
Properties of Melt and Thermal Processes during Solidification in Jewellery Casting*

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Dedicated to the memory of William S Rapson

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A survey is made of the significant thermal properties pertaining to liquid and solidifying jewellery alloys, and some properties of the investment are also considered. Values found in the literature, or measured in our own investigations are used together with estimates. A relatively simple model for solidification is presented. Some parameters such as volume/surface area ratio, superheat and solidification temperature are discussed. The solidification behaviour of a simplified ring is investigated in more detail using the model. In addition, some observations were made whilst casting spirals.

The success of a casting process depends on many factors, such as the size and shape of the cast item and the gating (sometimes also called spruing); the pressure and other forces applied (determined by the equipment and the procedure used); and the properties of the alloys and the investment etc. Temperature and thermal processes dominate all the other factors which influence these processes but there are strong interconnections between all the factors, and all of them need to be taken into account.

In a previous publication (1) the effects of pressure, flow rate and some of the other factors were considered. In this present paper we deal more extensively with thermal effects. In order to establish a complete and realistic model of an investment casting process we first need a model for the thermal processes. In general this problem remains unresolved, and only simplified models are currently available.

There are several reasons for the difficulty in establishing a comprehensive model:

- (a) An almost infinite number of interactions between the various influencing factors.
- (b) The casting conditions cannot be reproduced precisely (even when excellent equipment is available and there is a capability for external process control).
- (c) The great variety of cast items with their complicated designs.
- (d) The small dimensions of a jewel.

- (e) The lack of knowledge of thermal properties of jewellery alloys in the liquid state and at solidification.

Also, insufficient data on the thermal properties of the investment are available.

In the following discussion, some aspects of thermal processes will be considered, and some measured values for liquid and solidifying jewellery alloys given.

SURVEY OF THERMAL PROCESSES IN INVESTMENT CASTING

The process starts with the melting of the alloys by induction heating, resistance heating or using a flame. Various aspects of this part of the casting process have already been considered previously (1).

During the casting process itself, two contradictory thermal processes occur:

- (a) The *introduction* of heat by the molten metal into the mould. The quantity of heat is governed by four factors: mass of melt, temperature of melt, specific heat, and heat of solidification.

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(b) The *dissemination* of heat which occurs by radiation, by heating the investment, and by thermal conduction. Factors which influence this are: the mould (flask) temperature (respectively temperature difference between melt and flask), the specific heat of the investment, the thermal conductivity of the investment, and the (thermal) interface resistance between the melt and the investment wall.

Some simplifications may be allowed: A loss of heat by radiation into the surroundings is unlikely as soon as the melt has entered the cavity. The wall thickness might be considered as unlimited in most cases. The low thermal conductivity of the investment makes it unlikely that the heat reaches the outside of the flask before the solidification process is finished, although an exception to this may occur if the item comes unusually close to the flask wall (In some cases this was performed intentionally in order to obtain a kind of directional cooling effect).

However, the factors mentioned above are not alone sufficient to characterize the thermal processes occurring during investment casting. The shape and size of the castings as well as the sprues and gates have a dominant influence on the introduction, dissemination, and consumption of heat. In addition, metallurgical factors such as melting range, grain structure and grain size must be considered. For example, the formation of dendrites and the interdendritic spacing are well known for their influence on the formation of pores.

Thermal and Physical Properties of the Melt

The outcome of a casting process is determined by two groups of properties:

Properties directly influencing the metal flow, and indirectly the solidification:

- Density
- Viscosity
- Surface tension

These factors influence the flow rate and the decrease of melt temperature between entering the mould and reaching the fine details of the cast item. The actual temperature also directly affects the solidification rate.

Properties influencing solidification, and therefore indirectly the metal flow:

- Solidification range
- Heat of solidification
- Specific heat
- Thermal conductivity

All four of these factors determine the heat transfer. However, their magnitude is quite different. Specific heat and heat of solidification deliver thermal energy. Thermal conductivity is ambivalent. Heat is

transported from hotter places to cooler ones *eg* from the sprue to the gate, a process which delays solidification. On the other hand heat is transported from the core of an item to the cooler interface with the investment, a requirement for solidification.

