

## 33 Years in Portugal as a Materials Researcher from Japan

A Special Contribution  
expressing appreciation to *Sociedade Portuguesa de Materiais*  
on awarding *Prémio de Carreira e Reconhecimento*

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### 1. Introduction

I feel profoundly honored to be awarded with *Prémio de Carreira e Reconhecimento* (Career Recognition Prize) by *Sociedade Portuguesa de Materiais* (*SPMater*; Portuguese Society for Materials Research; although the institute name is often shortened to be *SPM*, it might be confused with *Sociedade Portuguesa de Matemática* and thence I inclined to use shortened expression *SPMater*) in 2015. To express my deep gratitude to *SPMater* for deciding to award me this prestigious *Prémio*, I would like to summarize my footpath as a materials researcher in Portugal started in July 1982 at then *LNETI - Laboratório Nacional de Engenharia e Tecnologia Industrial* (now *LNEG - Laboratório Nacional de Energia e Geologia* through sequence of institute name changes, *INETI - Instituto Nacional de Engenharia e Tecnologia Industrial* and again *INETI* but representing *Instituto Nacional de Engenharia, Tecnologia e Inovação*). During last 33 years working at National Industrial Research Institute with occasionally changing names in sequence, *LNETI - INETIndustrial - INETInovação- LNEG*, I managed to publish nearly 100 papers on peer-reviewed journals and to present more than 70 communications at national and international conferences including bi-annual *Materiais xxxxx* conference series of *SPMater* started in 1983 thanks to friendly and productive cooperation with several colleagues at the institute, especially Eng<sup>a</sup> Teresa Marcelo (Eng<sup>a</sup> (Engenheira) is a unique title used in Portugal for female graduate from Engineering Faculty of University; corresponding title for male is Eng<sup>o</sup> (Engenheiro)), Dr. Jose Brito Correia and Dr. Fernando Almeida Costa Oliveira (in order of starting year of collaboration) as well as with colleagues outside the institute including Prof. Luís Guerra Rosa and Prof. Jorge Cruz Fernandes at *IST (Instituto Superior Técnico)* in *UTL (Universidade Técnica de Lisboa)*.

Nowadays, it is not very difficult to access list of publications and, in many cases, to acquire PDF copies of full text of the published works on web pages (e.g., Refs. 1 - 4). Noting this modern reality, I would like to present in this manuscript thanking *SPMater* for awarding me of the *Prémio* some back-stories or episodes that were not described in formal scientific and technical publications.

## 2. Before Arriving Portugal

### 2.1. Apprenticeship years at Osaka University in Japan

In Japan, education system starts with 6 years primary school followed by 3 years junior high school. After these 9 years of compulsory education, 3 years high school follows before 4 years of university course (6 years for medical and dental schools). Graduate school thereafter consists of 2 years Master Degree Course and 3 years Doctor Degree Course.

I chose to study Nuclear Engineering at Faculty of Engineering in Osaka University entering April 1968. In science and engineering faculties in Japanese universities, student in the final year is assigned to a specific laboratory to start final year project on given subject to get primary hand-on experience in research work. I chose to enter Prof. Tadao Sano's laboratory for the final year project in April 1971 and Dr. Masahiro Katsura was assigned as my supervisor. Broad scope of research program assigned to me was evaluation of thermodynamic stability of ternary U-M-N systems where M represents transition element. The first M assigned for me to work with in this line of research work was Ce (cerium). More specifically, I was assigned to carry out measurement of decomposition pressure  $p(N_2)$  of cerium mononitride CeN. Under comparatively low  $p(N_2)$ , MN dissociates incongruently



to yield molten M(l) releasing  $N_2$  gas while, at above certain threshold  $p(N_2)$ , MN would melt congruently



In the regime of incongruent melting, melting temperature  $T$  would vary depending on  $N_2$  gas partial pressure  $p(N_2)$  whereas congruent melting temperature would become constant irrespective of  $p(N_2)$ .

