LIQUID PHASE SINTERING OF NICKEL BASE SUPERALLOYS

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Summary

Liquid phase sintering accounts for close to 90% by value of sintered products. Superalloys with a wide melting range (≃100°C) are candidates to this densification mode. Two processes were considered in a laboratory study (scale 100 g - 10 kg) with Astroloy or René 95 :

Liquid Phase Sintering Under Vacuum produces closed porosity(⩾ 95% t.d.) preforms with shapes reproducing that of the ceramic container, for sintering temperature ranging from 1280 to 1300°C. Cylindrical or annular preforms are further densified by hot isostatic pressing (H.I.P) or forging without enveloppe.

Liquid Phase Sintering Under Moderate Uniaxial Pressure (⩽ 5 MPa) produces net shape materials. Optimum conditions are derived from rheological studies on the powder deformation and the friction with the mold.

The main advantage in having a liquid phase is the activation of sintering. With up to 35% liquid, pressureless densification is obtained by capillary forces and solution/precipitation processes. Adding a uniaxial pressure forms the alloy to intricate shapes without liquid-solid separation. The flow stress is a few tenths of MPa, hundred times less than in the solid state. Supersolidus hot pressing (S.H.P.) requires alumina or zirconia molds to limit reactions.

Liquefaction heterogeneities concerning primarily titanium and metalloids can be eliminated by a 1h homogeneization step below the solidus (1200°C). To avoid precipitation of fragile phases (sulfocarbides, borides) the powder composition should be specified ⩽ 50ppm S, ⩽ 200ppm B. Grain size is about that of the particle but forging can restore a fine grain structure or lead to a partial recrystallization at the grain boundaries ("necklace" structure). Depending on heat treatments liquid phase sintered Astroloy can offer a classical or a more original precipitation morphology. Static mechanical properties are satisfactory whereas in some cases fatigue life is still to be improved for sintered + HIPped (or forged) material. Near-net shape products may be produced by uniaxial supersolidus hot pressing of Astroloy to substitute for cast and machined grades with lower mechanical properties.

Introduction

To date, the consolidation of superalloy powders relies on solid phase sintering at temperatures closer to the γ' phase solvus than to the solidus for p.m. disk alloys under pressures exceeding 100 MPa for usual H.I.P. practice. Much attention has been paid to densification processes operating under moderate or atmospheric pressure but at high temperatures for superalloy powders and others (2). The research conducted at the School of Mines on nickel base superalloy liquid phase sintering led to the evaluation of several processes discussed here. The material was primarily of the Astroloy type (Table I) with a René 95 type powder for parts of the study. The prealloyed powders were produced either by argon or centrifugal atomization ("REP" or "PSV" processes (3,4)) with a mean particle size ranging from 50μm to 300μm.

Table I. Chemical Composition of Alloys - Wt %*

Alloy (Ni-Base)	C	S	B	Ti	Al	Nb	O_2
Astroloy A.A.	0,042	0,005	0,021	3,49	4,12		0,008
Astroloy A.A.	0,026	0,002	0,023	3,60	4,00		0,008
Astroloy C.A.	0,048	N.A.	N.A.	3,2	4,0		0,004
Astroloy C.A.	0,084	0,001	0,014	3,52	4,80		0,007
René 95 A.A.	0,05	N.A.	N.A.	2,97	7,66	2,11	N.A.

*Only the elements of special importance in liquid phase sintering are given, others are to specification.
A.A = Argon atomization, C.A = centrifugal atomization.

No particle treatment or blending according to composition or size distribution was included before sintering. Both alloys have solidus temperature from 1200 to 1215°C. Processes may be divided into two classes (Figure 1).

