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Review: A Decade of Quenching from the Melt

T. R. ANANTHARAMAN, C. SURYANARAYANA
Department of Metallurgy, Banaras Hindu University, Varanasi-5, India

The technique of rapidly quenching metals and alloys from the melt developed in 1960 by Duwez and his collaborators has gained wide popularity. The extremely high cooling rates (10^6 to 10^8 °C/sec) attainable with these techniques have yielded supersaturated solid solutions, non-equilibrium crystalline phases and also amorphous alloys. The fascinating results obtained so far, particularly the unusual structures and properties of the new products, are extensively reviewed in this article.

1. Introduction

The technique of quenching or rapid cooling of a material from an elevated temperature to room temperature or below, followed by annealing either at room temperature or elevated temperatures to develop suitable microstructures and hence desired properties, has always enjoyed considerable popularity among metallurgists and materials scientists. However, quenching treatments have until recently been confined to the solid state, the main purpose being either the retention of phases stable only at high temperatures as in precipitation-hardening studies, or the utilisation of non-equilibrium transformations as in the production of martensite in steels. While diverse liquid quenching media such as oils, water, iced brine or molten metallic baths have been used widely in practice, rapid cooling has also been effected occasionally by projecting gas streams against hot specimens. In all such quenching techniques heat is abstracted by *convection* and the highest cooling rates so achieved are restricted to values of the order of a few tens of thousands of degrees Celsius per second [1-3].

In an effort to achieve still higher cooling rates, Falkenhagen and Hofmann [4] decided to take advantage of heat removal by *conduction* and, in 1952, tried out an ingenious method wherein a molten alloy was sucked into a copper mould maintained at liquid nitrogen temperature and chilled against the refrigerated mould surface. With this technique, these workers obtained an appreciable increase in solid solubility of the elements of the first transition period in aluminium. It is rather surprising that this observation did not create enough enthusiasm among metallurgists as regards the inherent potentiality of this technique in obtaining supersaturated solid solutions, until Duwez and his collaborators [5] developed the "gun" technique for quenching liquid metals and alloys just over a decade ago.

The necessity of having thin liquid films in perfect contact with a good heat conductor to obtain spectacular cooling rates was realised for the first time by Duwez. The importance of thin liquid films was completely overlooked by Falkenhagen and Hofmann [4] and thus the credit for opening up the virgin field of quenching metals and alloys from the melt goes in full measure to Duwez. Following his "gun" technique, many more devices have been developed on the same principle and no less than 200 technical papers have been published on rapid solidification in the last decade. The innumerable results obtained by the application of these techniques have been periodically reviewed [6-11] from different angles. The present article constitutes a systematic and exhaustive review on the structure as well as properties of rapidly solidified alloys.

2. Experimental Devices

A large number of devices have been developed in the course of the last decade to quench metals and alloys from the liquid state. Their efficacies vary widely depending on the extent to which the above-mentioned requirements for rapid solidification are satisfied. The salient features of these devices are brought out in the following paragraphs.

2.1. The Gun Technique

This technique developed by Duwez and Willens [12] has proved by far to be the most popular one. Essentially, a small quantity (up to 100 mg) of the metal or alloy is melted in this method by induction or resistance heating in a graphite crucible with an orifice of about 1 mm in diameter at the bottom. The melt does not fall through the orifice because of high surface tension. Ejected by means of a shock wave, the molten metal passes through the orifice rapidly and spreads onto a copper substrate in the form of thin foils (up to 15 μm in thickness). When desired, the substrate can be maintained at subzero temperatures.

The shock wave is generated by the rupture of a thin (0.008 cm) mylar diaphragm located between the high- and low-pressure chambers through an inert gas at high pressure. The velocity of the shock wave is estimated to be approximately 150 to 300 m/sec [13], which is capable of atomising the melt. The shock wave in some cases can also be produced by detonating an explosive charge.

Graphite appears to be the best material for the container for metals and alloys which do not react with carbon. In case of reactive and refractory metals like tantalum, tungsten and zirconium, either a ceramic insert can be kept at the bottom of the crucible or the metal can be melted with concentrated radio-frequency induction-heating over a silver hearth [14]. Because of the rapid heating rate even metals and alloys with high vapour pressure constituents can be melted with a minimum loss of material.

Metallic melts have been shown to solidify at cooling rates of the order of 10^6 to 10^8 °C/sec [13] when quenched with the "gun". The product is made up of irregular thin foils, porous in nature and with varying cross-sectional area. The thickness of the foils can vary from a fraction of a micron at the edges to many microns in the centre. Near the edges and holes the foils are transparent to the electron beam and hence can be directly examined in an electron microscope [15]. However, because of their uneven cross-section, the foils obtained with the "gun" device are not suited for the measurement of either physical or mechanical properties.

2.2. The Piston-and-Anvil Technique

The next technique developed both chronologically and in terms of popularity to quench melts is due to Pietrokowsky [16], who utilised the concept of catching a molten droplet between a stationary anvil and a fast-moving piston, both faced with beryllium copper. In the original apparatus, the alloy was melted by a gas flame in a fused silica tube and ejected at negligible speed by applying a slight positive pressure to the silica tube. During its path the molten droplet cuts a beam of light directed towards a photocell and thus triggers the piston actuated by high-pressure gas.

Based on this simple model a number of variations of this device with differences in either the melting technique or the process of releasing the piston have come up over the years. For example, Esslinger [17] demonstrated that levitation-melting can be used, thus eliminating the need for a container. Galasso and Vaslet [18] noted that electron-beam melting of the sample placed on a copper plate acting as a track for the moving piston coupled with actuating a solenoid to sweep it can be employed for high-melting materials without any container problem. The complex triggering system can be dispensed with here since the electron beam can be kept "on" while the piston and the anvil come together. The apparatus can also be modified for heating with either laser beam or arc image. Baker *et al* [19] designed an apparatus wherein the sample is levitation-melted and dropped to be rammed between two conducting metallic plates activated by a fluid-operated piston system. In the device developed by Harbur *et al* [20], rapid movement of the piston was effected by an electromagnet drive, rather than gas pressure.

In all these variations, the whole assembly can be kept in a high-vacuum chamber and both the piston and the anvil can be cooled to low temperatures, if necessary.

A novel method of quenching the melts was developed by Caryll and Ward [21], wherein a levitation-melted sample is dropped through a pyrex tube when a swinging pendulum, by its motion, switches off the high frequency generator. The droplet is then squeezed between a piston and an anvil, both faced with copper. Although this technique was initially developed to study the slag-metal equilibria in the Fe-Mn-O system and later employed by Booth and Charles [22] to study the liquid phase equilibria in the Fe-Mn-S-O system, it can also be applied to metallic melts.

The final product obtained in all the above cases is made up of foils of almost uniform thickness suited for both physical and mechanical property studies. The thickness may well be up to about 100 μm, i.e. roughly ten times that obtained in the "gun" technique, but the cooling rate is considerably reduced. However, since the extraction of heat is from both the surfaces of the foil, the overall cooling rate in this technique is still of the order of 10^5 °C/sec [20].

Most recently, Ramachandrarao *et al* [23] have developed an ingenious method of quenching metallic melts by combining the gun and piston-and-anvil methods in such a manner that the product of the "gun" is rammed between a stationary anvil and a fast-moving piston. By synchronising the release of the piston with the rupture of the diaphragm, these workers could always get foils of uniform thickness. Qualitatively it could be shown that the cooling rates attainable in their apparatus could be comparable, if not superior, to those attained in the "gun" technique.

2.3. The Centrifuge

Kumar and Sinha [24] built a simple apparatus to solidify a melt rapidly into foils with an average thickness of 0.15 to 0.20 mm. This was achieved by melting the material in a graphite crucible with a 0.6 mm diameter hole near the top, and then centrifuging the melt in the crucible with the aid of a motor running at a speed of 1400 rpm. The centrifugal force thus developed was enough to eject the metal and allow it to solidify on impact with a copper drum surrounding the crucible. Since the flakes are quite thick, and also since cooling is only from one of the surfaces, the cooling rates are expected to be at least two to three orders of magnitude less than those obtained by the "gun" technique.

2.4. The Torsion Catapult

Roberge and Herman [25] developed a technique based on the spring-loaded catapult device designed earlier by two Russian workers [26]. In this technique the alloy melted in a graphite or boron nitride crucible placed at the end of a torsion bar is catapulted against a cold copper substrate. During its motion, the torsion bar is abruptly stopped when it strikes a shock absorber, while the melt continues to travel at a high speed until it strikes the cold conducting substrate. With this device, the authors were able to obtain bulk foil specimens solidified at quenching rates comparable with those of the piston-and-anvil technique. The greatest advantage of this method is that continuous foils (without any porosity) with an average thickness of 40 to 60 μm and suitable for physical and mechanical tests can be obtained. In contrast to the piston-and-anvil technique, foils obtained by the catapult technique are free from effects of plastic deformation.

Mechanical properties of the foils obtained with this technique have been studied by Toda and Maddin [27]. In spite of the continuity of the foils, the thickness along their entire length tends to be irregular and hence the data obtained do not represent the true mechanical behaviour of the material. The original "wedge" technique of Falkenhagen and Hofmann [4] has been modified by Hinesley and Morris [28] to obtain thin cylindrical specimens eminently suitable for tensile testing. In this method, the wedge-shaped mould was replaced by a cylindrical one with an internal diameter of 0.5 mm. Further, in addition to evacuating the mould, a positive pressure of argon was maintained to drive the liquid alloy into the refrigerated copper mould. The cooling rate in this apparatus was estimated to be of the order of 25000° C/sec.

In all the techniques described so far, the severe limitation concerns the size and amount of the product. If very fast cooling rates have to be realised, the thickness of the foils will, necessarily, have to be small. But it is possible that there need not be any restriction as regards the length of the sample. Some efforts made in this direction towards obtaining rapidly-quenched foils in large quantities are described hereunder.