Another factor to be considered is *shrinkage*. We have to distinguish between the relatively smooth decrease of the volume of liquid or solid metal with decreasing temperature and the sharp drop in volume during the solidification process itself. The latter is the cause of the most frequent defects in jewellery casting.

Thermal and Physical Properties of Investment

Three factors are important:

Gas permeability influences the back pressure, and therefore the flow rate. Again the solidification behaviour is affected.

Specific heat is responsible for heat uptake

Thermal conductivity (together with specific heat) determines the heat transfer, and consequently, the solidification rate. Properties affected are form filling and porosity.

In addition the mechanical strength, and the thermal and chemical stability have to be taken into account.

Interface Resistance

The interface resistance controls the heat flow through the mould-metal interface, and is determined by the properties of both the melt and the mould. Factors such as shrinkage, oxidation, and chemical reaction with the investment would be expected to have an influence, but no information is available, and experimental determination is extremely difficult.

AN APPROACH TO MEASUREMENTS, AND CHARACTERIZATION DATA

In general, data are not available for the characterization of liquid or solidifying jewellery alloys or for the properties of mould material (investment). Research work carried out in our laboratory has given some of the values, and some others were in the literature (2). In many cases, however, only estimated values could be obtained.

Solidification Range

The determination of the solidification range is not usually a problem using differential thermal analysis (DTA). Data obtained in our laboratories for some typical alloys are given in Table 1.

Heat of Solidification and Specific Heat

The heat capacity of a melt is determined by the specific heat, the temperature difference between the melt temperature and the onset of solidification (liquidus temperature), and the mass. The heat introduced during solidification is given by the heat of solidification and the mass. Both values influence form filling and solidification behaviour and therefore the porosity. The heat of solidification and the specific heat of the melt can be determined using differential scanning calorimetry (DSC). In order to provide the reader with a feel for the factors involved, values for some typical jewellery alloys are listed in Table 1. The data for heat of solidification (for the alloys) are measured values. The values for the specific heat were estimated using values for the pure elements.

Usually the values are based on the mass. However, for casting the quantity of heat introduced into the mould is determined by the volume. Table 2 gives values based on the volume. The values of the specific heat are small compared with the heat of solidification. With a superheat of 100 K the heat delivered by the melt in advance of solidification is about a third of the heat of solidification and might influence the solidification behaviour. (In most cases it can be supposed that the real superheat is much smaller when the melt reaches the pattern).

Thermal Conductivity

No certified values for thermal conductivity of liquid jewellery alloys were available. Judging from values for the pure alloying elements thermal conductivity might be

Table 1 Data from Thermal Analysis for some Typical Jewellery Alloys

Au %	Ag %	Cu %	Heat of Solidific. J/g	Specific Heat J/(g*K)	Liquidus Temperature °C	Solidus Temperature °C
91.7	6.2	2.1	60	0.174	1032.8	1009
75.0	16.0	9.0	72	0.212	933.3	902.8
58.5	30.0	11.5	76	0.242	891.4	850.9
	90	10	111	0.320	901.6	779.8
100			65*	0.157*	-	-
	100		107*	0.310*	-	-
		100	205*	0.494*	-	-

*Values: Edelmetall Taschenbuch²

Table 2 Data from Thermal Analysis for some Typical Jewellers Alloys, Volume Based

Au %	Ag %	Cu %	Heat of Solidific. kJ/cm ³	Specific Heat kJ/ (K*cm ³)	Heat due to Superheat		
					100 K kJ/cm ³	50 K kJ/cm ³	20 K kJ/cm ³
91.7	6.2	2.1	1.002	0.0029	0.289	0.144	0.058
75.0	16.0	9.0	1.096	0.0032	0.323	0.161	0.065
58.5	30.0	11.5	1.056	0.0034	0.336	0.168	0.067
	92.5	7.5	1.004	0.0029	0.290	0.145	0.058
100.0			1.126	0.0027	0.272	0.136	0.054
	100.0		1.011	0.0029	0.293	0.146	0.059
		100.0	1.644	0.0040	0.397	0.198	0.079

in the range of $\sim 50 \text{ W/m}^2\text{K}$. The thermal conductivity of the investment (gypsum bonded) was measured to $0.50 \text{ W/m}^2\text{K}$. This means that the cooling behaviour is determined by the low conductivity of the investment. The conductivity of the melt plays no significant role during the solidification process. In addition, the small dimensions of the cast items minimize the effect of thermal conductivity. A substantial thermal gradient within an item is not expected.

