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Innovative Induction Melting Technologies: A Historical Review

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Abstract

Two innovative induction-melting technologies with widespread but very particular applications in metallurgy as well as in the semiconductor-silicon industry will be considered here. The first is the induction melting of high reactive metals and semiconductor silicon in water-cooled metallic crucibles. The second one is the growth of silicon single crystals by the floating-zone technique for the application in the semiconductor industry.

Introduction

The melting of extremely reactive materials in conventional ceramic crucibles at high temperatures leads to an inadmissible contamination of their liquid phase. This prevents the manufacturing of high purity metals such as, e.g., Titanium, Tantalum, Niobium and Molybdenum. However, the induction cold crucible process makes it possible to melt down these metals without them being contaminated by the crucible material.

In the case of floating-zone silicon, the crystallographic perfection of homogeneously doped dislocation-free single crystals of today's 200 mm diameter is a further challenge for the manufacturers. Only the contact-less induction melting technology can fulfil such manifold requirements.

1. Induction Cold Crucible Processing of Metals and Semiconductors

This very pure melting process is based on the water-cooled metallic crucible, which makes the melt solidify immediately when coming into contact with the cold crucible wall (Fig. 1). A solid crust is formed. This so-called skull protects the crucible against the hot melt and permits a melting process without any disturbing impurities. The energy, necessary to heat-up, melt down and overheat the charge, is transferred via the electromagnetic field of an inductor. To provide sufficient electromagnetic transparency, the metallic crucible is usually slitted, and consists therefore of several segments that are electrically isolated against each other.

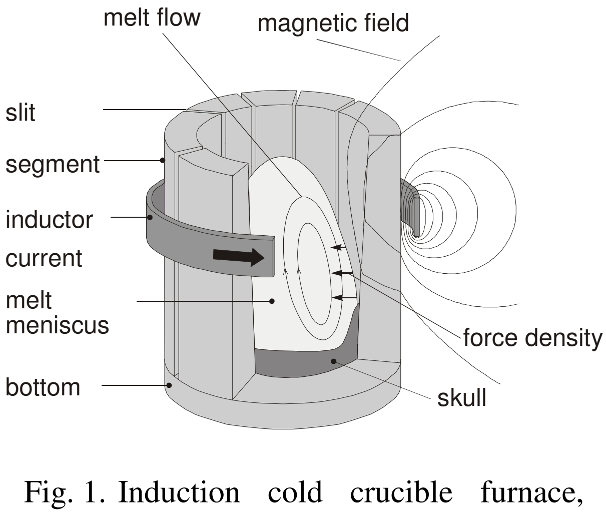

Fig. 1. Induction cold crucible furnace, schematically

The fascinating idea of preventing any contamination of highly reactive melts by the application of water-cooled metallic crucibles instead of ceramic ones is not new. The ceramic-free induction melting of such metals and their alloys in a water-cooled container was already patented in 1931 by the Siemens und Halske Company, Germany [1].

1.1 Silicon processing

Decades later, in 1957 and 1961, H.F. *Sterling* and R.W. *Warren*, UK, reported on the induction heated zone refining process of silicon, using a horizontal water-cooled silver boat (Fig.2) [2]. In the same year, 1961, A. *Berghezan* and E. *Bull Simonsen*, Belgium, reported on the horizontal induction zone melting of refractory metals and semiconductor materials in a water-cooled metallic boat as well [3]. Two years later, in 1963, H.F. *Sterling* and R.W. *Warren* again informed about the growth of high purity silicon crystals from a water-cooled cold crucible [4]. They used the Czochralski method, well introduced into the silicon industry worldwide. In this particular case the cold metallic crucible prevented any contamination from the container (Fig.3), in contrast to the conventional technique. In the end, all those experiments did not succeed, although these technologies had been applied and tested around the globe for the melting and zone-refining of semiconductor silicon in a horizontal boat under high purity conditions, as well as for the growth of Czochralski crystals from a water-cooled metallic crucible. Therefore, these technologies were never used for production purposes in the related industry.

