

Properties of melt and thermal processes during solidification in jewelry casting

by

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Abstract

A survey is given on significant thermal properties of liquid or solidifying jewelry alloys. Also some properties of investment are mentioned. Values found in literature, measured in own investigations or estimations are given.

A relatively simple model for solidification is presented. Some parameters such as volume/surface ratio, superheat and solidification temperature are discussed.

The solidification behavior of a simplified ring is investigated more detailed using the model.

Some observations made with casting of spirals are shown.

Keywords

Investment casting, thermal properties, solidification behavior, modeling

Introduction

The success of a casting process is defined by many factors, such as size and shape of the cast item, gating (spruing), pressure and forces (determined by the equipment and the procedure), properties of alloys and investment etc.

However, temperature and thermal processes dominate all other influencing factors and processes. There are strong interconnections between all the factors. Neglecting this fact would be a mistake.

In a previous publication¹ the influence of pressure, flow rate etc. was considered. Thermal problems were only mentioned briefly.

This paper shall deal more extensively with thermal problems.

Establishing a complete and realistic model of an investment casting process requires a model for the thermal processes on the first place. In general this problem remains unresolved, only simplified models are available.

There are several reasons for the difficulty to establish a comprehensive model:

- a) an almost infinitive number of interactions
- b) non reproductive casting conditions (even with excellent equipment and possibility for extern process control) .
- c) the great variety of cast items with their complicate design.
- d) and last not least: the missing knowledge of thermal properties of jewelry alloys in the liquid state and at solidification.

The thermal properties of investment are insufficiently known, too.

In the following some aspects of thermal processes will be considered, some measured values for liquid and solidifying jewelry alloys will be given. However, completeness could not be achieved.

¹ The Santa Fe Symposium on Jewelry Manufacturing Technology 1998, p. 457 - 491

Survey on thermal processes at investment casting

The process starts with melting of the alloys by induction heating, resistance heating or by flame. Aspects of this part of the casting process were already considered in a former presentation¹.

Considering the casting process itself, two contradicting thermal processes occur:

- a) Introducing heat by the molten metal into the mold. The quantity of heat is given by four factors: - mass of melt, - temperature of melt, -- specific heat, and heat of solidification.
- b) Dissemination of heat will occur by radiation, by heating up the investment, and by thermal conduction.

Influencing factors are: - Mold (flask) temperature (respectively temperature difference between melt and flask), - specific heat of investment, - thermal conductivity of investment, - (thermal) interface resistance between melt and investment wall.

Some effects can be neglected: - 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 as long the solidification process is not finished. An exception may be if the item comes unusually close to the flask wall. (In some cases this is/was performed intentionally to obtain a kind of directional cooling effect.).

Unfortunately the influencing factors mentioned above are not sufficient to characterize the thermal processes with investment casting. Shape and size of the castings inclusively sprues and gates have a dominant influence on introducing, dissemination, and consumption of heat. Metallurgical factors e.g. melting range, grain structure and grain size have to be mentioned, too. For example, the formation of dendrites and the inter-dendritic spacing are well known for their influence on the formation of pores.

Thermal and physical properties of melt

The result obtained by 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 drop of melt temperature between entering the mold and reaching fine details of the cast item. The actual temperature again is decisive for solidification rate.

Properties influencing solidification, and therefore indirectly the metal flow:

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

All four of the 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 e.g. from the sprue to the gate. This might delay the 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.

An other property 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 of volume at solidification. The latter is the cause of the most frequent defects in jewelry 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 behavior is affected.

Specific heat is responsible for heat uptake

Thermal conductivity determines the heat transfer (together with specific heat), and therefore the solidification rate. Influenced properties are formfilling and porosity.

In addition the *mechanical strength* has to be considered.

Interface resistance.

It controls the heat flow through the mold-metal interface, and is as well determined by metal/melt properties as by mold properties. It may be supposed that e.g. shrinkage, oxidation, and chemical reaction with the investment have an influence. However, no information is available, and experimental determination is extremely difficult.

Measurements, and characteristic data, an approach

In general there is a lack on data for characterization of liquid or solidifying jewelry alloys. The same is valid for properties of mold material (investment). Research work done in our laboratory gives some values. Other values could be obtained from literature². In many cases only estimated values could be achieved, which might be sufficient for many purposes.