Surface Tension

Surface tension is not only a factor influencing form filling of small details of filigree items, it may also affect surface quality. A great deal of the typical dendritic surface structure of castings can probably be attributed to the relatively high surface tension of precious metal alloys. Actually surface tension is not quite the variable which we need. It is the interface tension which is really the characteristic which needs to be known, and this is determined by the surface tension of the liquid metal, the investment properties, and the atmosphere. (This value will also depend on temperature, and in practice the tension near the solidus temperature is important.). The surface tension of the liquid alloy itself can be strongly influenced by alloying elements. Published values (2) show, for example, a significant effect of germanium and silicon on the surface tension of gold.

One of the reasons for adding silicon to jewellery alloys might be the decrease of surface tension. Possibly the effect of silicon on the interface tension between melt and investment is still more pronounced. The standard alloying elements for yellow gold (*ie* copper and silver) do not influence the surface tension to any great extent. For binary alloys values are given in the literature (2); our own measurements were performed recently with standard jewellery alloys (interface tension alumina/melt in a reductive atmosphere, sessile drop method). The measured values are between 1,000 and 1,200 mJ/m^2 .

Shrinkage at Solidification

Shrinkage at solidification (abbreviated simply as 'shrinkage') cannot be called a 'thermal property', but it is an integral part of solidification and is the predominant factor influencing shrinkage porosity. Shrinkage can be deduced using the densities of solid alloys at solidus temperature and the density of the melt at the liquidus temperature. The sessile drop method can help to determine these values approximately. Table 3 gives some values for the pure alloying elements (calculated using literature values for densities) and an approximate value measured for a carat gold alloy.

Table 3 Examples of Shrinkage at Solidification

Compound	Shrinkage at Solidification %
Gold	4.8 ¹
Silver	7.3 ¹
Copper	5.4 ¹
18 ct	6 ²
AuAgCu	

¹ calculated using densities given in literature

² estimated from measurements

Viscosity and Fluidity

No simple relevant method for measuring the viscosity is known. The standard methods used in metallurgy need sophisticated equipment and a large quantity of material. Foundry men often use 'fluidity' instead of viscosity. Fluidity is only partially determined by viscosity. It also takes into account casting conditions and other thermal properties of alloys. Consequently, for comparison of a number of alloy samples, casting conditions must be kept as uniform as possible. For practical use the fluidity is of great value. The most frequently used method for the determination of fluidity is the casting of spirals.

Properties of Investment

Only a few data on thermal properties are available. (Mechanical properties have been measured more frequently (3)):

Specific heat and thermal conductivity

The specific heat of the investment is in the range of $0.8 \text{ J/(g}^{\circ}\text{K)}$ (4), *ie* approximately four times the value of jewellery alloys. The same quantity (in mass) can absorb four times the energy that the melt delivers (same temperature difference). For real casting conditions, however, values related to the volume must be considered; then the relationship changes:
Heat capacity of melt per volume: *ca* $3 \text{ J/(cm}^3\text{K)}$
Heat capacity of investment per volume: *ca* $1 \text{ J/(cm}^3\text{K)}$.

This means that one volume of melt cooling down is able to increase the temperature of about three times the volume of the investment with the same temperature difference.

The thermal conductivity of the investment was measured with $0.50 \text{ W/(m}^2\text{K)}$ at 600°C , a low value similar to (or even lower than) values for good

insulating material. Fireclay refractory (chamotte) has a thermal conductivity of approximately 0.6 to 0.9 W/(m*K) at 600°C.