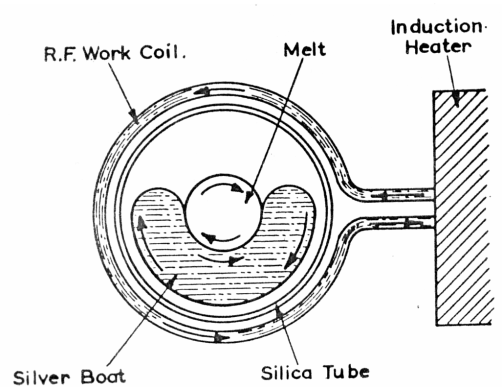

Fig. 2. Induction heated horizontal zone refining of silicon, using a water-cooled silver boat

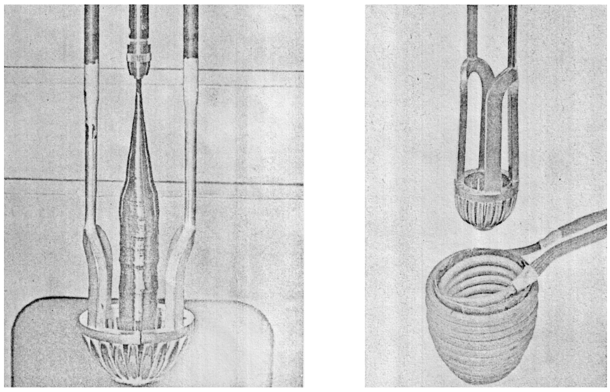

Fig. 3. Water-cooled silver crucible and pulled silicon crystal (left), cage crucible and induction coil (right)

In the years after, many other experts have investigated this technology. In 1969, one of the pioneers in the field, J. *Reboux*, France, obtained the US patent 3,461,215 for the application of inductive cold crucible processing of massive multi-crystalline silicon blocks as a base-material for the production of solar cells [5]. Many years later, in 1985, T.F. *Ciszek*, USA, was the first who proposed to apply the cold crucible technique for the silicon remelting and casting by using an open-bottom type of the crucible for the vertical continuous casting of solar-grade silicon for solar cells [6]. He performed the casting of a 25x25 mm^2 cross sectional ingot with 170 mm length. Since the 1990s the MADYLAM- group under M. *Garnier* in Grenoble, France, has adopted this innovative technique successfully [7]. Several modifications have been introduced to take into account the physical characteristics of silicon, particularly its electrical conductivity, strongly dependent on temperature, and the volume expansion when solidifying. The crucible is segmented at the bottom part and not at the top (Fig.4), a graphite susceptor above the crucible is used to heat

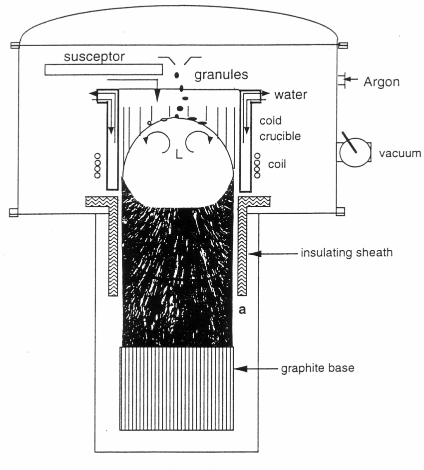

Fig. 4: Continuous casting of solar-grade silicon, using a cold crucible

up the low conducting starting solid raw silicon granules, whereas the cooling rate of the solidified material is controlled by an additional graphite heater just below the crucible. Ingots of up to 130x130 mm^2 were produced and processed into solar cells. Similar investigations have been performed not only in the USA and in Europe but also in Japan, where K. *Kaneko* et al. reported in 1990 on their results obtained from cold crucible induction melting and casting of silicon solar cell material [8].

Up to now, however, the cold crucible continuous casting of multi-crystalline silicon ingots has not played an important role in the industrial fabrication of solar-grade silicon for photovoltaic cells.

1.2 Metals processing

In 1961, G.H. *Schippereit* et al. presented in the United States of America a cold crucible furnace for the induction melting of reactive metals [9].

