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AN EXPERIMENTAL STUDY OF
SOME QUENCHING TECHNIQUES AS APPLIED
FOR CERTAIN FCC METALS AND ALLOYS

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The experiments revealed the drop method as developed in our laboratories to provide the most reliable operation. Typical quenching rates are of the order of 4×10^4 °C/sec in water and 500 °C/sec in LN_2.

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ABSTRACT

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KEYWORDS

QUENCHING	SILICONES
FCC	NITROGEN
METALS	CALCIUM CHLORIDES
ALLOYS	AMMONIA
TEMPERATURE	HELIUM
WATER	AIR

List of contents

I. Introductory Remarks to the Quench Problem

For point defect studies, quenching has become one of the most important methods for evaluation of the characteristic data of vacancies and vacancy clusters. The significance of quenching lies in the fact that the only type of defect likely to be frozen-in in appreciable concentration are vacancies and vacancy associates, respectively. Thus quench experiments offer the possibility of studying behaviour and properties of vacancy-type defects without the complications which arise when appreciable concentrations of other defects such as interstitials, for example, are present.

It is a familiar result of statistical thermodynamics that the equilibrium concentration of any species of defect at temperature T is given by:

$$c = c_o \exp \{ - (Q_f - T\Delta S_f) / kT \} \tag{1}$$

where Q_f is the formation enthalpy (energy) and ΔS_f the change in entropy associated with the defect. This equilibrium concentration is achieved and maintained in a crystal by diffusion of defects from and to internal and external surfaces.

In an ideal quenching experiment the high-temperature-concentration of defects is preserved unchanged at a lower temperature at which the defects are frozen-in. With a finite cooling rate this cannot be achieved because of various processes which tend to maintain thermodynamic equilibrium by eliminating excess defects. Already NABARRO (1) has pointed out that dislocations can act as sinks for vacancies and BARTLETT and DIENES (2) have indicated that in non-equilibrium conditions such as encountered in quenching, some vacancies will combine to vacancy pairs (or clusters).

At any temperature the rate of establishing a new equilibrium defect concentration is determined by the mean free path between defect sources and sinks, the migration energy of defects, the binding energy between defects and by the temperature itself. The sink concentration c_s, the migration activation energy Q_m and the binding energy of vacancy clusters (e.g. divacancies) Q_b being considered constant for a certain material, only the quenching temperature and quenching rate can be varied by the experimentator.

For reliable detection of point defects by electrical resistivity measurements, the main requirement is to freeze-in a (single) defect concentration as high as possible. Normally this makes the fastest quench desirable since otherwise appreciable losses of (single) vacancies may arise by migration to and annihilation at sinks or by formation of vacancy associates (during quench). The higher the quench temperature is, the higher the quench speed applied has to be since defect mobility and concentration increase exponentially with temperature and hence the loss rate during quenching too. In consequence for a fixed quench rate the thermodynamic equilibrium concentration of vacancies at quench temperature can be retained almost completely only up to a certain temperature. Above this temperature losses become appreciable and the logarithm of the quenched-in resistivity does not increase anymore linearly with the reciprocal temperature.

On the other hand quenching always produces some thermal stress since the inner and outer

parts of the specimen cool at different rates. If the thermal stress becomes sufficiently large to cause plastic deformation, moving dislocations will be generated which can act as sinks or sources for defects. Obviously this process which is forming an upper limit for the allowable quench rate, is related to the sample's dimensions and its thermodynamic data (specific heat, thermal conductivity etc.).

For interpreting thoroughly some recent experiments and results of quenching on FCC alloys [e.g. on a-brass (3)], an exact investigation of the various quench techniques applied to these materials and their characteristic quench rates appeared to be worthwhile.

2. Quenching Techniques

The various quenching methods described hereafter are most commonly used to quench materials as FCC metals and alloys from medium temperatures up to 1000°C. As quenching media we considered water, liquid nitrogen and to some extent He-gas, silicon oil, $CaCl_2-$ and NH_4OH –solutions. Water is the most suitable quenching medium because of its high thermal capacity, thermal conductivity and heat of vaporization. It is specially used for non-reactive materials, whereas silicon oil, liquid nitrogen LN_2 or He—gas are utilized for quenching of materials which tend to oxidize or react with water (for example UC) and for materials in which the defects migrate already at very low temperatures. In the latter case also certain aqueous solutions cooled to rather low temperatures (ca. −40°C) by a cryostat may be applied succesfully.

The equipments have been installed in our laboratories, and some of them have already been described in connection with other experiments (3,4,5). Therefore we give here only some brief indications.

2.1 Tilt Method.

With this technique, the sample to be quenched is inserted inside a quartz tube into a horizontal resistance furnace (Fig. 1). For real quenches, the specimen can be kept under an inert gas (He,Ar) atmosphere to prevent oxidation and evaporization. For our present experiments, the tube was open at one end and a thin thermocouple was attached to the sample. Having reached the quenching temperature, the tube is quickly taken out of the furnace, tilted over a nearby quench bath (water, liquid nitrogen etc.), and the specimen is falling by its own weight into the bath. To compensate for the stiffness of the measuring thermocouple (diameter of wire 0,2mm) an additive stainless steel piece has been attached to it.

2.2. Pull Method

The furnace, tube and sample are in the same arrangement as above. In contrary to method 2.1, here the quench bath is brought directly to the opening of the quartz tube and the sample for quenching is drawn out of the furnace by means of a thin wire which is attached to it and passing below a fixed axis inside the bath (Fig. 2).
For rate determinations the wire has been substituted by a thin thermocouple (no additive weights being used).

2.3 Drop method

This technique has recently been developed for our laboratory and utilizes a vertical resistance furnace (Fig. 3). In this furnace a quartz tube supplied with connections to a vacuum system and a (inert) gas inlet valve is installed. The lower end of the tube is closed during the heating period by a stopper. At the top the tube is closed by a feedthrough for current leads and a thermocouple. The current leads end in a filament wire (0,05 m/m) at which the specimen is attached by means of a thin nickel wire charged by an additional stainless steel weight (ca. 50 g.). To start quenching, the filament wire is heated till it breaks and having removed the ground stopper before, the sample drops into the quench medium put beneath. Since the sample tube is immersed at its lower end into the quench bath, the quenches can be performed almost perfectly in an inert atmosphere.
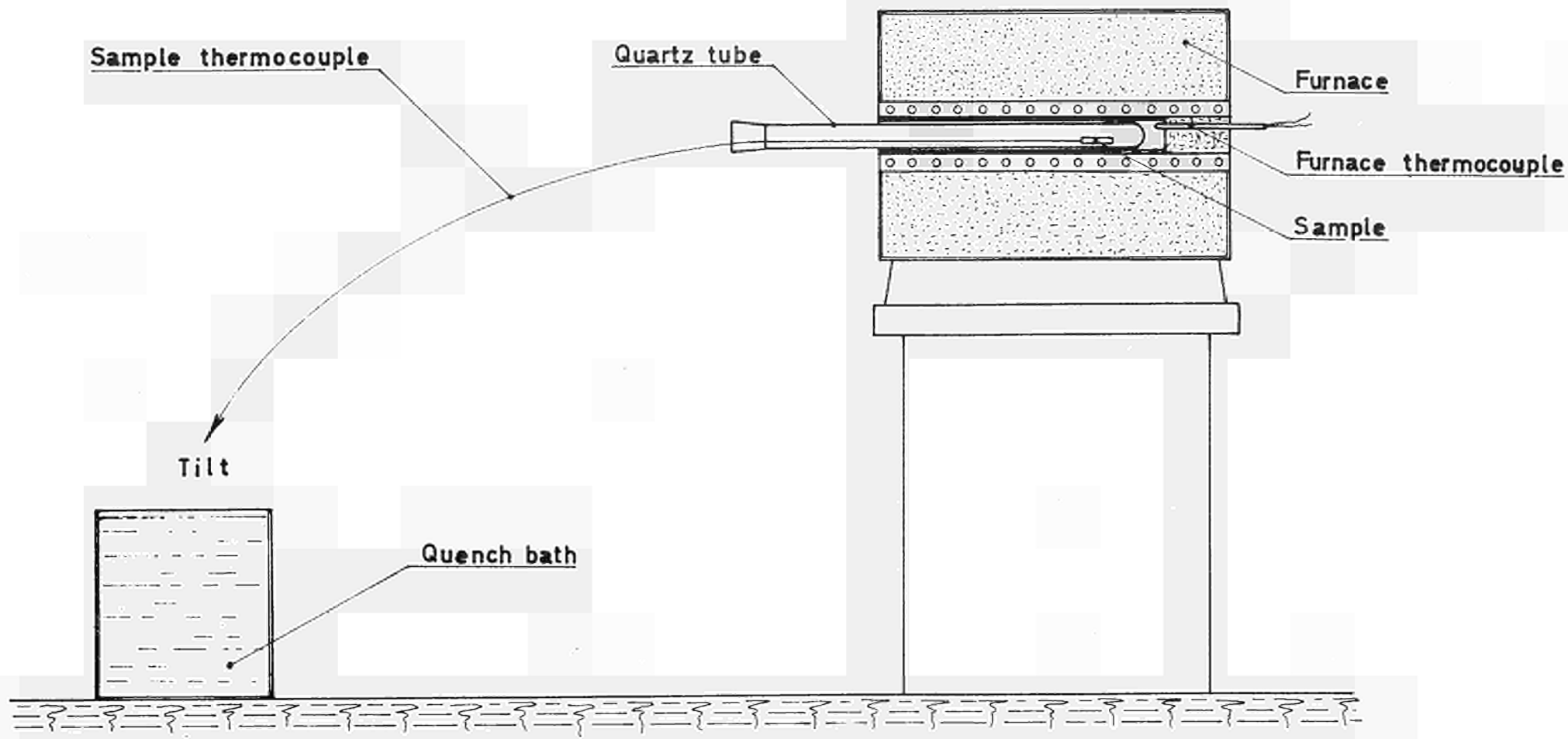
Sample thermocouple

Quartz tube

Furnace

Furnace thermocouple

Sample

Tilt

Quench bath

Fig. 1 Schematic drawing of the experimental arrangement for "tilt method" quenching.

Sample thermocouple(drawing wire)

Quartz tube

Pull

axis

Furnace

Furnace thermocouple

Sample

Quench bath

Fig. 2 Schematic illustration of the experimental installation for "pull method" quenches.

