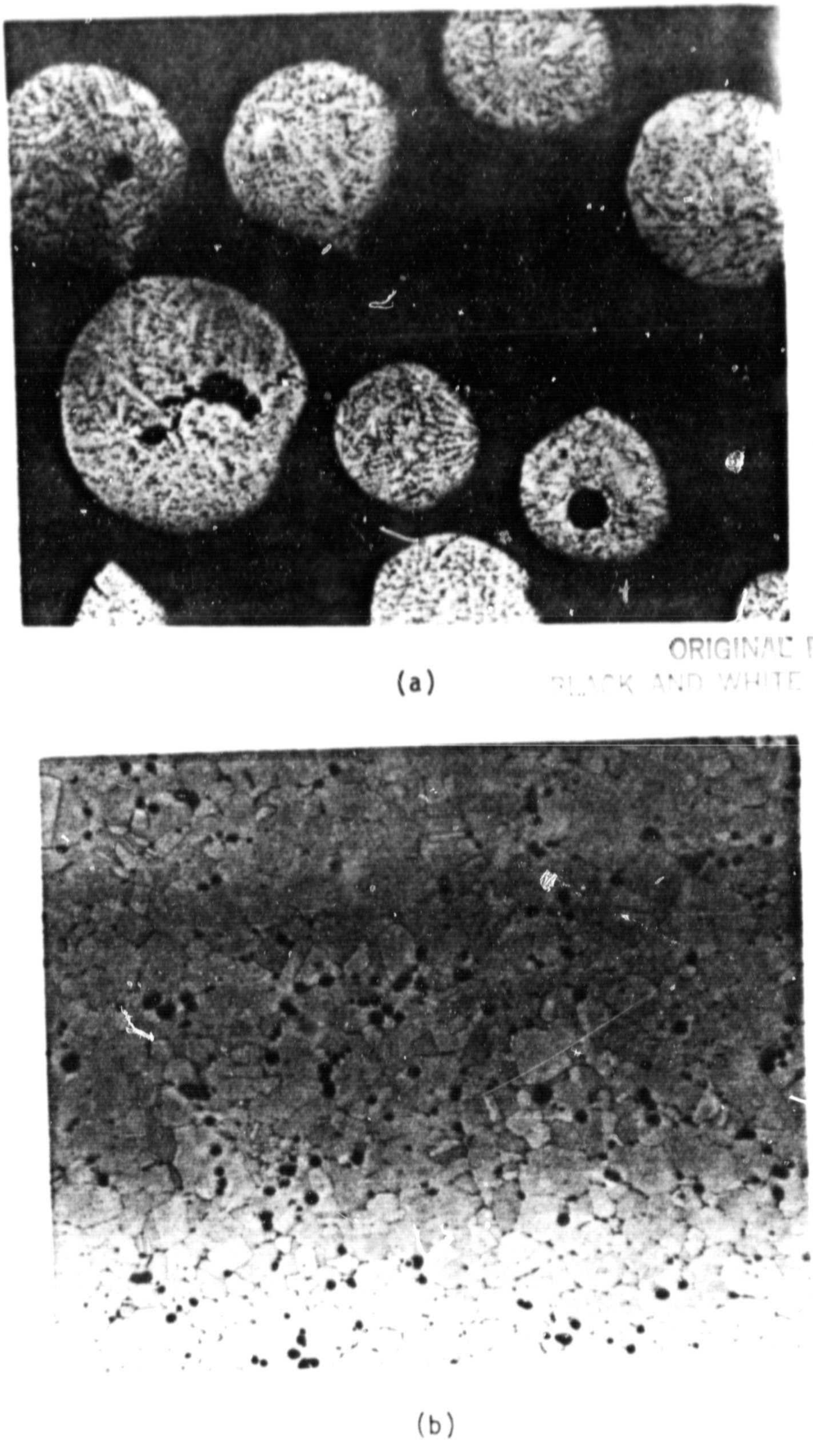
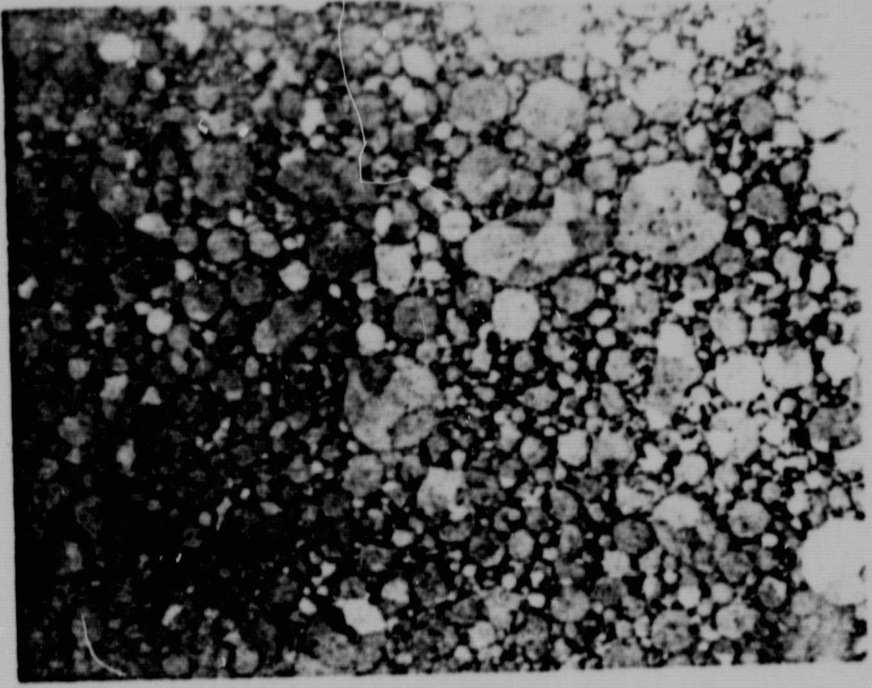
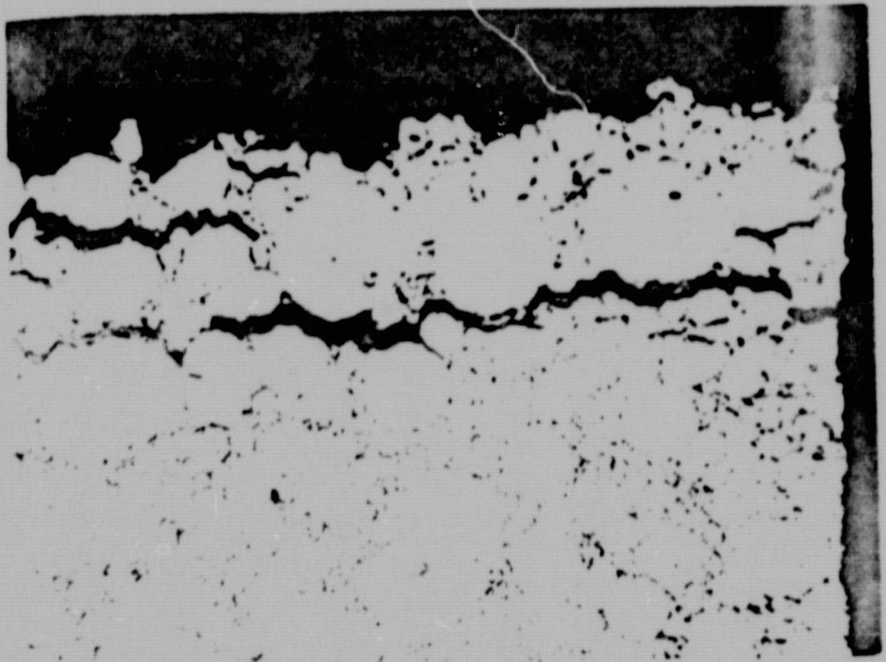


Fig. 8. Astroloy 700. (a)Subsonic gas atomization with argon showing argon entrapment. (b) After HIP treatment 2 hours at 1204°C (1477K) followed by 2 hours solution heat treatment at 1204°C (1477K). 128x and 26x.



(a)



(b)

Fig. 9. IN-100 RS material. (a) As hot isostatically pressed 2 hours at 2204°C (1477K). (b) Stress-rupture failure at 982°C (1255K); interparticle and intergranular failure; elongation about 10 . 100x and 200x.