Solidification range

The determination of the solidification range in general is not a problem. It is performed in many laboratories. The values for standard alloys are well known.

The usual measuring method is differential thermal analysis (DTA). Data for some typical alloys are given in table 1.

Heat of solidification and specific heat

The heat capacity of melt is determined by the specific heat, the temperature difference between melt temperature and 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 formfilling and solidification behavior and therefore porosity.

The heat of solidification can be determined in a similar way as the solidification range. The procedure has to be modified a bit, and is called differential scanning calorimetry (DSC). In principle the specific heat of the melt can be measured using the same apparatus.

For a first orientation values for some typical jewelry alloys are listed in table 1. The data for heat of solidification (for the alloys) are measured values. The values for the specific heat are estimations using the values for the pure elements.

² Edelmetalltaschenbuch 2nd Edition published by Degussa, Hüthig 1995

Table 1 Data of thermal analysis for some typical jewelry alloys

Au	Ag	Cu	Heat of solidification	Specific Heat	Liquidus Temperatur e	Solidus Temperatur e
%	%	%	J/g	J/(g*K)	°C	°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 Taschenbuch ²

Table 2 Data of thermal analysis for some typical jewelry alloys, volume based

Au	Ag	Cu	Heat of solidific.	Specific Heat	Heat due to superheat		
					100 K	50 K	20 K
%	%	%	kJ/cm ³	kJ/ (K*cm ³)	kJ/cm ³	kJ/cm ³	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

Usually the characteristic values are based on the mass. However, for casting the quantity of heat introduced into the mold is determined by the volume. Table 2 gives values based on the volume.

The specific heat is small compared with the heat of solidification. However, superheat multiplies the value. With a superheat of 100 K ($^{\circ}\text{C}$) the heat delivered by the melt in advance of solidification is about a third of the heat of solidification and might influence the solidification behavior. In most cases it can be supposed that the real superheat is much smaller when the melt reaches the pattern, even if the measured temperature of the melt in the crucible is 150 K ($^{\circ}\text{C}$) above liquidus temperature.

The subject will be considered more detailed later.

Thermal conductivity

No certified values for thermal conductivity of liquid jewelry alloys were available. Judging from values for the pure alloying elements thermal conductivity might be in the range of $\sim 50 \text{ W/m}\cdot\text{K}$. The thermal conductivity of investment (gypsum bonded investment) was measured to $0.50 \text{ W/m}\cdot\text{K}$.

That means that the cooling behavior is determined by the low conductivity of investment. The conductivity of melt plays no significant role during the solidification process. In addition, the small dimensions of the cast items minimize the effect of thermal conductivity. These facts together prevents generating a substantial thermal gradient within an item compared with the thermal gradient build up in the investment.

Surface tension

Surface tension is not only a factor influencing formfilling of small details of filigree items, it is supposed to effect also surface quality. Probably a great deal of the typical dendritic surface structure of castings can be attributed to the relatively high surface tension of precious metal alloys. Actually surface tension is not quite the variable which we need. More exactly interface tension is the characteristic one which is

necessary to be known. It is the result of surface tension of the metal, investment properties, and atmosphere. (Of course the value depends also on temperature. For practical use the tension near solidus temperature is important.). The surface tension of the liquid alloy itself can be strongly influenced by alloying elements.

Published values ² show e.g. a significant effect of germanium and silicon on surface tension of gold.

One of the reasons for adding silicon to jewelry 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, copper and silver do not influence the surface tension to a great extend.

For binary alloys values are given in literature ², own measurement were performed recently with standard jewelry alloys. Only a preliminary result with some uncertainty can be given. The investigations will be continued and extended within a current research project. It has to be stated that the results of our measurements give the interface tension melt/ alumina ceramic in a forming gas atmosphere.

Some remarks on the measuring method:

Among several methods described in literature the sessile drop method appeared to be most suited to our problem. A few grams of alloy are molten in a protective atmosphere on an inert support. A picture is taken from the droplet of melt. The contact angle and some measurements of the size can be used to calculate the surface (interface) tension.

For calculation the *density* of the melt is necessary, which is usually unknown. A method was developed to use the sessile drop method also to get a estimation for the density of the liquid metal. The estimation might be a relatively rough value, but it is sufficient for the purpose.

