

# TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

## PRESIDENT'S LETTER

Dear Friends,

Time is flying! At the time you read this Bulletin, we shall have held our April meeting of the Executive Committee in Brussels to review the matters of the T.I.C. and to work on the programme for our Forty-eighth General Assembly in Rio. Although there is still a lot of detailed work to be done, we feel we have put together a very attractive programme, in terms of both the technical and the social issues. We appreciate very much the help and the input of our hosts Industrial Fluminense and CBMM.

However, it goes without saying that most of the burden was carried by our Secretary General Judy Wickens and our Technical Promotion Officer Ulric Schwela. Both have not only covered the workload for the Forty-eighth General Assembly but also worked hard on the further progress of the Transport Committee. Judy and Ulric: thank you very much for your input!

Two major events are due to come shortly:

1. As mentioned above, the Forty-eighth General Assembly in Rio de Janeiro will take place in approximately four months from now. Please register early for this event and do come to in Rio.
2. We will have a new Secretary General, Ms Emma Wickens, who will take over the business of running our association as of July 1st. We wish Emma all the best for promoting the further development and growth of our organisation and also a lot of fun in working with our crowd!

Looking forward to seeing you all in Rio.

Axel Hoppe, President

### Secretary General

Ms Emma Wickens becomes Secretary General of the T.I.C. in July 2007. She is a chemical engineer, with more than 10 years of experience in industry.

### Transport problems?

A new system for reporting transport denials and delays for Class 7 materials is being established by a UN agency. If you have experienced difficulties with the transport of minerals and raw materials, please contact the T.I.C. so that we can inform you about the procedure.

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## FORTY-EIGHTH GENERAL ASSEMBLY AND TECHNICAL MEETING

The 2007 meeting of the Tantalum-Niobium International Study Center will be held in Rio de Janeiro from October 21st to 24th. Following the formal General Assembly on the morning of Monday October 22nd there will be a session of technical presentations, and a second technical session will be held on the morning of Tuesday October 23rd. On Wednesday October 24th there will be plant tours, when delegates will be able to choose to visit either Industrial Fluminense or CBMM. A welcome reception on the evening of Sunday October 21st and a gala dinner jointly hosted with CBMM on the evening of Monday October 22nd will complete the programme. Sightseeing tours for accompanying persons will be arranged. The conference will be held at the Sheraton Barra Hotel.

Invitations will be sent to nominated delegates of member companies by early July. Others interested and who have not yet contacted the T.I.C. should do so as soon as possible.

### Technical programme

The following papers are expected (not in running order):

- **T.I.C. statistics, transport project, IMO denial reporting procedure**  
Ulric Schwela, Technical Promotion Officer, Tantalum-Niobium International Study Center
- **MIBRA's pegmatite (Volta Grande) and improved mining performance**  
Itamar Resende, Industrial Fluminense
- **Current production capacity expansion at CBMM**  
Tadeu Carneiro and José Isildo de Vargas, Companhia Brasileira de Metalurgia e Mineração
- **Mining in Nigeria – Mekios and tin sheds**  
Sele Obomhense, Mekios UK
- **Very high CV tantalum-powder-paste – a new technique for very small capacitors**  
Ralph Otterstedt, Marianne Gottschling, Helmut Haas, H.C. Starck GmbH
- **High reliability and critical applications of tantalum capacitors**  
Y. Freeman, R. Hahn, Ph. Lessner, and J. Prymak, Kemet Electronics
- **A new era for high CV tantalum powders**  
John Koenitzer, Tomoo Izumi and Larry A. Mann, Cabot Supermetals
- **New high performance tantalum solutions for abrasive corrosion media**  
Dr Bo Gillesberg, Danfoss Tantalum Technologies
- **Growth in the use of niobium oxide capacitors**  
W.A. Millman and Dr Tomas Zednick, AVX
- **The actuality and future development of China's superconductive niobium materials**  
He Jilin, Zhong Jingming, Chen Lin, Xie Weiping, Ningxia Orient Non-ferrous Metals Group Co., Ltd.

## REACH IN

by Judy Wickens

The European Union REACH regulation, the New Chemicals Policy, entered into force on June 1st 2007. The full text, which runs to 278 pages, can be found on the EU web site [eur-lex.europa.eu](http://eur-lex.europa.eu), or by entering into Google 'Regulation (EC) no 1907/2006', making sure that it is the version published on May 29th 2007 that is located (the header is 29.5.2007).

This is the legislation on Registration, Evaluation and Authorisation of Chemicals which has been discussed, drafted and amended for many years, and been the subject of much lobbying by environmentalists and by industry. The purpose of REACH, as the EU sees it, is to unify the legislative framework with two main aims: to improve protection of human health and the environment from risks of chemical hazards, and to enhance the competitiveness of the EU chemicals industry. The distinction between 'existing' and 'new' chemicals should be smoothed out, numerous different rules should be brought together into one system, and information will be passed both up and down the supply chain, to include downstream users. The onus will be on industry to ensure that chemicals it manufactures and markets do not adversely affect health or the environment.