- 9 -
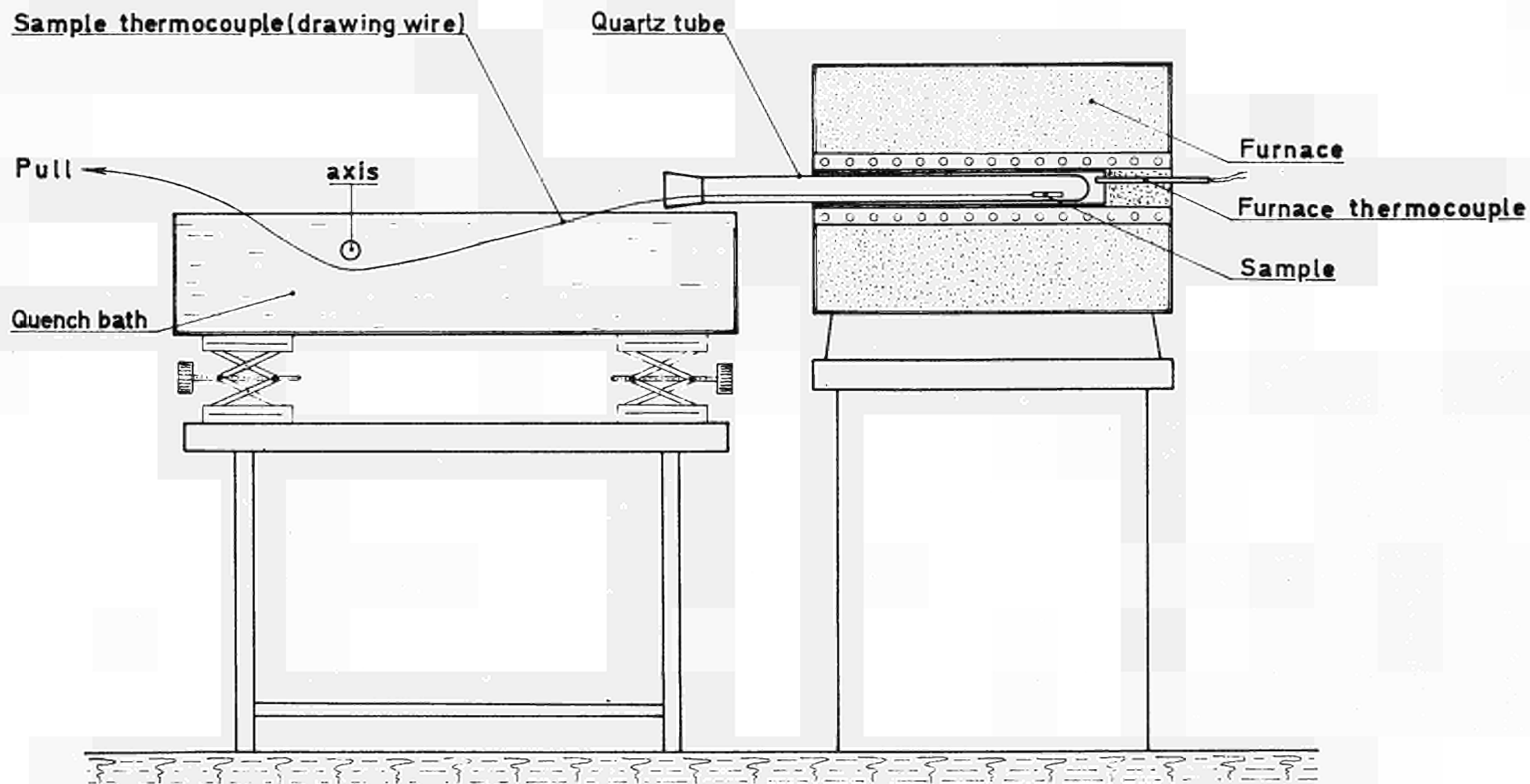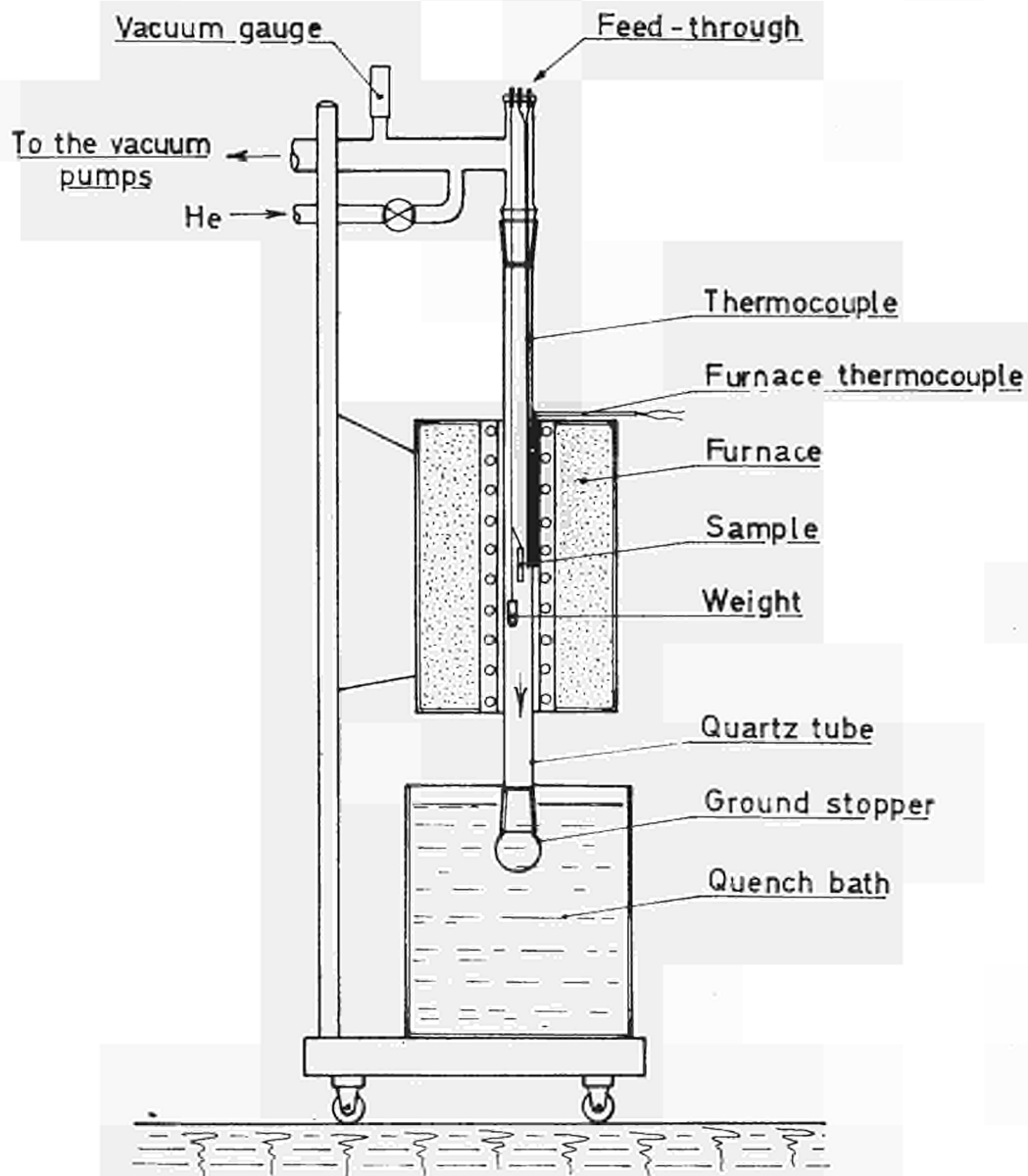
Fig. 3 Schematic draft of the experimental arrangement for "drop quenches"

From above it is already evident that this technique should provide a rather reproducible quench because manual operation is eliminated. In addition the real sample (quenching) temperature can be measured more precisely by means of the sample thermocouple nearby.

For our rate determination experiments, the upper end of the tube had to be kept open, and the nickel wire was replaced by the measuring thermocouple.

Some improvement of the technique described above can be achieved by utilizing a HF-generator instead of the resistance furnace *). Thus, higher quenching temperatures —as needed for other materials (UC, refractory metals etc.)— can easily be obtained and moreover the duration of fall (fall length) could even be reduced. Varying properly the fall height, the sample will arive with different speeds at the quench bath surface and thereby various quench rates can be settled. Attention should be paid to the fact, that with greater fall length also the temperature (heat) losses of the sample will increase.