Table 3 Influence of some additions on the surface tension of gold

Metal/Alloy	Surface tension	Temperature
	mJ/m ²	°C
Au	1093	1300
Au + 4 % Ge	982	1300
Au + 1.6 % Si	965	1300

Table 4 Surface tension of some gold alloys

Metal/Alloy	Surface tension	Temperature
	mJ/m ²	°C
Au	1200	1200
Au + 24% Cu	1120	1300
Au + 27% Ag	1031	1300
Au58.5Ag32Cu9.5	1000	940

Table 5 Shrinkage at solidification , examples

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

¹ calculated using densities given in literature

² estimated from measurements

Shrinkage at solidification

Shrinkage at solidification (abbreviated simply as 'shrinkage') is not just a thermal property. However, it is strongly related to solidification. Furthermore it is the central point concerning shrinkage porosity. For judging newly developed alloys it should be known how shrinkage is affected.

Shrinkage can be deduced using the densities of solid alloys at solidus temperature and density of melt at liquidus temperature. The sessile drop method can help to determine these values approximately. More precise measurements need more sophisticated equipment and greater quantities of alloy, which is unpractical for development of jewelry alloys.

Table 5 gives some values for the pure alloying elements (calculated using literature values for densities) and an approximate value for a carat gold alloy.

Viscosity and fluidity

No simple method for measuring viscosity is known. The standard methods used in metallurgy need a sophisticated equipment and a great quantity of material.

Foundry men often use 'fluidity' instead of viscosity. Fluidity is only partially determined by viscosity. It takes also into account casting conditions and other thermal properties of alloys. Therefore for comparison of alloys casting conditions has to be kept as constant as possible. For practical use the fluidity is of great value.

The most often used method for determination of fluidity is casting spirals.

Trials are under way testing the usability of this method in jewelry casting. Final results can not be presented. However, preliminary tests with temperature measurements gave a good insight in solidification behavior of alloys (see later).

Properties of investment

Only a few data on thermal properties are available. (Mechanical properties were measured more thoroughly ³.)

Specific heat and thermal conductivity

The specific heat of investment is in the range of $0.8 \text{ J}/(\text{g} \cdot \text{K})$ ⁴, that means it is approximately four times the value of jewelry alloys. The same quantity (in mass) can uptake four times the energy that the melt delivers (same temperature difference). For real casting conditions, however, values related on volume have to be considered.

The relations changes:

Heat capacity of melt/ volume: approximately $3 \text{ J}/(\text{cm}^3 \cdot \text{K})$

Heat capacity of investment/volume: approximately $1 \text{ J}/(\text{cm}^3 \cdot \text{K})$.

That 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.

Or an other example: If no thermal equilibrium by thermal conduction would occur, a volume of melt with 50 K ($^{\circ}\text{C}$) superheat would increase the same volume of investment for about 150 K ($^{\circ}\text{C}$) until solidification starts.

The thermal conductivity of the investment was measured with $0.50 \text{ W}/(\text{m} \cdot \text{K})$, 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 $0.9 \text{ W}/(\text{m} \cdot \text{K})$ at $600 \text{ }^{\circ}\text{C}$.

³ e.g. D.Ott, Properties of Investment, The Santa Fe Symposium 1988, p. 47 - 62

⁴ D.J. Browne, Kimmitt Sayers, Modelling of Casting, Welding and Advanced Solidification Processes VII, 1995, 441 - 448

Gas permeability

Only one of the non-thermal properties of investment shall be mentioned. Gas permeability is a crucial factor for melt flow (together with the pressure situation given by casting conditions). Furthermore the porosity of the investment influences specific heat, thermal conductivity and density of the investment. All these values effect directly the solidification.

With a given type of investment powder, the permeability depends primarily on the mixing ratio. For obtaining the correct values the permeability has to be measured at working temperature (mold temperature). Cooling down the burnt investment to room temperature causes micro-cracks. Irrelevant values for permeability will be measured.

The gas flow should be a linear function of pressure difference with gas permeability as a constant factor (fig. 1). Investigations proved this fact.

Table 6 gives values for some properties of commercial investment brand, measured after burn-out.

Modeling the process

The aim of this task was to demonstrate the influence of the various parameters on solidification time enabling more precise adjusting casting parameters. The model ⁵ is very much simplified, and only applicable to simple shaped items (rods, spheres, plates e.g.). However, it might provide a feeling for the processes acting at casting.