2.5. The Plasma-Jet Spray Technique

Moss *et al* [29] developed the plasma-jet spraying technique with the advantages of quenching the melts at cooling rates of the order of 10^7 °C/sec and at the same time producing the material continuously at the rate of a few grams per minute. Incidentally, both reactive and refractory metals can be quenched since there is no container problem.

In this method, fine powder of the alloy is injected into a high-temperature plasma and the molten droplets impinge at a high velocity onto a cooled roughened copper substrate. Although the products of this technique have been used for the measurement of mechanical properties, the fact that they are only 89 % dense suggests that the properties may not be truly representative of the mechanical behaviour of the material.

2.6. The Filamentary Casting Technique

This technique of casting flat filaments with a thickness of 5 to 50 μm and up to 7 metres in length was successfully developed by Pond and Maddin [30]. In their technique, the molten alloy is forced through a sapphire orifice from a graphite ejection mould and allowed to strike the interior of a spinning drum. A pneumatic cage raises the mould slowly so that the impinging melt spreads into a flat filament before it completely solidifies. By adjusting the variables such as orifice size, ejection pressure, drum velocity etc., the thickness and width of the filament can be controlled. The metastable effects observed in Cu-Ag alloys by the gun technique [5] have been realised by this technique also.

The latest development in this direction is due to Chen and Miller [31], who obtained thin uniform films of amorphous solids ranging in thickness from 10 to 100 μm by controlling the variables. Their technique consists of melting a few tenths of a gram of alloy and then dropping it between a pair of rapidly rotating steel rolls, which are held together under pressure. The drop solidifies while passing through the rollers and the cooling rate is estimated to be 10^5°C/sec. A similar technique, with rolls covered with a hard chrome surface rotating at a speed of about 7000 rpm, has been reported by Babic *et al* [32].

2.7. Nomenclature

The very first technique to be developed in the field of quenching melts originates from the California Institute of Technology, Pasadena, USA, and owes its origin, as already indicated, to Pol Duwez. He named this the "*gun*" technique of rapid quenching from the liquid state. It was called the "gun" technique since the liquid metal is shot against a good heat conductor. However, Grant of the Massachusetts Institute of Technology preferred to call it the *splat-cooling* technique since the melt is splattered onto a substrate. Duwez objected to the word "splat-cooling" because of its colloquial nature and its being not perhaps even good English.

Alternate expressions like *liquid-quenching* [33], and *Duwez technique of liquid-quenching* [34] were suggested for this technique. Objections to these suggestions came from Srivastava [35], who felt that liquid-quenching might mean quenching of the sample into a liquid and hence suggested *liquisol-quenching*, meaning thereby that the quenching is from the liquid to the solid state. Similarly *Vaposol-quenching* can be used to describe the transition from the vapour to the solid phase. "Liquid-Quenching" and "Vapour-Quenching" may then connote rapid cooling of liquids and vapours from a high to a low temperature. Although this seems perhaps to be the most appropriate and least controversial, it has unfortunately not caught on and splat-cooling has come to be commonly used.

3. Measurement of Cooling Rate

In spite of a decade of active research in the field of liquisol-quenching and the development of more than a dozen devices, relatively few serious attempts have been made to measure the cooling rates achieved in these techniques. A knowledge of the cooling-rates helps in the first instance in evaluating the relative efficiencies of the different quenching techniques. Further, an understanding of the variables affecting the rates of cooling enables one to optimise the conditions to achieve the maximum possible cooling rates.

3.1. Theoretical Estimate

The only attempt to calculate the cooling rates developed in the gun technique theoretically is due to Ruhl [36], who assumed the problem to be one of uni-dimensional heat flow. Depending upon the nature of contact between the splat and the substrate, three types of cooling have been realised. The first is "ideal cooling", wherein the heat transfer coefficient h, has a value of ∞ and the thermal gradients in the splat and the substrate are large. The second is "Newtonian cooling", wherein h is quite small. The thermal gradients in the splat and the substrate are negligible and the cooling is completely interface-controlled. The last is "intermediate cooling", in which the thermal gradients are not negligible and the contact between the splat and the substrate also is not ideal. The dimensionless Nusselt number can be employed to differentiate quantitatively between the above three types of cooling. The Nusselt number is given by hx/k, where x and k are the thickness and thermal conductivity of the splat, respectively. When the Nusselt number has a value > 30, cooling is ideal; when it is < 0.015, it is Newtonian; intermediate values refer to intermediate cooling conditions. In the majority of splat-cooling experiments, the cooling is either Newtonian or intermediate and it is near the ideal condition only in exceptional cases when the contact and adhesion of the splat to the substrate is very good.

Temperature matrices were evaluated by carefully choosing a large number of position and time increments and from these the cooling rates were evaluated. It has been observed that the time-temperature plots exhibit arrests corresponding to the start and the finish of solidification stages and from these the cooling rates were evaluated for both liquid-state and solid-state cooling. A careful analysis of about ten variables indicated that the splat thickness, the interface heat transfer coefficient, h, and the instantaneous splat temperature are the most important in determining the cooling rates. The cooling rate varies inversely as the square of the splat thickness in ideal cooling and inversely as the splat thickness in Newtonian cooling. Under otherwise identical conditions, the cooling rate is proportional to h/x in intermediate cooling. The instantaneous splat temperature is important because even though the cooling rate decreases with fall in temperature, it remains at a very high level down to quite low temperatures in ideal cooling, while in Newtonian cooling the relationship is very different, especially at low temperatures. Other variables such as substrate temperature, initial splat temperature, etc. have also been considered and shown to have only a minor effect on the rate of quenching. A higher initial temperature, for example may result in a lower cooling rate because of greater heating of the substrate, which may have a moderate effect in low-melting alloys. The calculated cooling rate for a one-micron-thick iron splat on a copper substrate is 8.1×10^9 °C/sec in ideal cooling and 6.9×10^7 °C/sec in Newtonian cooling.

3.2. Experimental Evaluations

Experimental determination of cooling-rates in the gun technique of quenching melts was first reported by Predecki *et al* [13]. In their method, the splat is allowed to land on a pair of dissimilar metals – nickel and silver in their experiment – kept close to one another in an insulating base, thus forming the hot junction of a thermocouple. This generates a thermo-emf between the splat material and each of the dissimilar metals which can be recorded on an oscilloscope. Making the critical assumptions that the peaks in the oscilloscope traces are due to the individual droplets landing on the substrate and that the emf generated is directly proportional to temperature, the cooling-rates for a gold-14 at. % antimony alloy and for silver, are calculated to be about 10^6 °C/sec and 1.0 to 5.0×10^8 °C/sec, respectively.

Even though a large number of questionable assumptions such as (i) a uniform splat thickness of one micron, (ii) constancy of substrate temperature and (iii) invariance of heat transfer coefficient with temperature, were necessary in arriving at the cooling rates, the results are nevertheless valuable and interesting, since this first attempt gave an impetus to the development of other techniques for determining the cooling-rate.

Although it has always been generally believed that the cooling-rates attainable in the piston-and-anvil technique are lower than in the gun technique, the first experimental proof for this came through Harbur *et al* [20], who measured the cooling rates in the piston-and-anvil technique on the same lines as adopted by Predecki *et al* [*13*]. The only difference in their technique is that the hot junction was made up of 0.125 cm thick iron and aluminium plates. The resultant emf was fed to an oscilloscope and from the emf-time plots, the cooling rates were calculated with the assumption that the heat flow from the splat into the plates is controlled by interface resistance. This assumption seems to be valid in view of the very low value of Nusselt number ($\sim$0.05). It has, however, been observed that the cooling rates can vary both radially and through the thickness within a splat. Also, the cooling rate is different in the liquid-phase and solid-phase cooling stages. For example, in the case of splat-cooled aluminium, a cooling rate of 7×10^5 °C/sec was achieved in the liquid phase followed by a millisecond of isothermal delay, during which period the heat of solidification was released. Finally, in the solid state the foils cooled at a rate of 3×10^4 °C/sec.

These measurements were later followed up by Löhberg and Müller [37] who measured the cooling rates in the piston-and-anvil technique with an entirely new variable. Their method was based on the principle of focusing the infra-red radiation emitted by the solidifying melt and getting an estimate of the temperature and cooling rate therefrom. A unique feature of this method lies in its ability to estimate the amount of undercooling before solidification starts. For example, it was noted that copper and copper-nickel melts undercooled by as much as 106 to 135 °C before the onset of solidification [38]. A cooling rate of nearly 10^5 °C/sec has been estimated for the apparatus used by these workers.

All the above-mentioned methods of estimating cooling rates in liquisol-quenching techniques suffer from one or more disadvantages, and no perfectly satisfactory method has so far been evolved. Even if reliable estimates of cooling rates were to be obtained by employing any one of the above methods, unfortunately none of these takes into consideration any of the structural characteristics of the splat.

An improved method based on a very different criterion has been developed by Matyja *et al* [39]. A correlation is here arrived at between *secondary dendrite arm spacing* (DAS) and the cooling-rate. A relation of the type

$$d \,.\, r^a = C$$

where d = secondary DAS,

r = rate of cooling,

and a and C are constants,

is developed and a is shown to have a value of 0.32. This method has the advantage of simplicity and is based on the fact that DAS is a function of supercooling, which in turn depends on the rate of quenching. A diagram correlating DAS and cooling rates up to ~ 3 × 10^4°C/sec was first developed by Dean and Spear [40] and was later extended to ten orders of magnitude of cooling-rates by Matyja *et al* [39] by measuring DAS and cooling rates in several Al-base alloys subjected to splat-cooling. These correlations, represented in the form of master diagrams, are very usful since the measurement of DAS will directly give the cooling-rates. Using these master diagrams and measuring DAS by the method due to Levy *et al* [41], it has been shown by Suryanarayana and Anantharaman [42] that liquid Al-Ge alloys solidified at a rate of 2 × 10^6°C/sec when quenched with the gun technique, and at a rate of 4 × 10^4°C/sec when the melt was just dropped onto a copper substrate. Such master diagrams for other alloy systems will be a welcome addition to the literature on splat-cooling.