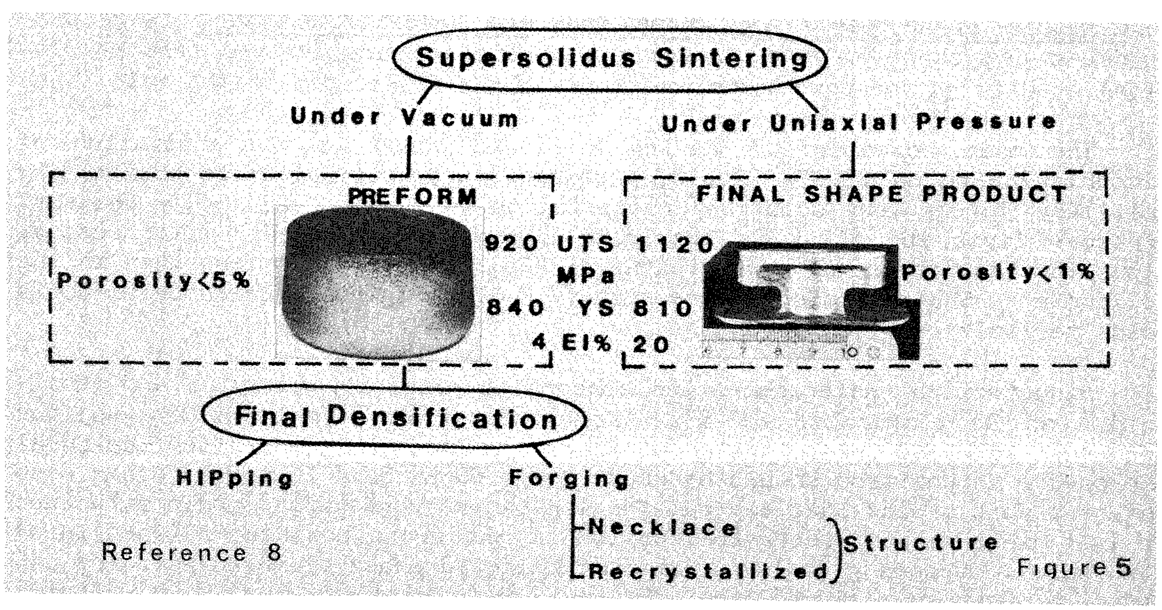


Figure 1 : Various processes based on supersolidus sintering of superalloy powders

Liquid phase sintering leads to special microstructural features which will be presented in a further section, but conventional microstructures can also be secured by forging liquid phase sintered preforms.

Influence of Sintering Parameters

Densification occurs primarily under the action of capillary forces and presumably involve the three stages described in the phenomenological description of sintering (Figure 2). With the presence of a liquid phase stages 1 and 2 are greatly activated (5). The influence of sintering parameters on the densification will only be summarized here (Figure 3) as it has been presented elsewhere (6).

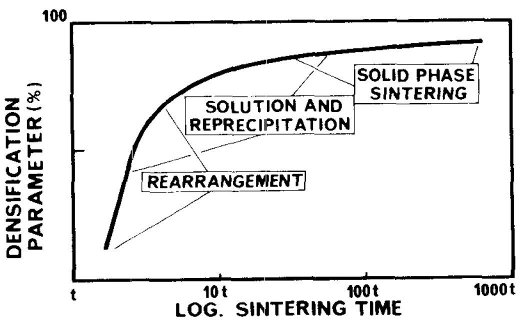


Figure 2 : The three stages of liquid phase sintering (after (5))

Temperature. An increase in temperature results into an increase in liquid fraction (estimated in Figure 3a from differential thermal analysis) and in turn into an increase in density. The kinetics of sintering derived from interrupted isothermal sintering tests show some difference between A.A. and C.A. powders (Figure 3a-b) which is likely to reflect a difference in chemical homogeneity or in particle size distribution. To avoid separation of the liquid from the solid phase under the effect of gravity, liquid fraction should not exceed 0.4.

Particle size. Isothermal sintering on powder batches with a well-defined particle size showed a superior sintering tendency for smaller particles as well as a strong correlation between grain and particle size. The optimal conditions inferred from isothermal sintering tests are : 1) temperature to be determined for each powder within the range 1280°C-1300°C, 2) sintering time of about one hour, 3) vacuum from 10^{-5} to 10^{-4} torr*.