Remark: One of the simplifications is neglecting the interface resistance (thermal resistance on the interface between melt and investment). Especially due to gas formation an influence might be expected. Gas formation can be caused by chemically reaction between melt and investment.

⁵ The model is based on the following publication:
Merton C. Flemings, Solidification Processing, McGraw Hill 1974, p. 7 - 12

Investment: Influence of pressure difference on gas flow

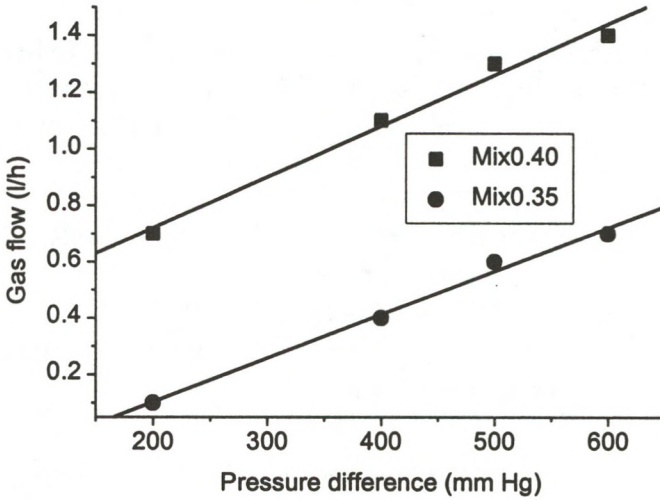


Fig.1 Influence of mixing ratio and applied pressure on gas flow

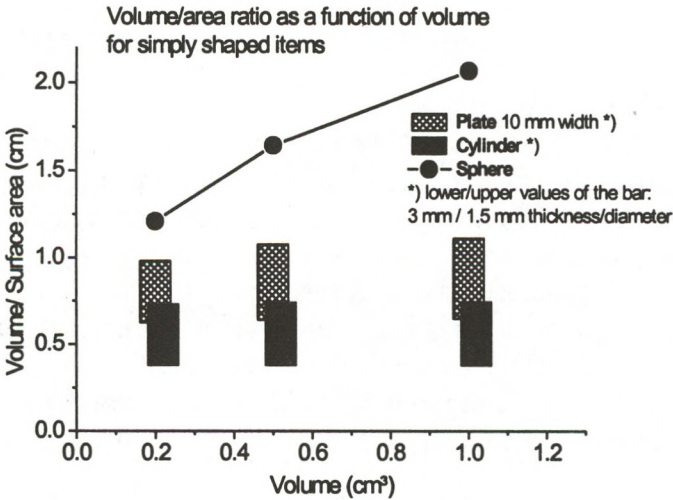


Fig. 2 Influence of volume on volume/surface ratio for spheres, cylinders (rods) and plates

Table 6 Some characteristic values for investment properties

Mixing ratio	100:37	100:40	Temperature.	Pressure difference
Density g/cm	1.29		20 °C ¹	
Gas permeability ml/sec*cm*bar	0.39	0.54	600 °C	670 mbar
Thermal conductivity W/m*K	0.50		600 °C	

¹ after burn out, measured at room temperature

Table 7 Comparison of measured solidification time with computed values

Shape	Alloy	"Solidific. temp." °C	Solidification time (sec)	
			measured	computed
Sphere 10 mm	Au585Ag200	880	34	30
	Cu115			
Sphere 15 mm	Au585Ag200	870	75	69
	Cu115			
Rod (Cylinder) 2.6 mm	Au750Ag160 Cu90	917	2.8	3.9

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

$$t_f = c * (V/A)^2 \quad \text{(equation 1) or}$$

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

where

t_f freezing time

V/A volume/ surface ratio

T_0 'solidification' temperature

The alloy is considered to solidify at a **constant temperature, the solidification range is neglected** in this case). This is a simplification which will effect the validity of the model to a small amount.

T_m mold (flask) temperature (temperature of the investment surrounding the pattern)

C A constant including thermal properties of melt and investment: Heat of solidification (per volume), specific heat of investment (per volume), thermal conductivity of 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 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 in the system shall be simply increased by a term which takes into account specific heat of melt (per volume) and the difference between actual melt temperature and 'solidification' temperature.

Volume / surface ratio

A critical value for using the model mentioned above is the ratio of volume to surface (abbreviated as 'volume ratio'). In general it can only be computed for simply shaped items.

