DEVELOPMENT AND APPLICATIONS OF ULTRAFINE ALUMINIUM POWDERS

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Abstract

Over the last twenty years or so, a variety of new technologies has been developed to produce sub-micron powders. Among the products attracting interest is nanoaluminium which is being evaluated in specialist propulsion and exothermic end-uses. This paper examines the advances made in ‘nanopowder’ production in the context of the existing aluminium powder industry where finest commercial grades have a median size of ~6µm (one or two orders of magnitude coarser than nanopowders) and which today supplies the markets being targeted by nanopowders with coarser, but effective products. Are there genuine market opportunities for nanoaluminium and if so, how will they be produced? One the one hand there are the novel nanopowder production methods which are high yielding but generally slow and costly, while on the other, there is the very fine fraction from conventional atomising routes which generate a very low yield of sub-micron powder but which nevertheless can translate into a meaningful rate as part of the bulk production. Can conventional routes ever hope to make sufficient volumes of nanopowders cost effectively and which will be the favoured routes in future? Moreover, what of the ‘ultrafine’ size range (~0.5-5µm) which is of more immediate potential interest to today’s powder users. This paper seeks to identify the near term opportunities for application of low volume/high value ultrafine and nano powders.

1 Introduction

Annual sales of aluminium powders and granules (~<1mm) worldwide is estimated at ~ 200k tonnes per annum (tpa) primarily comprising sales to the metallurgical, chemical and paint & pigment industries (1). Specialist end uses include rocketry, explosives, thermal spray, powder metallurgy, etc. The vast majority of powders are produced by conventional air or inert gas atomisation though significant quantities are made by granulation of foils. Several of the bulk applications where aluminium is used as a powerful reductant or as a precursor in the chemical industry attract low premiums. There is therefore an economic drive to maximise production of superfine fractions (those defined as having median particle sizes in the range 5–15µm) which are precursors for the manufacture of increasingly sophisticated pigments for decorative finishes on automotives and domestic appliances.

For other end uses, such as thermal spray or powder metallurgy, removal of superfines can be advantageous in improving powder flow characteristics and reducing the hazards associated with airborne superfines and associated dust collection systems (2). For the powder producer, there is a drive to develop a balance of customers requiring complementary size fractions in order to sell the entire atomised size distribution. In order to increase the value of the portfolio, gas atomising technology has focused on achieving higher yields of fine powders to satisfy the demand for fine pigments. The natural progression is towards nanopowders, but with the exception of a few specialist niches, the focus is on stepwise size reductions to service established Al powder markets. Atomising technologies are therefore being geared towards maximising the yield of superfines. While gas atomisation processes are generally regarded as inefficient, with as little as 1% of applied energy being utilised in size reduction, significant amounts of sub-micron material are generated during atomising. It is debatable how much further the technology can be developed to produce superfines, but it will almost certainly be unable to bridge the gap to nanopowder production methods (Ref 3-11). Ultrafines (~0.5-5µm) would, however, be a more realistic target.

Fig.1 shows a schematic relationship between 'product size' and approximate price range for aluminium. In the 'coarse' limit, 660kg sows or T-bars are available on the LME at ~ £0.9-1.1/kg and this contrasts with a quoted price of up to £700/kg for nanopowders (12). Fig.2 is an approximate indication of the volumes of aluminium produced in different sizes. Without attaching too much significance to the relationship, there is a striking trend between the world's aluminium product capacities and the physical size of the product – from smelter to nanopowders: this suggests an ultimate market size of 10-100tpa.