Gas permeability

Only one of the non-thermal aspects of investment need be mentioned here. Gas permeability is a crucial factor for melt flow. Furthermore the porosity of the investment influences the specific heat, thermal conductivity and density of the investment. All these values directly affect the solidification process. With a given type of investment powder, the permeability depends primarily on the mixing ratio. In order to obtain the correct values the permeability has to be measured at the working temperature (mould temperature). Cooling down the heated investment to room temperature causes micro-cracks and irrelevant values for permeability will be measured. The gas flow should be a linear function of the pressure difference with gas permeability as a constant factor. Preliminary results show that a phosphate bonded investment has a higher gas permeability than a gypsum bonded one, in spite of the higher strength of the phosphate bonded investment.

MODELLING THE PROCESS

The aim of this approach was to demonstrate the influence of the various parameters on solidification time, enabling a more precise adjustment of casting parameters to be made. The model (5) is considerably simplified, and only applicable to items having simple shapes (for example, rods, spheres and plates). However, the model might provide a basis for monitoring the processes operating during the casting process. One of the simplifications is the neglect of the interface resistance (thermal resistance at the interface between the melt and the investment), caused especially by gas formation. This gas formation can arise from a chemical reaction between the melt and the investment.

In its simplest form the equation can be written as follows (if no superheat is applied) :

$$t_f = c * (V/A)^2 \quad (1)$$

$$\text{or } t_f = C * (V/A)^2 * 1/(T_0 - T_m)^2 \quad (2)$$

where

t_f = freezing time

V/A = volume/ surface area ratio

T_0 = 'solidification' temperature (The alloy is considered to solidify at a *constant temperature, ie the solidification range is neglected* in this case. This

simplification affects the validity of the model to a certain extent)

T_m = mould (flask) temperature (temperature of the investment surrounding the pattern)

C = a constant derived from the thermal properties of the melt and the investment: *ie* the heat of solidification (per volume), the specific heat of the investment (per volume), and the thermal conductivity of the investment

c includes the temperature difference in addition and is only valid for constant casting conditions.

Equation (1) is also known as *Chvorinov's rule*, and is proved by experiments in foundries. In practice, superheat has also to be taken into account. Some modifications of Equation (2) were necessary. For a first rough estimation and a small superheat (as it occurs in reality) the heat introduced into the system will be simply increased by a term which takes into account the specific heat of the melt (per volume) and the difference between the actual melt temperature and the 'solidification' temperature.

Volume/Surface Ratio

A critical value when using the model described above is the ratio of volume to surface area (abbreviated as 'volume ratio'). In general, this can only be computed for items with simple shapes. For real jewellery castings only estimates are possible. Figure 1 gives an indication of the influence of shape and volume on the volume ratio. A sphere shows the largest ratio, indicating the longest cooling time compared with a plate or a cylinder (under identical casting conditions). The ratio strongly depends on the volume (and diameter) of the sphere. The volume ratios of cylinder and plate are almost independent of the volume, but depend on the diameter of the cylinder and the thickness of the plate (at constant width). The smallest ratio and the highest cooling rate is given by a cylinder. A retarded rate of solidification is desirable for gates. Unfortunately they are (in most cases) cylinders with a relatively small volume ratio, and therefore have a fast cooling rate. 'Plates' will behave similarly to cylinders when their cross-section comes closer to a square.

Testing the Model

Temperature measurements have been performed using micro-thermocouples in items with simple shapes such as spheres and rods. The measured values can be compared with calculated ones. Table 4 gives some examples. The values agree fairly well, when we bear in mind that a very simple model was used, and that the values for several parameters could only be estimated. The model could of course only be tested with items having relatively large cross-sections. In small ones the temperature measurement