For real jewelry castings only estimations are possible.

Fig. 2 gives an impression on the influence of shape and volume on the volume ratio.

A sphere shows the largest ratio, that means the longest cooling time compared to a plate or a cylinder (under identical casting conditions). The ratio depends strongly 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 respectively the thickness of the plate (at constant width). The smallest ratio and the highest cooling rate shows the cylinder.

A retarded solidification is desired for gates. Unfortunately they are (in most cases) cylinders with a relatively small volume ratio, and therefore a fast cooling rate.

'Plates' will behave similar to cylinders when the cross-section becomes more square.

Testing the model

Temperature measurements have been performed using micro-thermocouples in simply shaped items such as spheres and rods. The measured values can be compared with calculated ones. Table 7 gives the results of some examples. The values agree fairly well, taking into account that a very simple model was used, and that the values for several parameters could only be estimated. (It is an important task in future to obtain the missing values for such parameters.)

Of course the model could only be tested with relatively large cross-sectioned items. In small ones the temperature measurement is not possible respectively measurements are unreliable.

The computes values do not match so well with the measured ones concerning the time needed for cooling down from melt temperature (superheat) to 'solidification' temperature.

Reasons for might be:

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

A modification of the model should be tested in future.

Despite of the uncertainties of the current model it can provide some insight in the casting process. The cooling and solidification behavior of small items can be visualized. Whereas direct measurements are no more possible in such fine structures.

Fig. 3 and fig. 4 give two examples. Fig. 4 demonstrates the sharp decrease of solidification time for spheres with decreasing diameter. An increase of the diameter from 5 mm to 15 mm changes the solidification to a factor of approximately seven. The time which the melt needs to cool down from superheat to solidification temperature is comparatively short.

That means that solidification can not be much influenced by increasing the melt temperature. On the other hand metal flow is possible only for a short time, and depends strongly on superheat (if other parameters are kept constant).

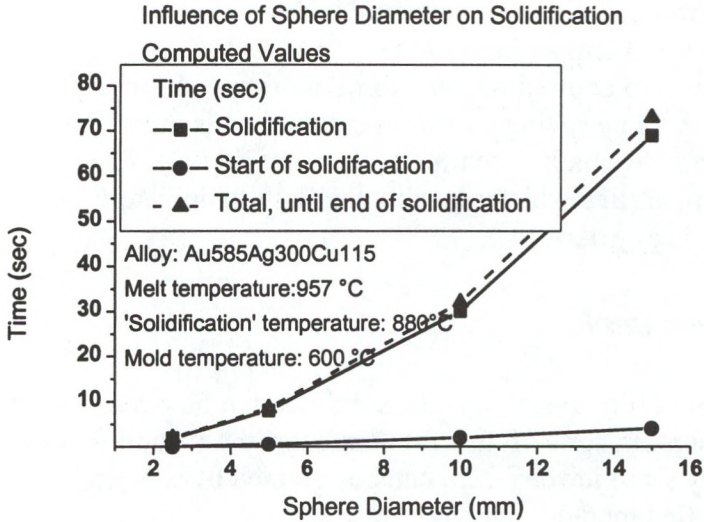


Fig. 3 Relation between sphere diameter and cooling respectively solidification time of spheres (computed values)

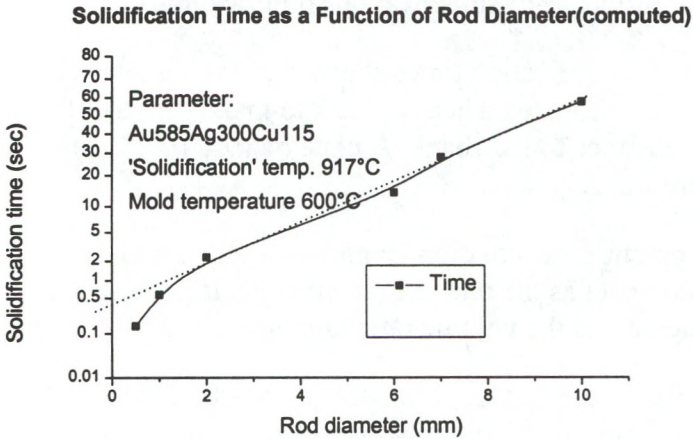


Fig. 4 Relation between rod diameter and solidification time of rods (cylinders), computed values

The influence of mold (flask) temperature is shown in **fig. 5**. Decreasing the mold 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. (Remark: The time scale is not linear!) The old and simple rule is quantified which says that the flask temperature should be decreased with heavy parts.

