Klaus Schulze Symposium

on

PROCESSING AND APPLICATIONS OF HIGH PURITY REFRACTORY METALS AND ALLOYS

Edited by

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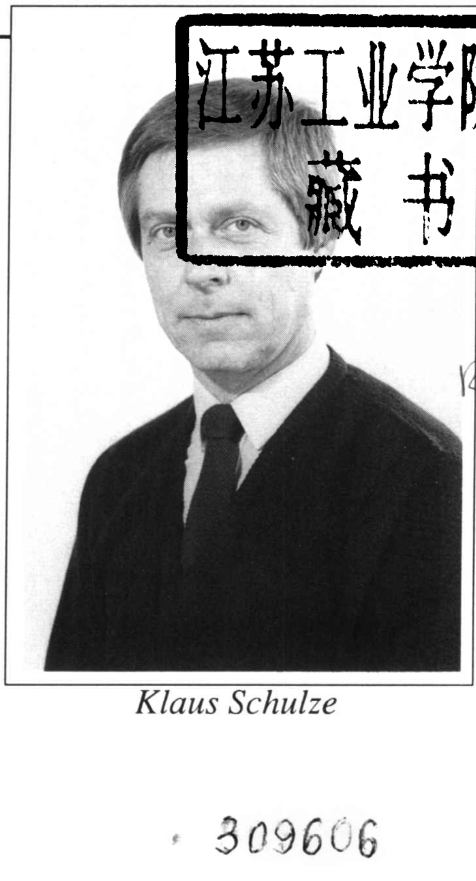

Klaus Schulze

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FOREWORD

Klaus Schulze Symposium on Processing and Applications of High Purity Refractory Metals and Alloys was held on 18-19 October 1993 at the Fall Meeting of The Minerals, Metals and Materials Society, TMS, in Pittsburgh, Pennsylvania, USA. As its title would indicate, this Symposium was held to honor Dr. Klaus Schulze of MaxPlanck Institute of Metals Research, Germany. He passed away in 1991 at the age of 51 after significant contributions to the materials world in general, and to the ultrahigh purity refractory metals in particular. Dr. Schulze, whose accomplishments are recognized throughout the world, and include preparation of the highest-purity niobium in the world. He will be missed not only as a great scientist but also as a very good friend by all of us.

This timely Symposium was sponsored by the Refractory Metals Committee of the Structural Materials Division of TMS. It brought together a select international group of scientists to honor the memory of Dr. Schulze and to share their latest findings on the processing and applications of refractory metals.

During the three-session symposium, over twenty papers were presented. These papers covered the new advances in the area of processing and applications of high purity refractory metals and alloys as well as a review of the previous developments. The topics ranged from extraction and recovery to ultrapurification of refractory metals, and from physical, chemical metallurgy and kinetics of their alloys to the latest analysis and characterization techniques. Current and potential uses as well as advantages and limitations of the refractory metals and alloys were also among the subjects covered.

The first session was devoted to niobium and tantalum and consisted of eight papers. The second session consisted of six papers on niobium and tantalum compounds. During the third session seven of the nine scheduled papers on molybdenum, tungsten, iridium and vanadium were presented. All the sessions were very well-attended. The papers were clear, concise and informative, and were presented in a well-organized fashion. Each presentation was followed by a very stimulating discussion which continued beyond the sessions outside the conference room.

This volume contains most of the papers presented at the Symposium. The editors wish to thank the authors, organizers, session chairpersons, the Refractory Metals Committee and TMS for their help in organizing the Symposium and in publishing the Proceedings.

H. A. Jehn
P. Kumar
M. Uz

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Tribute to Dr. Klaus Schulze

Günter Petzow, Peter Majewski

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Klaus Schulze was born at Dortmund in February 11th, 1941.