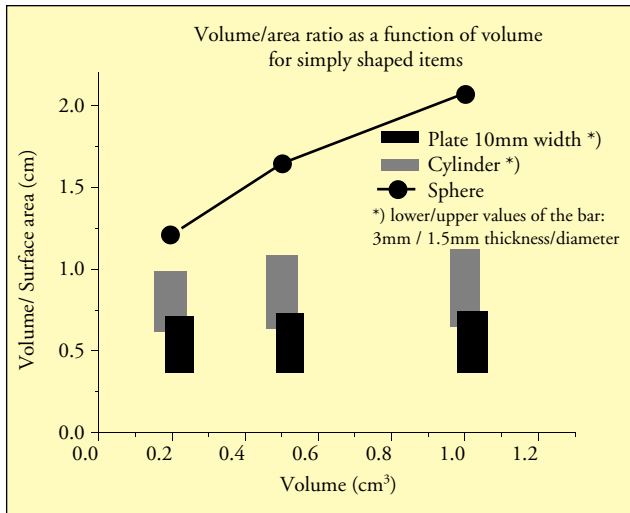


Figure 1 Influence of volume on volumel/surface ratio for spheres, cylinders (rods) and plates.

is not possible and measurements are unreliable. The computed values for the times needed for cooling down from melt temperature (superheat) to 'solidification' temperature do not agree with the measured values.

The reasons for this might be:

- unreliable measured values for this short time interval
- the model was developed for an almost constant reference temperature. This may be a permissible approximation for the relatively small solidification range and the relatively large amount of solidification heat.

Despite the uncertainties of the current model it can nevertheless provide some insight into the casting process. The cooling and solidification behaviour of small items can be envisaged. Direct measurements are not possible in such fine structures. Figure 2 demonstrates in principal the sharp decrease of solidification time for spheres with decreasing diameter. The figure is based on computed values and can only be used as an estimate. An increase of the diameter from 5 mm to 15 mm changes the solidification by a factor of approximately seven. The

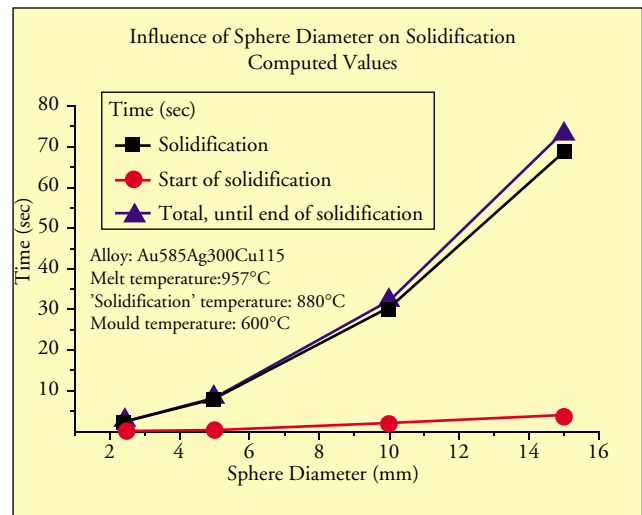


Figure 2 Relation between sphere diameter and cooling solidification time of spheres (computed values).

time which the melt needs to cool down from superheat to the solidification temperature is comparatively short. The melt flow is possible only within this short time interval. The influence of the mould (flask) temperature is shown in Figure 3 Decreasing the mould temperature from 600 to 400°C decreases the solidification time to approximately a third, independent of sphere diameter. The absolute saving on solidification time is more significant with heavy items. (The time scale is not linear!)

A Ring as an Example

It is not possible to simulate the solidification of a real jewellery item having a complicated design, but some insight into the solidification of a relatively heavy sized jewellery item can be obtained using a highly simplified shape. It consists of a flat shank with rectangular cross-section with a sphere or plate as a head. The dimensions were varied to some degree. Figure 4 gives the results of the computations as an estimated approach. One more simplification was made neglecting the superheat. The estimate of solidification time shows that even a relatively

Table 4 Comparison of Measured Solidification Time with Computed Values

Shape	Alloy	'Solidification Temperature'	Solidification Time (sec)	
			Measured	Computed
		°C		
Sphere 10 mm	Au585Ag200Cu115	880	34	30
Sphere 15 mm	Au585Ag200Cu115	870	75	69
Rod (Cylinder) 2.6mm	Au750Ag160Cu90	917	2.8	3.9