*) For non-metallic samples an auxiliary pre-heating might then be necessary.
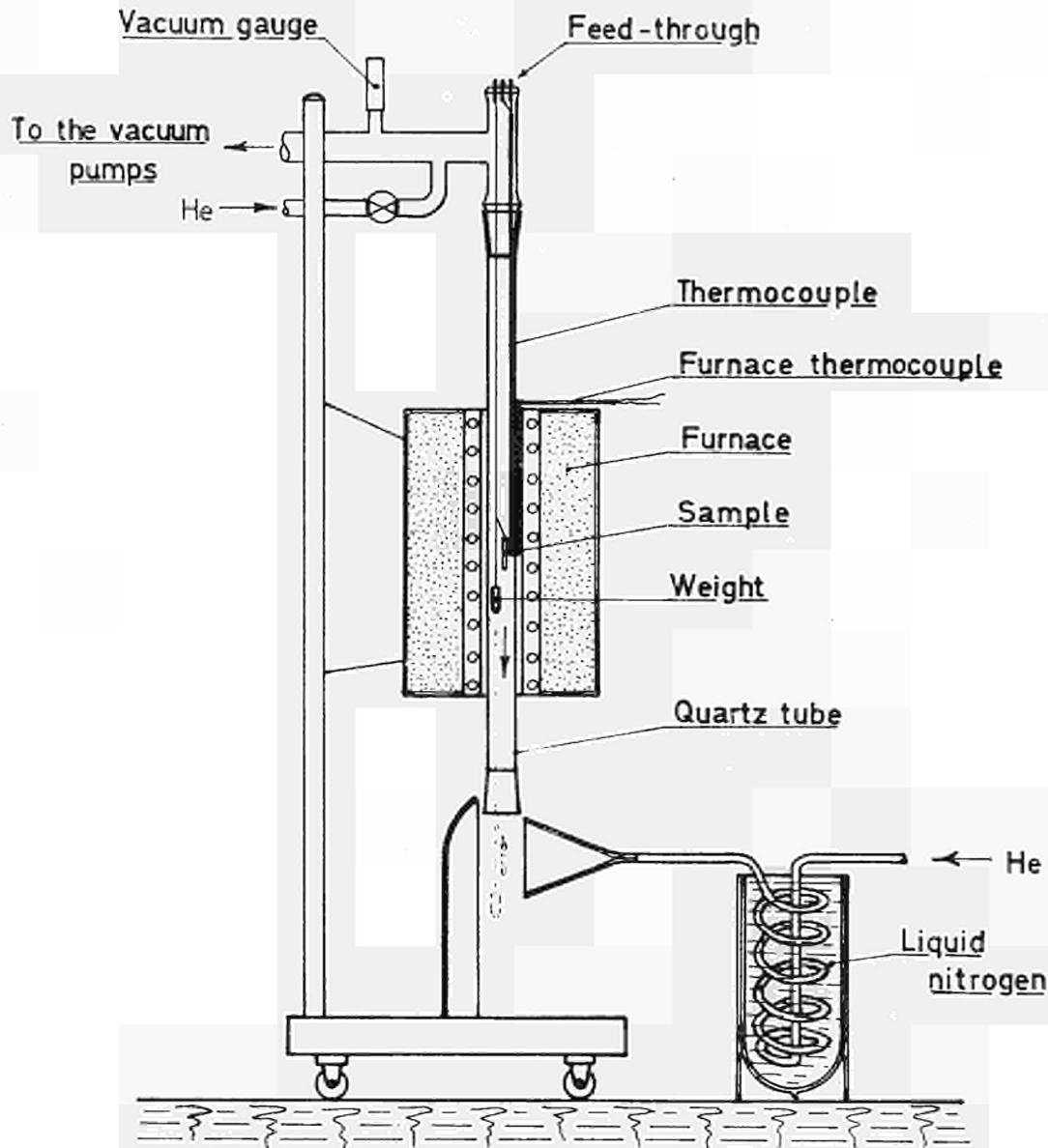
Fig. 4 Schematic drawing of the experimental installation for "gas quenches"

For a more flexible way of setting different quench rates, we may here also suggest another modification of the drop method: to the lower end of the sample a thin wire is connected passing through an u-shaped tube filled with the quench medium. By winding up this wire by means of a high speed motor, the specimen can be drawn into (and through) the quench bath. Attention must be paid to a proper performance of the experiment in order to prevent eventual deformation of the sample during the quench.

To determine the exact quench temperature for temperatures higher than 1200°C an automatic pyrometer or a calibrated photocell focussed onto the bath surface might be proposed as a con-

venient means. However the determination of the quench rate will be rather difficult since the fall of the specimen can hardly be pursued by a pyrometer, and might only be executed by resistance measurements.

For the high temperature region and for quenching from melt it may also be suggested to make use of the levitation technique as described for example by Van AUDENHOVE and JOYEUX. (6) Here the sample is levitated and heated by a H.F. electromagnetic field inside a suitable formed coil.

A further improvement of the actually used drop method is foreseen by the installation of an electromagnetically operated shutter in place of the ground stopper. For higher temperatures a tube of Al_2O_3 instead of the quartz tube will be used.

2.4 Gas quench

A convenient method for quenching highly reactive materials is the "gas quench" by means of blowing a precooled gas blast onto the sample. To this purpose after its heating period, the sample is dropped suddenly just outside the lower end of the tube blowing simultaneously a stream of cold heliumgas on it. This helium becomes precooled in a liquid nitrogen heat-exchanger to about $-150°C$. (see Fig. 4)

Using HF- or direct resistance heating, the sample could remain at the heating position, current switched off and the gas blast sent directly onto it.

3. Performance of Experiments

The quench rate of the various techniques had to be determined by quenching a sample from different temperatures into different quench media and recording the temperature vs time decrease.

Measurements of quench speeds are considered to be somewhat difficult due to a possible error caused by the method of temperature detection.

Both applicable temperature control techniques —either measurement of the sample resistance or detection of the EMF output of a thermocouple are subjected to a temperature deficiency due to the thermal conduction along the leads attached to the sample *).

We decided here for temperature measurements by a thermocouple because of the more direct correlation between the measured voltage output and temperature (specially in case of an alloy sample) and because of only two — instead of four — wires being applied.

It should be mentioned that for the rate determinations a linear dependence of the thermocouples' EMF on temperature is assumed which is, of course, only valid in a first approximation. The sample was made of α-brass and had about the dimensions of the samples used for our resistivity measurements (50 x 5 x 0.1 mm) and a weight of ca. 0.4 g.

For the quench bath we used either a 30 cm high container of 25 l water or oil (T = $18^\circ \pm 1^\circ$C) or a 20 cm high styropor vessel containing ca. 7 liters of liquid nitrogen or of the aqueous solutions **).

The temperature was measured by a thermocouple the wires of which were spot welded ca. 5 mm distant from each other onto the sample by a condensator discharge. Thus one can be rather confident to measure the real surface sample temperature and to avoid the heat capacity of a hot junction of the thermocouple. The temperature measured is that of a certain area and not only that of one point. Furthermore it could be controlled by this arrangement if the thermocouple had lost contact to the sample during quenching.

As can be seen from the results in section 4, the choice of a suitable thermocouple may influence considerably the curve shape. It became evident that the use of very thin wires is strongly recommended in order to avoid heat conduction from or to the sample giving rise to a temperature deficiency. For this reason we took asbestos insulated Fe-Konst-thermocouples (0,45 mm ϕ) the wires of which were of 0,2 mm diam.

Due to the fact that the heat conductivity of brass (0,26 cal cm/cm^2 sec $^\circ$C at 18°C) is greater by orders of magnitude than that of water (0,00143 cal cm/cm^2 sec $^\circ$C at 20°C) or nitrogen (0,00034 cal cm/cm^2 sec $^\circ$C at -196°C) and due to the small sample thickness (0,1 mm), the

*) An ideal measurement would mean contactless temperature detection as it could be provided in certain limits by an automatic pyrometer or a UR-sensor — although with rather great experimental difficulties (see 2.9).

**) For method 2.2 a 30 cm high container with 100 l water was used.

measured surface temperature can be assumed to correspond in good approximation to the real sample temperature, i.e. there should exist no great temperature gradient which may give rise to thermal stresses (see Par. 5).

The thermocouple signal has been recorded by a Tectronics Type 556 Dual Beam Oscilloscope (reference temperature 25 ± 1°C). The oscilloscope was triggered either by self-triggering or by manual external triggering — the latter mode being more secure if executed with rather good simultaneousness. The oscilloscope display curve itself was recorded by a Polaroid Land Camera *).

Some previous rate determination experiments had been performed by means of a recorder oscillograph (galvanometric system Visicorder-HONEYWELL [3]) providing the possibility of long time recording, i.e. no triggering was needed. Further the time scale was greater by a factor 5. However using for data evaluation an enlarged copy of the oscilloscope display curve, the data obtained with the two different techniques agree fairly well.

*) Normally, in addition to the quench curve there has been also recorded the initial ¡sample temperature T_F and the final (bath) temperature) T_E.

4. Results

Indications on quenching speeds found in literature (9,19) are often lacking of a proper definition. Sometimes the time for half of the total temperature drop is taken as quench rate. We consider this not adequate since the loss of vacancies by annihilation or clustering is possible in the whole temperature range where vacancies have a marked mobility. Rate determinations depend on the cooling law being assumed. LOMER (11) considered for his fundamental retention calculations an exponential cooling law:

$$dT/dt = -\beta \, (T - T_L), \qquad T_L = \text{quench bath temperature} \qquad [1]$$

whereas MORI, MESHII and KAUFMANN (12) assumed a constant cooling rate:

$$T = T_Q - t.V, \qquad \begin{aligned} T_Q &= \text{quench temperature} \\ V &= \text{quench rate} \end{aligned} \qquad [2]$$

Indeed, the initial cooling rate of the exponential law can also be approximated by a linear cooling rate. The quench curves reported below have also indicated that the early temperature drop can be considered as quasi linear. But it has to be emphasized that in reality due to the various, not yet clearly understood heat transfer mechanisms (as heat conduction in gas and liquid phase, nucleate and film boiling etc.), the temperature-time-relation during quenching as shown by our photographs is neither straightly linear nor a simple functional relation. This statement is valid —with some distinction— for quenches into water as well as in liquid nitrogen, helium etc. But for the sake of simplicity and for comparisons we have calculated a mean quench speed V taking the time for the temperature drop from the quench temperature T_Q to 100°C — a temperature at which vacancies in fcc alloys just start to migrate in appreciable amount. We agree that this method sometimes may result in an underestimation of the real quench rate and therefore the values listed in Table I might not be compared directly to literature data but should be valuated mainly in a relative manner.

In the following the characteristics of quenches from temperatures in the range of 300, 500 and 700°C into water, liquid nitrogen, silicon oil, two aqueous solutions and gas (He, air) performed by the various techniques are explained in some detail *).

4.1 Quenching of thermocouples

In order to detect the response of the thermocouple itself, some quenches of two types of thermocouples (0,5 and 0,2 mm wire diam.) were accomplished by method 2.1 and 2.3 from about 500°C into water and liquid nitrogen. Fig. 5 — 8 show typical quench curves and some significant results are listed in Table I.

The results clearly point out that the thicker thermocouple (2) due to its greater mass and heat capacity, responds very slowly. For the quenches into water, the quench rates achieved with the two thermocouples differ by a factor 3, for liquid nitrogen it reaches 5 — what might be due to the smaller heat of vaporization and thermal conductivity of nitrogen as compared to water.