The diligent atmosphere of this city in the centre of the Ruhr-area characterized by the steel industry influences his youth - and supposedely the influence of this environment has caused his interest for the technical matters of his domestic industry and his preference for metallurgical engineering. Consequently, after his final examination qualifying for admission to a university and after one year at the army he started to study metallurgical engineering at the technical university of Clausthal. In november 1971 he became a PhD scientist. His academic teachers were Profs. Engell, Schmalzried and Wassermann, learned persons with highest reputation in their field of research. Prof. Engell supervised for Klaus Schulze's thesis "Kinetic of the electrolytical reduction of aluminum and silver in alcalichloraluminat-liquids".

He took his examination in Clausthal but he performed his experimental work at the Max-Planck-Institute for Metals Research in Stuttgart. The reason for this situation was that Prof. Engell was called to be the successor of Prof. Köster at the University of Stuttgart and in addition, to become a Scientific Member of the Max-Planck-Institute for Metals Research. Logically, Engell asked his best scientists to follow him to Stuttgart - one of these scientists was Klaus Schulze.

During his PhD work Klaus Schulze constructed a unit for the preparation of extremely pure and tantalum free niobium out of fluorit-liquids. These activities were part of his work at the laboratory of high purity metals, which was set up and directed by Profs. Haessner and Tölg. Immediately after Klaus Schulze had graduated as a PhD scientist, he was employed as a scientist at the laboratory. In the early seventies, Klaus Schulze and his group who were working on the preparation of high purity refractory metals came to the Powdermetallugical Laboratory, where he worked until his end. He substantially contributed to the set up and reputation of the Powdermetallurgical Laboratory.

Schulzes scientific research included more than 100 publications and was characterized by a special originality and exactness. He knew that the phase diagrams are the basis of each investigation of multi-component systems. Consequently, his studies of the phase diagrams in order to clarify the heterogeneous phase equilibria and to understand the microstructure and the properties of multi-component materials were the centre of his prime research activities.

He always considered the scientific and technical relevance of his work very important. He studied the binary and ternary systems of niobium primarily in terms of the preparation of high purity niobium.

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Beside the studies aiming at an understanding of the structure and properties of the refractory metals and both low temperature and high temperature superconductors, the preparation of high purity materials was the main important part of Schulze's work. In the early seventies, he started to prepare high purity niobium. The extremely tantalum poor niobium, which he prepared form fluorit melts, was the raw material used for additional preparation steps aiming at a further purification of the material. Generally, he applied the zone melting technique with an electron beam and heat treatment in ultra high vacuum. In particular, he studied the metal gas reactions, the knowledge of which is improtant for the preparation of refractory metals with an extremely poor oxygen and nitrogen content.

Finally, Klaus Schulze was able to prepare metals of such extreme purity that the chemical analysis techniques had to be refined in order to quantify the purity of the prepared material. This development was the basis for the founding of the laboratory for high purity materials analysis, as a branch of the Max-Planck-Institute for Metals Research.

Apart from the chemical analysis, Schulze applied the measurement of the internal friction using a torsion pendulum and the measurement of the residual resistance for the quantification of the purity of the metals.

Finally, Klaus Schulze was able to prepare the purest niobium of the world. This record, which has not yet been surpassed, was honored with the Charles Hatchet Award in 1983.

In addition to ultra pure niobium, Klaus Schulze prepared ultra pure tantalum, molybdenum, vanadium and beryllium. Schulze also studied various aspects of the toxicity of beryllium in cooperation with Prof. Zorn.

The ultra pure metals prepared by Klaus Schulze have been desired substances for metals physicists all over the world. For example, the diffusion of charged myons and their interaction with traces of impurities were successfully investigated using Schulze's niobium. In addition, the ultra pure niobium is extraordinarily suitable for the application in terms of dosimeter of fast neutrons. In this context, it is remarkable that Klaus Schulze's ultra pure niobium was normed to EC-NRM 526 in the frame of research and developement projects of the European Communities. Until now, this niobium is applied as reference material for the neutron dosimetry in nuclear reactors.