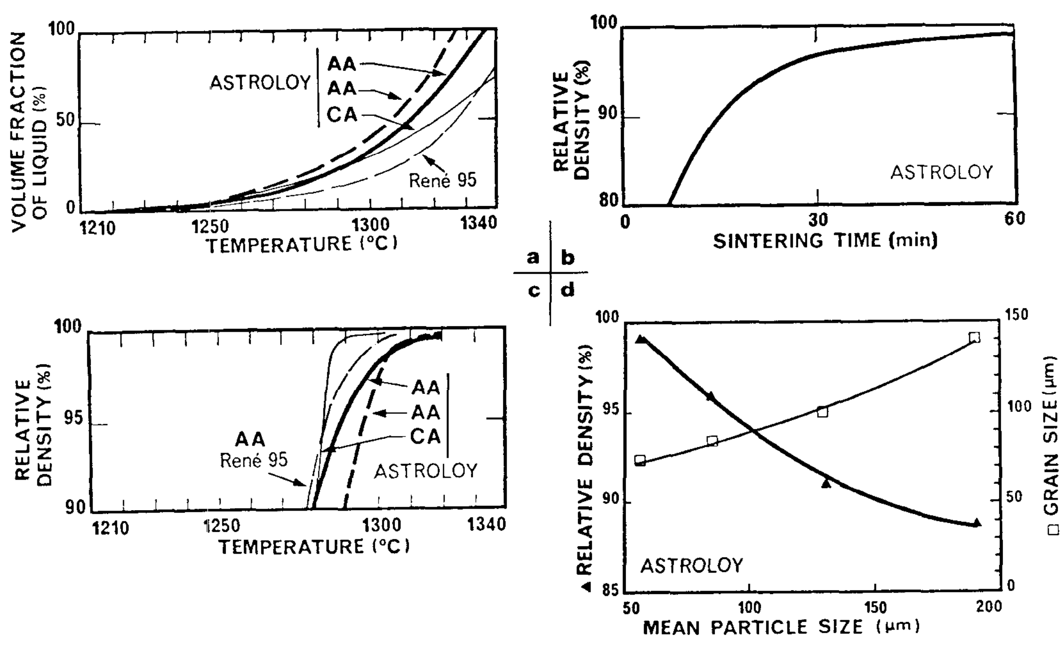


Figure 3 : Influence of sintering parameters.

a) Liquid fraction vs temperature for AA or CA Astroloy and AA Rene' 95.
b) Density vs isothermal sintering time-1305°C,C.A. Astroloy
c) Density vs temperature for the same powders - 1h sintering time.
d) Density and grain size vs particle size, AA Astroloy- 1h sintering time.

* 1 torr = 133.322 Pa.

The powder is simply poured in a ceramic container, without tapping or vibrating. Contrary to solid state consolidation practice, degassing does not seem to be a requisite, the liquid phase being responsible for particle bonding. Under optimal sintering conditions, shrinkage is almost isotropic and close to 12% which restricts shape reproduction primarily to convex parts, for instance cylindrical preforms.

The sintered preform shows a closed porosity, usually below 5%, which leads to rather weak tensile properties (Figure 1). Further densification is required and will be dealt with later in the text. Superficial chromium losses and evaporation are limited. With standard superalloy foundry ceramic molds, no large scale reaction was evidenced in contact areas and there was no sign of ceramic inclusion.

Particularities Linked to Liquid Phase Sintering

Most important features are : 1) a large grain size related to particle size (Figures 3,4) but a fine grain size typical of usual p.m. superalloys may be secured by forging, 2) porosity usually located at triple points, eliminated by HIPping or forging, 3) chemical heterogeneities due to partitioning of some elements in the liquid during sintering (Figure 4). Equilibrium partition ratios C_s/C_L are of the order of 0.8 for Mo, 0.6 for Ti, and much lower for C and S (7). A mere 1 hour homogeneization step just below the solidus (Figure 4) eliminates the Ti heterogeneities and also