At the beginning stage of the cold crucible technology, the complexity of the physical interaction of the electromagnetic, the thermal and the fluid-flow field in the melt, together with the formation of a solid crust between the cold crucible wall and the hot melt, allowed only empirical investigations of the induction cold crucible melting. Intensive experimental studies have been carried out since the beginning of the 1980s. Several groups of physicists and engineers have been active in this field, particularly at Research Institutes in Moscow, Russia, in Grenoble, France, and at several places in Japan. Therefore many fundamental investigations were carried out and published. In 1984, L.L. *Tir* at al., Moscow, presented new results [10]. However, the MADYLAM-group around M. *Garnier* especially has shaped this technology distinctly: In 1982, D. *Delage* et al. [11] and in 1988 A. *Gagnoud* et al. [12], and others of the group presented remarkable theoretical and experimental results. At the same time, several groups in Germany were engaged in this field. Here the team around A. *Choudhury* [13-16] at the ALD Company has to be mentioned, a manufacturer of modern melting units, including ICCF. ALD concentrated on developing production processes for innovative and competitive TiAl parts for the automobile industry. Mathematical models of the electromagnetic, thermal and fluid flow fields in an ICCF were developed by the team of A. *Mühlbauer* at the Hanover University [17,18]. Besides these theoretical studies experimental melting and casting tests of TiAl exhaust valves for automotive applications were also performed in Hanover [19-21]. Intensive investigations of the cold crucible processing of reactive metals were undertaken in the United States [22], at the United Kingdom [23,24], in Korea [25], and in other countries as well.

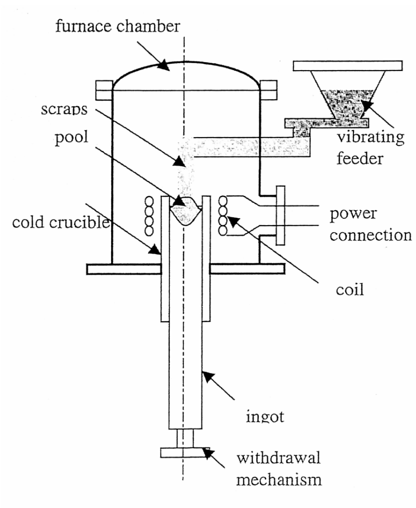

Fig. 5. Cold crucible continuous casting, schematically

The induction cold crucible melting and pouring of various materials is meanwhile widely used in industry since the middle of the 1990s. The intermetallic compounds in the γ-phase of TiAl show an excellent temperature resistance that qualified them as materials for automotive exhaust valves at very high temperatures.

The manufacture of TiAl-valves for the automobile industry serves as an example for the successful application of ICCF for mass production. A new concept for the low cost production of a high number of pieces is based on a melting process that uses ICCF as well as a casting device with a preheated centrifugal mould [17,19]. The decisive advantage is the integration of the operating steps melting, alloying, over-heating and casting in only one process. Because no pre-alloys are required, rather cheap scrap can be recycled. These characteristic features lead to considerable economical benefits.

In 2005, A. Umbrashko et al. gave results of recent investigations of the fluid flow in cold crucibles using the 3D transient Large Eddy Simulation (LES) method [26].

The induction cold crucible continuous casting of materials is an important application of the ICCF technology, not only for the processing of multi-crystalline solar grade silicon, as shown above, but also for the recycling of TiAl scrap resulting from several sources. At the end of the 1980s, the CEZUS Company, France, developed this process, in a joint research program with MADYLAM, for a first application on an industrial scale [27]. This technique, referred to as the 4C process, comprises continuous induction melting of feeding materials in a water-cooled copper crucible, followed by a downward solidification of the liquid from the crucible due to a continuous pulling of the solidified ingot, see Fig.5 . The segmented crucible acts as a container for the melt and as a mould for the cast material. A combined experimental and numerical approach [28] was necessary to determine the operating conditions by solving the strongly coupled phenomena between the 3D magnetic field, the fluid flow in the melt and the temperature.

The more recent development of the 4C process in metallurgy is its application to steel manufacturing. Resulting from a Japanese national project started in 1995 involving 9 Japanese and two European companies, the project aimed to improve cast steel quality and productivity through electromagnetic continuous casting using cold crucibles [29].

2. Floating-Zone Process

Transistor technology, which began in 1948, called for semiconductor materials such as germanium and silicon with impurity concentrations as small as 10^{14} cm^{-3} or even less. From the conventional chemical point of view, this demand seemed to be utopian in those years. Thus W.G. *Pfann's* report on a zone refining process created a sensation in 1952, as he provided a simple solution for the purification problem [30]. The process begins with a charge of relatively impure germanium being placed in a horizontal quartz or graphite boat. A narrow zone is then molten by induction or radiation heating and passed through the boat from one end to the other. This way, most of the impurity atoms are transported together with the travelling liquid zone to one end of the ingot. This purification process can be intensified by a multiple-pass zone refining technique that leads to the required high-purity material. However, this technology was not applicable for the highly reactive silicon because of the unacceptable silicon contamination by the boat material.