### SUBSTANCES, PREPARATIONS, ARTICLES

The regulation applies to 'substances' and 'articles', but, again, the simple classification has become more complicated as the regulation developed. Chemical terms such as metals, elements and compounds are not used, and all such materials are called 'substances'. Substances can be on their own, or also can be part of preparations, intermediates, by-products and articles. 'Articles' are composed of various 'substances', and the need for registration depends on whether a substance is foreseen to be released during the use of the article or not. 'Preparations' consist of several substances mixed together but without a chemical reaction taking place, as in a solution, and all the substances in the preparation can be registered separately. Alloys are 'special preparations', and guidance is being developed to apply to these. Particular rules cover 'intermediates' which are not isolated for sale and which do not leave the site where they are made.

All substances are covered by the scope of the regulation unless they are explicitly exempted. In spite of the aim to have a unified framework, some substances (see Annex V) have been exempted for various reasons, such as being covered by other regulations. Exemptions include medicines, radioactive substances, non-isolated intermediates, waste, pesticides, polymers, foods, foodstuffs and animal feed, some elemental gases such as hydrogen, and minerals.

Minerals, ores and ore concentrates are exempted as 'substances which occur in nature, if they are not chemically modified'. Thus minerals which have been subject only to physical treatment, by manual, mechanical or gravitational means (Article 3 point 39), are at present exempted. According to Annex V point 8 they are not exempted if 'they meet the criteria for classification as dangerous according to Directive 67/548/EEC'. However, this exemption is expected to be reviewed within a year, and readers whose principal concern is with concentrates should not stop here or cease giving their attention to the regulation.

The difficulty of defining waste which is or is not a secondary raw material continues, and, for the present at least, waste is not covered by REACH but it remains subject to regulations on waste.

### PRE-REGISTRATION

Although the process beginning with registration originally appeared simple, it has gradually increased in complexity, so that the first stage which now requires urgent attention from industry is 'pre-registration'. The period for pre-registration was fixed by the entry into force, and will run from June 1st 2008 to December 1st 2008, a specific and limited period of time.

Each manufacturer or importer (M/I) of a substance in quantities of one tonne or more per year is obliged to submit a registration to the European Chemicals Agency (ECHA). This means each company separately, and for a corporation with a number of legal entities in the EU a registration is required for each entity. Companies established outside the EU may appoint a representative or agent within the EU. If a substance will be manufactured or imported by several companies, the detailed information can be submitted by one company, called the 'lead registrant', while each company submits basic information about its identity and the substance but without the details: this is 'joint submission of data by multiple registrants'. The informal and voluntary groupings called 'consortia' would be likely to produce such submissions. Consortia will be superseded by SIEFs.

Substances listed in the European Inventory of Existing Commercial Chemical Substances (EINECS), which were on the market by 1981 are also called 'existing' or 'phase-in' substances. About 30 000 substances in this category are expected to be pre-registered in the defined period, and thus benefit from the transitional regime of an extended period for registration. For 'new' or 'non-phase-in' substances which have not been pre-registered, further rules and restrictions apply, as in Article 26 and other provisions.

### ECHA AND SIEF

The European Chemicals Agency (ECHA, or 'the Agency') will be established in Helsinki, with a Management Board, an Executive Director and about 350-400 scientists on the staff when fully operational. ECHA will deal with technical matters and scientific dossiers, although problem issues will be referred to Member States.

One month after the close of pre-registration, by January 1st 2009, ECHA will publish on its web site a list of the names of pre-registered substances, with identifying EINECS or CAS codes. If a downstream user does not find on the list a substance which it wishes to use, it can notify the ECHA.

If several companies have pre-registered one substance, the ECHA will form a Substance Information Exchange Forum (SIEF) in which those companies will be obliged to participate. Thus a SIEF will replace the voluntary and relatively informal arrangements of the 'consortium'. As a SIEF will be set up for each substance, that implies the formation of 30 000 SIEFs, and they will run until June 1st 2018. The purpose of the SIEF is to facilitate the collection and sharing of data, to identify data which are missing and arrange to carry out testing, and to share

the financial burden. The way in which this burden is shouldered will be imposed by ECHA unless it is agreed between the SIEF members in their own way.

An initial submission to the Agency will be quickly checked for completeness, and if no rejection is received by the registrant within a fixed period it will be allowed to produce or import the substance. This does not amount to approval by the Agency. The Agency will evaluate the dossiers over a period of 11 years, starting with substances perceived as dangerous and those produced or imported in large tonnages.

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## COSTS AND FEES

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The total cost of the REACH system is expected to be partly or largely offset by savings in healthcare costs as human health and the environment are better protected by the improved management of risk, and as hazardous chemicals are prevented from being released.

For the registration process, a scale of the fees to be paid to the Agency will be defined in a separate regulation, varying by tonnage of the substance and also according to the registrant. A preliminary scale indicates a basic fee which increases with the tonnage band of the substance, a lower rate for members of a consortium, a further reduction for small and medium sized companies (SME), and with the lowest rate for SME in a consortium, ranging in all from about 500 to 24 000 euro, but this is not yet fixed and the rates are only an indication. The fee for submission will be far from being the only charge on industry, as further costs will be incurred, such as the time taken for staff to do the work, or fees for research and laboratory testing, or the use of agents or perhaps the expense of personnel travelling to attend educational seminars.

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## INFORMATION SHARING

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The well-known Safety Data Sheets will be carried over into the REACH system, with some possible modifications and additions, and Annex II of the Regulation describes the provisions for these. Annex I addresses the chemical safety reports, which must include all identified uses. As downstream users are also involved in the system they have to take account of the stated uses and make their own arrangements if they wish to employ the substance for other uses. Correct identification of each substance is important.