*) Method 2.2. only from 700°C into water, method 2.4 only quenches from 500°C into a precooled gas stream and still air

Fig. 5 Response curve of a 0.2 mm φ Fe-Konst.-thermocouple quench-
ed from ca. 500°C in water by the "drop method". Time scale:
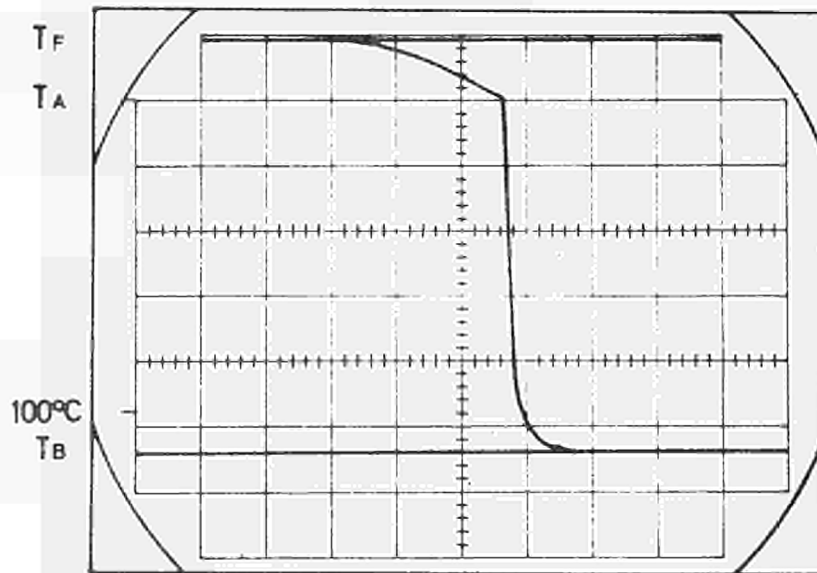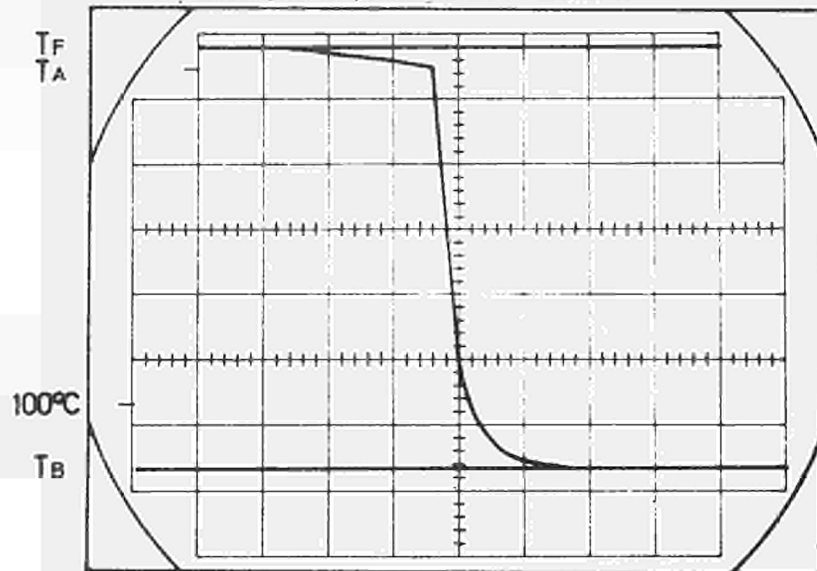50 msec/unit, temperature scale: 5 mV/unit.

Fig. 6 Response curve of a 0.5 mm φ Fe-Konst.-thermocouple quench-
ed from ca. 500°C in water by the "drop method". Time scale
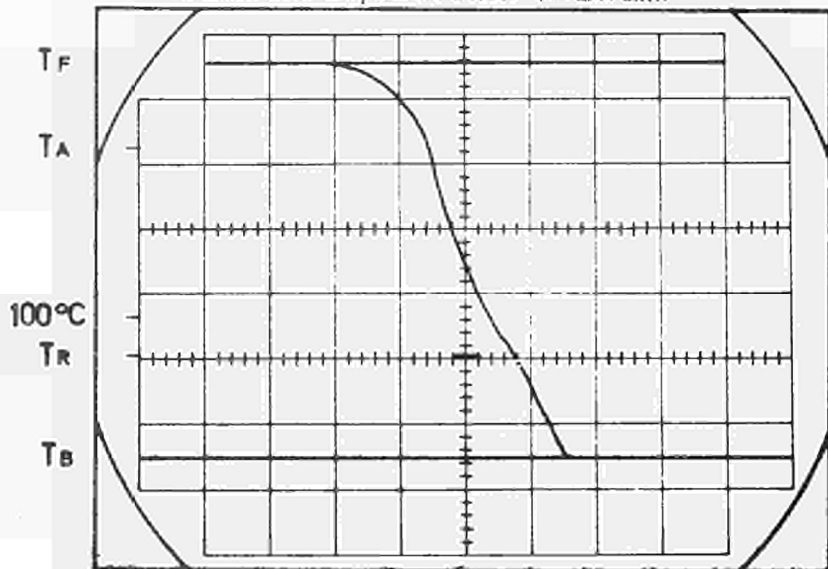50 msec/unit, temperature scale: 5.55 mV/unit.

Fig. 7 Response curve of a 0.2 mm φ Fe-Konst.-thermocouple quench-
ed from ca. 500°C into LN_2 by the "tilt method". Time scale:
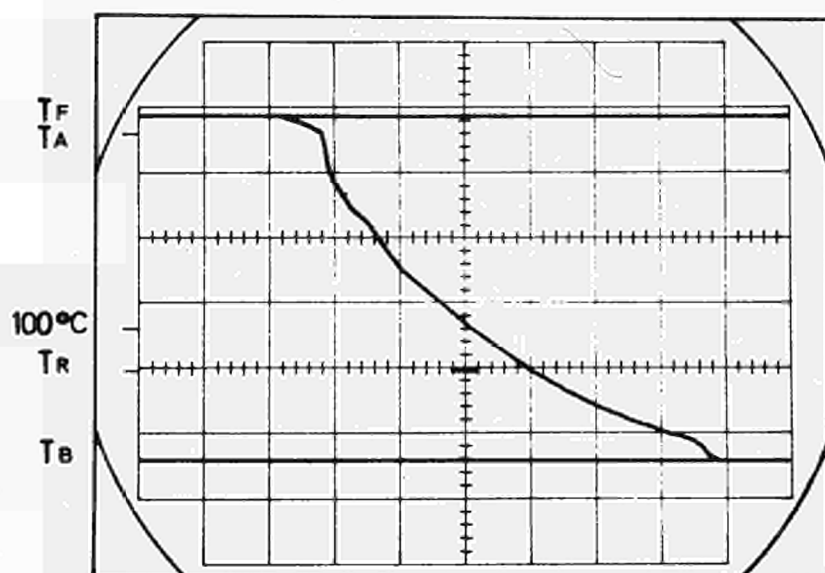0.2 sec/unit, temperature scale: 6.66 mV/unit.

Fig. 8 Response curve of a 0.5 mm ⌀ Fe-Konst.-thermocouple quench-
ed from ca. 500°C into LN₂ by the "tilt method". Time scale:
0.5 sec/unit, temperature scale: 6.66 mV/unit.

These physical data determine mainly also the great difference in quench speed between quench-
es in water and in nitrogen (by a factor (30-40). The faster response of the thinner thermocouple
is also indicated by its higher ΔT-values (temperature drop during extraction).

It is evident that for rate measurements on a sample, the influence of the measuring thermo-
couple should be negligible. But infact this cannot be achieved completely and even using —as
we did— the very thin thermocouple wire, there is always involved a greater heat capacity.
Due to the fact that the insulation of the thermocouple prevents immediate heat exchange with
the quench bath, the heat from the hot part of the wires will flow to the bare "hot junction" to
be exchanged.

This process is, of course, more marked in quenching a sole thermocouple than one attached to
a sample, i.e. with increased mass and surface. Therefore the quench rates reported below have
to be considered as lower limits.

All quench rate measurements according to our method proved to be reproducible within limits
of ± 10% whereby the estimated error in data evaluation is about 5%.

4.2 Tilt method

Figures 9, 10 and 11 represent some typical quench curves. The total time for sample extraction
from the furnace could be evaluated from curves at a time scale of 50 msec/cm (see Fig. 10),
whereas for rate determination the curves have preferentially been taken at shorter time scales
(20 or even 10 msec/cm, see Fig. 11). The results proved the method to be rather reproducible,
the extraction time varying between 250 and 350 msec. Typical data are listed in Table I. From
this it follows:

a) the temperature decrease during extraction amounts to about 10% of the furnace temperature,

b) the quenching rate increases somewhat with quenching temperature, reaching a maximum speed of about 27000°C/sec from 700°C for quenches into water,

c) quenches into LN_2 have a much lower quench rate, by a factor 40-50,

d) quenches into silicon oil seem to be faster by a factor 2 than LN_2-quenches as is demonstrated by one experiment (Fig. 12). Water and silicon oil as well as the aqueous solutions of NH_3 and $CaCl_2$ (see 4.4) represent real "liquid" quench baths whereas LN_2 as all cryogenic liquids has to be considered as a "gaseous" quench medium.

It should be mentioned here that the curves of quenches into LN_2 —as well as the gas quenches reported below— show an even more complex temperature characteristics than water quenches. Therefore calculations of quench rates assuming a linear cooling law may result in somewhat inadequate values. For that reason it might be recommended to refer here directly to the quench times $(t_Q = <T_Q \div 100°C>)$ as characteristic evidence of the quenching efficiency.

Fig. 9 Quench curve obtained for a brass-specimen quenched from ca. 500°C into LN_2 by the "tilt method". Time scale: 0.2 sec/unit, temperature scale: 5 mV/unit.

Fig. 10 Quench curve obtained for a brass-specimen quenched from ca. 500°C into H_2O by the "tilt method". Time scale: 50 msec/unit, temperature scale: 5 mV/unit.