Due to his very successful scientific work, Klaus Schulze was a popular speaker at conferences. Based on this fact, he travelled many countries in the world. But his particular predilection was focused on Brazil - the country with the greatest niobium resources of the world. He was a member of the Advisory Board of the Fundacao de Technologia Industrial of the Brazilian government. From the German Minister of Research and Technology Klaus Schulze was called to direct the Niobium Project as part of the German-Brazilian technology convention. He gave lectures at the University of Sao Carlos and Campinas and recommended both governments for joint research activities and bilateral scientist exchange. In doing so, he united business and hobby, because his particular preference concentrated on the Latin-American countries and their cultures; Klaus Schulze spoke Spanish fluently. It was a serious concern and a great satisfaction for him that he was able to contribute substantially to the understanding between Germany and Brazil.

Klaus Schulze was conscious that a well working infrastructure of the institute is the necessary basis for his scientific work and success. Consequently, he contributed significantly in this sense. His talent in managment and his pronounced sense of duty was an advantage for him. During 1986 and 1987 he managed the construction of the new Ceramic Building and the clean room facility of the Powdermetallurgical Laboratory. Due to his effective cooperation with the architects the construction work was finished within only one year and in 1987 the scientific work could begin in the well equipped laboratories.

We are admiring his achievements and we are thankful to him.

Klaus Schulze died on June 20th, 1991 - he was only 50 years old.

We remember Klaus Schulze as a kind man, who was constructive, critical, achievement-orientated and with a positive approach to life.

I

THE PRODUCTION OF HIGH THERMAL CONDUCTIVITY NIOBIUM FOR

HIGH FREQUENCY SUPERCONDUCTORS ON A TECHNICAL SCALE

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Abstract

In the temperature range 2 to 20 K the thermal conductivity of Niobium depends on the sum of the interstitial impurities (COHN). The interstitial impurity content can be determined integrally by measuring the specific Residual Resistivity Ratio: RRR. For commercial niobium qualities the RRR value is 20 to 40 corresponding to a total COHN content of 200 to 250 μm/g and a thermal conductivity range of λ 8 - 10 W/mK.

These parameters are used as sensitive parameters for quality assurance aspects in the control of subsequent production steps such as forging, rolling and annealing. After several melting cycles in the EB-furnace, ingots with a weight of up to one ton were produced with a total COHN content of 65 μg/g, RRR values 100 to 140 and a thermal conductivity up to 35 W/mK.

As a result Niobium sheets with high interstitial purity: RRR = 180 and λ (4.2K) = 45 W/mK could be produced from this ingot material, taking suitable precautions during sheet manufacture.

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Introduction

With the increasing use of superconductivity in science and technology, niobium and its alloys have found a wide field of application. In particular the alloy Nb-46.5Ti and the intermetallic compound Nb_3Sn are now indispensable as standard materials for high-field superconductors. Like the pure metal, both these materials are classical representatives of the Type II superconductors [1)2)].

The development of NbTi and Nb_3Sn was pursued particularly intensively. The current state of the art in the metallurgy and processing of these materials permits the attainment of extreme requirements concerning critical currents and/or magnetic fields. On the other hand, the unalloyed metal was not subject to a similar development because of the different nature of the technical requirements associated with the physical properties. This situation is changing at present due to the further development of high-frequency superconductivity [3)4)5)] for the acceleration of "elementary particles" such as electrons, protons and positrons in linear accelerators and storage rings.*

* Projects: CERN/Geneva, DESY/Hamburg, University/Wuppertal, Cornell University/Ithaca/USA and KEK/Japan.

When accelerating elementary particles to relativistic velocities, energy losses Δ E occur as a result of synchrotron radiation. These losses are inversely proportional to the mass of the particles and increase with the 4th power of the particle energy. To compensate for radiation energy losses and to accelerate the particles further, additional energy must be supplied. This is achieved using hollow resonators, known as cavities, by applying phase-corrected high-frequency fields in the microwave range [3)6)7)], see Figure 1.