There is provision for more extensive transfer of information both up and down the supply chain than has been usual in the past, and information will be available to the public. Sharing of scientific information between companies is required, with the intention of reducing costs, although there is some allowance for restriction of sharing where there may be commercial sensitivity, but how this will be discerned is not clear. Toxicological testing on vertebrates is strictly limited and must be carried out only once.

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## GUIDANCE AND HELP

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Alongside the Regulations, the Commission has launched REACH Implementation Projects (RIPs) involving experts from stakeholder

groups. RIP 3 is developing guidance documents for industry, with subsections such as RIP 3.2 on 'Chemical safety report and SDS' and RIP 3.4 on 'Data sharing'. Most of the RIP guidance is still being developed, and people involved are working as fast as possible to complete the tasks. Also national helpdesks are to be set up to advise on various aspects of the regulatory system.

There are increasing numbers of seminars and workshops to broaden industry's knowledge and to support those who need to know more. Eurometaux holds workshops which are highly informative, and it is setting up a REACH Gateway focussed on the metals industry. The European organisation CEFIC has been closely involved as the regulation was developed; it has established a REACHCentre with a useful web site, and will offer a workshop on 'REACH for Business Managers', combining technical and commercial aspects, on September 20th 2007 in Brussels.

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## WELDING WITH NIOBIUM

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### **Influence of niobium on mechanical properties and hot cracking susceptibility of nickel-base cored-wire weld metal types 70/20 and 70/15**

*This article was prepared from the paper by G. Posch and W. Klagges, Böhler Schweisstechnik Austria GmbH, R. Vallant and H. Cerjak, Institute for Materials Science, Welding and Forming, Graz University of Technology, presented by Dr Posch at the T.I.C. meeting in Innsbruck, October 2006*

Welding is a process that joins metal pieces by melting the parts, sometimes with an added filler, to form a pool of molten material so that a strong joint is formed when the metal cools, useful in the construction of complex items such as turbine engines.

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## ABSTRACT

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In the last few years new types of welding electrodes have been evolving on the market: flux-cored wires (FCW) and metal-cored wires (MCW) are replacing solid wire in the standard gas metal arc welding (GMAW) process. These new types are produced by using various metal and/or mineral powders to fill a tube or a rolled strip before drawing to diameters equivalent to those of solid wires used for GMAW. Using this technique the benefits of the slag systems process and easy variation of alloying concepts known from the shielded metal arc welding (SMAW) process can be applied to the very economical GMAW welding process, with additional advantages in the welding behaviour.

This paper explains briefly the production technology and possibilities of nickel-base cored wires and deals with the influence of different niobium/carbon-ratios on the hot cracking susceptibility and mechanical properties, especially in nickel-base 70/20 and 70/15 weld metals. Using the PVR-hot-cracking test facility and tensile testing an optimum Nb/C-ratio could be found to minimize the hot cracking susceptibility at requested mechanical properties.

The results achieved by the use of different nickel-base cored wire weld metals will be set out in relation to those achieved with the SMAW and the solid wire GMAW processes.

T.I.C. Member Survey 2007 results: Products available from firms which responded

Company	Raw materials	Carbides	Alloy additives	Metalurgical grade products	Capacitors, capacitor material	Services & Other
	Columbite Pyrochlore Struverite Synthetic Concentrate Tantalite Tin Slag	Binary carbides Carbide tools Mixed carbides Niobium carbide Tantalum carbide	Ferro-niobium (steel grade) Ferro-niobium (vacuum grade) Ferro-niobium-tantalum alloy Nickel-niobium Nickel-tantalum Niobium-copper Niobium-titanium (aerospace) Niobium-titanium (superconductors) Niobium-zirconium Tantalum-niobium	Niobium ingot (unalloyed) Niobium melting stock Niobium mill products (alloyed) Niobium mill products (unalloyed) Scrap (Nb & Ta) Tantalum ingot (unalloyed) Tantalum ingot (alloyed) Tantalum melting stock Tantalum mill products (alloyed) Tantalum mill products (unalloyed)	Anodes Capacitors (niobium) Capacitors (tantalum) Cases Foil Powder, EB-melted Powder, sodium-reduced Scrap (Ta capacitor material) Wire	Assaying, analysis Potential mining and exploration Weighing and sampling Other
A&M Minerals and Metals	X X X X			X		
A&R Merchants				X X X X X		X X
Alfred H. Knight International				X X X X X		
Advanced Material Japan	X			X X X X X	X X X X	
Anglo American Brasil				X		
Angus and Ross						X
ATI Wah Chang				X		
AVX						
CBMM				X X X	X X	
DM Chemi-Met				X		X
Duoluoshan Sapphire Rare Metal				X X X X X	X X X X	X X X X
Elite Material Solutions				X X X X X	X	
Exotech	X					
Firadec						
Gestion Iamgold-Quebec				X		
H.C. Starck GmbH & Co. KG (Germany)		X X X X X	X X X X	X X X X X	X X X X X	X X X X X
H.C. Starck Inc. (U.S.A.)		X X X X X	X X X X	X X X X X	X X X X X	X X X X X
H.C. Starck Ltd. (Japan)		X X X X X	X X X X	X X X X X	X X X X X	X X X X X
H.C. Starck Co., Ltd. (Thailand)		X X X X X	X X X X	X X X X X	X X X X X	X X X X X
Hi & M Corporation					X X X X X	
Industrial Fluminense	X			X		
Jiujiang Tanbre Smelter		X X X X X	X X X X X	X X X X X	X X X X X	X X X X
Kemet						
Malaysia Smelting	X					
Mamoré Mineração e Metalurgia				X		
Metal Do						X X
Metherma		X X		X X X X		X
Mitsui Mining and Smelting		X X X X	X X X X			
NEC Tokin					X	
Ningxia Nonferrous Metals		X X X X X	X X X X X	X X X X X	X X X X X	X X X X X
Niotan						X
Noventa	X					
Plansee				X X		X
Plazaminerals	X					
Reading Alloys				X X X		X
Rittenhouse International Resources	X			X X X X		
Simmonds (Metal Trading)	X			X X		X
Solikamsk Magnesium Works		X X X X X	X X X X X			
Stapleford Trading	X X X X			X		
Thailand Smelting and Refining						
Trademet	X X X					
Treibacher Industrie				X X		X X X X
W.C. Heraeus				X X X X X		
Zhuzhou Cemented Carbide		X X X X X	X X X X X			X X X