4.3 Pull method

Fig. 13 a-c shows a series of quenches from 700°C into water. It is obvious that there is little reproducibility since the sample sometimes during being pulled through the quench bath seems to have jumped out of the water or to have touched the container wall (or the fixed rod, see Fig. 2) or entered the bath in different manner. Furthermore this technique is strongly dependent on the individual performance of the extraction. Performing a good quench, the extraction time may be in the order of 50-100 msec, i.e. very short and the temperature decrease is equally relatively small (compared to results 4.2). The quench rate itself as calculated from Fig. 13 a, corresponds about to that achieved by method 2.1. and might be even higher. Because of the bad reproducibility no further quenches at other temperatures have been executed. The method is considered to be somewhat "dangerous" since in a normal quench (without attached thermocouple) there does commonly not exist ad hoc the possibility to prove the efficiency of the quench experiment but a complete annealing curve is needed for.
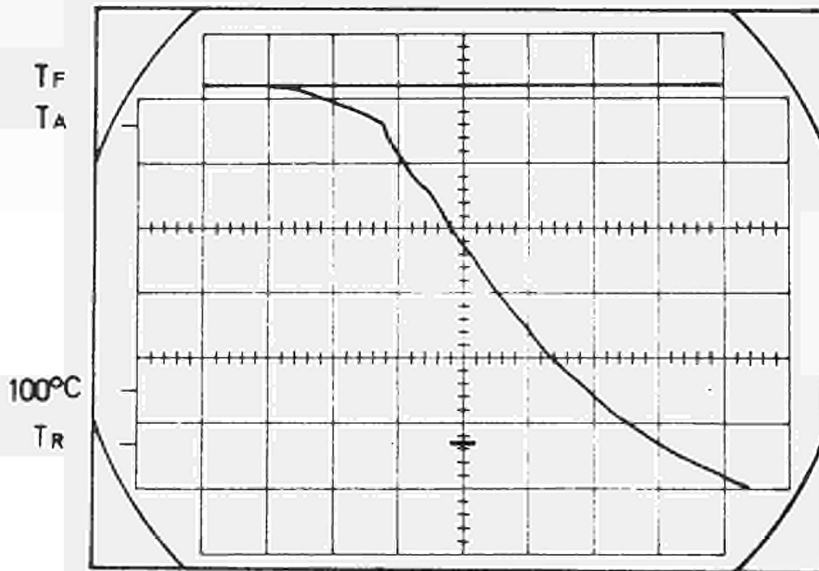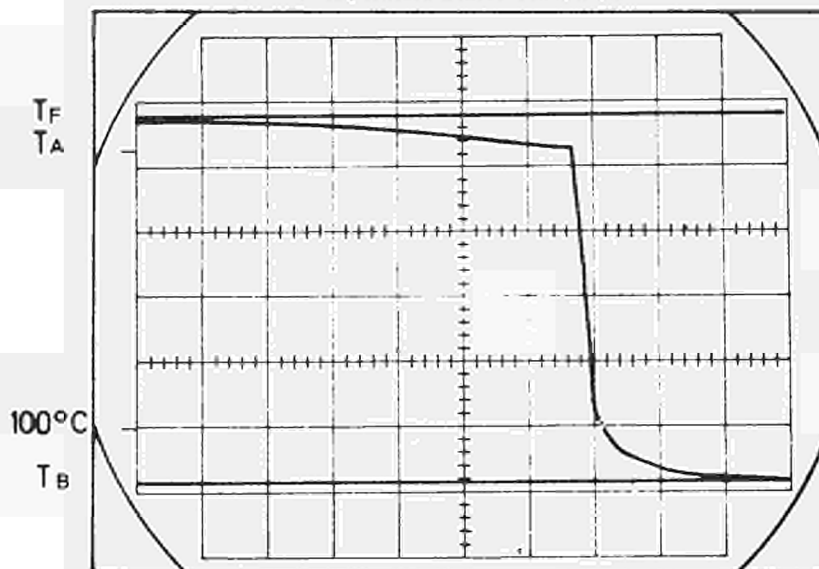

Fig. 11 Quench curve obtained for a brass-specimen quenched from ca. 300°C into H₂O by the "tilt method". Time scale: 20 msec/unit, temperature scale: 2.94 mV/unit.

Fig. 12 Quench curve obtained for a brass-specimen quenched from ca. 500°C into silicon oil by the "tilt method". Time scale: 50 msec/unit, temperature scale: 5 mV/unit.

Fig. 13 Three quench curves obtained for a brass-specimen quench-
ed from ca. 700°C into H_2O by the "pull method" and show-
ing the low reproducibility of this technique. Time scale:
50 msec/unit, temperature scale: 7.15 mV/unit.

Fig. 14 Quench curve obtained for a brass-specimen quenched from ca. 500°C into H_2O by the "drop method". Time scale: 20 msec/unit, temperatuur scale: 7.15 mV/unit.

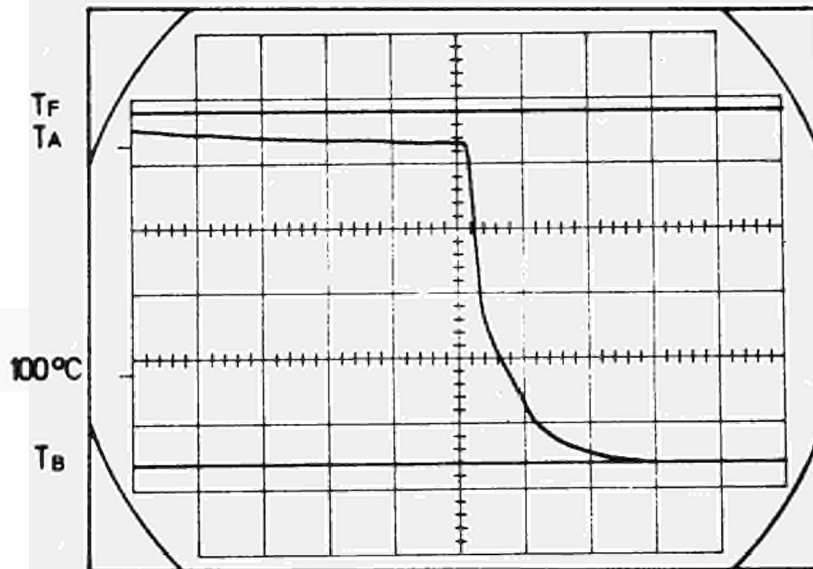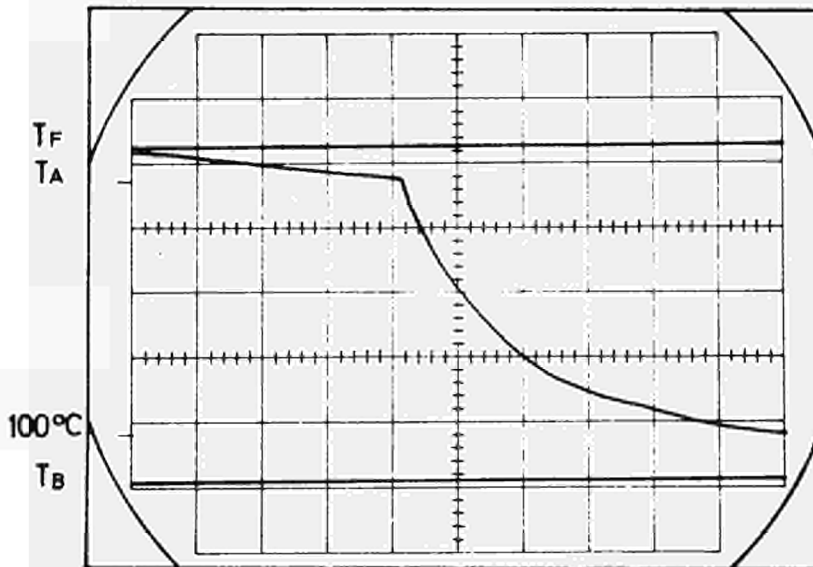Fig. 15 Quench curve obtained for a brass-specimen quenched from ca. 700°C into H_2O by the "drop method". Time scale: 50 msec/unit, temperature scale: 7.15 mV/unit.

4.4 Drop method.

Figures 14 – 19 represent some typical quench rate curves from different temperatures (500, 700°C) into water, into aqueous solutions of NH_3 and $CaCl_2$, respectively, into silicon oil and LN_2. Typical results obtained by this technique are listed in Table I. As main topics we note:

a) The quench rates are for all quench temperatures of the same order of magnitude as obtained by the previously described techniques. For water quenches a somewhat higher quench speed can be revealed which might be caused by a higher speed of the sample when hitting the quench bath surface. Although running off with much lower rates, quenches into silicon oil show the same phenomenon (see Fig. 12 and 19). For LN_2-quenches, the quench rate is is not altered by the quench method (see Table 1) what probably is due to another heat transfer mechanism in LN_2 not being influenced by the sample motion in the quench medium.

b) Quenches from 500°C into aqueous solutions of NH$_3$ as well as of CaCl$_2$ (at about −40°C) revealed quench rates which are somewhat lower than those for plain water.

c) As for method 2.1 the quench rate increases slightly and not proportionally with temperature. A maximum speed of 4×10^4 °C/sec could be achieved for a quench from 700°C into water.

d) The extraction time is rather short (100 − 150 msec), and therefore the temperature drop $\Delta T = T_F - T_Q$ markedly lower than for the other methods.

e) The quenches are rather well reproducible.

The data listed in Table 1 reveal a somewhat higher temperature drop ΔT for LN$_2$-quenches than for quenches into water. That is probably caused by the experimental arrangement used for the rate determination: the top of the sample tube has been kept open and when putting the LN$_2$-container beneath, the hot tube worked as chimney sucking a stream of cold nitrogen which cooled more efficiently the sample already during its fall.

Fig. 16 Quench curve obtained for a brass-specimen quenched from ca. 700°C into LN$_2$ by the "drop method". Time scale: 0.2 sec/unit, temperature scale: 0.35 mV/unit.