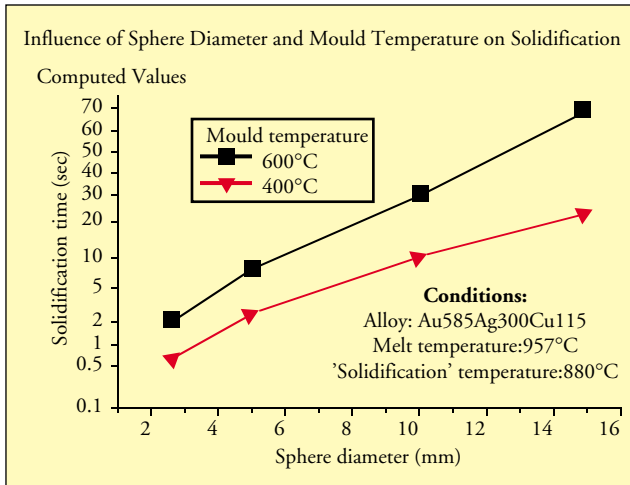


Figure 3 Influence of mould temperature on solidification time versus sphere diameter (computed values)

moderate head size will need a heavy shank to make sure that the head will solidify in advance to the shank. A plate of 10 x 10 x 2 mm would need a 3 x 5 mm shank. Fortunately in practice the situation is more favourable in most cases. The head is not as compact as the one used for testing. Real rings have a structured design which decreases the volume ratio, and therefore the solidification time. Increasing the flask temperature from 400 to 600°C does not change the ratio between the solidification times. However, the absolute difference increases between the solidification time of the shank and that of the head, which seems to be a disadvantage.

STRUCTURAL ASPECTS

Dendritic Structure

Coming back to the example of the ring, even if the computed solidification time ratio is favourable and uncertainties can be excluded, a pore-free casting is not guaranteed. Standard jewellery alloys solidify with formation of a dendritic network. A spongy state exists, and this causes a high flow resistance for the residual melt. In order to equalize the shrinkage of the head, the melt has to flow through the spongy part of the shank. Pressure must be applied to overcome the flow resistance, avoiding porosity.

Thus, we have a structural problem, which can probably be minimized if alloys with less dendritic structure are available. Alloys solidifying with a 'grainy' (or more precisely: equiaxed structure) have a lower flow resistance, and are more favourable for the casting process. The casting method can also play its part in solving the problem. A higher pressure difference could reduce this kind of shrinkage porosity.

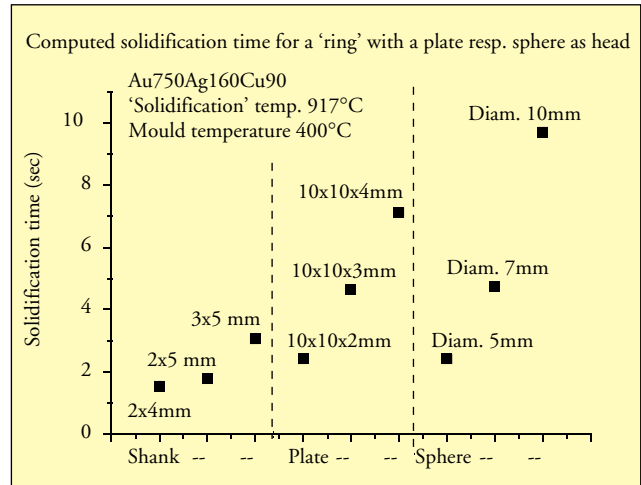


Figure 4 Computed solidification time for different parts and sizes of simplified ring, mould temperature 400°C.

EXAMPLE OF SOLIDIFYING ROD-SHAPED SPIRAL

When evaluating the flow behaviour of alloys, the spiral test is a common procedure used in foundries. It can also be used for the investigation of solidification behaviour. For this purpose a spiral of 2.6 mm diameter and 400 mm length was cast. The horizontally positioned spiral was directly connected with the sprue ('stem of the tree'). At certain distances from the sprue micro-thermocouples were fixed along the spiral. Figure 5 shows a typical plot of temperature versus time for a 18 ct yellow gold alloy.