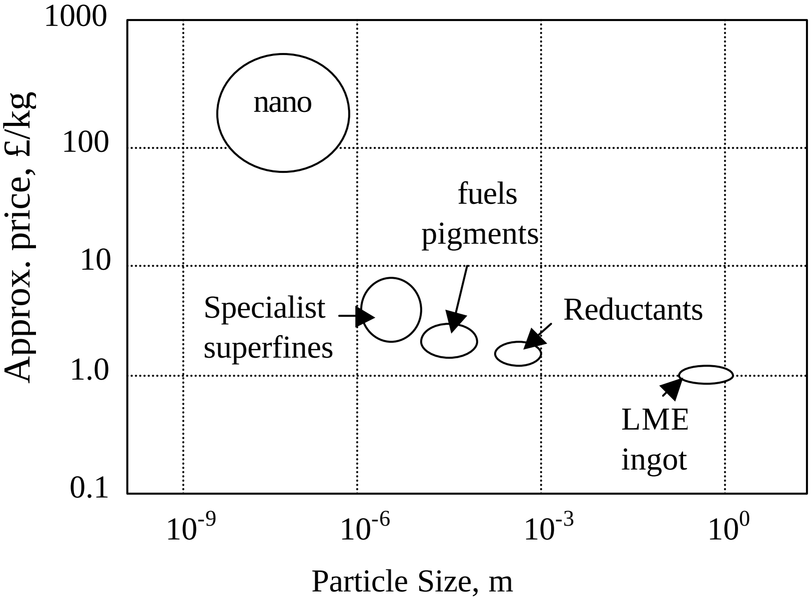

Fig. 1 Approx prices for Al as a function of the product size: from ingot to nanopowders

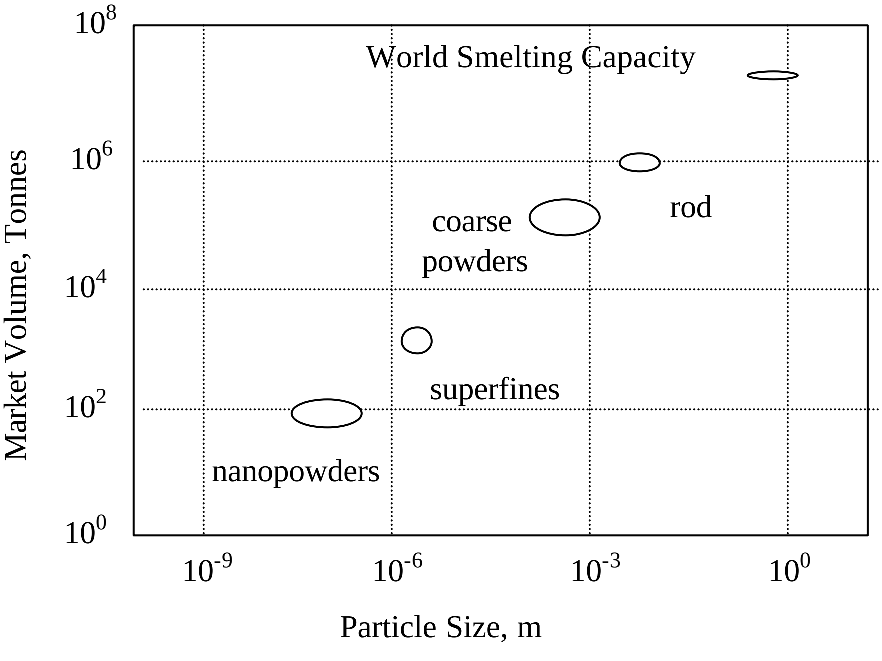

Fig. 2 Approx market size for Al as a function of product size: from ingot to nanopowder

2 Production of Aluminium Powders

A variety of methods is available for production of aluminium powders from the melt but the most significant volumes of fine powders are prepared by air and gas atomisation. For gas atomisation an empirical relationship has been determined relating the metal/gas ratio to the median particle size. For a given molten metal flux, then increasing the incident gas flux will reduce the median particle size resulting in an increase in the yield of fines. The width of particle size distribution is also dependent on the design of the atomising head and detailed process variables and this also affects the yield of the fine fraction.

The efficiency of gas atomising processes is low (typically quoted as ~ 1%) and whilst several process innovations have enabled reasonable yields of superfines to be achieved (type and temperature of atomising gas, nozzle and manifold design), there are difficulties in achieving stable running conditions if parameters are set to achieve very fine median sizes.