Most recently, Burden and Jones [43] have developed yet another method to determine the cooling rates produced in splat-cooling techniques. They undertook electron-microscopic studies of plastic/carbon replicas of splat sections normal to the substrate plane and observed well-resolved lamellar microstructures in splat-cooled Al-$CuAl_2$ eutectic alloys. They measured the interlamellar spacing λ and arrived at the freezing velocity R from the relation

$$\lambda = A_2 \, R^{-n}$$

where A_2 is a constant

$$1.04 \times 10^{-5}\,\mathrm{cm}^{3/2}\,\mathrm{sec}^{-1/2}$$

and $n = 0.5$.

The above equation was formulated from the known relationship developed earlier [44, 45]. From a measurement of R, the heat-transfer coefficient h can be calculated and hence the cooling-rate. The latter was calculated to be 7 × 10^5 and 3 × 10^4°C/sec, respectively, when the quenching from the melt was done onto grit-blasted and mechanically polished copper substrates. These values are, however, at least two to three orders of magnitude less than the usual cooling-rates associated with the gun technique. Apart from this, the method suffers from a few other obvious disadvantages. A knowledge of the foil thickness is necessary; this varies from point to point, and was assumed to be 3 × 10^{-3} cm by these investigators. The freezing temperature and the proportion of microconstituents were calculated from the equilibrium diagram. This is, however, not justified in view of the drastic undercooling involved, which changes the proportion of the microconstituents present in the splat. Yet another assumption was that the heat-transfer coefficient is not greatly affected by different alloying elements. In view of the above questionable assumptions and also the fact that Newtonian cooling was assumed to prevail when calculating the heat-transfer coefficient, the above method may not be expected to yield reliable values of cooling rates for splat-cooling techniques.

Although a number of methods for estimating the cooling rates are reviewed above, no method can claim to yield the exact cooling-rate unequivocally. Further the cooling-rate depends upon the type of alloy that is quenched and is also a function of the individual efficacy of the particular apparatus. Hence it seems desirable that the cooling rate is designated for any specific alloy with reference to the apparatus used.

4. Structural Characteristics of Quenched Products

Metallurgists are familar with the technique of quenching by which some alloys can be made to undergo martensitic transformations in the solid state. In some cases it is also possible that the high-temperature phase is retained with the same crystal structure in a supersaturated condition. Liquisol-quenching has now been shown to lead to the retention of supersaturated solid solutions at composition ranges far beyond what can be obtained by conventional quenching techniques. New non-equilibrium intermediate phases have also been prepared by this process in a variety of alloy systems in which no equilibrium intermediate phase exists. Thanks again to this novel experimental technique, metallurgists have been able to get metallic materials in a glassy state, which probably represents the ultimate in quenched products. Added to these exciting results, researchers in this field have also observed unusual properties in materials prepared by liquisol-quenching, such as striking improvements in the mechanical properties and unexpected semiconducting and superconducting properties. The splat-cooled alloys offer interesting possibilities for the study of structure and properties of liquids. Even in those alloys where there is neither extension of solid solubility nor amorphous solidification nor even any non-equilibrium effect, the alloy foils can be expected to be microstructurally different and also to represent more homogeneous solid solutions.

Some of the interesting results obtained so far by the application of splat-cooling techniques will now be discussed under the following headings:
Supersaturated solid solutions,
Non-equilibrium crystalline phases,
Amorphous alloys.

4.1. Supersaturated Solid Solutions

Metastable supersaturated solid solutions are of common occurrence in metallurgy and often constitute stepping-stones to precipitation-hardened alloys. In their formation, an equilibrium transformation in the solid state is suppressed. When the same result is achieved starting from the liquid state, the liquidus and solidus transitions may be crossed fast and the nucleation of a second phase may also be prevented in the solid state. This was first demonstrated by Falkenhagen and Hofmann [4] when they dissolved more of many transition elements in aluminium in the solid state than indicated by the relevant binary equilibrium diagrams.

An unbroken series of solid solutions is expected in a binary alloy system if the two constituent elements have very little atomic size difference, same valency, same crystal structure and little or no electronegativity difference. These prerequisites are contained in the Hume-Rothery rules for solid solubility, which were empirically formulated from a series of experimental observations. Serious violations of these rules are to be found in systems like Ag-Pt, Cd-Zn, Cu-Ag and Cu-Rh, where either a eutectic or a peritectic reaction is met with in place of a continuous series of solid solutions. Duwez *et al* [5] were the very first to show that the separation of the alloy melt into two phases can be completely suppressed in some of these systems by quenching from the melt at a rate of 10^6 to 10^8 °C/sec. Following their pioneering work on the Cu-Ag system, isomorphous solidification has so far been achieved in the Ag-Pt [46], Cu-Rh and Ni-Rh [47] systems. Cd-Zn still appears to be the exceptional system in which there is a little extension of solid solubility of one metal in the other [48]. It is rather difficult to explain this behaviour, unless still higher cooling-rates and lower substrate temperatures lead to the expected isomorphous solidification. A large number of chromium and manganese systems which satisfy all Hume-Rothery rules and do not exhibit isomorphous solidification still await experimentation.

The phenomenon of complete solid solubility in all proportions is not restricted to binary systems involving pure elements only. The pseudo-binary system GaSb-Ge also satisfies all requirements for complete solid solubility, even though under equilibrium conditions it features a eutectic reaction. By subjecting alloys of this system to splat-cooling it was shown that an unbroken series of solid solutions could be obtained [49].

Extensive solid solubility of one element in the other is precluded if any of the Hume-Rothery criteria is not satisfied. Even in such cases, it is possible to retain a higher concentration of the solute in the solvent by splat cooling. For example, the fcc solid solutions in noble metal systems have been found to be generally stable up to a valence electron concentration (VEC) value of 1.4. However, quite a few exceptions have been reported in literature. Especially in the Ag-Si and Au-Si alloys, there is no measurable solid solubility of one element in the other and in the Ag-Ge and Au-Ge systems, a maximum 9.6 and 3.2. at. % Ge only goes into solid solution, with a VEC value far below 1.4. It has been possible by quenching from the melt to extend the solid solubility of Ge in Ag to a maximum value of 13 at. %, which corresponds to an electron-to-atom ratio of 1.39 [50]. In the other three systems, however, it has not been possible with the existing techniques to reach the maximum solid solubility limit.

In the Au-Co and Cu-Co alloy systems, where extensive solid solubility of one element in the other can be expected, there is only a marked increase in the solubility [51]. It is quite likely that these alloys first solidify into a homogeneous solid solution at all compositions and then decompose quickly into two supersaturated solid solutions. A similar situation has been observed with regard to the Ag-Cu system [52] with somewhat lower solidification rates than in the earlier experiments that established isomorphous solidification.

Systematic investigations of the solid solubility of various elements in Co and Ni were undertaken by Luo and Duwez [53] and Klement [54]. They found a marked increase in the solid solubility of the IIIB and IVB group elements and arrived at the interesting conclusion that extension of solid solubility is limited in such cases to either the eutectic or the peritectic composition. For example, Ga dissolves up to 10 at. % in Co under equilibrium conditions and by liquisol-quenching the solubility can be increased to about 21 at. %, while the eutectic composition is 27 at. %. Similar results have been obtained in many systems, although some rare exceptions do seem to exist. This is understandable because beyond the eutectic composition the nucleation of the second phase becomes of primary importance, and cannot be easily suppressed unless the equilibrium solid solubility is exceeded very much on the other side also. An extreme case of this type will result in a continuous series of solid solutions. Table I lists all the results obtained to date on the extension of solid solubility limits of various solutes in different solvents. The above correlation can also be observed from this table.

Interstitial solid solubility of elements such as boron and carbon in solvents like iron, cobalt and nickel has also been investigated [61, 96, 97]. The extension was found to be considerable, especially in the Fe-C system.

In all cases of extension of solid solubility, the lattice parameter of the metastable solid solution generally follows the same trend as under equilibrium conditions. Beyond the maximum limit the lattice parameter naturally remains constant. Surprisingly, exceptions to this behaviour are to be found in the Co-Cu [51] and Al-Si [74] systems, where the lattice parameters are found to deviate in the two-phase regions. This is explained on the basis of the existence of a miscibility gap in the undercooled liquid for the cobalt solid solutions in the Co-Cu system and on the basis of a preferential nucleation and growth of silicon in the undercooled alloys in the Al-Si system. Attempts are also being made to find out the effect of a third element on binary solid solubility [82, 98].