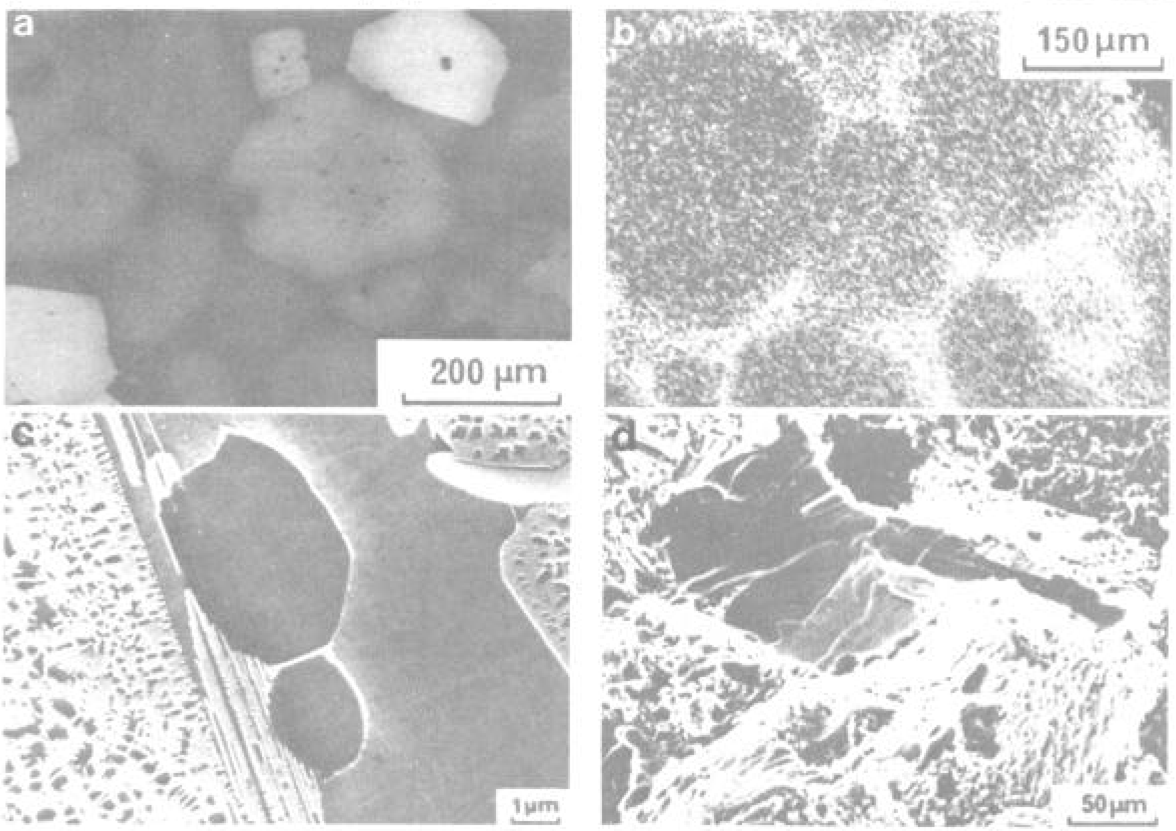


Figure 4 : Microstructure of liquid phase sintered nickel base superalloys.

a) Large grain size of sintered-only Astroloy. Optical micrograph.
b) Titanium X-ray (Kα) image of non homogeneized Astroloy.
c) Eutectic (γ-γ') pool in René 95 (non homogeneized), SEM image.
d) Sulfocarbide plate in Astroloy (sulfur content ≃ 25%), SEM image.

the eutectic pools (more abundant in René 95 than in Astroloy). More deleterious effects are attached to boron (small molybdenum borides at grain boundaries), but above all to sulfocarbide platelets (Figure 4). Allowances for sulfur must be lower than conventional limits for HIPped materials. Primary carbides are scattered in the matrix or clustered at the triple points. Gamma prime phase precipitation is both coarse (1-2 μm) at grain boundaries and fine in the grain; the final γ' precipitate distribution will of course be set by heat treatment (8).

Complete Consolidation After Sintering
Supersolidus-Sintered and Forged Materials

To attain a high level of performance, the residual porosity of the sintered-only preforms must be suppressed by HIPping or forging. Forging seems more attractive since it limits the scatter of the p.m. materials properties and brings large microstructural changes. This section deals only with forging supersolidus-sintered preforms, however, HIPping remains interesting in the case of closed porosity preforms (like supersolidus-sintered ones) since it is not necessary to use a container. Morever, the properties of the final materials compare well with those of as-HIP'ed products (8).

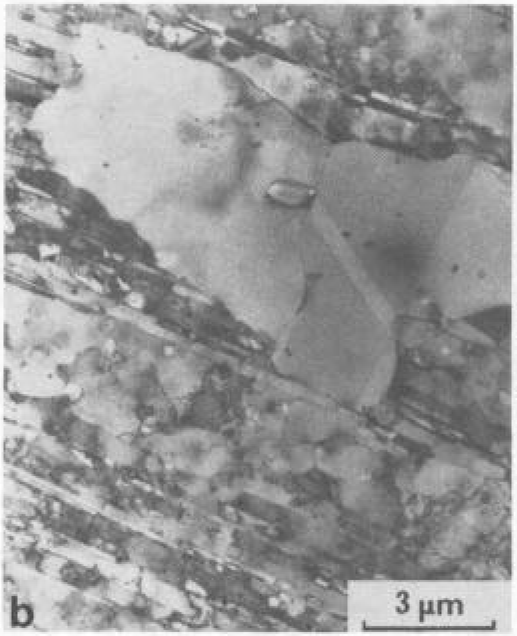
After forging, the completely densified material exhibits a warm-worked structure. The degree of recrystallization increases with increasing forging ratio (for a given forging temperature). Unrecrystallized structures were obtained for rather low deformation ratios (< 30%) whereas fully-recrystallized structures for high ratios (⩾ 50%). These structures and the corresponding properties were detailed in previous publications (7).