Some remarkable observations are:

- 1 Solidification starts with considerable undercooling. At the first measuring point of the spiral the supercooling is 19 K (°C). After onset of solidification the temperature increases with approximately 6 K (°C) and remains constant for a while. The end of solidification cannot be detected precisely in the diagram. The solidus temperature has to be used as a criterion for determination of solidus time.
- 2 More surprising is the temperature at the final point reached by the melt. This temperature is far below the solidus temperature but the thermocouple is covered by the melt. The liquid metal has positively reached this point, but the temperature remains constant for an interval which indicates solidification; and as yet this is unexplained.
- 3 The temperature loss of the melt whilst running through the length of the spiral depends on the flow rate. Casting with low (hydrostatic) pressure

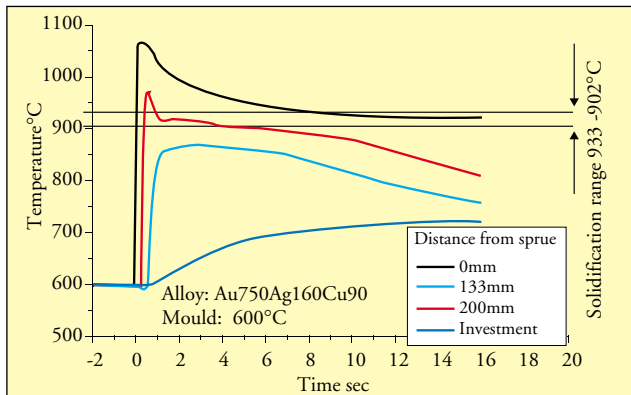


Figure 5 Casting spirals: temperature and solidification behaviour.

results in a stronger decrease of temperature than casting with higher pressure (pressure/vacuum assisted casting) see Figure 6.

Repeated measurements verified the results, especially point 2 above.

CONCLUSIONS

- * Two contradictory processes determine the manner in which a jewellery item solidifies:
 - The *introduction of heat* by the melt is influenced in the main by temperature, mass, specific heat and heat of solidification of the melt.
 - The *dissemination of heat* is in the main influenced by the surface/volume ratio of the item, the mould temperature, specific heat and thermal conductivity of the investment, and the thermal interface resistance.
 - Some of the characteristic values needed for evaluation of the solidification behaviour are

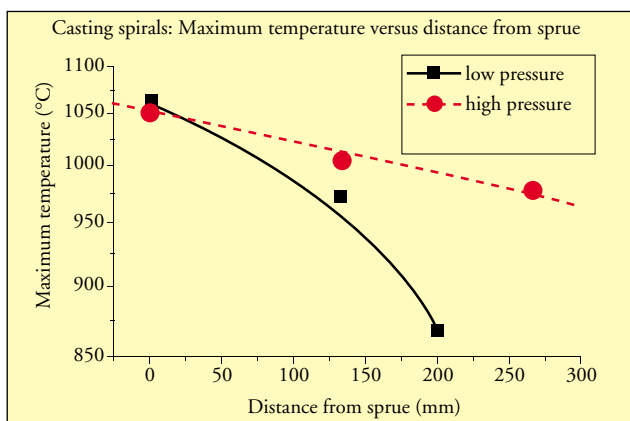


Figure 6 Temperature drop within a spiral as a function of the distance from sprue.

available from the literature or can be determined from recent research work. However, many more or more precise estimates are still required.

- * A model which is used in foundries has been adapted for the investment casting process for jewellery. Experimental work with a simplified 'jewellery' item has indicated that the model can be used to give an initial characterization of the processes.
- * Solidification time was used as a key value. The volume to surface ratio and the difference between solidification and mould temperature are variables. They have parabolic influence. For example the (computed) solidification time of a sphere varies from more than 60 sec for a 15 mm diameter to about 2 sec for a 2.5 mm diameter 14 ct alloy (standard casting conditions).
- * An estimate can be made of the dimensional relationships within a simply shaped item (including the gate) in order to avoid shrinkage porosity in the relatively heavy parts of the item.
- * The model discussed is a 'static' one. A flowing melt would have a modified behaviour as some trials with spirals have demonstrated; but this effect could not yet be included in the model.
- * It has been shown how some estimations of the solidifying behaviour can be made which might help to reduce such factors as shrinkage porosity. However a great deal of further research is necessary to come closer to reality

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