WELDING

Commonly used welding processes

The welding processes most often used are Manual Metal Arc (MMA), Metal Inert Gas/Metal Active Gas (MIG/MAG), Flux-Cored Wire (FCW) and Submerged Arc Welding (SAW). All these welding processes use an electric arc to melt the base material and filler metal (electrode). MMA and SAW use a solid wire as filler material with additional components to form slag and shielding gas to optimise metallurgy and welding characteristics and to protect the arc and weld surface from oxidation and contamination. But these techniques are limited in their use by low efficiency or restrictions on the possible welding position. MIG/MAG uses a solid wire as filler and a shielding gas, provided externally, to protect the arc. This process is known as a highly economical means of producing welds even in difficult positions, but it has the disadvantage that slag forming components are not present. FCW as the 'latest' development among the standard welding processes combines the benefits of slag forming components with the high efficiency of the MIG/MAG process by using tubular wires which are filled with slag forming

components.

A market survey in Europe from 1975-2000 [1] shows that the market share of MMA is continuously decreasing while MIG/MAG increases, and FCW is slightly increasing. Comparing the European market with U.S.A. and Japan, the tendency is similar, except that the market share of FCW is much larger in U.S.A. and Japan.

FLUX- AND METAL-CORED WIRES

As already mentioned, FCW combines the benefits of welding processes which use slag forming components and the high efficiency of the MIG/MAG process by using tubular wires which are filled with slag forming compounds and special alloying powders. If only alloying elements and no slag forming compounds are used in the filling, the tubular wire is known as metal cored wire (MCW). In Figure 1 the production technology of FCW and MCW is shown.

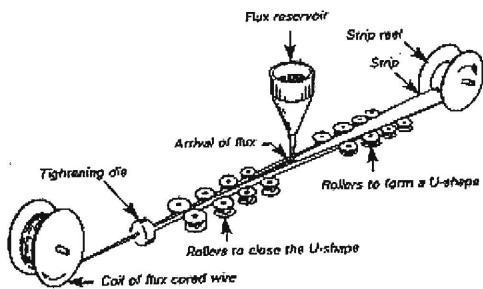


Figure 1: Production of Flux-cored wires

## Principles of Welding

The main principle of welding is melting the base materials to form a common melt pool. To improve the joint, or to fill up the joint, filler metal can be added. After solidification of the weld pool the joint is formed. As welding is a process with a localised high heat input created by an electric arc or some other highly energetic source (e.g. laser), an inhomogeneous temperature field is built up near the heat source.

This temperature field affects also the base material near the joint and can cause metallurgical effects in the base metal. If the temperatures are high enough to cause microstructural changes in the base metal the region is called a 'heat affected zone'. In addition to various microstructural effects high internal stresses are also built up by the temperature field caused by welding.

## CRACKING IN NICKEL-BASED WELDMENTS

### Solidification cracking

All metals show a typical relationship between ductility and temperature (Figure 2): increasing temperature in the solid state up to the solidus temperature ( $T_s$ ) leads to higher ductility. But above  $T_s$  a sharp decrease in ductility due to the presence of a second phase, a liquid phase, occurs. This region is called the Brittle Temperature Range (BTR). If stresses are applied within the BTR, solidification cracking can take place.

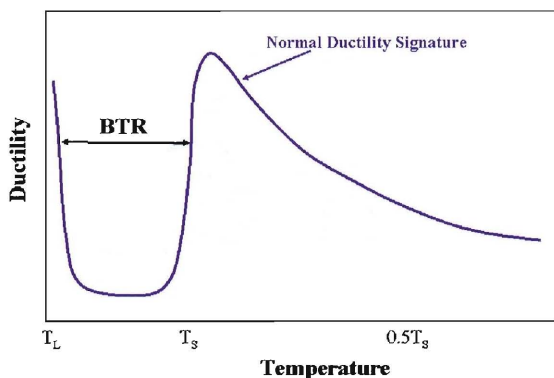


Figure 2: Dependence of ductility and temperature [3]

To minimise the BTR and consequently to prevent solidification cracking, the presence of elements which can form phases with low melting points should be avoided. Such elements are, for example, sulphur, phosphorus, bismuth and antimony. During cooling from the liquid weld pool these critical phases remain as a liquid at the solidification front (Figure 3). Additional stresses caused by the inhomogeneous welding temperature field can lead to hot cracking.