"Necklace" Structure Materials.

Intermediate forging ratios can lead to the so-called "necklace" structure, a fine "necklace" of recrystallized grains surrounding large warm-worked grains. This duplex structure conventionally achieved by forging preforms HIPped above the solvus temperature often offers the best compromise between good creep-rupture properties (large grains) and a high resistance to crack initiation and propagation (fine recrystallized grains). 40% reduction at 1080°C are the optimal conditions to achieve a well-marked "necklace" structure with conventional hot pressing (the densification conditions would be nearly the same for isothermal forging) followed by standard heat treatments for Astroloy, HT1 et HT2.

HT1	HT2
4h/1080°C - OQ	4h/1100°C - OQ
+8h/870°C - AC + 4h/980°C - AC	+24h/650°C - AC + 8h/760°C - AC
+24h/650°C - AC + 8h/760°C - AC	

Microstructural aspects : Hot deformation initiates recrystallization which grows by post forging static annealing. The fraction of recrystallized grains around the "pancaked" warm-worked grains reaches about 0.15 for 4 hours annealing at 1100°C (Figure 5). The forged material microstructure depends primarily on the chemical composition of the powder and on the heat treatment. These parameters govern nucleation and growth in recrystallization and the recovery mechanisms (refer to previous publications for more details (9-10)).



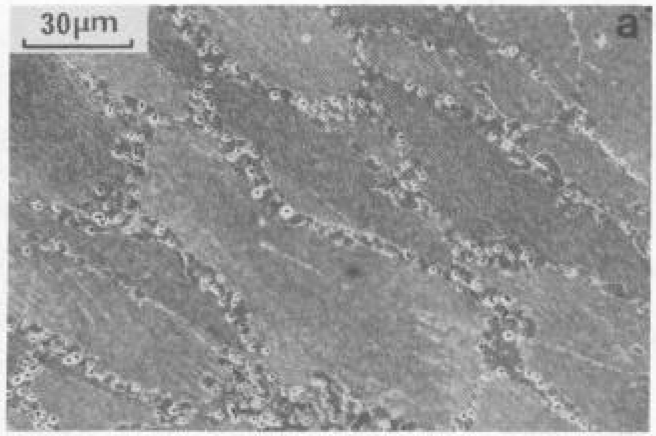


Figure 5 a) "Necklace" structure, A.A. Astroloy, SEM image of the HT2 forged material. b) Deformation twinning near grain boundaries. TEM image of twins in the vicinity of recrystallized grains.

Mechanical properties: Static and dynamic properties were determined in the axial direction. Static properties are satisfactory in comparison with the specifications or with conventional p.m. products (Figure 6). However, for the dynamic behavior, if the crack propagation resistance is adequate (10) the low-cycle fatigue resistance is not because of 1) the possible residual porosity resulting from a loose control of the forging conditions, 2) the rather narrow interval between conventional 0.2% yield strength and ultimate tensile strength.