4.2. Non-equilibrium Crystalline Phases

A limited number of transitional phases which are highly metastable at room temperature are obtained during the ageing of supersaturated solid solutions. Familiar examples for these are the Al-Cu and Al-Zn systems. Therefore, it is logical to expect that non-equilibrium phases may be formed on quenching alloys from the liquid state also. In addition, one would be

TABLE I Extension of solid solubility limits in binary alloys on quenching from the melt

Solvent	Solute	Solid solubility limits (at.%)		Concentration of eutectic (E) or peritectic (P) (at. %)	Ref.
		Equilibrium	Extended		
Ag	Cu	14.1	100.0	E – 39.9	5
	Ge	9.6	13.0	E – 25.9	50
	Pt	40.5	100.0	P – 40.5	46
	Sb	7.2	8.0	P – 8.8	55
	Sn	11.5	13.0	P – 14.5	55
Al	Ag	23.8	25.0	E – 37.5	56
			40.0		57
	Au	0.041	0.35	E – 0.72	27
	Co	0.01	0.5	E – 1.0	58
	Cr	0.45	2.85	P – 0.45	4
			2.2		59

TABLE I continued on next page

TABLE I—*continued*

Solvent	Solute	Solid solubility limits (at. %)		Concentration of eutectic (E) or peritectic (P) (at. %)	Ref.
		Equilibrium	Extended		
			2.0		60
			3.0		61
	Cu	2.5	18.0	E – 17.3	62
	Fe	0.026	0.082	E – 0.9	4
			4.4		63
	Ga	9.5	65.0	E – 90.0	64
	Ge	2.8	7.2	E – 30.3	42
			—*		65
	Mg	18.9	36.8	E – 37.4	66
	Mn	0.9	4.7	P – 1.0	4
			3.0		67
			4.3		68
			7.7		69
			5.0		70
			5.1		59
			5.0		60
	Mo	0.07	0.18	P – 0.07	71
	Ni	0.023	5.2	E – 5.7	72
			7.7		73
	Pd	0.0	7.0	E – 7.5	58
	Si	1.59	11.0	E – 11.3	74
	Sn	0.02	0.26	E – 97.8	75
	Ti	0.085	0.19	P – 0.085	4
			0.22		76
	V	0.18	0.55	P – 0.18	4
			0.63		71
			0.65		77
	W	0.024	0.15	—†	71
			0.95		78
	Zr	0.28	2.2	P – 0.28	79
Au	Co	23.5	42.0	E – 27.0	51
Bi	Pb	0.5	6.0	E – 44.0	80
Co	Al	15.5	17.2	E – 19.5	53
	C	3.8	7.8	E – 10.8	61
	Cu	12.0	25.0	E – 94.5	51
	Ga	11.0	18.2	P – 27.0	53
	Ge	15.0	17.4	E – 25.0	53
	Si	14.0	15.0	E – 22.0	53
	Sn	2.5	5.0	E – 20.5	53
Cu	Ag	4.9	100.0	E – 60.1	5
	Be	16.4	19.0	P – 23.6	58
	Co	5.5	15.0	P – 5.5	51
	Cr	0.8	1.8	E – 1.8	4
	Fe	4.5	20.0	P – 4.5	81
	Pb	0.09	1.3	—‡	69
	Rh	18.5	100.0	—†	47
Fe	C	0.3	16.2	P – 0.6	82
	Cu	7.2	15.0	P – 7.2	81
	Ga	17.4	50.0		83
	Ti	9.8	16.0	E – 14.0	58

TABLE I —*continued*

Solvent	Solute	Solid solubility limits (at. %)		Concentration of eutectic (E) or peritectic (P) (at. %)	Ref.
		Equilibrium	Extended		
Ga	Al	0.0	8.0	E - 10.0	64
GaSb	Ge	2.0	100.0	E - 35.0	49
Gd	Ce	—†	30.0	—†	84
	La	25.0	30.0	P - 30.0	84
	Nd	—†	50.0	—†	84
	Pr	—†	35.0	—†	84
In	Bi	4.0	6.0	E - 22.0	85
Mg	Al	11.6	22.6	E - 30.1	66
	Mn	1.55	2.5	P - 1.55	86
	Zr	0.2	0.32	—†	86
Ni	C	2.6	8.2	E - 10.0	61
	Ge	12.0	20.0	P - 22.0	54
			22.0		87
	Nb	14.0	15.1	E - 16.2	88
	Rh	—†	100.0	—†	47
	Si	12.7	15.0	E - 21.4	54
			20.0		87
	Sn	10.4	17.0	E - 19.3	87
			12.0		54
	Ta	15.4	16.6	E - 16.0	88
	V	43.0	51.0	E - 52.0	89
Pb	Ca	0.51	0.93	P - 0.51	4
	Cd	5.9	7.0	E - 28.0	90
			20.0		58
	Mg	5.3	9.5	E - 15.7	90
	Na	12.0	23.8	E - 20.0	4
	Sb	5.9	8.0	E - 11.1	91
			17.0		80
	Sn	29.0	30.0	E - 73.9	90
Pd	W	22.0	44.0	P - 18.5	92
Pt	Ag	22.5	100.0	P - 59.5	46
	W	63.4	67.0	P - 63.4	92
Rh	Cu	9.2	100.0	—†	47
	Ni	—†	100.0	—†	47
Sb	Pb	2.5	11.0	E - 88.9	80
Sn	Al	0.0	2.0	E - 2.2	93
	Au	0.2	4.0	E - 5.9	93
	Bi	13.1	50.0	E - 43.0	93
	Cd	1.5	3.0	P - 2.05	93
	Cu	0.01	6.0	E - 1.3	93
	Mg	0.2	9.0	E - 9.0	93
	Sb	10.2	15.6	P - 10.3	93
	Zn	2.0	3.0	E - 15.0	93
V	Ni	8.0	18.0	P - 34.0	89

Note: *not clearly indicated, †phase diagram not available, ‡ neither a peritectic nor a eutectic system. All the equilibrium data are taken from Hansen [94] and Elliott [95].

interested to know whether the missing Hume-Rothery phases in case of the noble metal systems could be synthesised with the help of rapid solidification techniques.

The first non-equilibrium crystalline intermediate phase to be prepared by rapid quenching from the liquid state is the hcp phase in Ag-Ge system [99]. This initiated further research into other systems and by now no less than 60 non-equilibrium intermediate phases have been reported in literature. Out of these, a few are found to occur with the composition-structure correlations of the so-called Hume-Rothery phases, but in other cases the phases have entirely new crystal structures.

After an extensive study of binary equilibrium diagrams, Hume-Rothery came out with the suggestion that some phases, which he named as electron phases, occur at particular VEC values and with a definite crystal structure. For example, he showed that electron phases with electron-to-atom ratios of 21/14 (1.5), 21/13 (1.62) and 21/12 (1.75) occur in many noble metal systems with the bcc, complex cubic and hcp crystal structures. As in the case of other empirical rules, this rule also is not followed in some systems namely, Ag-Ge, Ag-Si, Au-Ge, Au-Sb, Au-Si, Au-Sn, etc., wherein the Hume-Rothery electron phases are either completely or partially absent. With the application of splat-cooling techniques it has been possible to produce some of these missing phases. For example, hcp phases at VEC values of 1.75 are obtained in Ag-Ge, Ag-Si and Au-Ge systems [100]. Complex cubic γ-brass-type structures are reported in Au-Si [65] and Au-Sn [101] systems at VEC values of 1.62. It is disheartening to note at this stage that even in strictly homologous systems similar phases have

TABLE II Non-equilibrium intermediate phases produced by quenching from the melt

System	Composition range (at. % solute)	Lattice parameter		VEC	Ref.
		a(Å)	at. % solute		
A. SIMPLE CUBIC					
Bi–Au	20–25	3.123	25	4.0 –4.2	105
Sb–Au	16–28	2.984	16	3.88–4.36	105
–Cr	13–24	3.074	10	5.0	106
–In	32	3.050	32	4.36	107
–Mn	20	3.090	10	5.0	106
–Ni	10–20	3.030	15	5.0	105
	10–19	3.030	15	5.0	106
–Pb	50	3.113	40	4.6	80
–Pd	11–25	3.022	11	5.0	105
Te–Ag	20–30	3.055	25.5	4.5 –5.0	103
–Au	20–45	2.960	37.5	3.75–5.0	103
B. BODY-CENTRED CUBIC					
Au–Gd	50	3.593	50	—	108
–Nd	50	3.659	50	—	108
–Pr	50	3.680	50	—	108
–Sm	50	3.621	50	—	108
–Y	50	3.559	50	—	108
Cu–Sn	50	3.528	50	—	109
In–Bi	35–40	3.832	35	3.7 –3.8	85
C. FACE-CENTRED CUBIC					
Ag–In	70–80	4.658	70	2.4 –2.6	110
Au–Si	5–25	7.844	—	1.15–1.75	104
	25–50	19.503	—	1.75–2.50	104
Cd–In	20–85	4.440	20	2.2 –2.85	110
–Sn	10–25	4.443	10	2.2 –2.5	110
Mg–Pb	16–23	4.158	16	2.32–2.46	111
–Sn	13–18			2.26–2.36	112
Zn–Ga	23–37	3.977	23	2.23–2.37	110