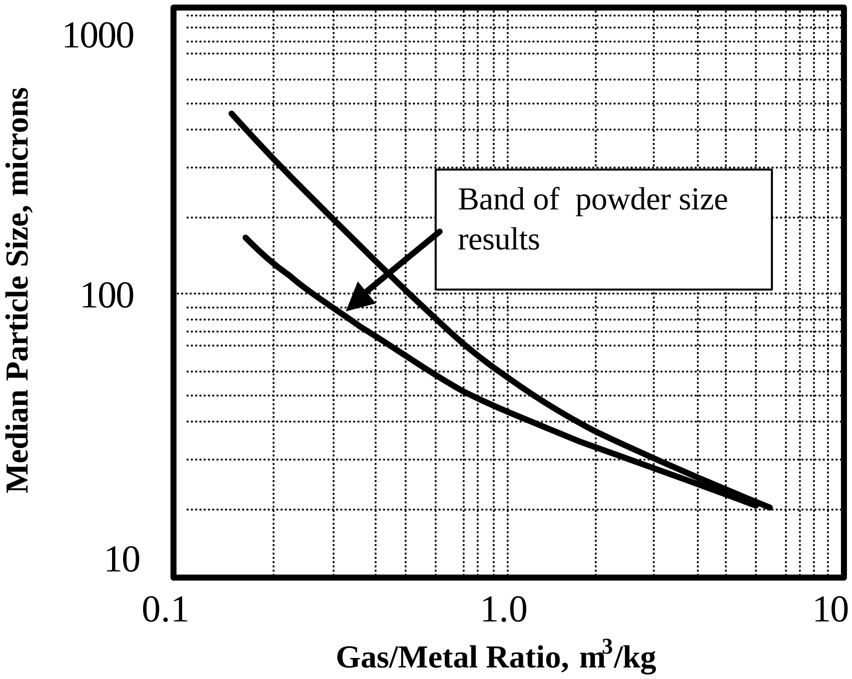

Fig.3 Gas/Metal Ratio vs Al Particle Size for close-coupled atomization processes.

Fig.3 shows that the median particle size achievable by gas atomisation (13) tends towards an asymptotic limit with increasing gas/metal ratio, suggesting that direct atomisation of nanopowders would require unsustainable gas / metal ratios. Nevertheless, as the median size decreases, the proportion of sub-micron product increases and while yields will inevitably be low, this is compensated for by the fact that the atomising process runs continuously at relatively high throughputs (tonnes/day) compared with nanopowder methods (typically kgs/day). Therefore, meaningful net production rates may be achieved for nanopowders if effective separation can be achieved.

3 Ultrafine aluminium powders from gas atomisation

Fig.4 shows SEM images of a fine fraction of gas atomised powder which has been separated from a coarser, gas atomised distribution. The SEM images confirm that individual particles are effectively spherical and that there is a large size range from ~100 to 2000nm. Laser particle size analysis (Malvern Mastersizer) in Fig.5 shows a median size of ~ 1.9um and that there is ~ 20% by mass which is sub-micron.