A ring as an example

We have no possibility to simulate the solidification on a real ring with a complicate design. In spite of this fact some insight in solidification of a relatively heavy sized jewelry item can be obtained by studying a strongly simplified model.

It consists of a flat shank with rectangular cross-section and a sphere or a plate as head. The dimensions were varied to a certain amount.

Fig. 6 and fig. 7 give the results of the computations. One more simplification was made neglecting the superheat. (As shown previously there is no great influence of superheat on solidification.)

The estimation of solidification times shows that even a relatively 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 favorable in most cases. The head is not as compact as the one used in practice. It has a structured design which decreases the volume ratio and the solidification time.

Increasing the flask temperature from 400 °C to 600 °C does not change the ratio between solidification times. However, the absolute distance increases between solidification time of the shank and that of the head, which seems to be disadvantageous.

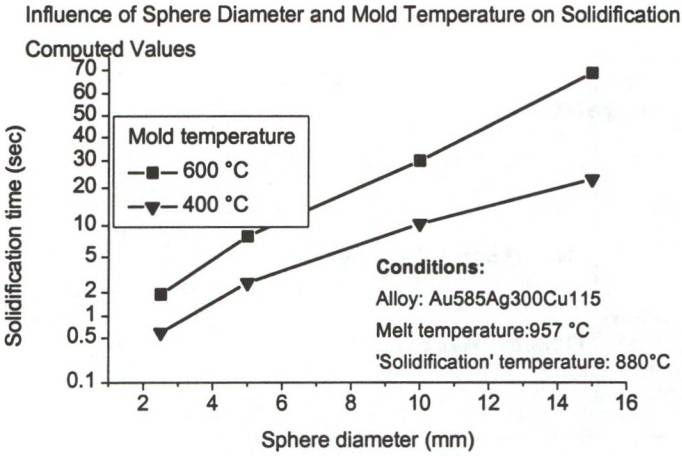


Fig. 5 Influence of mould temperature on solidification time versus sphere diameter (computed values)

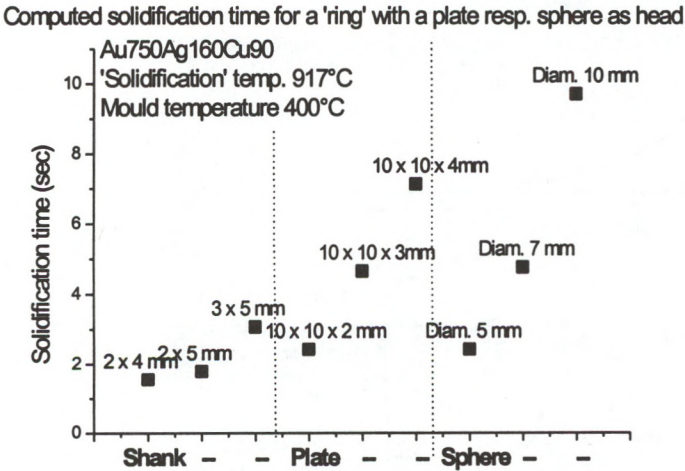


Fig. 6 Computed solidification time for different parts and sizes of a simplified ring, mold temperature 400°C

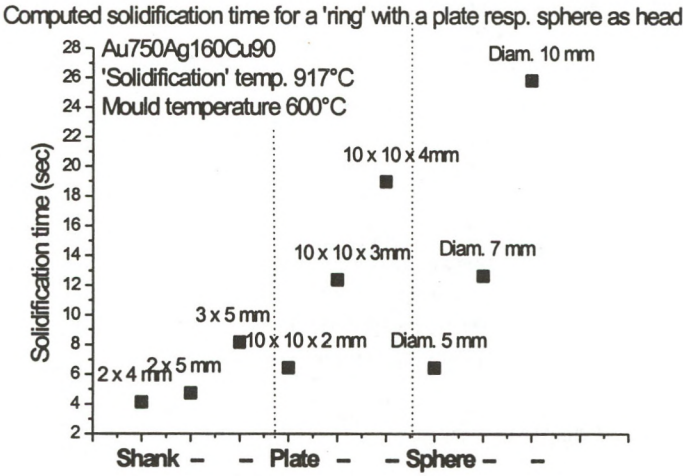


Fig. 7 Computed solidification time for different parts and sizes of a simplified ring, mold temperature 600°C