TABLE II continued on next page

TABLE II—*continued*

System	Composition range (at. % solute)	Lattice parameters				VEC	Ref.
		a (Å)	*c* (Å)	*c*/*a*	at. % solute		
D. HEXAGONAL							
Cd–Bi	40–60	3.246	3.066	0.945	40	3.2–3.8	110
Cu–Zn	36–42	4.318	9.996	2.315	—	1.36–1.42	113
In–Bi	39–45	3.278	3.084	0.941	45	3.77–3.90	85
	55–72.5	3.318	3.115	0.939	55	4.10–4.45	85
In–Sb	20–40	3.205	2.980	0.930	—	3.4–3.8	114
In–Sn	55	3.190	2.990	0.937	55	3.55	110
Sn–Ag	4	3.174	2.957	0.932	4	3.88	93
–Al	50	3.181	2.980	0.937	50	3.5	93
–Au	4–16	3.177	2.957	0.931	8	3.52–3.88	93
–Ca	10–16	3.151	2.994	0.948	15	3.70–3.80	93
–Cd	15–45	3.173	2.982	0.939	30	3.10–3.70	93
–Cu	10–35	3.188	2.976	0.933	35	2.95–3.70	93
–Ga	20	3.143	2.922	0.930	20	3.8	93
–Mg	12–15	3.186	3.011	0.945	15	3.70–3.76	93
–Pb	10–26	3.220	3.027	0.940	26	4.0	93
–Pd	4–8	3.125	2.979	0.927	8	4.0	93
–Tl				No Details Available			10
–Zn	10–25	3.181	2.963	0.931	15	3.50–3.80	93
E. HEXAGONAL CLOSE-PACKED							
Ag–Ge	10–30	2.897	4.716	1.628	25.7	1.3–1.9	99
		2.898	4.723	1.630	49.7		50
		2.899	4.716	1.627	26.0		29
		2.900	4.712	1.625	21.0		9
Ag–Si	5–25	2.870	4.528	1.578	—	1.15–1.75	104
Au–Ge	10–30	2.885	4.737	1.642	—	1.3–1.9	115
		2.876	4.732	1.640	21		65
Au–Sb	13–15	2.898	4.731	1.633	—	1.52–1.60	65
Fe–C	16.2	2.622	4.318	1.646	16.2		82
Mo–Ru	40	2.764	4.462	1.614	40		29
Ni–Nb	17–21	2.581	4.220	1.635	—		88
Ni–Ta	20–25	2.585	4.229	1.636	—		88
F. TETRAGONAL							
Ag–Ge	15–22	8.116	20.52	2.523	15	1.45–1.66	9
Al–Ge	15–40	13.03	12.04	0.924	30	3.15–3.40	116, 42
	40–80	14.98	16.03	1.07	50	3.40–3.80	117, 42
Au–Ge	25–65	16.444	44.982	2.736	40	1.75–2.95	115
	27	4.127	38.54	9.342	27	1.81	118
		12.39	20.17	1.623	27	1.81	118
		12.97	12.47	0.961	27	1.81	118
Ga–Al	18–35	—	—	1.086	18	3.0	64
In–Bi	15–30	5.014	4.304	0.858	22	3.3–3.6	85
	78–83	6.145	3.296	0.536	78	4.56–4.66	85
Pb–Bi	52–65	14.78	14.99	1.015	52	4.52–4.65	113
Sn–Bi	25	5.88	3.196	0.543	25	4.25	93
	50	6.07	3.251	0.536	50	4.50	93
Tl–Au	28–33	7.07	5.55	0.785	33	3.0	58

TABLE II continued on next page

TABLE II—*continued*

System	Composition range (at. % solute)	Lattice parameters					VEC	Ref.
		a (Å)	b (Å)	c (Å)	α	at. % solute		
G. γ-BRASS-TYPE								
Au-Si	17–20	9.60	—	—	90°	20	1.51–1.60	65
-Sn	28–35	9.80	—	—	90°	29	1.84–2.05	101
H. β-Mn-TYPE								
Au-Si	16–25	6.75	—	—	90°	16	1.48–1.75	113
I. RHOMBOHEDRAL								
Au-Bi	53.5		—	—			3.38	58
Bi-Au	14–45	3.031	—	—	89° 06′	40	3.8 -4.44	105
Sb-Mn	18–25	3.106	—	—	86° 39′	20	5.0	106
J. ORTHORHOMBIC								
Al-Ni	7	6.40	7.56	9.56	90°	7	3.0	73
In-Bi	75	6.26	6.03	3.30	90°	75	4.50	85

not been obtained. To cite an example, the complex cubic γ-brass-type phases are absent in Ag-Ge, Ag-Si and Au-Ge systems and a phase with the hcp structure is not to be found in the Au-Si system. Efforts until now have been concentrated on the production of new phases and the time is perhaps now ripe to think seriously about the seeming ambiguities and apparent contradictions.

Although many investigators had confirmed that extensive solid solutions can form in the Cu-Ag system, Stoering and Conrad [102] had reported the existence of an hcp phase in splat-cooled Cu-Ag alloys by their electron-microscopic studies.

Apart from these electron phases in noble metal systems, a large number of non-equilibrium intermediate phases have been obtained in a variety of alloy systems. These have unit cells ranging from as small as simple cubic with one atom per unit cell [103] to as large as complex fcc with 500 atoms per unit cell [104]. Table II lists all these phases according to the structures in which they crystallise. From a critical examination of this table, it becomes apparent that the crystal structures adopted by the phases can generally be correlated with their VEC values. For example, the simple cubic phases are obtained by adding various solute elements such as Au, Ni, Pd, etc. to solvents like Bi and Sb, which are pentavelent elements. Both Bi and Sb are known to adopt the simple cubic crystal structures under pressure by a slight rearrangement of the atoms. The addition of alloying elements with a smaller atomic size seems to achieve the same purpose and the VEC range over which the simple cubic phase occurs is from 4.4 to 5.0. Simple cubic structures have also been observed in Te-base alloys with Ag and Au. As explained by Luo and Klement [103], the atomic packing in pure Te can be regarded as that of a distorted simple cubic structure. A Te atom in the hexagonal structure of the element has six nearest neighbours – two at a distance of 2.866Å and four at 3.471Å – which lie in three approximately orthogonal planes. In the monoclinic equilibrium Te$_2$Au phase, the six Te neighbours to an Au atom lie in nearly orthogonal planes and the three Au and three Te atoms surrounding a Te atom also lie in nearly orthogonal planes. If the bonding between the two types of atoms can be removed or at least minimised, it is possible that this can result in a simple cubic structure [119]. This is precisely what seems to happen in Te-base alloys.

In a systematic investigation of Sn-base systems with as many as 15 alloying elements, Kane *et al* [93] observed that a simple hexagonal phase with one atom per unit cell (HgSn$_{6-10}$ type) could be obtained by quenching the alloys from the melt. They noted further that the axial ratio for the hexagonal phase decreased with an increase in VEC. It is to be noted in this connection that the simple hexagonal phase occurs in a limited VEC range of 3.00 to 3.80. Soon after these phases were discovered, Weaire and Williams [120] justified the observed axial ratio on the basis of the Ewald energy criterion.

The rapid quenching techniques have also yielded non-equilibrium crystalline phases with entirely new structures which have no parallels in the literature. As pointed out earlier, these phases can be very complex with a large number of atoms per unit cell.

A new hcp phase has been detected [82] in the Fe-C system. This phase is considered to be similar to the high-pressure hcp polymorph of iron [121] and not isomorphous with the hcp ϵ-carbide. A similar correlation has also been observed in the Ga-Al system [64].

Some of these new non-equilibrium phases are found to have either semi- or superconducting properties. This will be taken up in a later section.

4.3. Amorphous Alloys

Vapour-deposition has been a favourite technique for producing amorphous films of various materials. The advent of the gun technique of quenching melts showed for the first time that metallic amorphous phases can be synthesised by techniques other than vapour deposition. By very rapidly cooling from the melt Klement *et al* [122] could solidify Au-Si alloys near the eutectic composition in an amorphous state. This discovery has since been followed up by the production of an appreciable number of amorphous phases in a variety of binary and ternary alloy systems through liquid-quenching.

The presence of an amorphous phase in alloys is generally identified by the lack of diffraction contrast in electron micrographs recorded at high magnifications and the presence of only two or three diffuse rings in the electron diffraction patterns recorded at high voltages. While such observations have been inferred by Duwez and his associates [8] as due to "amorphous" phases, Grant and his co-workers [88, 129] have preferred the word "microcrystalline" to refer to such products. It is rather difficult to choose between the two words since we are probably dealing in both cases with extremely small particles, often less than 20Å, which represents the limit of resolution of the average electron microscope. Until a clear and unequivocal definition of these two expressions is formulated and generally accepted, some confusion in this regard is bound to prevail in the literature. The study of physical properties like specific heat may be expected to throw some light on the nature of the phase, but it is perhaps the field-ion microscope which will eventually offer a conclusive solution of the problem. However, in the following paragraphs, only the word "amorphous" will be used to refer to these unusual phases.

Since the atomic mobility is the highest in the liquid state, the very fast quenching-rates obtainable with liquisol-quenching techniques may be expected to retain the random arrangements of atoms in the liquid state, even after solidification. Although this would appear to represent the very ultimate aim of quenching, the presently attainable cooling-rates are fast enough to prevent crystallisation in quite a few alloy systems. Still higher cooling-rates should in principle be capable of producing amorphous phases in almost all alloys, although their stability at room temperature would be a problem. Table III lists all the composition ranges in alloy systems around which amorphous phases have been produced by fast quenching techniques.

It has long been well known that Se solidifies in an amorphous form even at appreciably low cooling-rates, and that Te, similar to Se in all other respects, solidifies into a crystalline form at comparable cooling-rates. Even on subjection to high enough cooling-rates (as can be obtained in the liquisol-quenching techniques), it was found impossible to prevent the crystallisation of Te. However, addition of alloying elements such as Ga, Ge or In was found to be conducive to the formation of amorphous phases after rapidly quenching the alloys from the molten state. The presence of the amorphous phase in these alloys was identified by broad peaks in X-ray-diffractometric records and diffuse rings in electron diffraction patterns. Foils containing the amorphous phase crystallised, on heating, in a dendritic fashion and their initially poor conductivity was found to increase rapidly after such crystallisation.