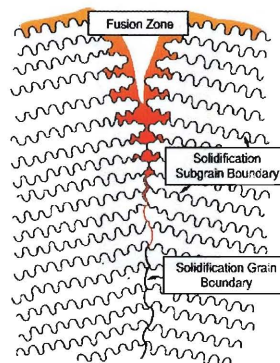


Figure 3: Solidification front of a weldment [3]

Comprehensive investigations [2] have shown that the solubility of these critical elements at high temperatures is higher in cubic body-centred lattices than in cubic face-centred structures. This explains the high hot cracking sensitivity of nickel-base alloys.

### Liquation cracking

Liquation cracking can occur if materials sensitive to hot cracking are heated up to temperatures above the melting point of the low melting critical phases but below the 'main' solidification temperature of the alloy. Also in this case, stresses can lead to cracking.

### Ductility dip cracking

High chromium nickel-base alloys show in a temperature range between  $0.6-0.8T_s$  a solid-state grain boundary embrittlement phenomenon which is called Ductility Dip Cracking (DDC) (Figure 4).

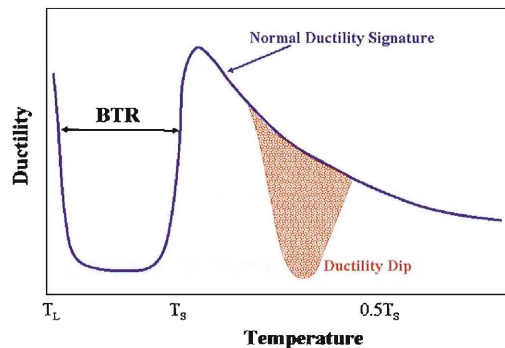


Figure 4: Appearance of Ductility Dip [3]

The mechanism of Ductility Dip Cracking has not yet been completely understood, but various investigations [3] have shown that fine particles at the grain boundaries, especially carbides of the type  $M_{23}C_6$ , can prevent grain boundary gliding and thus the formation of voids and small cracks along grain boundaries.

### Testing of hot cracking behaviour

For the quantification of the hot crack susceptibility of weld metals the controlled deformation crack test or controlled flat tension test (PVR-test) was developed [4, 5, 6]. This test procedure uses flat specimens of base metal or 'all weld metal' (AWM) clamped into a special tension fixture of a horizontal servohydraulic tensile test equipment (Figure 5).

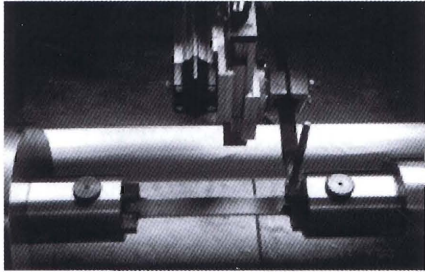


Figure 5: PVR-test equipment

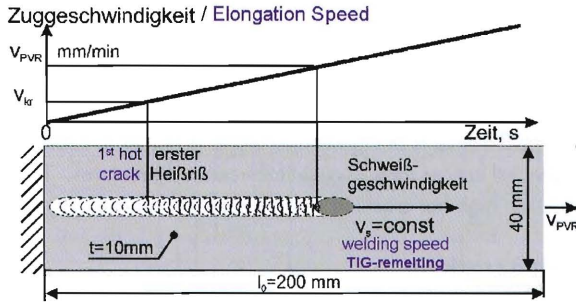


Figure 6: Principle of PVR-testing

The welding arc, moving with constant speed, is superposed by a linearly increased tension speed in the welding direction (Figure 6). The standard PVR-test procedure is carried out with tension rates linearly increasing from zero to 60mm/min, using bead-on-plate TIG-welding (TIG: tungsten inert gas) with argon shielding gas at various heat inputs.

For quantification of the hot cracking susceptibility the critical tension speed ( $v_{cr}$ ) or critical elongation speed (CES) is determined. The CES should correspond to the first hot crack detected visually at a specified magnification. It can be determined for each of the hot crack types: solidification cracks (SC), liquation cracks (LC) and Ductility Dip Cracks (DDC). In Figure 7 the surface of a PVR test specimen after testing is shown. The different types of hot cracks can easily be detected.

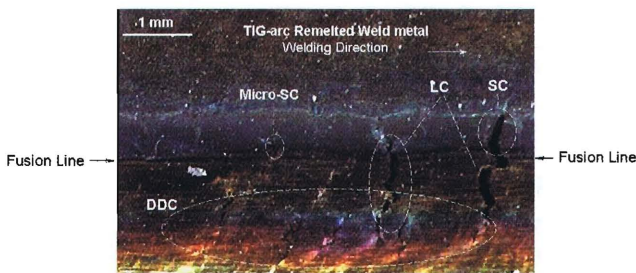


Figure 7: Surface of PVR-test specimen with different kinds of detected hot cracks [7]

## EXPERIMENTAL PROCEDURES

### Design of filler material

The aim of this work was to determine the appropriate niobium and carbon content for flux- and metal-cored wires. Because of the novelty of this kind of filler material, no standards are available so far from which the chemistry of the weld metal can be derived. In Figure 8 various standards for filler metals and different welding processes of type 70/15 and 70/20 are listed. The specifications regarding carbon and niobium content are different depending on the applied welding process for the filler and base metals.