Fig. 17 Quench curve obtained for a brass-specimen quenched from ca. 500°C into silicon oil by "drop method". Time scale: 50 msec/unit, temperature scale: 6.66 mV/unit.
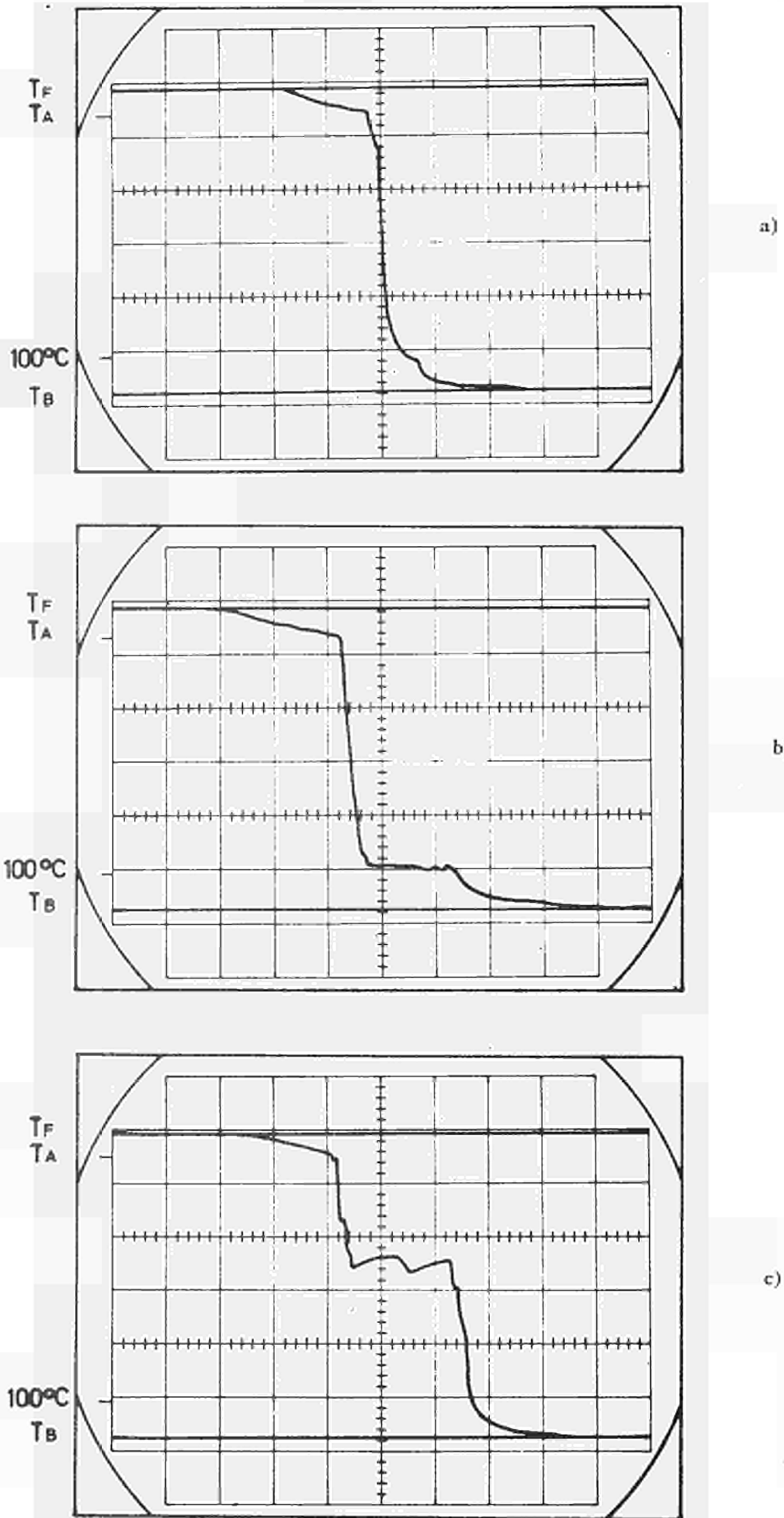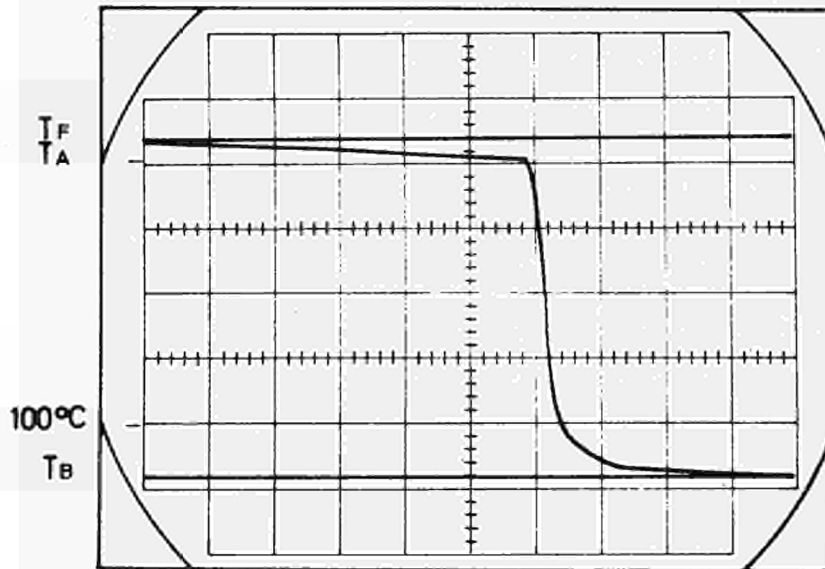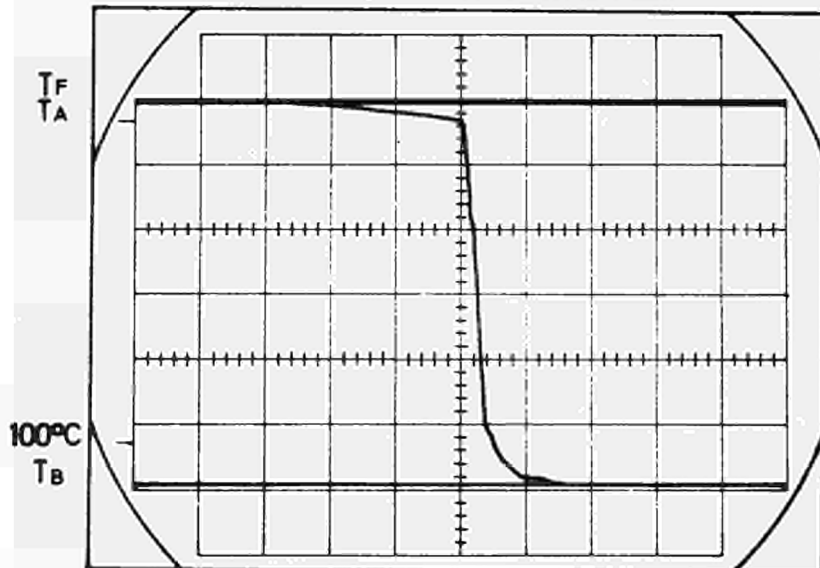
Fig. 18 Quench curve obtained for a brass-specimen quenched from ca. 500°C into an aqueous solutions of CaCl₂ at–40°C by the "drop method". Time scale: 20 msec/unit, temperature scale: 5 mV/unit.

Fig. 19 Quench curve obtained for a brass-specimen quenched from ca. 500°C into an aqueous solution of NH₃ at–40°C by the "drop method". Time scale: 20 msec/unit, temperature scale: 5 mV/unit.

Fig. 20 A quench curve for a brass-specimen quenched from ca. 500°C by a pre-cooled He-gas stream. Time scale: 0.5 sec/unit, temperature scale: 5 mV/unit.

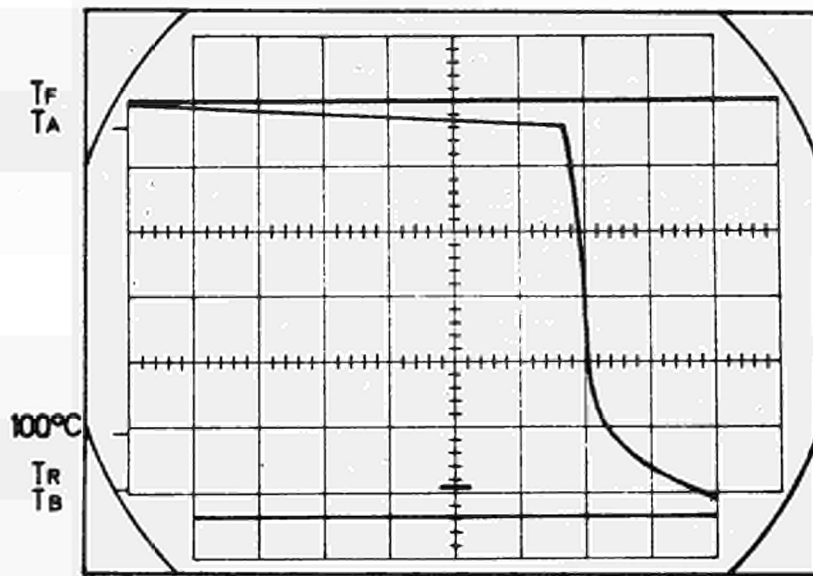Fig. 21 A quench curve for a brass-sample extracted vertically from the furnace (at ca. 500°C) and cooling by naturally convecting air (25°C). Time scale: 1 msec/unit, temperature scale: 5 mV/unit.

4.5 Gas quench

Only one experiment (at $T_N = 500°C$) has been executed by quenching with precooled He-gas; the curve obtained is shown by Fig. 20. Here the extraction time and the corresponding temperature drop are about the same as for quenches by method 2.3 due to the same sample extraction operation from furnace. The quench rate however is about twice that of quenches from the same temperature into LN_2.

Further it should be taken into account that our experimental arrangement was not the best one in what concerns a) the method of blasting helium-gas against the specimen *) and b) its suspension at the thermocouple passing through the furnace. For these reasons the indicated quench times and rates should be considered as lower limits which could be easily improved.

For a comparison we made with the same arrangement a simple air quench from the same temperature ($T_N = 500°C$). The sample was vertically removed at its thermocouple and cooled down by naturally convecting air (see Fig. 21). The quench rate (see Table I) was slower by a factor of about 20 with respect to a He-quench and by a factor 10 compared to LN2-quench. The difference in quench speed between LN_2- and air-quench will mainly be caused by the lower quench medium temperature in the former case. The similarity of the quench curves in all cases (LN_2-, He-, air-quench) indicates that the same heat transfer mechanism has to be assumed.

*) It is suggested to blast the pre-cooled helium through two frits at both sides onto the sample.

5. Discussion

Discussion of the results should start with some remarks to the quench curves obtained by the various techniques. Here we first have to distinguish between quenches in "real" liquids (as plain water, silicon oil, $CaCl_2$-solution and NH_3-solution) and in "gaseous" media (LN_2, He-gas and convecting air).

Quenches in water exhibit independently of the applied technique three stages in the total temperature drop: a) a quasi linear temperature decrease during the extraction of the sample from the furnace, the shape of which is clearly dependent on the quenching method. It is follow-ed by b) an abrupt temperature drop when the specimen hits the quench medium surface. This stage shows also an almost linear character which is changing at lower temperatures ($T_C \approx 100°C$) into c) a slower exponential decrease. This experimental statement is in contradiction to to results obtained by KAUFMANN and MESHII (13), who claim for a rather low quench rate just below the quench temperature which is increasing lateron markedly.