Nonetheless, this new technique opened the way to new material purification procedures, and crystal growth modifications. The crystal growth application, which will be considered here, branched off from zone refining as the **floating-zone technique**. Its basic features were first shown in 1952 in USA by H.C. *Theuerer's* fundamental patent [31]. Typical for this container-free method is the freely floating zone, suspended between the freezing and the melting interfaces (Fig. 6). P.H. *Keck* and M.J.E. *Golay* grew the first silicon crystal with this new method, still without rotating the

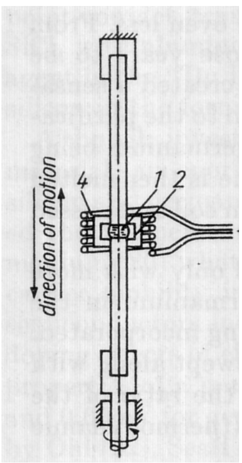

Fig. 6. Vertical zone refining technique

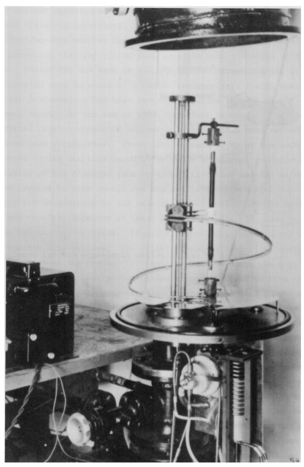
Fig. 7. R. Emeis's floating zone apparatus (1954)

crystal [32]. R. *Emeis* independently invented and initiated the floating-zone activity at Siemens, Germany [33]. He rotated the growing crystal, thus producing straight cylindrical crystals with diameters up to 10 mm. S. *Müller* and P.H. *Keck* et al. applied high frequency induction heating, whereas their predecessors had used radiation heating [34, 35]. The end of 1954 had thus established the basic techniques for the industrial crystal growth of high purity silicon. Fig. 7 shows an early floating-zone apparatus that was designed by R. Emeis in 1954. The multi-turn coil could be moved up and down and was fed by high frequency power; only the seed could be rotated. Again, the advantage of the floating-zone technique lies in the high purity of the silicon crystals resulting from the absence of a container.

The floating-zone method was also tried at the Bell Laboratories, USA, during the late 50s. E. *Buehler* worked with an automatic gas zoner and was able to grow 15 mm crystals. In Germany, Siemens was growing ultrahigh purity silicon crystals with a vacuum zoner, applying the stretch-squeeze multi-pass automation method. Step by step it became possible to improve the crystal quality and increase the diameter. In 1956, *W. Keller* introduced a slim seed to reduce the dislocation density. Some years later, in 1959, *W.C. Dash* presented a special seeding technique for the dislocation-free FZ crystal growth of silicon, which used a thin seed, tip etched down to 0.25 mm [36]. In 1960, *G. Ziegler* modified Dash's seeding method by applying the so-called bottleneck technique that opened the way to grow dislocation-free silicon crystals at an industrial scale [37]. In 1959, W. *Keller* invented and introduced the needle-eye FZ growth (Fig. 8), which enabled the growth of larger diameter dislocation-free silicon crystals.

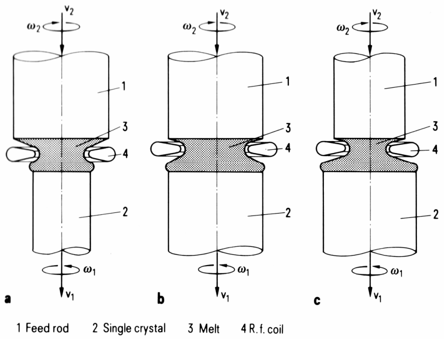

Fig. 8. Needle-eye FZ growth: (a) stretched, (b) diameter unchanged, (c) squeezed (1959)

The further development and production of float-zoned (FZ) silicon crystals took place in many countries. In Germany particularly the Wacker Company has pushed this technology as one of the largest manufacturer in the world. Until the end of the 1950s the crystal diameter size did not exceed 25 mm, whereas during the 60s and 70s a dramatic increase from 33 mm to 50 mm and 75 mm was achieved. This diameter enlargement was a prerequisite for the development and fabrication of high power discrete devices like thyristors and others. In the last decades a further increase of crystal diameter has taken place, which lead to an additional improvement of the device manufacturing. The 100 mm crystal appears at the end of the 1970s, the 125 mm one in 1986, and the 150 mm one some years later, at the end of the 1980s for 1-0-0 crystals and at the end of the 1990s for 1-1-1 crystals. The worldwide first 200 mm 1-0-0 dislocation-free silicon crystal was grown at Wacker-Siltronic Company in September 2000 (Fig. 9).