Classification / Standard	W.-No./UNS No.	C	Si	Mn	P	S	Cr	Ni	Nb	Fe	Ti	Mo	Cu	Others*	
Bare Electrodes / All-weld metal	NiCr20Nb DIN 1738 Bare Electrodes and Rods	min		2,5			18,0	65,0	1,5						
		max	0,05	0,5	3,6		0,015	22,0	3,0	3,0	0,8		0,5		
	NiCr15FeMn DIN 1736 Weld Metal MMA-Electrode	min			5,0			13,0	61,0	1,0	2,0				
		max	0,10	1,0	10,0		0,015	17,0	3,5	9,0	1,0		0,5	0,3 Ta	
	ERNiCr-3 AWS A5 14 Bare Electrodes and Rods	min			2,5			18,0	67,0	2,0					
		max	0,10	0,5	3,6	0,03	0,015	22,0	3,0	3,0	0,75		0,5	0,5	
	ENiCrFe-3 AWS A5.11 Weld Metal MMA-Electrode	min			5,0			13,0	58,0	1,0					
		max	0,10	1,0	9,5	0,03	0,015	17,0	2,5	10,0	1,0		0,5	0,5	
	NiCr20Mn3Nb prEN ISO 14172, Weld Metal MMA-Electrode	min			2,0			18,0	63,0	1,5					
		max	0,10	0,5	6,0			22,0	3,0	4,0	0,5	2,0	0,5		
NiCr15Fe6Mn prEN ISO 14172, Weld Metal MMA-Electrode	min			5,0			13,0	60,0	1,0	2,0					
	max	0,10	1,0	10,0			17,0	3,5	10,0	1,0		0,5	0,3 Ta		
NiCr20Mn3Nb prEN ISO 18274, Bare Electrodes and Rods	min			2,5			18,0	67,0	2,0						
	max	0,10	0,5	3,5			22,0	3,0	3,0	0,7		0,5			
NiCr18Fe8Nb prEN ISO 18274, Bare Electrodes and Rods	min			15,0	70,0	1,5	5,0								
	max	0,08	0,3	1,0			17,0	3,0	9,0				0,5		
Base metal	NiCr15Fe, Alloy 600	min					14	72	6						
		max	0,08	0,5				17		10	0,3		0,5	0,3 Al	
Base metal	LC-NiCr15Fe, Alloy 600 L	min					14	72	6						
		max	0,03	0,5				17		10	0,3				

Figure 8: Standardised chemical composition of various filler metals of types 70/15 and 70/20 [7]

To investigate the influence of different niobium and carbon contents in the weld metal, various cored wires with different chemical compositions were produced and welded, then compared with the results of flux-cored wires and fillers already existing on the market for other welding processes. To evaluate the influence of niobium and carbon the other alloying elements (Cr, Mn, Mo) were kept constant in the laboratory-produced cored wires (Figure 9). Cr was at about 20%, Mn was around 3% and no Mo was added.

Consumable	Solid wire	MMA-Electrode	Metal-cored wires MCW										Flux-cored wires FCW											
			Testing wires										Market products											
			Ni-base 70/20		Ni-base 70/20								Ni-base 70/20		Ni-base 70/20		Ni-base 70/15							
Consumable	Alloy type	Alloy No.	1	2a	2b	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18a	18b		
			Nb [%] in Filling	2,5	n.k.	0,0	1,0	2,0	3,0	3,5	1,0	2,0	3,0	n.k.	2,4	n.k.	n.k.	1,9						
			C [%] in Filling	≤0,03	n.k.	0,05	0,05	0,05	0,1	0,05	0,1	0,05	0,05	0,1	0,05	0,05	0,05							
			Nb/C-ratio	83	n.k.	0	20	40	20	60	30	70	35	20	40	80								
Heat Input	Nb- C-content	AWM [kJ/cm]	12,2	9,8-10,3	-	11,9	12,8	12,5	9,5	12,2	9,5	14,8	9,7	9,5	9,3	9,3	9,5	10,4	8,5	9,1	-	-		
			PD [kJ/cm]	13,4	9,8-10,5	8,2	8,6	8,7	8,4	8,3	8,2	7,9	8,2	7,9	6,5	6,5	6,3	-	-	-	-	13,0	7,0	

Figure 9: Variation of Nb and C in the laboratory produced cored wires [7]

### Welding of test specimens

To evaluate the mechanical properties and the hot cracking susceptibility test specimens of 'all weld metal' (AWM) and 'plate deposits' (PD) were established (Figure 10) [7].

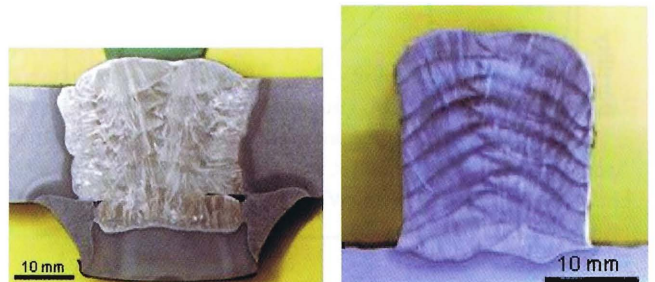


Figure 10: Test specimens: left: AWM acc. EN 1579-1 (AWM); right: plate deposit (PD) [7]

The making of an 'AWM' specimen is exactly defined in the European standard EN 1579-1. In principle it can be seen as an approximately 20cm long joint with a gap approximately 20mm broad and 20mm high. The two sides of the gap have the same chemical composition as the filler metal to prevent dilution effects. In practice this is achieved by buffering the plates which are used for establishing the joint with the same filler material. This

procedure guarantees that test specimens consist of almost 'pure' weld metal. Plate deposits are a kind of multilayer cladding. To create samples of pure weld metal it must be ensured that the first two overlays are not taken into account when preparing the samples. To establish a bar of more or less 20cm in length with a rectangular 20mmx25mm cross section copper moulds are used.