Measurement of radial distribution functions from X-ray patterns showed that the first-nearest neighbours of atoms are at almost the same distance in all amorphous alloys irrespective of the solute element added to Te [6]. A similar observation has been made for the second-nearest neighbours also. A point of interest here, however, is that the distances of the first and second nearest neighbours in the amorphous alloys are the same as those in liquid Te. Again the atomic arrangement in liquid Te seems to be very similar to the structure of hexagonal crystalline Te. This observation shows clearly that the alloying elements either effect greater undercooling of the melt or increase the viscosity

TABLE III Amorphous phases produced by quenching from the melt

System	Composition range (at. % solute)	First nearest neighbours		Second nearest neighbours		Ref.
		Distance (Å)	Number	Distance (Å)	Number	
Ag–Si	17–30	—	—	—	—	65
Au–Ge	27	—	—	—	—	115
Au–Si	15–40	2.5	—	—	—	122, 57, 104
Au–Si–Ge	13.7 Ge, 9.4 Si	—	—	—	—	123
Au–Sn	29–31	—	—	—	—	101
B	—	—	—	—	—	124
Cu–Ti	30–35	—	—	—	—	125
Fe–P–C	13P, 7C	2.6	7	4.3	19	126
Fe–Pd–P	10.5 Fe, 20 P	2.76–2.80	13.2–14.6	4.65–4.66	—	127
Mn–P–C	15 P, 10 C	2.63	12	4.47	—	128
Nb–Ni	33–78	2.50–2.68	—	—	—	129
Nb–Ni–Al	39 Ni, 13 Al	2.59	—	—	—	129
Ni–Pd–P	10–70 Ni, 20 P	2.70–2.78	12.7–13.3	4.51–4.60	—	127
Ni–Pt–P	40–80 Pt, 25 P	—	—	—	—	130
Ni–Ta	35–45	2.56–2.63	—	—	—	129
Pb–Au	25	—	—	—	—	65
Pb–Sb	48	—	—	—	—	91
Pd–Ge	18–20	—	—	—	—	8
Pd–Si	15–23	2.79	11.6	4.78	—	131, 132
Pt–Ge	17–30	—	—	—	—	132
Pt–Sb	33–37	—	—	—	—	132
Pt–Si	25	—	—	—	—	132
Rh–Si	22	—	—	—	—	132
Te–Ag	33–40	—	—	—	—	103
Te–Cu–Au	25 Cu, 5 Au	2.70	—	—	—	133
Te–Ga	10–30	2.65–2.70	1.3–2.2	4.05–4.10	11.4–12.7	134, 135, 136
Te–Ge	10–25	2.60–2.70	1.3–1.6	4.00–4.05	11.1–11.9	134, 135, 136
Te–In	10–30	2.70–2.80	2.0–2.3	4.15–4.25	10.8–14.0	134, 135, 136
Zr–Co	28	—	—	—	—	125
Zr–Cu	40–75	—	—	—	—	125
Zr–Ni	20–40	—	—	—	—	125
Zr–Pd	20–35	—	—	—	—	125

of the molten alloy or do both. Further confirmation for the inference that the distribution of atoms in the amorphous phase is the same as that in crystalline one for Te came from the work of Tsuei and Kankeleit [137], who undertook an investigation of the Mössbauer effect and confirmed the existence of a chain structure in an amorphous Te-base alloy. Amorphous phases have been detected in ternary Te-Cu-Au alloys also.

The most interesting potentialities of the rapid quenching techniques lie in their capability to produce metallic glasses or amorphous alloys. The discovery of Au-Si amorphous phase triggered such interest in metallurgists, that as many as 25 amorphous phases were synthesised in a decade in alloys – both binary and ternary – based on Au, Pd and Pt.

Soon after the discovery of the Au-Si amorphous phase, Cohen and Turnbull [138] proposed that a deep eutectic near the metallic element in a noble metal-nonmetal binary system is most conducive to the formation of non-crystalline phases. They put forward the idea that impurity additions, which raise the energy of the crystalline state more than that of the amorphous state, will cause the formation of glassy structures. Such a criterion was found to be not necessary in Zr-base alloys, where non-crystalline phases were detected without the presence of a deep eutectic in the concerned alloy system [125]. Hume-Rothery and Anderson [139] suggested that the stable structures adopted by certain liquid compositions result in a lowering of the melting point at such compositions. Hence the alloy with the eutectic compositions can be expected to have the most stable liquid structure which could be retained by ultra-rapid quenching techniques. This proposal is supported by the observation that most of the amorphous phases in metallic systems are obtained at or around eutectic compositions. There is only the exception in the Pb-Sb system, where the amorphous phase was observed in a hypereutectic (Pb-48 at. % Sb) alloy [91]. An excellent review has recently been prepared by Turnbull [140] to predict the conditions for the formation of amorphous phases. His criterion of a relatively low eutectic temperature in comparison with the melting point of the metallic element, coupled with a metal-rich eutectic composition, has been a very useful guide for choosing systems to observe amorphous solidification. On the basis of these criteria, Pd-Ge, -Sb, -Si and Pt-Ge, -Sb, -Si systems have been chosen and all the eutectics have been found to solidify in an amorphous state after rapid cooling [132].

A point of difference between the crystallisation characteristics of Te-base and metallic amorphous phases is the absence of dendritic crystallisation in the latter, suggesting that the metallic amorphous phases have high thermal conductivities. Some of the interesting properties of both types of amorphous phases are discussed in a later section.

4.4. Constitution Diagrams for Non-equilibrium Solidification

The constitution of liquisol-quenched alloys is generally found to be a sensitive function of the thickness of the foil and hence the cooling rate. Therefore, the non-equilibrium constitution in any alloy system at a given temperature can be correlated with the cooling rate. The constitution can be determined by X-ray techniques and the cooling rates can be measured with any of the techniques described earlier (section 3). An attempt to arrive at a constitution diagram for non-equilibrium solidification was first made by Anantharaman *et al* [115] for rapidly quenched Au-Ge alloys and later on extended to Ag-Si and Au-Si [104] systems. More recently, Suryanarayana and Anantharaman [42] have established a semiquantitative diagram for the Al-Ge system.

In these diagrams, somewhat similar to the usual equilibrium constitution diagrams, the alloy composition is plotted as the abscissa, the ordinate representing the cooling-rate. Similar to melting points of pure metals, we have here the cooling-rates necessary for solidifying the metals in an amorphous state plotted on the *Y*-axis. Similarly, for the alloys of the system, the locus of the points representing the minimum cooling rates for bringing about amorphous solidification of the melts constitutes the "liquidus" of the non-equilibrium constitution diagram. Naturally, the equilibrium eutectic composition will correspond to the cusp in the "liquidus" line of the metastable constitution diagram, since the probability of retaining the liquid structure has been shown to be the highest at or around eutectic composition in various systems [139].

Since the solidification in the liquisol-quenching techniques is instantaneous, a "solidus" line, separate from the "liquidus" cannot be visualised. The line representing the increasing solid solubility of one metal in the other with increasing cooling-rate can be equated with the "solvus" line of normal equilibrium diagrams. In this manner, the whole non-equilibrium constitution diagram can be mapped out incorporating the probable intermediate phases that may be produced. A great advantage of these diagrams is that possible transformation even after the solidification is complete can be incorporated. Such diagrams not only assist in the interpretation of the observed constitution, but also predict the latter under given conditions of composition and cooling-rate.

A somewhat similar type of diagram has been proposed by Giessen and Willens [11] with the difference that the ordinate in it represents the degree of supercooling instead of the cooling-rate. Since the extent of supercooling and cooling-rate are in some way directly related, the nature of the diagrams in both cases is the same. However, as already pointed out, since the diagram proposed by Anantharaman *et al* [115] "uses a directly measurable parameter, and also incorporates the results of possible solid-state reactions, the cooling-rate diagram probably has got greater potential practical applicability than the supercooling temperature diagram" [11].

Giessen [10] had proposed yet another type of diagram for representing the non-equilibrium constitution obtained by rapid quenching from the melt. He suggested that pseudopotential and VEC can be utilised as the two axes to construct "phase" diagrams. Areas representing a particular crystal structure were outlined and these composition ranges were found to have the lowest energy for that structure in comparison to the various competing structures. Hence, any composition which falls in this phase region should have the same crystal structure. Such diagrams obviously have their use, but the phase-boundaries cannot be fixed with certainty in them in the absence of sufficient data and also the impact of cooling-rate cannot generally be taken into account.

Of all the available representations of non-equilibrium constitution, the cooling-rate composition diagrams seem to be the most practical, since they incorporate all necessary details.

5. Properties of Quenched Products

The splat-cooling technique has become very popular in a short time not only because of its ability to produce extremely high cooling-rates, but also because of the unusual properties associated with its products. Thanks to the variations of this technique, it has been possible to produce amorphous ferromagnets, superconducting intermediate phases made up of non-superconducting elements and supersaturated solid solutions with vastly superior mechanical properties. An intensive study of the properties of such non-equilibrium phases is bound to lead to a better understanding of the origin of alloy phases. Some of the important properties of these unusual phases will be discussed in the following paragraphs.

5.1. Supersaturated Solid Solutions

In the early years of splat-cooling, the attention of researchers was concentrated only on extending the solid solubility limits and hence the properties of such supersaturated solid solutions received very little attention. Although the extremely fine grain-size (~ 500 Å) associated with such rapidly solidified alloys was realised as early as 1962 [15], for some years no one attempted the measurement of their mechanical properties to establish the striking increase in strength with supersaturation. Studies were also hampered, to some extent, by the non-availability of suitable samples for mechanical testing. The high dislocation density due to the extremely fine grain-size coupled with solid-solution hardening and, in some cases, dispersion-hardening due to fine dispersion of an intermediate phase may be expected to lead to a tremendous increase in mechanical properties. Such a right combination of effects was achieved by Toda and Maddin [27] in rapidly solidified Al-Au alloys, with as much as a six-fold increase in yield strength in case of an Al-5 wt % Au alloy. As expected, the percentage elongation in such alloys is very low. However, by stabilising the fine grain size with Al_2Cu precipitate along the grain boundaries, superplasticity (elongations up to 600%) has been observed in rapidly solidified Al-17 wt % Cu alloy [141]. A summary of the results obtained so far is presented in table IV.