Ce is very reactive to  $O_2$  and its handling in air demands very special care. When pure Ce was purchased from Johnson Matthey (England), it was delivered in form of sponge immersed in inert mineral oil. The university had no sophisticated laboratory to synthesize CeN from the purchased Ce sponge. Thus, it was sent to Central Research Laboratory of Mitsubishi Metal and Mining Corp. in Omiya near Tokyo for synthesizing CeN from the purchased Ce. Such technical services of industries to universities in those days in Japan were done as special favor without involving payment. Prepared CeN samples at Mitsubishi were sent back to our laboratory in Osaka University in several vacuum-sealed glass tubes. Once some fragments of CeN samples were taken out of the sealed glass tube, it was kept in storage system made of glass held in dynamic vacuum to avoid undesired oxidation degradation of the CeN before the dissociation pressure measurement was undertaken. In fact, simple dynamic vacuum was not sufficient to retard progress of oxidation of CeN and the zone of the storage system in which CeN fragments were stored must be submerged in liquid nitrogen to keep at low temperature. Although we arranged special automatic liquid  $N_2$  supply system for the CeN storage apparatus, its function was not very reliable. Thus, during the period while I was working with CeN, I had to go to laboratory even on Sundays to ensure level of liquid nitrogen for CeN storage system.

#### 2.1.1. Statistical thermodynamic approach to interstitial non-stoichiometric compound $MX_x$

Probably, concerned with my situation of such technical difficulty in undertaking assigned experimental work using CeN that might lead to retarded progress of experimental work resulting in failure to complete my Master and subsequent Dr. degree work within specified years (in Japan, empirical academic rule was to publish 4 - 5 papers in peer-reviewed journals before submitting Dr.

degree thesis to the university for review), Dr. M. Katsura arranged me a safe-guard option to study statistical thermodynamics to be able to make some publications making use of statistical thermodynamic analysis for available experimental data in case of serious delay of experimental work. We read together intensively a classical textbook on statistical thermodynamics co-authored by Fowler and Guggenheim [5] for me to get acquainted with statistical thermodynamic analysis procedure. It was not an easy task at all for me. There was once a serious difficulty for me to interpret either Bose-Einstein or Maxwell-Boltzmann statistic formula (I do not remember which one it was) and it took me a couple of months just to proceed a few lines of Fowler and Guggenheim's text book. It was an enlightening experience to overcome this difficulty and it was not the only single case but, in fact, sequences of such enlightening experiences had to be repeated many times thereafter.

To justify concern of Dr. M. Katsura over my delayed experimental work, my first publication [6] emerged in 1974 (the year of bloodless revolution on 25 April in Portugal) was not report of experimental work but statistical thermodynamic model calculation for hypo-stoichiometric sub-nitride Cr<sub>2</sub>N of Cr. In those days, there was no personal pocket scientific calculator available although such inconvenient situation would be outside the imagination of modern students in 21st Century. Only luxury in our laboratory was single massive Casio table-top calculator of dimension about 20 x 20 x 5 cm that costed about 300,000 JPY (Japanese Yen) then but had capacity to undertake only four basic arithmetic operations (+ / - / x / ÷) alone. So, to undertake calculations desired for my first publication including logarithm and other scientific functions, I had to spend quite long hours at a library consulting massive classical numerical handbook by Landolt-Börnstein (*LB*). I committed stupid mistake in numerical calculation. I confused *ln* (natural logarithm) and *log<sub>10</sub>* (engineering logarithm) on taking values from *LB* Numerical Handbook (*ln X / log<sub>10</sub> X ≈ 2.3026*). As the consequence, term *R ln f(N)* referring to electronic contribution of entropy term was erroneously calculated although evaluated values for nearest neighbor interaction energy term *E(i-j)* between atom *i* and atom *j* were not affected by this careless mistake (*f(N)* refers to atomic partition function of *N* in hypo-stoichiometric *hcp* (hexagonal close packed) Cr<sub>2</sub>N phase and *R* universal gas constant). This careless mistake in confused *log<sub>10</sub>* and *ln* remained unnoticed for quite a while and reproduced in my Dr.Eng. thesis presented to Osaka University in 1977 [7] and it was corrected only a decade later in Chapter 5 of Ref.[8] published in 1985.