With these two procedures macro-sized specimens for determination of chemical analysis, hot cracking sensitivity and mechanical properties can be established. Nevertheless it must be taken into account that the distribution of the internal stresses within the samples is completely different. In the case of 'AWM' sample preparation, free shrinkage of the plates is possible; internal stresses caused by the welding process are reduced by plastic deformation of the already existing weld. In contrast, plastic deformation is hindered in the case of plate deposits. This leads to a much higher level of internal stresses within the specimen.

### Tensile properties

In the longitudinal direction of the AWM and PD test specimens, tensile test samples were prepared and tested using a tensile testing machine. In Figure 11 and Figure 12 the results of the tensile testing are shown. The beneficial effect of niobium addition can clearly be seen, as both fracture elongation and tensile strength increase as the niobium content is increased.

In the case of flux-cored weld metal (Figure 12), it must be taken into account that slag systems also have an additional influence on the mechanical properties. Commercially available flux-cored wires have a variety of different slag systems – more basic systems with better mechanical properties but worse welding properties, or rutile systems with superior welding characteristics but lower mechanical properties. Besides the alloying concept and the slag system, the heat input seems also to have an influence on the mechanical properties, as can be seen in Figure 12 for FCW 18.

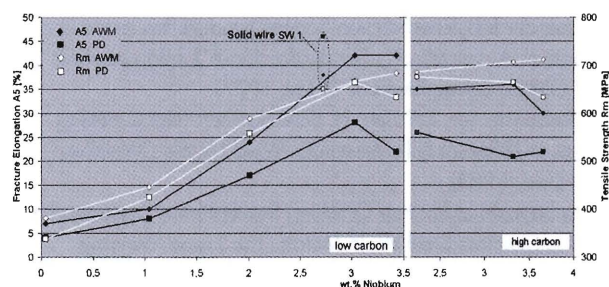


Figure 11: Metal-cored weld metal tensile test specimen: fracture elongation and tensile strength versus niobium and carbon content [7]

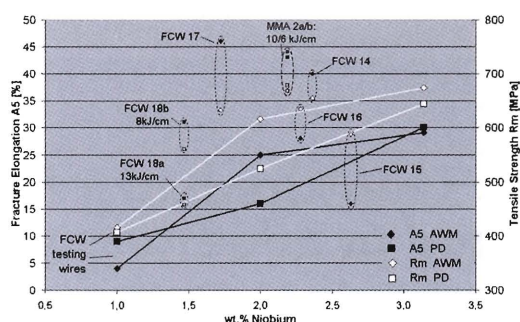


Figure 12: Flux-cored weld metal tensile test specimen: fracture elongation and tensile strength versus niobium content [7]

After the tensile testing the broken specimens were visually inspected. Besides the main fracture, minor cracks were found on the surface of the broken test specimens. Due to their appearance they were called 'hook cracks' (Figure 13). The formation of these hook cracks can be explained by defects which already exist in the tensile test specimen before testing. Application of the tensile stresses causes these defects to become enlarged and opened so that they can easily be seen on the surface. In the case of nickel-base alloys such defects are often small hot cracks, especially ductility dip cracks (DDC).

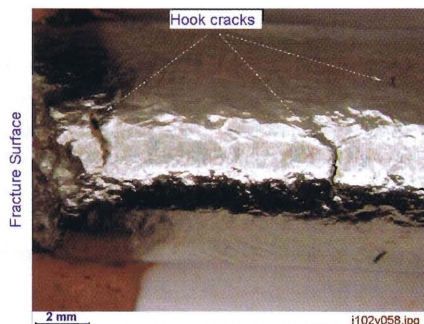


Figure 13: 'Hook cracks' on the surface of a broken tensile test specimen [7]

These hook cracks in the broken tensile test specimen can be counted and related to results of the tensile test. A clear correlation between the hook cracks and the reduction of area can be found for metal cored filler metal (Figure 14). In Figure 14 it can also be seen that more hook cracks were always detected in the plate deposit specimens (PD) than in the AWM specimens. The niobium content of the weld metal can also be correlated with the appearance of hook cracks: the more niobium present, the fewer hook cracks and the higher the reduction of area.

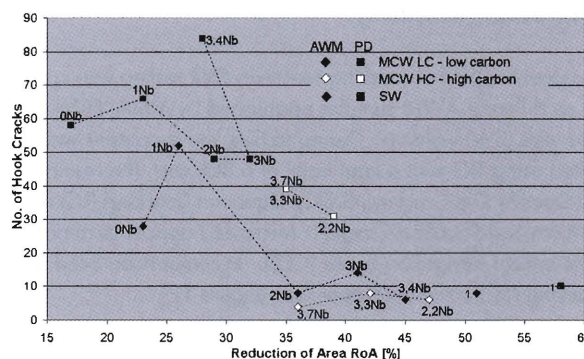


Figure 14: Metal cored-weld metal tensile test specimen: relation between hook cracks and reduction of area [7]

In principle, similar results can also be obtained for flux-cored filler metal but it must be mentioned that there is an additional significant influence of the type and basicity of the slag on the number of hook cracks and reduction of area. In Figure 15 fractographs of broken tensile test specimens of AWM flux-cored wires with different niobium contents are shown. As the niobium content increases, in addition to oxides, increasing amounts of small particles of niobium carbide NbC appear, having a positive influence by making the grain size smaller.