Varich *et al* [79] made an interesting observation on Al-Zr alloys rapidly solidified by catapulting the melt onto a brass substrate. They found that when the alloys were quenched either from the homogeneous liquid phase or from the two-phase (liquid + solid) region, the lattice parameter and the microhardness value of the Al-solid solution increased with increasing temperature of the melt to be quenched. This trend continued

TABLE IV Mechanical properties of liquisol-quenched alloys

System	wt. % solute	Hardness (VHN)	0.2% offset yield strength (kg/sq.mm)	UTS (kg/sq.mm)	% elongation	Ref.
Al-Al_2O_3	1.2	50	16.9*	19.0*	—	142
Al-Au	5	—	18.3	21.7	low	27
Al-Cr	5	—	—	38	—	17
Al Cu	17	—	—		600	141
Al-Fe	8	260	—	—	—	143
	8	—	—	48	—	17
Al-Mn	2.4	—	26.0*	29.2*	5	28
	9	—	—	48	—	17
Al-Si	11	110	—	50	—	17
Al-V	—	28	—	—	—	77
	4.9	130	31.0*	35.2*	4	144
Al-Zr	2.2	64	—	—	—	79
Pd-Si	6.2	—	84.4*	—	0.1	145

*Converted from values expressed in psi

only up to a certain temperature depending upon the Zr content and beyond that temperature the lattice parameter and microhardness assumed constant values. They did not, however, offer any explanation for this observation.

Relatively few attempts have been made to undertake a systematic investigation of the defects produced in splat-cooled metals and alloys. Furrer and Warlimont [146] did not observe any vacancy complexes in splat-cooled Al-Fe samples, owing to the formation of solute-vacancy pairs or clusters. Thomas and Willens [147] observed an increased vacancy concentration in rapidly quenched Al. Kirin *et al* [148] made use of this observation to explain the observed low value of the lattice parameter of rapidly solidified Al. A similar observation has been made in regard to Al-Sn solid solution [75]. However, the change in lattice parameter is too small to be measured accurately. Further, if this were to be true, even solid-state quenching should result in lowering of the lattice parameter at least in a few cases. But there is no report in the literature so far to this effect. Thomas and Willens [147] as well as Rastogi and Mukherjee [149] measured the vacancy formation energies in Al and Pb, respectively, and showed them to be only 0.11 eV in the liquid against 0.76 eV in the solid state for Al, and 0.35 eV in the liquid state against 0.63 eV in the solid state for Pb.

Although the possible existence of stacking faults in rapidly quenched alloys was suggested earlier [115], a systematic study of their effects on the broadening of X-ray line profiles has only recently been undertaken [150-152]. The occurrence of faulting in liquisol-quenched Ag-Ge alloys was also observed in the electron microscope [153]. The first experimental proof for the absence of lattice strain in quenched foils came from a study of liquisol-quenched Ag and Ag-Ge alloys, which also showed that all the broadening could be attributed to small particle size. Another interesting observation concerns the possible formation of the non-equilibrium hcp phase in the Ag-Ge system through increasing faulting of the close-packed planes of the supersaturated fcc solid solution with increasing solute content.

The thermal stability of the supersaturated solid solutions has generally only been qualitatively investigated to get some idea of their decomposition behaviour [154, 155]. Only one systematic investigation has so far been reported in the literature [156], wherein the decomposition of supersaturated Ag-Cu solid solutions was followed by measurement of X-ray intensity and electrical resistance. Linde [156] found that the activation energy for the transformation to the equilibrium phases was of the order of 33 000 ± 2000 cal/g-mole.

Linde [157] has also measured the enthalpy of solid solution in a splat-cooled Ag-25 at. % Cu to be 1150 ± 200 cal/g-atom in an acid calorimeter.

The process of decomposition in Ag-Cu alloys according to Linde [156], is by the formation of nuclei of the stable phase and proceeds in a discontinuous fashion. However, Nagakura *et al* [52] found in their studies of the same system that in the early stages of decomposition, Cu-rich and Ag-rich supersaturated solid solutions are formed, which at a later stage decompose to equilibrium solid solutions. They conclude that "the mechanism of precipitation from non-equilibrium phase is different from the mechanism of precipitation from the ordinary supersaturated solid solution". The recent electron-microscopic and X-ray investigations of Stoering and Conrad [102] have supported the hypothesis of Nagakura *et al* [52] that solute-rich supersaturated solid solutions are formed at low annealing temperatures in this alloy system.

The decomposition behaviour of supersaturated Al-Si alloys was investigated by Itagaki *et al* [74] by X-ray and electron-microscopic studies, and an activation energy of about 14 to 20 Kcal/mole was arrived at for precipitation in case of alloys with different Si contents. They observed that the very fine Si particles grow to sizes of the order of 0.1 to 0.2 μm when aged at 300°C for an hour. In spite of the absence of any crystallographic relationship between the precipitate and the matrix, the latter was found to be considerably strained, resulting in a lowering of the lattice parameter.

Optical metallographic examination of the surface of the foils obtained by liquisol-quenching has been shown to display interesting structural features which aid in a better understanding of the solidification sequence [158-161]. Recently Kranjc and Paić [162] showed that contact X-ray microradiography helps in detecting undissolved Fe particles in splat-cooled Al-Fe samples, which otherwise is difficult either by X-ray or by electron microprobe techniques.

5.2. Non-equilibrium Crystalline Phases

In spite of the production of a large number of intermediate phases in a variety of alloy systems, any generalisation is made difficult because of apparently dissimilar behaviour in homologous systems. To cite an example, Hume-Rothery electron compounds at VEC values of 1.75 with the hcp structure are observed in Ag-Ge, Ag-Si and Au-Ge systems, but such a phase seems to be absent in the Au-Si system. Similarly, two tetragonal intermediate phases are produced under non-equilibrium conditions in the Al-Ge system, but not a single intermediate phase could be synthesised in the Al-Si system. However, empirical correlations are slowly emerging between the thermodynamic properties of liquids and the intermediate phases [163, 164]. For example, it has been shown that the inflections in $\overline{\Delta S}{}^{\mathrm{xs}}_{\mathrm{A}}$ versus N_{B} plots, where $\overline{\Delta S}{}^{\mathrm{xs}}_{\mathrm{A}}$ is the partial excess entropy of species A and N_{B} is the atom fraction of species B, correspond to the compositions of non-equilibrium intermediate phases [164].

A somewhat exciting result has recently been reported by Ramachandrarao and Anantharaman [118], which indicates that the temperature from which the melt is quenched may have a pronounced effect on the constitution in solidified alloys. They have shown that three different non-equilibrium intermediate phases could be produced by quenching the Au-Ge eutectic melts from 480, 550 and 800°C. All these three tetragonal phases are structurally interrelated and their structures seem to be related in some way to the existence of different sizes of atom clusters in the liquid state. If one assumes that a given alloy can exist in the liquid state with different arrangements of atoms at different temperatures and that such atom clusters can prove sources of nucleation, it is not difficult to understand the formation of a series of interrelated structures on quenching the alloy from the melt. However, such a phenomenon has not been reported in any other system.

The stability of a number of intermediate phases has been investigated both after deformation and/or annealing. It has been observed that certain phases are stable only at liquid nitrogen temperatures [93], while a few are stable up to temperatures as high as 870°K [129]. The metastable simple cubic phase in a Te-37.5 at. % Au alloy did not transform to the equilibrium phases even after 50% reduction in thickness at liquid nitrogen temperature [103].

Very few investigations have been reported as regards the thermodynamic stability of the non-equilibrium intermediate phases [165-167]. From a knowledge of the variation of free energy with temperature in Au-Sb [165], Pb-Bi [166] and Au-Sn [167] systems, it has been concluded that the intermediate phases produced by splat-cooling are unstable at all temperatures. The amount of undercooling required for the formation of non-equilibrium phases has also been deduced from the above investigations.

Some of the intermediate phases produced by quenching the alloy melt are found to be superconducting at temperatures rather close to absolute zero. An interesting example is that of the Au-Ge tetragonal phase which is superconducting up to 1.63°K [168] although neither Au nor Ge is superconducting. Equilibrium intermediate phases when quenched from the liquid state are found to have higher superconducting transition temperatures, probably because of better homogeneity. Table V lists the

TABLE V Superconducting transition temperatures and structures for some non-equilibrium phases

System	at. % solute	Crystal structure	Transition temperature, °K	Ref.
Ag–Ge	20	hcp	0.85	168
Ag–Te	66.7	Simple cubic	2.6	168
Al–Cu	0.85	fcc	2.95	169
Au–Ge	50	Tetragonal	1.63	168
Au–Te	62.4	Simple cubic	1.62	168
Mo–C	50	fcc	14.3	170, 171, 172
Mo–Ru	40	hcp	8.7	29
Nb–Al	25	bcc	3.1	14
Nb–Ge	25	Cubic	17.0	173
Ta–Al	25	bcc	1.59	14
Ta–Au	25	bcc	0.82	14
W–C	50	fcc	10.0	170

superconducting transition temperatures of some of the non-equilibrium intermediate phases along with their crystal structures.

The possibility of optical metallographic identification of non-equilibrium intermediate phases has been highlighted recently by Suryanarayana and Anantharaman [174] by their identification of the tetragonal Al-Ge phase in the form of regular six-faced pyramids.

5.3. Amorphous Alloys

Amorphous phases constitute the majority of non-equilibrium phases whose properties have been studied in great detail. Efforts have been made to relate the structure of these phases to that of the liquid. Although the problem is quite complicated, the large number of investigations carried out so far indicate that there is a definite relationship between the properties of the liquid and those of the amorphous phases. As has already been pointed out, the arrangement of atoms seems to be the same in the melt and in the amorphous phases in Te-base alloys.