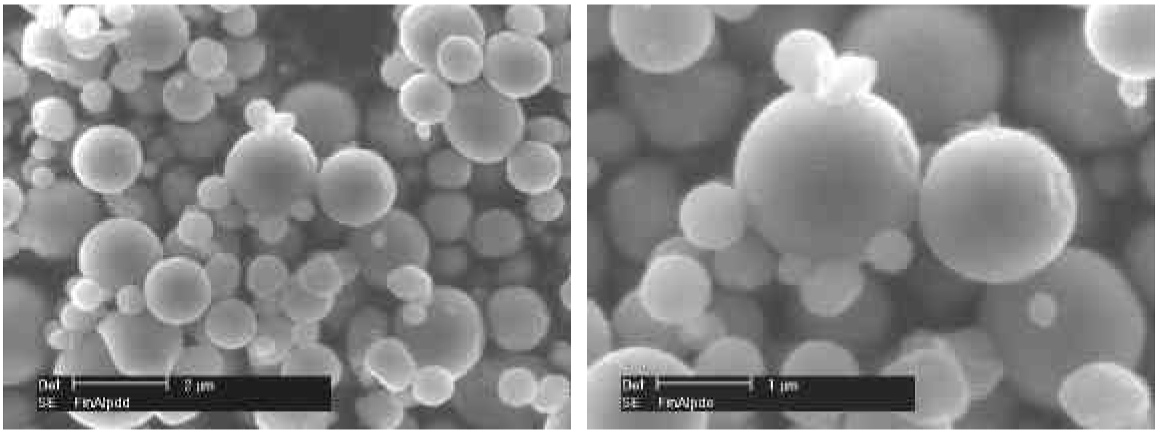

Fig.4. SEM images of 2µm median size gas atomised aluminium powder

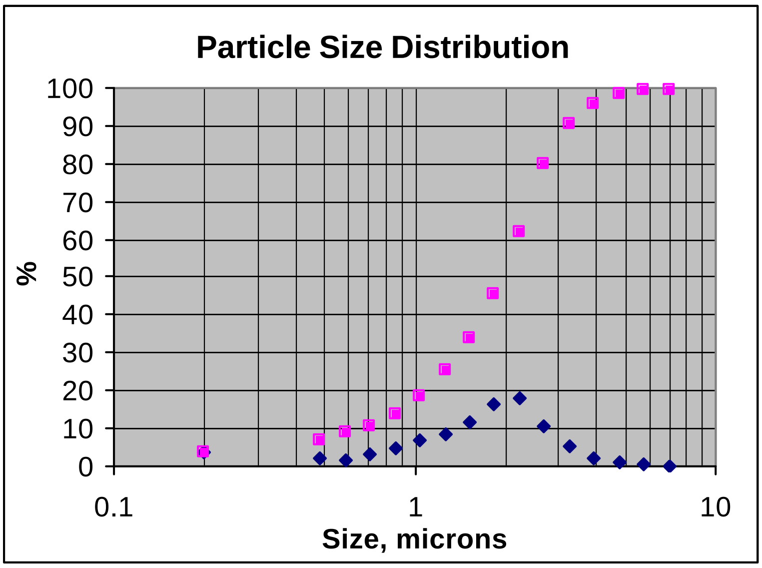

Fig 5. Malvern Mastersizer size analysis: Alpoco 2µm secondary collector powder

The fact that atomisation has been performed in inert gas and the particle size is relatively coarse results in a relatively pure powder product with a relatively low oxide content. Analysis shows that there is 0.55% oxygen and 0.02% C. The low carbon level contrasts with levels found in some powders produced by plasma technology (5). Depending on the final application, this is potentially advantageous since it is known that adsorbed carbonaceous species can stifle surface activity of Al powders (14). The specific surface area (SSA) of this sample was determined by BET (surface adsorption) analysis to be ~$2m^2g^{-1}$. This value is consistent with that predicted from an assumption of the oxide thickness and the measured oxygen content of the powder. Values measured elsewhere on fine powders are in the range ~2-4nm (Ref 3-5). Tetronics quote a typical analysis of 15% oxygen (33% Al_2O_3) in their ‘aluminium’ nanopowder.

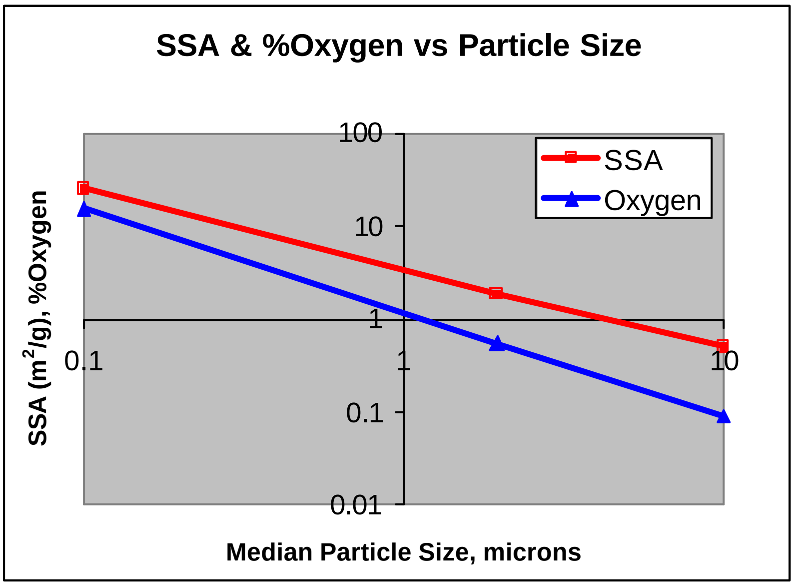

Fig 6. Relationships between median particle size and specific surface area (SSA), oxygen content. Includes data for atomised powders and quoted values from refs 4 & 2.

Fig.6 shows the relationship between median particle size and SSA and oxide content for selected gas atomised products. For comparison, published data for nanopowders prepared elsewhere are included in the figure. It appears that the gradient of the relationship between the SSA and median size is < 0.5 (0.5 is the value expected of monodisperse spherical powders) while the gradient for % oxygen vs median size is > 0.5. The deviation from the expected gradient may indicate different size distributions and different oxide thicknesses on different particle sizes. There is very good agreement with the values determined by Higa et al (6) for chemically-produced powders and by Tetronics (5) for plasma-produced nanopowders. Argonide's Alex powder appears to have a slightly thinner oxide in relation to its size, but overall there is a remarkably good correspondence between the amount of active aluminium (oxide level) and the particle size. Technanogy (12) claim to be able to control oxide thickness in their product and so the relationship in Fig 6 would not necessarily apply to their products.