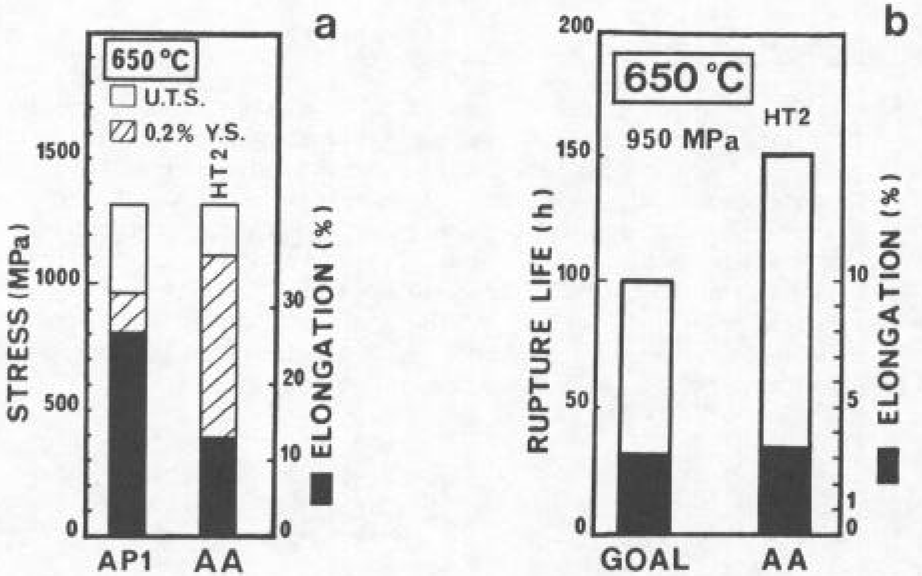


Figure 6 : Static properties of supersolidus-sintered and forged Astroloy at 650°C in comparison with HIPped Nimonic Alloy AP1 (17) or specification.
a) Tensile tests b) Creep-rupture tests.

Supersolidus Hot Pressing (S.H.P., moderate uniaxial pressure)

The study of net shape supersolidus hot pressing first led to investigate rheological parameters, then the densification of Astroloy with containers of increasing shape intrication.

Rheology of Solid-Liquid Astroloy

We considered solid/liquid mixtures with a liquid fraction below 0.4 (symmetrical to those usually mentioned for "rheocasting") in which the solid phase is a rigid particle skeleton. Residual porosity was restricted to less than 5% (liquid phase sintered preforms, HIPped and machined for some of them).

Intrinsic rheological parameters. Compression tests under constant load were conducted on 20mm dia, 6mm high cylinders in a hot pressing chamber (11). Barrelling of the sample remained limited in most tests indicating a negligible influence of friction on the alumina pressing plates. The kinetics of the change in height for a porous material demontrates that sintering is completed before creep starts(Figure 7). Dependence of deformation on temperature may be linked to that of liquid fraction (Figure 3). Conventional flow stress inferred from compression tests plotted vs liquid fraction show a near continuity with solid state deformation (HIP or superplastic forging) (Figure 8). This kind of comparison may be extended to the strain-rate sensivity coefficient crudely estimated from compression tests. At 1300°C values of $m = \frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}}$ are in the range 0.6-0.8 and are more typical of the high temperature superplastic deformation of nickel base alloys than of the newtonian liquid behavior. Strain-rate sensivity coefficients derived here are significantly higher than those reported by Suéry and Flemings (12) for dendritic solid/liquid Sn-Pb mixtures.

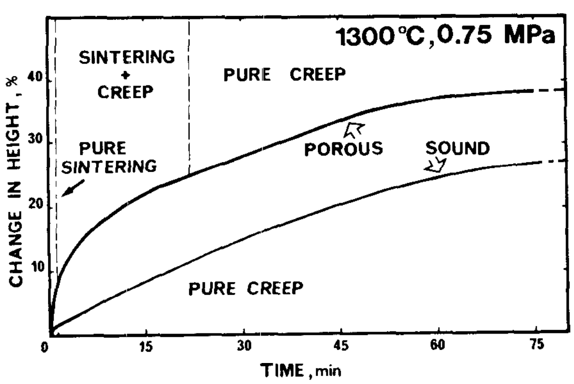


Figure 7 : Compression tests on full cylinders (sound and porous), 1300°C - 0.75 MPa. Relative heigh reduction v.s. time (after (11)).

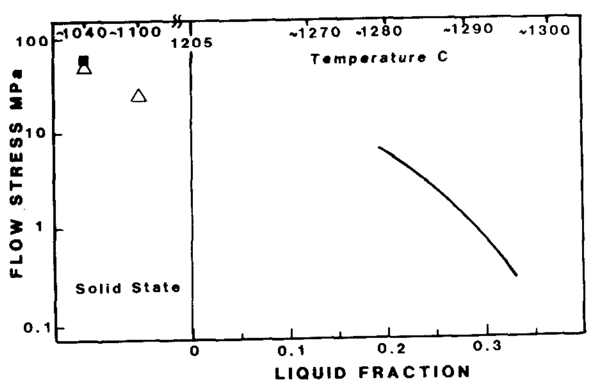


Figure 8 : Conventional flow stress for semi-solid Astroloy. Comparison to measurements on solid state deformation of △ Astroloy (13) and ■ superplastic IN 100 (14). $\dot{\varepsilon} = 5 \cdot 10^{-4}\ s^{-1}$.