Our results indicate further that one has to distinguish between the sample tempera-ture T_F in the furnace and the real quench temperature T_A i.e. the sample tempe-rature at the moment of hitting the quench bath surface. From calculations of LOMER (16) it can be concluded that in well annealed fcc metals the time for the re-establish-ment of the thermodynamic defect concentration after a small temperature variation at high temperature (i.e. at relatively high defect mobility) is of order of some 10 msec. Therefore we can assume, that the equilibrium concentration will be maintained during the temperature decrea-se due to specimen extraction ("quench rate" of some $100°C/s$), and "efficient" quenching does not start before immersion into the quench medium.

For the evaluation of the formation energies of vacancies the resistivity increase by quenching is determined as a function of the reciprocal quenching temperature. Since it follows from our results that the temperature drop during sample extraction is strongly dependent on the tech-nique to be applied, this fact should always be taken into account for an exact data evaluation and the quench temperature corrected correspondingly.

The extraction temperature loss increases obviously with the furnace temperature and with the time needed to transfer of the sample from the furnace to the quench bath. It became evident that the drop method yields the best results with respect to temperature loss and reproducibility The quench rate itself is determined by
a) quench temperature
b) temperature and thermodynamic data of quench medium
c) speed of motion of specimen through the quench bath, which is dependent on the quench tech-nique.

Quenches into water yielded for all methods rate values of the same order of magnitude, being somewhat higher for the drop method which may be caused by a faster motion of the specimen in the quench bath. For this method the immersion speed can be properly adjusted in certain limits by selecting different fall heights.

With the $CaCl_2$- and the NH_3-solutions only a few runs have been performed. In general they indicate the same features as water quenches, but the corresponding quench rates are somewhat different (see Table I). It became evident by these experiments that not the quench bath temperature but its thermodynamic data are the most important point. The $CaCl_2$-solution (of $-40°C$) has about the same heat capacity as water (see Table II) whereas the thermal conductivity is a little lower. But the liquid surrounding the sample surface has to be heated up ca. 151°C ($-40°C + 111°C$) instead of $80°C$ as in case of water ($20°C + 100°C$) until the vaporization process can start which carries off the sample heat more efficiently.

With regard to ammonia we have to state that both heat capacity and thermal conductivity are lower than for water and $CaCl_2$-solution . On the other hand, vaporization of NH_3 starts earlier than for water and $CaCl_2$-solution, but the latent heat of vaporization is almost only half that of water and the thermal conductivity of the NH_3-gas is markedly worse than that of water vapor; therefore we have to expect a lower quench rate.

Thus the importance of thin film boiling as heat transfer mechanism in quenching experiments is impressively demonstrated. The results and conclusions are also supported by the quenches in silicon oil where we found much lower quench rates. In this case, thermal conductivity as well as heat capacity are fairly low, whereas the boiling point of the medium is rather high. Therefore the vaporization process should not become important, and all heat has to be transfered by conduction and/or convection. It should be emphasized here, that for a more sophisticate and complete discussion of these phenomena, one has to take into account also other properties as viscosity and surface tension as well as heat transfer by radiation and/or convection.

The quench curves into liquid nitrogen show approximately the same temperature characteristics as those of quenches in precooled helium-gas or in air. In contrary to "liquid" quenches, these curves do not exihibit a sharp break at the moment when the sample enters the quench medium which would indicate a change in the heat transfer mechanism.

When immersing the hot sample into boiling nitrogen, due to the small heat capacity, low boiling temperature and bad heat conductivity of nitrogen as compared to "real" liquids, a vapor layer on the sample surface is formed instantaneously which prevents good heat exchange to the bath. Since the latent heat of vaporization of LN_2 is rather small (s. Table II), the contribution of the vaporization process to heat removal should be small, too. But as a matter of fact seems to us the presence of a N_2-vapor layer on the sample surface during the whole duration of the quench process. This layer cannot even be removed by the sample's motion in the quench bath and due to the low heat conductivity of N_2-vapor, heat transfer by conduction is rather bad. *)

The similarity of the temperature curves of quenches in LN_2, helium-gas and air confirms the conclusion that quenching in LN_2 (and all other cyrogenic liquids) corresponds to a cooling in a gaseous phase. It is also evident that because of the altered heat transfer mechanism, the quench rates being achieved are much lower than for "aqueous" quenches.

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*) For quenching in a gaseous phase heat transfer by convection has probably to be considered as the only efficient process.

Despite of lacking of any vaporization process, quenches with a precooled He-gas stream are faster than in LN_2, by a factor 2, because of the higher values of specific heat and thermal conductivity (see Table II) of He in comparison to N_2. Furthermore, here a greater contribution of (forced) convection to the heat removal process has to be expected.

From our results we may conclude that quenching with He gas or LN2 (cyrogenic liquid *) is limited to following special cases:

a) The material to be quenched reacts with water and aqueous solutions, or it has a marked solubility for oxygen.

b) The vacancies in the material under investigation are expected to have a rather low migration activation energy, i.e. measurements and annealings have to be performed at cryogenic temperature.

c) Relatively low quench rates are needed as-for example-for freezing-in vacancy clusters.

d) The sample material itself has a very low heat conductivity, i.e. the heat transport inside the sample becomes the rate determining process.

e) The vacancies have a rather high migration activation energy, i.e. the total jump number and hence the corresponding defect loss during quenching remains small even at such a low quench rate.

MORI, MESHII and KAUFMAN (12) have demonstrated by quenches of well-annealed gold specimens that quench rates of the order of 2×10^4 °C/sec are sufficient to freeze-in almost completely the equilibrium defect concentration at quench temperatures up to 850°C. The quench rates reported here may depend somewhat on the specimen material —namely its specific heat and thermal conductivity— but we may state that the quench rates achieveable with our methods (see Table I) are sufficient to freeze-in equilibrium concentrations of defects even from higher temperatures — specially in alloys having a larger migration activation energy of vacancies than the pure metals. Furthermore in alloys smaller vacancy concentrations are detectable by resistivity measurements because of the ordering phenomenon associated with the migration of point defects in alloys .

There should be mentioned one point limiting the maximum quench speed to be applied. As pointed out already moving dislocations which may act as additional sinks or sources for defects can be created by thermal stresses in the sample. For metals Van BUEREN (13) has developed a formula which allows the estimation of the maximum permissible specimen thickness (or quench rate) to prevent thermal stresses which may cause dislocations:

$$d = \sqrt{5 (1-\gamma) \delta \sigma_{cr} / G V \alpha} \qquad [3]$$

*) Except quenches being executed in helium-II.

where:

$$\gamma = \text{poisson's number } (= 0.8 \text{ for } \alpha - \text{brass } *)$$

$$\delta = \kappa/\rho C = \text{thermal diffusivity } (= 0.434 \text{ cm}^2 \text{ sec}^{-1})$$

$$\alpha = \text{thermal expansion } (= 18 \cdot 10^{6} \, ^{\circ}C^{-1})$$

$$G = \text{shear modul } (= 4.2 \times 10^5 \text{ kpcm}^{-2})$$

$$\sigma_{cr} = \text{critical shear stress } (= 22 \text{ kp/cm}^2)$$

$$V = \text{speed rate } (= 3 \times 10^4 \, ^{\circ}C/\text{sec})$$

For the samples of our interest (α—brass), we obtain according to this relations a maximum allowable specimen thickness of 0,6 mm. Even taking this value only as a crude approximation, we can be rather sure to be not concerned with thermal stresses when utilizing samples of 0,1 mm thickness at the quench rates reported here.

By controlled variation of the sample's thickness, the influence of thermal stresses on the quenched-in vacancy concentration can be made evident by experiment.

With the quench speed data obtained by our experiments, one is now also able to calculate for a certain material und quench method the loss of (single) vacancies by annihilation at sinks and/or by formation of divacancies (clusters) during quenching. Such an estimation is normally desirable for a detailed analysis of annealing experiments after quenching.

We may give here a rough and simple estimation of the loss of single vacancies by annihilation during quench. The vacancies are assumed to decay according to the relation:

$$dc_v/dt = - c_s \, c_v \, \nu^*_o \, \exp \, (-Q_M/kT) \tag{4}$$

where

$$c_S = \text{sink concentration}$$

$$Q_M* = \text{migration activation energy of vacancies}$$

$$\nu_o = \text{pre-exponential factor}$$

We assume further a constant quench rate V, that means:

$$T = T_q - V t$$

Substitution for t in equ. (4) and integration gives:

$$\ln c_v/c_\infty = \frac{C_s \, \nu_o* \, \int_{Tq}^{T} \exp \, (-Q_M/kT) \, dT}{V} \tag{5}$$

Inserting in equ. (5) some reasonable values for c_s (10^{-7} molar fraction), Q_M (1.0 eV), T (273°K) T_q (973°K) and V = 4×10^4 °C/sec as deduced from our experiments, numerical integration yields a vacancy loss by annihilation during quenching of 5%, i.e. 95% of the vacancies present in thermodynamic equilibrium at temperature T_q will become frozen-in by a quench at the reported quench rate.

We should note from equ. (5) that the loss rate is direct proportional to the sink concentration and that at any given temperature $\ln c_v$ is expected to vary linearly with 1/V.

*) Numerical values are valid for M_s—80 according to ref. (17).

For a more sophisticate and complete consideration of the problem we may refer to the papers of DIENES and DAMASK (16) and KAUFMAN and MESHII (13), respectively.

For completeness we should add also some remarks on a quench technique not dealt with here: It is the quite convenient method of heating the specimen by a current passing through the sample; quenching is accomplished by switching off the current with simultaneous cooling in air or by gas blast as well as by dropping the sample with its current leads into a quench bath. Compared to the quench techniques described in this paper, thereby it is obviously difficult to achieve a homogenous temperature distribution along the sample during heating and quenching — which is yet a fundamental condition for a reliable quench. Further by this method some mechanical deformation of the sample during quench cannot be excluded.