Within measurement errors, Fig.6 appears to confirm that below 10µm, particles may be treated as spherical and have a consistent oxide thickness. If the relationship is examined at coarser sizes, there is a deviation towards relatively high oxide contents and surface areas which is indicative of increasingly irregular particle shape.

It is known that fine aluminium powders (<45um) can form explosive mixtures with air. Indeed it is the highly exothermic reaction of aluminium with oxygen ($\Delta H(298K)=-1678kJ/mol$ of Al_2O_3) that confers the desirable reducing and propulsive properties of the powder. The hazards associated with aluminium powders have been described recently (2) and it is not surprising that these become more acute as the powder size reduces, particularly below 45um. Increased reactivity of nanoaluminium has been commented on by Tepper (3) and Tetronics (5) and initial explosibility tests have been conducted on the gas atomised 2µm powder to examine its behaviour versus other commercial powders. Explosibility testing is used routinely for the safe design of production plant and this uses a 20 litre sphere apparatus for measuring explosion pressure transients following ignition of a dust cloud within. Among parameters characterising explosibility, the Minimum ignition Energy (MiE) is a measure of the reactivity of the powder and the minimum explosible concentration (MEC) is the threshold concentration that will support ignition.

Table 1 shows a selection of explosibility data for different aluminium powders.

Powder size	Sample origin	MiE, mJ	MEC, g m^{-3}	Test House
-75,+45	Screened air atomised	300-400	750	Chilworth
-38 µm	Screened air atomised	50-60	60	Chilworth
6 µm median	Gas classification	13	n/a	Chilworth
2 µm median	Secondary filter	8.5	70	Wolfson BS 5958

Tests were done by Wolfson Electrostatics on a sample of fine powder collected from Alpoco's secondary filtration system (15). The minimum ignition energy of 8.5mJ for 2µm aluminium powder is somewhat lower than typical values for superfines (Fig.7). Note that measurements on even finer samples may be affected by agglomeration of fines which will not allow true dispersion into the most potent dust cloud.

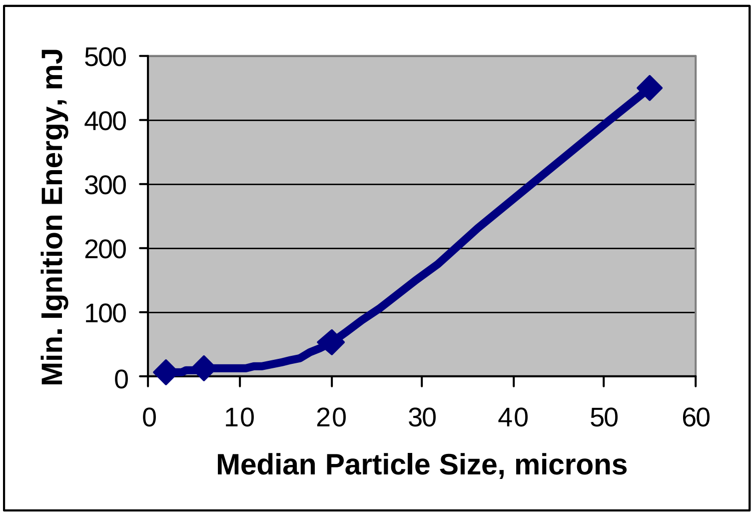

Fig. 7. Relationship between Minimum Ignition Energy and Aluminium Powder Size

The increased reactivity of superfine powders is further confirmed by DSC analysis in air which shows the early onset of oxidation (509°C (2µm) and 562°C (6µm)) and the much enlarged exothermic peak areas compared with coarser powder (see Fig. 8).