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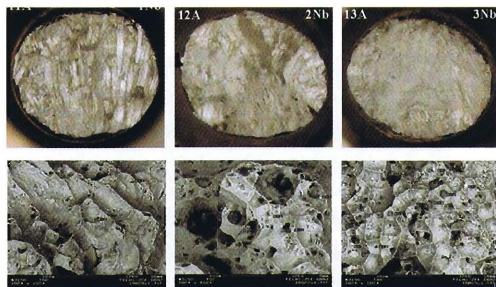


Figure 15: Stereomicroscopic and SEM fractographs of broken FCW tensile test specimens with different niobium contents [7]

### Toughness properties

In addition to tensile testing, ISO-V toughness testing at  $-196^{\circ}\text{C}$  was carried out. As can be seen from the results (Figure 16), in the case of metal-cored wires niobium-contents above about 2% decrease the toughness of the weld metal. In the case of flux-cored wires similar effects could not be detected. Carbon, as well as niobium, has an influence on the toughness properties: a higher carbon content leads to lower toughness values compared to weld metal with lower carbon.

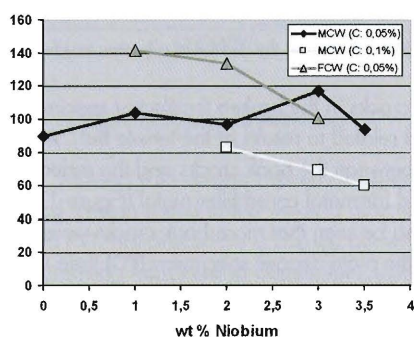


Figure 16: Toughness at  $-196^{\circ}\text{C}$  depends on niobium and carbon content

### Hot cracking sensitivity

To determine the hot cracking sensitivity PVR-testing was carried out on different AWM samples established by MMA, FCW and solid wire (SW) welding. During testing, the specimens were re-melted using TIG with a heat input of  $6.8\text{kJ/cm}$ . The results show that Ductility Dip Cracking (DDC), Liquation Cracking (LC) and the 1<sup>st</sup> Micro-Solidification Crack (1<sup>st</sup> Micro-SC) appear at almost the same critical elongation speed (CES). In comparison Solidification Cracking (SC) occurs at higher CES (Figure 17).

In the tests, AWM of solid wire welding shows a higher hot cracking resistance; fillers with slag systems have nearly the same, but slightly lower, CES. Compared to the AWM the base metal has the lowest hot cracking sensitivity [7].

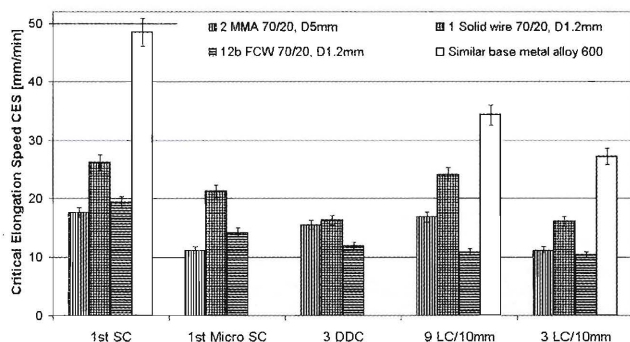


Figure 17: PVR-test results: AWM of MMA, FCW and solid wire compared to base metal TIG-re-melted ( $6.8\text{kJ/cm}$ )

## CONCLUSIONS

This investigation has clearly shown that niobium improves the hot cracking resistance of nickel-base filler metals of type NiCr15 (nickel-base 70/15) and NiCr20 (nickel-base 70/20). The formation of niobium carbide plays an important role in causing finer subgrain structures and carbide formation at grain boundaries which improves ductility and lowers the hot cracking susceptibility, especially ductility dip cracking. The optimum niobium content was found to be around 2–2.5%. Higher niobium contents decrease toughness and promote solidification cracking. It also pointed out a lower hot cracking resistance of the filler metals compared to the base metal, caused by higher amounts of elements in the weld metal which are critical in promoting hot cracking. Comparing different filler metals, the solid wire welding shows the best behaviour, but it must be stated that the welding of the other welding processes exhibits a better performance. But nickel-base flux-cored wires with optimised slag systems show the best welding behaviour, with highest efficiency at acceptable hot cracking susceptibility.

The authors thank Niobium Products Company and the Materials Center Leoben (Kplus programme of the Austrian government) for financing this investigation and Prof. Herold, Mrs Streitenberger and Mr Pchennikov from the Institute of Joining and Beam Technology at TU Magdeburg for performing the PVR-tests and for their evaluation.

They also offer special thanks to the senior welding metallurgists Mr Tösch from Böhler Schweißtechnik Austria and Mr Heinemann, UTP-Schweißmaterial for their helpful advice.

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