Extrinsic rheological parameters. Following an approach indicated by Hawkyard and Johnson (15) annular preforms (ID 12mm, OD 24mm, h 4mm) were uniaxially pressed at supersolidus temperatures between alumina plates. Friction coefficients are in the range 0.3-0.4 between 1295 and 1300°C but exceed 0.5 at 1280°C.Using the results of the rheological study supersolidus hot pressing was first tested on 52mm ∅ cylinders under 5 MPa at 1280°C for 2h (11). The tensile properties (Figure 1) are intermediate between HIPped Astroloy and best conventional cast nickel base superalloys. More intricate shapes were then considered using standard silicate bonded casting molds rather than alumina.

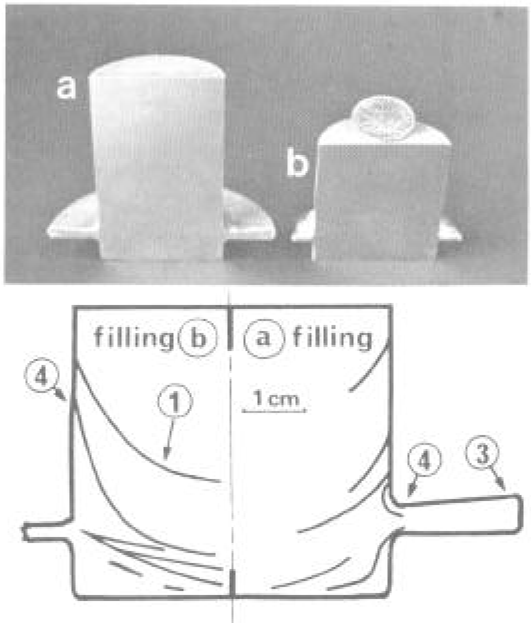


Figure 9 : Characteristics of SHPed rheology specimens (sketch).

Rheological tests were carried out in the conventional conditions 1290°C-5MPa but specimen shape was chosen to study a critical aspect of near-net shape capability : the filling of thin parts perpendicular to the axis of pressing (and symmetrical). The pressing duration was selected to leave enough porosity to enable the determination of flow lines (Figure 9b). Two ways of filling the mold were compared : a filling entirely with powder, b filling only the main cylindrical core. Axial polished sections exhibit rheological features (Figure 9) : 1 parabolic "flow lines" marked by stringers of porosities or segregation of powders, 2 an increasing porosity from top to bottom and a superfical porosity in the vicinity of the mold lateral surfaces, 3 a proper reproduction of the shape only in case of mold filling a 4 geometrical distorsion of the annular rim due to the creep of the thin shell.

These phenomena are linked to friction of the alloy on the mold wall and to an incomplete transmission of pressure. It was decided to further test this assumption on two product geometries with radically different surface/volume ratios (parameter which is linked to the vertical pressing stress gradient).

Application. SHP'ing of blades or frame bosses. Several blades or bosses were pressed under conditions derived from the rheological study with temperatures up to 1305°C, temperatures gradients were also measured and two different presses were compared. The characterization of the parts showed that 1) in the present state of the art the SHP process cannot be applied to asymmetrical parts with a large S/V Ratio such as blades, 2) on the contrary small symmetrical parts with lower S/V ratios (except for thin and intricate extensions) such as bosses could be produced with an excellent shape reproduction.