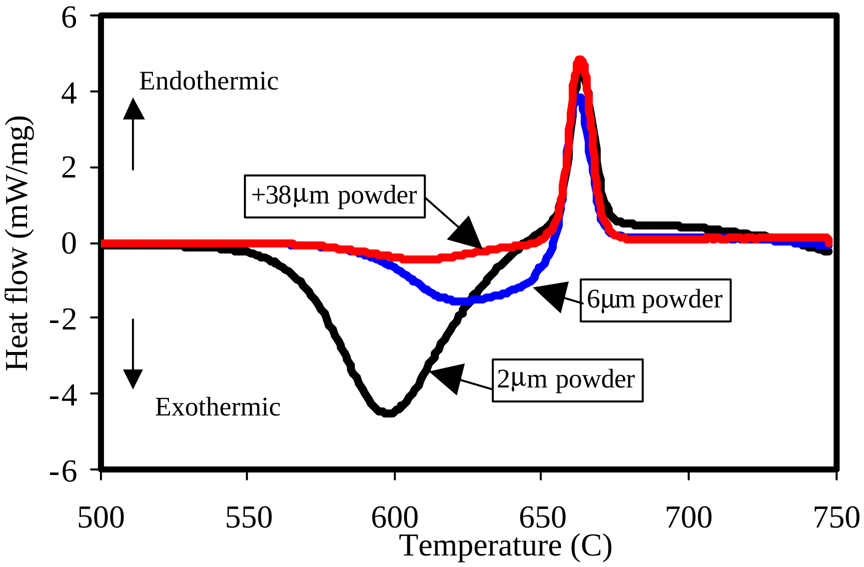

Fig. 8 DSC traces showing oxidation followed by melting of aluminium powders.

4 Production of Nanopowders

Several techniques are being developed today for the manufacture of nano aluminium. With the exception of gas atomisation, exploding wire and plasma wire fragmentation, most methods seek to grow powders from an induced gaseous phase (a 'bottom up' approach rather than a fragmentation method). Table 2 lists some of the leading practitioners: Alpoco's ultrafine gas atomised powder is included for comparison.
Table 2 shows a selection of manufacturing methods for nanopowders.

Method	**Producer**	**Quoted size, nm**	**Production rate**	**SSA m^2g^{-1}**	**Ref**
Electro-explosion of wire	Argonide	50-500	100's g/hr	10-15	3,4
DC Plasma torch	Tetronics	50-150	2kg/hr short run	25-30	5
Inert gas condensation Physical Vapor Synthesis	Nanophase Technologies	10-50	Tonnes pa	20-60	
Chemical: Alane adducts	US Navy	65-500	low		6
Sodium Flame Encapsulation (SFE)	AP Materials		Industrial scale		7
Gas condensation	Technanogy	20-200	kg/hr/reactor	>50	18
Inert gas atomisation	Alpoco	100-5000	0.5kg/hr	2	

In general the methods break down into chemical/pyrolysis methods and high energy plasma or current-assisted methods. Typical production rates for nanoaluminium are quoted at between ~200g/h and 2kg/h. The fastest production route appears to be flame pyrolysis which is claimed to be capable of delivering 1000-5000tpa from a single reactor for oxides and carbon black. APMaterials claim a unique sodium flame and encapsulation technology for pyrolysis and subsequent encapsulation of particles before agglomeration occurs. They claim advantages in scale of production and low cost vs IGC. Singhal et al (11) quotes ~$50/kg production cost for a reactor with burner diameter of 12.5cm scaled up to 100tpa for oxides. Particle size can be controlled by controlling pressure in the reactor. Reduced pressure in flame pyrolysis leads to rapid quenching and fine particles, but at normal pressure there is an opportunity for coarsening by coalescence.

Nanophase Technologies employs plasma evaporation of a metal substrate followed by cooling with carrier gas and collection (PVS: Physical Vapour Synthesis or Inert Gas Condensation (IGC)). The conditions in the carrier stage can determine size and level of agglomeration. Alumina with median size 10-50nm can be produced with SSA of 15-90m^2/g. Nanoalumina is offered at ~ $200/kg. The IGC method involves evaporation of the precursor followed by homogeneous nucleation/condensation of powder in a low partial pressure of inert gas. Importance is placed on control of the colloidal behaviour of nanoaluminium and complementary coating technology enables subsequent dispersion.

Technanogy also operates an IGC method (reactor output ~lbs/hr) and claim techniques for control of particle size within +/-10nm and control of oxide thickness between 1-5nm (12). They expect to deliver 20t nanoaluminium products in 2002. The SSA is >50m^2/g and the main application is in propulsion where the goal is to increase effective payload of space vehicles. IGC methods are also operated by Nanoproducts, Inc. who describe preparation of a precursor solution of the required stoichiometry which is then subjected to plasma evaporation. Higa et al. (6) have a solution method for decomposition of solutions using transition metal catalysts. Choice of catalyst and concentration of reactants determines particle size. In general, chemical methods appear to be advantageous in giving tight size distributions and low impurity levels but production rates are relatively low.