Fig. 9. Worldwide first 200 mm dislocation-free 1-0-0 silicon crystal (Courtesy of Siltronic AG)

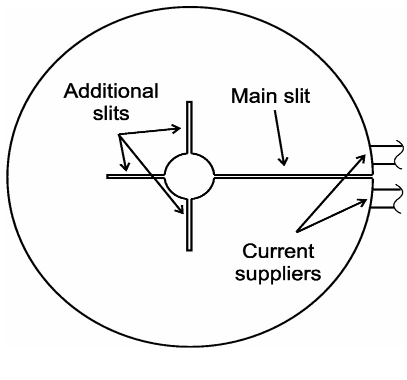

Fig. 10. Modern needle-eye inductor used in industrial FZ growth (Courtesy of Siltronic AG)

This dramatic increase in crystal diameter size involved many modifications of the original floating-zone technique [38]. It is not possible to describe all of them here. But the most important modifications should be mentioned: The use of a one-turn pancake coil instead of a multi-turn coil in a bottom- seeded needle-eye growth arrangement is common today [39, 40]. In Fig. 10 the schematic drawing of a modern coil used for the industrial growth of large diameter crystals is depicted. An important further modification of the needle-eye floating-zone method is the eccentric growth [41]. Here the axis of the growing crystal is slightly shifted to the axis of the inductor and the supply rod, which leads to a more homogeneous resistivity distribution across the crystal diameter by a better mixing of the liquid zone.

With rising crystal diameters, the growth of dislocation-free crystals that show the required homogeneity on the macroscopic and on the microscopic-scale became more and more difficult. That is why additional stirring means are helpful to improve the dopant homogeneity. A rotating magnetic field clearly improves the melt mixing and leads to a very homogeneous radial resistivity profile.

The development of the silicon floating zone process during the last 50 years is reflected by the increase of the crystal diameter as shown in Fig. 11.

The numerical modelling of the float-zone silicon process has turned out as an excellent tool for the modern crystal growth practice. Chains of models that cover the complete floating-zone process have been developed by A. *Mühlbauer* et al. [42]. These models have been improved over the last years. It is possible today to simulate numerically the growth situations precisely enough to improve the final crystal quality even for very large diameter sizes. This involves the calculation of electromagnetic, thermal, fluid-dynamic and dopant concentration fields in the system.

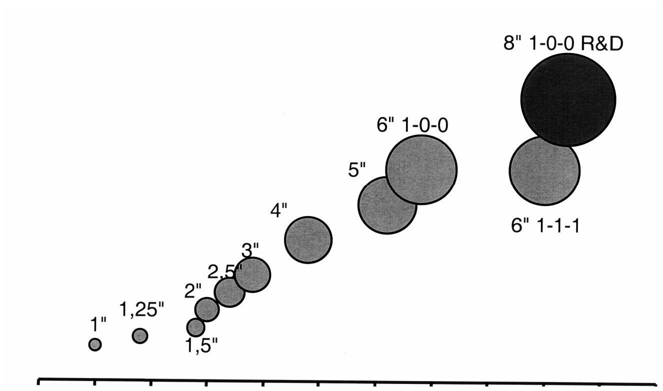

Fig. 11. Development of crystal diameter over the last 50 years (Courtesy of Siltronic AG)

A further critical parameter for the growing crystal is the mechanical stress field. Maximum values may not be exceeded; otherwise dislocations or even cracking occurs. Therefore, the detection of the mechanical stresses and the knowledge of the affecting parameters and their control is an important prerequisite for the successful float-zone growth of large crystals [43].

Moreover, it is now possible to calculate not only quasi-stationary situations but also transient growth processes as occurring during the growth of the start and the end cones of crystal rods [44]. The new model includes also the necessary adjustment of the HF inductor current and the velocity of the supply rod.

Conclusions

After the availability of electrical energy for heating purposes at the end of the nineteenth century, theoretical and experimental investigations in the field of induction heating were carried out worldwide. Conventional and innovative melting techniques were introduced into the industry step by step. In the 1930s of the last century the theoretical frame of induction heating together with many practical experiences made up complete set of knowledge. The development of the melting processes has always been closely connected with the availability of well-suited, stable and powerful electrical supply sources. A short historical review of the development and the practical use of some innovative induction melting technologies are given.

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