The efficiency of an electromagnetic cavity depends on various parameters. Apart from the basic mircowave technology, the type and structure of the material play a decisive role. Cavities were previously fabricated from copper and were operated in the normal conductivity state. In the course of the new conception of accelerators (LEP/CERN, Hera/DESY, Tristan/KEK), the storage ring energies have been substantially raised (> 50GeV). Thus, a major demand on cooling arises because of the high frequency losses in normal conducting operation. The loss, i.e. the energy which is lost from the electromagnetic waves by conversion into heat, is determined by the high-frequency resistance of the cavity walls. In the superconducting state, the high frequency resistance becomes very low and should decrease as the concentration of the unpaired electrons (conductance electrons) with decreasing temperature (< Tc). Thus, superconductors such as niobium used as the wall material lead to a tenfold reduction in the high-frequency losses.

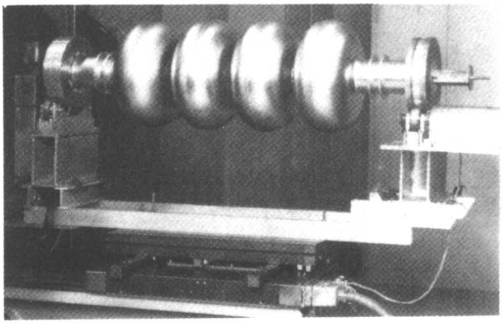

Figure 1: Four-cell Nb cavity structure, courtesy of CERN.

The efficiency of a cavity is characterised by the quality factor Q as the energy loss per oscillation (damping) and the accelerating voltage achieved E_a (V/m). The quality factor Q and accelerating voltage E_a are limited above all by the surface defects (roughness, oxide formation and similar effects) and by an inadequate thermal conductivity of the superconductor below the critical temperature (T_c) [8]. The technical development had stagnated in recent times because of the relatively poor thermal conductivity of commercial Nb-qualities of 5 to 9 W/mK at 273K.

Investigations of the thermal conductivity of superconducting niobium show that the thermal conductivity in the temperature range 0.5 to 10K is composed of phonon and eclectron components [9], and between 2 and 10K depends largely on the interstitial impurities of the niobium. For this reason, recent interest has concentrated on the production of high purity niobium on a technical scale. By means of ultra-high vacuum techniques such as high-temperature degassing, electron-beam zone melting and/or molten salt electrolysis, it was possible to produce extremely pure niobium on a laboratory scale [14]. These processes used in fundamental research cannot simply be applied to the production of large niobium sheets (1 to 2 m^2) such as are required for the construction of cavities. Not the least of the problems is that there is no suitable industrial equipment in which the required qualities can be produced economically on a tonnage scale. The aim was therefore to find a production route based on economic process steps which are available on an industrial scale such as aluminothermic reduction, electron beam melting, forming by forging and rolling and vacuum heat treatment.

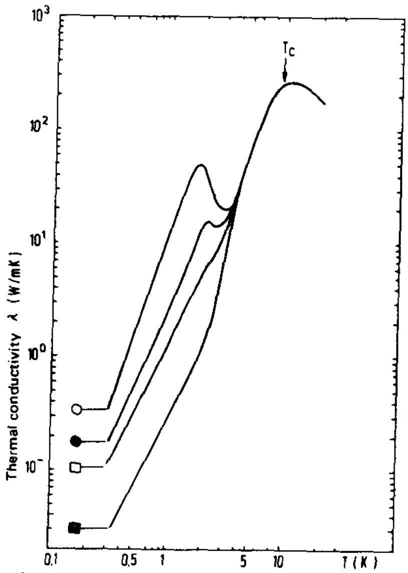

Figure 2: Thermal conductivity of cold deformed niobium samples, Wasserbäch [11]; undeformed; 1,.0 % deformed; 2,4 % deformed; 22,0 % deformed.