Measurements of electrical resistivity give considerable information on the nature of amorphous to crystalline transformation. Hence, electrical resistivity has proved a favourite tool in the study of amorphous phases obtained by rapid quenching from the melt [175]. In Te-base alloys containing Ga, Ge or In, measurement of electrical properties is rendered difficult because of low conductivity. This difficulty can be overcome by addition of Cu, which still results in an amorphous phase, while the addition of Ag or Au yields simple cubic crystalline phases. The electrical resistivity measurements of ternary Te-Cu-Au alloys can thus be expected to throw some light on the nature of amorphous-to-crystalline transformation.

The electrical properties of amorphous $Te_{70}Cu_{25}Au_5$ alloy obtained by the piston-and-anvil technique clearly indicate its semiconducting property [133]. Although theoretical arguments have been put forward for the occurrence of semiconduction in both liquids and amorphous solids, this amorphous phase constitutes the first experimental proof for this hypothesis. Gubanov [176] has shown that crystallinity is not a prerequisite for semiconduction and that a band structure can exist in amorphous solids also as long as there is short-range order. Duwez [8] clearly showed by means of two-dimensional simulated models that short-range order can be well visualised even in a random distribution of atoms. The intrinsic energy gap for this amorphous phase was found to be 0.2 eV. Further proof for semiconduction came from measurements of thermoelectric power [133]. It has been shown that the thermoelectric power of the amorphous semiconductor is about 50 times that of the same alloy in the equilibrium crystalline state and that it increases with temperature in the extrinsic range and decreases slowly in the intrinsic range. Further studies on amorphous semiconductors may be expected to allow an extrapolation of the band theory to non-crystalline solids.

In contrast, the metallic amorphous phases based on Au, Pd and Pt show that the room-temperature resistivity is between two to three times the resistivity of the corresponding stable crystalline phases obtained on annealing. The resistivity decreases with decreasing temperature with a small temperature coefficient of the order of $10^{-4}/^\circ C$ and the resistivity at $2.3^\circ K$ in a Pd-20 at. % Si alloy was observed to be approximately 95% of the room temperature value [131]. This increase in resistivity and small temperature coefficient of resistivity can be attributed to the large disorder of the amorphous structure which makes the contribution of phonon-scattering small.

Maitrepierre [177] undertook an extensive investigation on the structure of amorphous Ni-Pd-P alloys obtained by the piston-and-anvil technique and showed that the resistivity of the amorphous phase increases with temperature up to the crystallisation temperature at which it drops sharply at first, then reaches a minimum before increasing again up to the melting point of the alloy. As expected, the crystalline alloy exhibits a larger temperature coefficient of resistivity ($\sim 10^{-3}/^\circ C$) than the amorphous phase ($\sim 10^{-4}/^\circ C$). A similar observation has also been made with regard to the amorphous phase in Ni-Pt-P alloys [130].

In order to establish a clear relationship between the amorphous and liquid phases, it is necessary to carry out the resistivity measurements of the amorphous phase up to the melting point of the alloy. Unfortunately, the crystallisation at a lower temperature precludes that possibility. However, it is significant that Crewdson [142] reported that the electrical resistivity portions of the amorphous and liquid phases plotted against temperature can be joined together into a single smooth curve. This suggests that the structure of the amorphous phase is in some way related to that of the liquid.

A striking observation has been made in the low-temperature resistivity measurements of amorphous phases containing small amounts of a ferromagnetic element. It was found that the electrical resistivity reaches a minimum around 10° K, depending upon the alloy and its composition. This was attributed to the Kondo effect [178], which was earlier observed only in crystalline alloys. This effect is explained on the basis of the existence of localised magnetic moments in the alloy. It could explain the occurrence of a resistivity minimum in crystalline alloys, but fails to justify the same in the case of amorphous alloys [179, 180].

One of the exciting discoveries of the splat-cooling technique is the production of amorphous ferromagnets. The occurrence of ferromagnetism in noncrystalline solids has earlier been predicted by Gubanov [176]. He suggested that ferromagnetism does not require any long-range periodicity of atoms and his calculations based on d-d spin interaction between nearest neighbours in a non-periodic lattice give qualitative results similar to those obtained for crystalline solids. Because of an increased atomic distance in the amorphous state, the numerical value of the exchange integral can be different. Gubanov concluded that a crystalline solid which is not ferromagnetic may become so after transition to the amorphous state, and also that an amorphous solid could exhibit a lower magnetisation and a lower Curie temperature than its crystalline counterpart. Handrich [181] proposed a model in which the exchange integral always decreases owing to the structural fluctuations in the amorphous solid. Thus, an amorphous solid will always have lower magnetisations and Curie temperatures than the crystalline solids. This fact is amply borne out by experimental observations.

In order to study the magnetic properties of amorphous solids, either magnetic impurities such as Fe, Co or Ni are introduced into non-magnetic Pd-Si amorphous alloys or amorphous alloys are produced based on Fe, Co or Ni. The former are naturally weakly magnetic because of the limited quantity of the ferromagnetic element, while the latter are strongly magnetic. Most of the work in the former class seems to have been done on $(Pd_{1-x}M_x)_{80}Si_{20}$ alloy, where M is a ferromagnetic element and $x = 0.005$ to 0.07 for Fe, 0.12 for Co and 0.15 for Ni. During rapid heating of these alloys, about 1000 cal/g-mole of heat is released around 420°C, indicating the onset of crystallisation. Some of the important magnetic properties are tabulated in table VI.

In the second category of amorphous ferromagnets, namely those based on Mn, Fe or Ni, it has been observed that the magnetic moment of Fe is less in a Fe-P-C amorphous phase compared to that of pure Fe [182]. This was explained in terms of addition of electrons from the P and C atoms to the 3d band in Fe. The Curie temperature is also found to be approximately 60% lower than that of pure Fe, indicating considerable reduction in the exchange integral value.

Because of the great similarity between Fe and Mn atoms, Sinha [186] investigated the temperature- and field-dependence of magnetisation of a continuous series of amorphous solid solutions between $Fe_{75}P_{15}C_{10}$ and $Mn_{75}P_{15}C_{10}$. He found that the Fe-rich alloys are ferromagnetic and that the magnetic moment at 0°K decreases linearly from 2.07 μ_B/Fe atom in $Fe_{75}P_{15}C_{10}$ to 0.22 μ_B/(Fe, Mn) atom in $(Fe_{60}Mn_{40})_{75}P_{15}C_{10}$. He had also observed a peak in the magnetisation curves at temperatures between 15 and 40°K in the Mn-rich alloys, which was ascribed to the presence of ferrimagnetism in conjunction with parasitic antiferromagnetism over some local regions in the amorphous structure. How-

TABLE VI Magnetic properties of amorphous alloys produced by liquisol quenching.

System	at. % solute	μ_B	Curie temperature (°K)	Ref.
Fe–P–C	12.5 P, 7.5 C	2.10	586	182
Gd–Ce	30	4.2	160	84
Gd–La	30	17.0	185	84
Gd–Nd	50	1.7	145	84
Gd–Pr	35	3.5	165	84
Mn–P–C	15 P, 10 C	1.14	—	183
Pd–20 Si	1 Cr	3.58	—	184
	7 Cr	2.98	—	184
	7 Fe	5.6	28	185

ever, Hasegawa [183] did not find such a phenomenon in his investigations on amorphous Mn-P-C alloys.

Chen and Turnbull [187-190] measured the specific heat and glass transition temperatures of binary and ternary amorphous alloys based on Au-Si and Pd-Si alloys. Typically, the specific heat of amorphous Au-18.6 at. % Si alloy was measured with a differential scanning calorimeter and found to exceed that of the solid by 0.2 to 0.4 cal/g-mole°K [187]. This observation was attributed to changes in configurational entropy as a result of the random arrangement of atoms in the amorphous phase.

It is heartening that a considerable amount of work is at present being done at the CalTech Laboratories in Pasadena, where the gun technique of rapid solidification was originally developed, on the nature and properties of amorphous phases. A clear relationship between the liquid and amorphous alloys may well be expected to emerge in due course as a result of such studies.

6. Conclusion

In spite of the impressive volume of data on rapidly solidified alloys, it seems to be too early to think in terms of industrial applications of splat-cooled alloys. However, some contours of the possibilities in this direction are already visible.

Willens *et al* [191] fabricated an inductance-thermometer based on rapidly quenched vic-alloys with a temperature resolution better than 1 mdeg. Goldstein *et al* [192] have observed that the composition of the liquisol-quenched alloys is very uniform as revealed by electron microprobe analysis and hence such alloys may well be used as microprobe standards. Wang *et al* [193] found that tough transparent polyethylene films can be produced by quenching from the melt instead of through conventional extrusion and subsequent quenching of the film as it emerges from the hot rollers. Most recently, Tsuei and Duwez [194] have developed an amorphous alloy resistance thermometer that can measure temperatures from 1.5 to 300°K. The thermometer made up of the amorphous rapidly solidified $Cr_7Pd_{73}Si_{20}$ alloy has the special feature that its sensitivity increases with decreasing temperature. It has a thermo-emf of 48 μV/°K at 20°K and 60 μV/°K at 10°K with 2 mA current. Apart from all these applications, the liquisol-quenching technique has already proved its usefulness in preparing thin enough specimens for transmission electron microscopy [15]*.

Although the technique of rapid solidification is equally applicable to all types of materials, relatively little work has so far been done on non-metallic materials [195, 196]. The next few years may well alter this picture.

Looking back on a decade of quenching from the melt, it is safe to assert that liquisol-quenching has come to stay as an important experimental and research technique in metallurgy and materials science. The next decade will perhaps establish it as a standard production technique for materials needed in special industrial and laboratory devices.

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*Note added in proof
R. C. Dorward (*J. Nuclear Mat.*, **27** (1968) 235) has utilized the splat-cooled samples for neutron activation analysis standards because of their greater homogeneity in comparison to samples prepared by other techniques.
The authors are grateful to Professor R. W. Cahn for bringing the above reference to their notice.

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