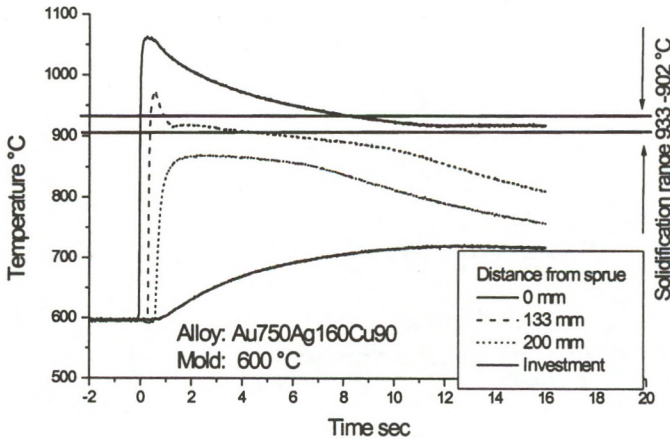


Fig. 8 Casting spirals: temperature and solidification behavior (example)

Structural problems

Dendritic structure

Coming back to the ring example. Even if the computed solidification time ratio is favorable (and uncertainties can be excluded), a pore-free casting is not guaranteed.

The standard jewelry alloys solidify with formation of a dendritic network in the mushy state causing a high flow resistance for the remaining melt. At times the solidification of shank and head occurs simultaneously. For equalizing the shrinkage of the head melt has to flow through the mushy part of the shank. This process needs some pressure on the liquid. If the pressure could not be provided, shrinkage porosity will occur even if the solidification of the shank is not finished prematurely.

We have a structural problem, which would need the developing of alloys with less dendritic structure.

Alloys solidifying with a 'grainy' (or more precisely: equiaxed structure) have a lower flow resistance, and are more favorable for the casting process.

Of course also the casting method can carry its part in solving the problem. Higher pressure (difference) would reduce this kind of shrinkage porosity.

Example for solidifying rod-shaped spiral

For testing flow behavior of alloys the spiral test is a common procedure used in foundries. It can also be used for investigation of solidification behavior. 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. The casting conditions were chosen in a way which would not allow complete formfilling because differences in flow behavior should be detected.

Fig. 8 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 ($^{\circ}\text{C}$). After onset of solidification the temperature increases with approximately 6 K ($^{\circ}\text{C}$) and remains constant for a while. The end of solidification can not be detected precisely in the diagram. The solidus temperature has to be used as a criteria for determination of solidus time.

2. More astonishing is the temperature at the last point reached by the melt. The temperature is far below solidus temperature but the thermocouple is covered by the melt. The liquid metal has positively reached this point. The temperature remains constant for an interval which indicates solidification. An explanation is not possible at the moment.

3. The temperature loss of the melt during running through the length of the spiral depends on the flow rate. Casting with low (hydrostatic) pressure results in a stronger decrease of temperature than casting with higher pressure (pressure/vacuum assisted casting), **fig. 9**.

These observations demonstrated on one example have been confirmed in several cases. The influence on casting quality has to be investigated in future.

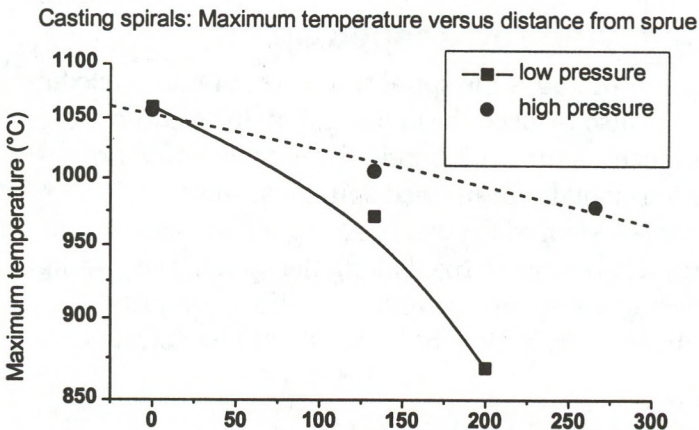


Fig. 9 Temperature drop within a spiral as a function of the distance from sprue