2. Fundamental Considerations and Metrological Requirements for the Material Development

The selection of the right process data for the individual process steps and their control demands a detailed knowledge of the influence of the individual impurities in the niobium on its thermal conductivity at low temperatures and also requires the availability of suitable analytical methods for their determination. For the control of the interstitial contents in the niobium after the various process steps, the determination of the residual resistivity ratio and gas analysis methods are particularly advantageous.

2.1 Material Condition and Thermal Conductivity

As is well known, the thermal transport in a solid body occurs via conductance electrons and lattice oscillations (phonons). In metals, the contribution of the electrons predominates, except at very low temperatures. When approaching the critical temperature (T_C), the transition to superconductivity, the electrons condense increasingly to Cooper-pairs, which do not contribute to the thermal transport. Thus, the phonon component of the thermal conductivity becomes more important, and at $T \sim 0.2T_C$ a significant phonon peak occurs, when scatterring processes due to a strongly distorted lattice structure (dislocations, grain boundaries, etc.) are avoided. Figure 2 shows the thermal conductivity, the relative contributions of the electron and phonon components, and the phonon peak of undeformed niobium [11].

The influence of the different lattice defects on the individual contributions to the thermal conductivity of body-centred cubic metals at low temperatures varies [11]. The electron component of the thermal conductivity is limited principally by the interstitial impurity atoms, as these reduce the free paths of the electrons by collision processes [11][1].

The influence of the substitutional impurity atoms and other lattice defects, such as dislocations and grain boundaries, on the electron component is relatively small [9]. On the other hand, the phonon conductivity is very strongly influenced by dislocations. As can be seen in Figure 2, the phonon peak disappears with increasing deformation.

The operating temperature of the cavities (temperature of boiling helium; 4.2K) lies, in the case of niobium, above the temperature at which an influence of the phonon peak occurs, so that the main interest in the material development has to lie in the improvement of the electron conductivity and thus in reducing the concentration of interstitial impurities i.e., carbon, oxygen, hydrogen and nitrogen (C, O, H, N).

For the determination of the thermal conductivity λ at 4.2K, a thermal flux $\Delta Q/\Delta t$ was maintained in niobium samples (2 x 2 x 50 mm^3) by means of silicon diodes as heat sources, and the temperature difference ΔT was determined over the sample length. The measurement cell for the determination of the thermal conductivity was installed in a helium-bath cryostat and evacuated to a final pressure of 10^{-5} m bar. The evaluation of the measured values was carried out with the aid of the equation [12]:

$$\frac{\Delta Q}{\Delta t} = \lambda_{T_c} \cdot \frac{F}{L} \cdot \Delta T \qquad (1)$$

F = cross section, L = length, t = time

As these measurements require special equipment and are relatively expensive, simple measurement methods were sought for the process control. Because of the dependence of the residual resistivity ratio (RRR) on the concentration of impurity atoms, it was natural to use this as a measure of the purity.

Furthermore, on the basis of theoretical calculations, there is a correlation between the thermal conductivity in the superconducting and normal conducting state 12). In combination with the Wiedemann-Franz law, a simplified relationship between the thermal conductivity and the residual resistivity ratio can be derived:

$$\lambda = \frac{RRR}{4}\bigg|_{T = 4.2\,K} \qquad (2)$$

According to this relationship, the thermal conductivity decreases just as the residual resistivity ratio with increasing concentration of the perturbing atoms. The determination of RRR values is a measurement technique which is not actually specific to certain elements but provides high sensitivity, accuracy and reproducibility.

It is known that the electrical resistivity is made up of partial resistances according to the following relationship (Matthiessen rule):

$$\rho_R = \rho_i(T) + \rho_{FA} + \rho_{EF} + \rho_{OF} \qquad (3)$$

ρ_i (T) resistance from electron scattering at phonons
ρ_{FA} impurity atom resistance
ρ_{EF} self defect resistance and
ρ_{OF} surface resistance