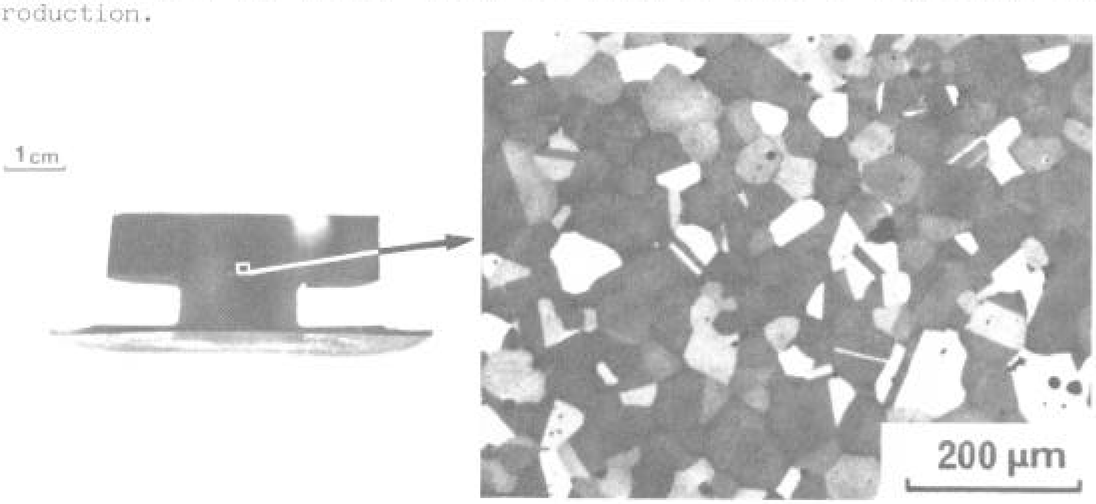


Figure 10 : Optical view of the microstructure in the core of a boss, Kalling etching.

The microstructure is quite typical of liquid phase sintered material (Figure 10). The importance of friction phenomena and part design being stated, it was important to further study what has been referred to as friction phenomena but should be designated as interaction in a broader sense.

The means to avoid contamination could be the use of pure alumina or zirconia molds or on the contrary the use of rather high silica contents to obtain a sufficient plasticity of the mold surface.

Alloy/Ceramic Container Interactions

When using conventional silicate bonded casting molds or boron nitride as container for SHP, alloy-mold interactions have been evidenced (Figure 11). Their origin is twofold : 1) mechanical phenomena : friction of the metal on the wall, abrasion of ceramic particles entrapped in the powder, 2) chemical reactions primarily reduction of the mold silica.

$$4\ \underline{Al} + 3\ SiO_2 \rightarrow 2\ Al_2O_3 + 3\ \underline{Si} \qquad [1]$$

The latter origin leads to an enrichment of grain boundaries in silicon to a depth measuring a few particle sizes and to an increase in carbide densitiy in the area already mentioned for disks HIPped in ceramic shells by Fleck et al. (16) and to the formation of small alumina particles (≈0.5 µm in diameter) or of thin alumina-rich layers stuck to the particle surfaces near the mold interface. Boron nitride molds also contaminate the alloy : segregation of titanium and aluminium and formation of titanium nitrides at the interface.

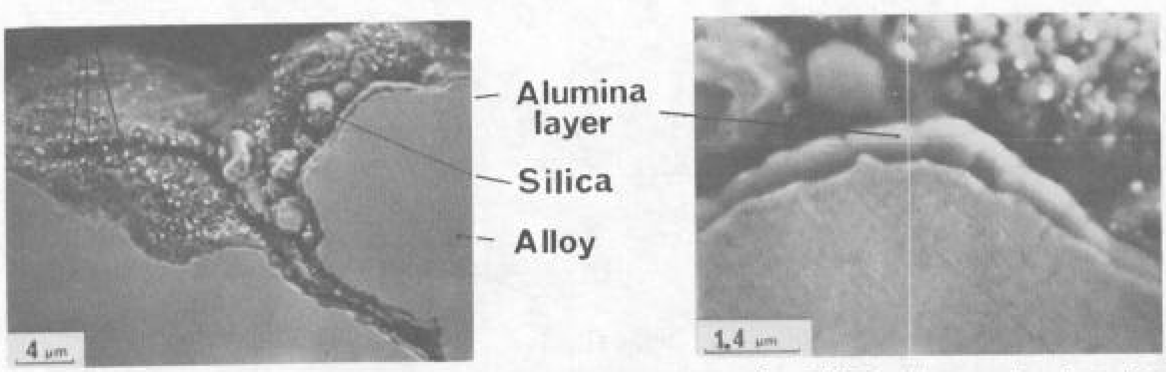


Figure 11 : SEM views of a section at the edge of a SHP'ed boss showing the morphology of alumina resulting from reduction of silica.

Conclusion

Liquid phase sintering may be considered to produce either forging preforms (sintering under vacuum at temperatures close to 1300°C)or near-net shape materials (supersolidus hot pressing-moderate uniaxial pressure). A tight control of process parameters (temperature-stress) is a requisite and the alloy composition must also be well specified. The results obtained with Astroloy are quite promising, with satisfactory mechanical properties of sintered + forged materials but further work needs to be done to qualify the process for the production of critical parts like turbine disks. Uniaxial supersolidus pressing of Astroloy in refractory (and inert) molds may produce small intricate shape parts otherwise obtained by casting and machining.

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