Argonide operate a unique exploding wire method for making aluminium powders by passing high currents through fine wires. This is a semi-continuous process and the plasma formed subsequently condenses to form fine particles (~100nm) in an Argon gas environment. This requires expensive equipment and production rates are low. Tetronics' DC Plasma route also has a wire feed, but the application of a plasma torch results in significantly finer particle sizes (see Table 2) and a noticeable level of carbon pick up (~2.4w/o) and other significant impurity levels. The very high surface area of nanopowders generally means that they are prone to adsorb impurities from the manufacturing environment. Other highly energetic sources such as spark discharge are also being applied to production of nanopowders (e.g. CyTerra Corp, Advanced Materials & Processes, November 2001).

The extremely high reactivity of fresh nanopowders means that each technique has a method for collecting the product in an inert atmosphere and must ensure a controlled passivation (e.g. controlled oxidation, salt or organic coating) before onward processing can be done safely. This is described in section 6.0 below.

5 Demand for Ultrafine and Nanopowders?

Demand for ultrafine and nanopowders can be expected from several quarters. Paint & pigment producers have driven the demand for finer powders for making products with high covering power and novel aesthetics. The pigment producers are interested in finer and more consistent products, because these will improve still further the covering power of the pigment. Allied to this, there are some consumers who produce conductive pastes and inks for electronic devices. As miniaturisation continues, so the need to offer thinner and more uniform/consistent coatings will grow.

Most of the projected applications for nanoaluminium aim to exploit the vast quantities of energy stored in nanoaluminium. Fuels for space and naval vehicles and propellants for the military are perhaps the areas of greatest interest for application of nanoaluminium. Aluminium powder is used today in solid rocket boosters e.g. for the Space Shuttle and Ariane 5 and there is an ongoing drive to reduce launch costs and increase payload. Tetronics refer to an increase in burn rate of between 2-10x when using nano versus regular aluminium powder fuel (5) and this is in line with Argonide's claim that their 'Alex' nanoaluminium doubles the burning rate and increases manoeuvrability and thrust compared with standard 20µm sized spherical aluminium powder (3,4).

Tepper describes a means for capturing their products directly in kerosene to produce a powerful fuel which is fully consumed before it exits the engine giving maximum burn efficiency. At the same time, it is clear that reliability and consistency are critical for successful missions and qualification trials will rightly be highly demanding. There is interest in the potential of the turbulent reaction of finely divided aluminium in contact with water to propel super-cavitating naval vehicles and ordnance (16). Specialist military pyrotechnics is another potential market: super-thermitic reactions are described by Lowe (12) which can be of particular interest for pyrotechnics, primers, detonators etc.

Powder metallurgy is an underdeveloped market for aluminium: a consequence of the difficulties in sintering powders with such a tenacious oxide layer. While nanosize powders will never be a commercial prospect for bulk PM, there is evidence that as initiators they could stimulate developments in Al and ferrous systems. Tepper (3) reports that pressed pellets with other powders such as B, Ni can be made to react at low temperatures and reference has been made to in situ formation of NiAl coatings. The use of conventional superfine (6µm) aluminium powder as a sintering aid for stainless steels has already been demonstrated by Degnan et al (17). In this case local thermitic reduction ($2Al + Cr_2O_3$ (surface oxide) = $2Cr + Al_2O_3$) generates heat to initiate early reaction.

Groza (18) reports that early sintering of nanopowders can occur at~0.2Tm for e.g. Fe, W compared with ~0.5Tm for conventional sintering. Tetronics report the onset of an oxidation exotherm at ~538°C and Argonide at 548°C (measured by DSC(5), DTA(19)). The attraction of nanopowders in this sense is not only in accelerated, lower cost sintering, but in allowing processing on thermally sensitive substrates, e.g. electronic interconnects described above. Another example is in the joining of dissimilar materials using a reactive interlayers e.g. joining stainless steel to aluminium.

In addition to sintering aids, then ultrafine alloy powders will also have interesting properties and strength levels are expected to be much enhanced as grain size decreases. In particular, dispersion hardening alloys should attain high strength and toughness. Such powders could be of interest for surface application via cold or thermal spraying techniques (20). Fig.9 shows a schematic of the cooling rate versus particle size. Rapid solidification in finer powders confers desirable microstructural refinement that is exploited in some powder metallurgical products to achieve e.g. optimum dispersion strengthening or superplastic forming properties in consolidated parts (21).