6. Conclusions

From the quench experiments described here, we have to conclude the following:

a) The tilt method although being a rather rudimentary procedure has proved to yield quite reliable and reproducible results which may be sufficient for many purposes.

b) The drop method may be recommended by its greater versability for quenches which must be performed under special requirements with respect to the variation of quench speed, quench medium, atmosphere, reproducibility, exact determination of quench temperature etc.

c) The quench rates achievable by our methods are sufficiently high to allow nearly complete retention of single vacancy concentrations in most fcc metals and alloys for quenching temperatures up to ca. 850°C. Using specimens of 0,1 mm thickness, we are not concerned with marked thermal stresses which might influence the quench efficiency.

d) Quenches in gaseous media yielded much lower rates than those in liquids.

e) The experiments indicate further that for the achievement of high quench rates, quench media have to be selected which allow to make use of a heat transfer process involving a great latent heat. The influence of the type of quench medium on the quench rate has been found more important than that of the quench bath temperature.

Acknowledgement

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8. Figure Captions and Tables

Fig. 1 Schematic drawing of the experimental arrangement for "tilt method" quenching.

Fig. 2 Schematic illustration of the experimental installation for "pull method" quenches.

Fig. 3 Schematic draft of the experimental arrangement for "drop quenches".

Fig. 4 Schematic drawing of the experimental installation for "gas quenches"

Fig. 5 Response curve of a 0,2 mm ϕ Fe-Konst.-thermocouple quenched from ca. 500°C in water by the "drop method". Time scale: 50 msec/unit, temperature scale: 5 mV/unit.

Fig. 6 Response curve of a 0,5 mm ϕ Fe-Konst.-thermocouple quenched from ca. 500°C in water by the "drop method". Time scale 50 msec/unit, temperature scale: 5,55 mV/unit.

Fig. 7 Response curve of a 0,2 mm ϕ Fe-Konst.-thermocouple quenched from ca. 500°C into LN_2 by the "tilt method". Time scale: 0,2 sec/unit, temperature scale: 6,66 mV/unit.

Fig. 8 Response curve of a 0,5 mm ϕ Fe-Konst.-thermocouple quenched from ca. 500°C into LN_2 by the "tilt method". Time scale: 0,5 sec/unit, temperature scale: 6,66 mV/unit.

Fig. 9 Quench curve obtained for a brass-specimen quenched from ca. 500°C into LN_2 by the "tilt method". Time scale: 0, 2 sec/unit, temperature scale: 5 mV/unit.

Fig. 10 Quench curve obtained for a brass-specimen quenched from ca. 500°C into H_2O by the "tilt method". Time scale: 50 msec/unit, temperature scale: 5 mV/unit.

Fig. 11 Quench curve obtained for a brass-specimen quenched from ca. 300°C into H_2O by the "tilt method". Time scale: 20 msec/unit, temperature scale: 2,94 mV/unit.

Fig. 12 Quench curve obtained for a brass-specimen quenched from ca. 500°C into silicon oil by the "tilt method". Time scale: 50 msec/unit, temperature scale: 5 mV/unit.

Fig. 13   Three quench curves obtained for a brass-specimen quench-
ed from ca. 700°C into H_2O by the ''pull method'' and show-
ing the low reproducibility of this technique. Time scale:
50 msec/unit, temperature scale: 7,15 mV/unit.

Fig. 14   Quench curve obtained for a brass-specimen quenched from
ca. 500°C into H_2O by the ''drop method''. Time scale:
20 msec/unit, temperatuur scale: 7,15 mV/unit.

Fig. 15   Quench curve obtained for a brass-specimen quenched from
ca. 700°C into H_2O by the ''drop method''. Time scale:
50 msec/unit, temperature scale: 7,15 mV/unit.

Fig. 16   Quench curve obtained for a brass-specimen quenched from
ca. 700°C into LN_2 by the ''drop method''. Time scale:
0,2 sec/unit, temperature scale: 0,35 mV/unit.

Fig. 17   Quench curve obtained for a brass-specimen quenched from
ca. 500°C into silicon oil by ''drop method''. Time scale:
50 msec/unit, temperature scale: 6,66 mV/unit.

Fig. 18   Quench curve obtained for a brass-specimen quenched from
ca. 500°C into an aqueous solution of $CaCl_2$ at-40°C by the
''drop method''. Time scale: 20 msec/unit, temperature scale:
5 mV/unit.

Fig. 19   Quench curve obtained for a brass-specimen quenched from
ca. 500°C into an aqueous solution of NH_3 at-40°C by the
''drop method''. Time scale: 20 msec/unit, temperature scale:
5 mV/unit.

Fig. 20   A quench curve for a brass-specimen quenched from ca. 500°C
by a pre-cooled He-gas stream. Time scale: 0,5 sec/unit,
temperature scale: 5 mV/unit.

Fig. 21   A quench curve for a brass-sample extracted vertically from
the furnace (at ca. 500°C) and cooling by naturrally convec-
ting air (25°C). Time scale: 1 msec/unit, temperature scale:
5 mV/unit.

Table I   Here are listed some significant data of quench rate measure-
ments executed by various techniques and with different
quench mediums.

Table II Some thermodynamic data of the materials involved in the
quench experiments, according to reference (17) and (18),

Method		Water					Liquid Nitrogen					Note
		T_F (°C)	T_Q (°C)	ΔT (°C)	t_q (ms)	V (°C/sec)	T_F (°C)	T_Q (°C)	ΔT (°C)	t_q (ms)	V	
I. Tilt method a) 0.5 mm ⌀ thermocouple	500°C	530	497	33	31.7	12500	479	430	49	1060	312	extraction time Δt 250–350ms
		559	528	31	31.7	13500	579	543	45	1335	325	
b) 0.2 mm ⌀ thermocouple	500°C	561	441	120	9.4	36200	519	392	127	195	1495	
		543	430	113	9.4	35100	601	490	111	289	1350	
II. Drop method a) 0.5 mm ⌀ thermocouple	500°C	492	473	19	27.0	13800	521	506	15	1265	321	
		486	466	20	25.2	14500	580	563	17	1600	289	
												Δt 100–150ms
b) 0.2 mm ⌀ thermocouple	500°C	681	587	94	11.75	41500	492	412	80	218	1475	
		725	633	92	13.5	39500	478	–	–	288	131	cooled in still air
III. Tilt method Sample Quench	300°C	335	307	28	10.0	20700	330	303	27	414	491	
		355					355	330	25	447	513	
												t 250–350ms
	500°C	511	468	43	12.9	28400	516	469	47	625	590	
							571	532	37	773	558	
	700°C	693	610	83	19.5	26100	693	592	101*	865	568	*very slow extraction
		696	619	77	18.8	27600	669	603	66	925	545	(400 ms)
	500°C	490	440	50	264	1280						silicon oil
IV. Pull method Sample quench	700°C	750	686	64	20.2	29000	–					
V. Gas-Quench method Sample quench	500°C						484	452	32	482	730	Δt 150ms quenched
							477	446	31	394	830	in precooled He-gas
							548	–	–	8860	50.6	
							556	–	–	7520	55.4	quenched in still air
VI. Drop method Sample quench	300°C	371	359	12	8.45	30600	281	266	15	334	497	Δt 100–150ms
		372	358	14	7.75	33300	262	246	16	305	478	
	500°C	494	469	25	9.87	37000	473	444	29	640	538	
							565	538	35	800	538	
	200°C	730	691	39	14.60	40600	727	674	53	1004	570	
							746	690	56	970	608	
	650°C	663	645	18	384	1420						silicon oil
	500°C	555	525	30	13.6	31200						aqueous solution of 34% CaCl2
		432	406	26	10.1	31000						
	500°C	523	496	27	27.0	23200						aqueous solution of 25% NH3
		483	457	26	26.6	23800						

Table I Here are listed some significant data of quench rate measurements executed by various techniques and with different quench mediums.

Material	Density	Specific heat	Viscosity	Thermal Concutivity cal/cm sec grd.	Latent heat of Vaporization	Boiling Point Ts
N_2 a) Vapor b) Liquid	1,2505 g/l at 20°C 0,808 g/cm³ at -196°C	0,248 cal/g grd at 20°C 0,474 cal/g grd at -200°C	55 μP at -192°C 0,172 cP at -192°C	$2,16.10^{-5}$ at -180°C $4,95.10^{-4}$ at -200°C	47,6 cal/g	-195,8°C
He a) Gas b) Liquid	1,2505 g/l at 20°C 0,13 g/cm³ at -268,94°C	1,25 cal/g grd at 20°C 1,08 cal/g grd at -268,94°C	139 μP at -100°C 30 μP at -269°C	$1,64.10^{-4}$ at -180°C $6,28.10^{-3}$ at -268,94°C	4,98 cal/g	-268,94°C
H_2O a) Vapor b) Liquid	0,95835 g/l at 100°C 0,99705 g/l at 25°C	1,007 cal/g grd at 100°C 0,998 cal/g grd at 20°C	1,05 cP at -20°C 0,282 cP at 101°C	$1,6.10^{-4}$ at -100°C $1,4.10^{-3}$ at 20°C	538,9 cal/g	+100°C
α – brass (Ms – 80)	8,67 g/cm³ at 20°C	0,094 cal/g grd at 20°C	–	0,338 at 20°C		
Silicon oil Ms 550	1,06 g/cm³ at 25°C	0,488 cal/g grd at 20°C	127 cP at 25°C	$3,5.10^{-4}$ at 25°C	–	?
aqueous solution of 30%CaCl$_2$	1,295 g/cm³ at -30°C	0,632 cal/g grd at -40°C	1,23 cP at 10°C	$1,055 \times 10^{-3}$ at -30°C	538,9 cal/g	111°C (Tf=-51,0°C)
Aqueous solution of 25% NH$_3$	0,907 g/cm³ at 20°C	0,995 cal/g grd at 20°C 0,967 cal/g grd at 2,4°C	0,276 cP at -40°C	$1,08.10^{-3}$ at 20°C (NH$_3$ - solution) $0,478 \times 10^{-4}$ at 0°C (NH$_3$ - gas)	332 cal/g	37,0°C

Table II Some thermodynamic data of the materials involved in the quench experiments, according to reference (17 and 18).
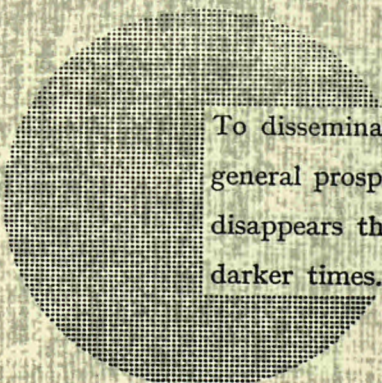
To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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