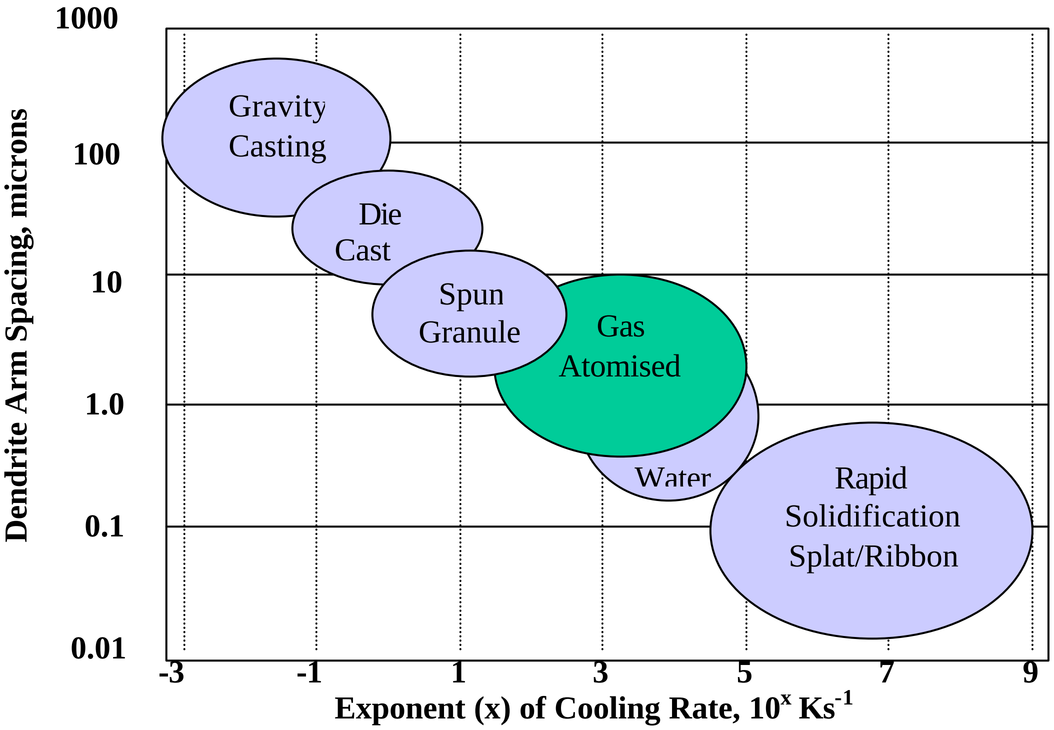

Fig. 9 Relationship between Cooling Rate and Microstructural refinement

Metallurgical reduction processes. Ultrafine aluminium may be exploitable in some metallurgical processes e.g. to enhance firing rates in the exothermic production of Cr, but there are some practical difficulties which may preclude its use. For example, control of the reaction, safe handling of fine mixes and extraction/collection of air-borne dust.

6 Practical Aspects

The very feature that makes nanopowders so attractive for some applications, namely its high reactivity, can also lead to problems in handling and the preservation of reactive properties. As described above, as powder size decreases, explosibility increases and safe collection and encapsulation methods are critical (2). It may be desirable for the product to be kept as active as possible, but unpassivated Al is pyrophoric and can not be safely air-freighted. Added care is required in the containment, packaging & transport of these products.

Various producers refer to controlled oxidation, varying thickness of the oxide film (12), capture in organic media, coating with salt or hydrophobic species etc. Specific methods will be geared towards certain end uses and it will be important to characterise the metastability and reproducibility of reactivity of such species if their ultimate performance is determined by the state of the film. Preservation of the surface condition during subsequent processing will need to be ensured for applications as critical as rocketry where a long shelf life is required and performance is absolutely paramount.

7 Conclusions

A variety of methods are emerging for the production of nanosized aluminium powders which are seen as having potential for application as propellants, high power metallurgical reductants/sintering aids and high efficiency coatings in particular. Each of the production processes discussed has limitations: all have low throughput and some demand expensive equipment and result in high oxide and impurity levels. Between the established superfines (5-15µm) market and the future nanosize market, an ultrafines category may be defined between 0.5-5µm which could be more accessible and of more immediate commercial interest.

Results shown here demonstrate that even at 2µm median size, there is evidence of exceptional reactivity. While this size is at the limit of what can be produced today by gas atomising, this may yet be a more feasible short-term prospect for supply of meaningful quantities of powder. Little work has been done so far to characterise this fraction, but the initial signs are that further work is merited.

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