Generalized fundamental formulae proposed for this line of analysis of interstitial non-stoichiometric condensed phase MX<sub>x</sub> are as follows.

$$A \equiv RT \ln \{[(\theta - x)/x][p(X_2)]^{1/2}\} = g(T) + \beta x E(X-X) \quad (3)$$

$$K(T) = g(T) - [D(X_2)/2 - RTC(T)] = Q - RT \ln Z_f(X)(T) \quad (4)$$

$$C(T) = -(1/2) \ln \{[(4\pi m_x)^{3/2}/h^3][(T^{7/2}/\Theta_r)(1 + \Theta_r/(3T))][\rho^2 v_0^*/2]\} \\ + \Theta_v/(4T) + (1/2) \ln [1 - \exp(-\Theta_v/T)] \quad (5)$$

$$\ln f_x(T) = -\int_0^\infty g(v) \ln[1 - \exp(-hv/(kT))]dv + \ln \rho v_0 \quad (6)$$

$$Q + \beta x E(X-X) = \partial E(MX_x)/\partial n_x \quad (7)$$

Symbols used in the above formulae are classified as follows:

**<universal constants>**

*R*: universal gas constant (= 8.31451 J·mol<sup>-1</sup>·K<sup>-1</sup>),

*h*: Planck constant (= 6.6260755 x 10<sup>-34</sup> J·s),

*k*: Boltzmann constant (= 1.380658 x 10<sup>-23</sup> J·K<sup>-1</sup>),

**<known materials constants>**

$m_X$ : mass of X atom

$\rho$ : nuclear spin weight

$\Theta_r$ : characteristic temperature for rotation of  $X_2$

$\Theta_v$ : characteristic temperature for vibration of  $X_2$

$\nu_0^*$ : electronic state of normal state of  $X_2$  molecule

$D(X_2)$ : dissociation energy of  $X_2$  molecule per mole

$\beta$ : factor determined from crystal structure consideration

$\theta_0$ : geometrically available number of interstitial site per M in  $MX_x$

$\nu_0$ : statistical weight of tightly bound electrons around X in  $MX_x$

$\nu$ : vibrational frequency of X atom in  $MX_x$  lattice

$g(\nu)$ : distribution function

**<experimentally measurable parameters>**

$p(X_2)$ : equilibrium pressure of ideal gas  $X_2$

$T$ : absolute temperature (K)

$x$ : composition (X/M atom ratio) in  $MX_x$

$n_X$ : number of X atoms in  $MX_x$

$n_M$ : number of M atoms in  $MX_x$

**<parameters to be evaluated>**

$Q$ : degree of stabilisation of X atom in  $MX_x$  lattice with reference to isolated X and M atoms in vacuum

$E(i-j)$ : interaction energy between  $i$  and  $j$  atoms in  $MX_x$  lattice

$E(MX_x)$ : lattice energy

$f_X(T)$ : partition function of X atom in  $MX_x$

$f_M(T)$ : partition function of M atom in  $MX_x$

$K$  &  $g$ : parameters determined by Eqs.(3) & (4) from the experimental  $P$ - $T$ - $C$  (pressure - temperature - composition) data

**<a factor to be assigned a priori>**

$\theta$ : number of the interstitial sites per M atom available for occupation by X atoms in  $MX_x$

**<a resultant model parameter referring to extent of blocking of interstitial sites>**

$Z$ : extent of blocking of interstitial sites by X in  $MX_x$  ( $= \theta_0/\theta$ ); that is, when one interstitial site in  $MX_x$  is occupied by an X atom,  $(Z - 1)$  neighbouring interstitial sites are blocked from occupation by other X atoms.

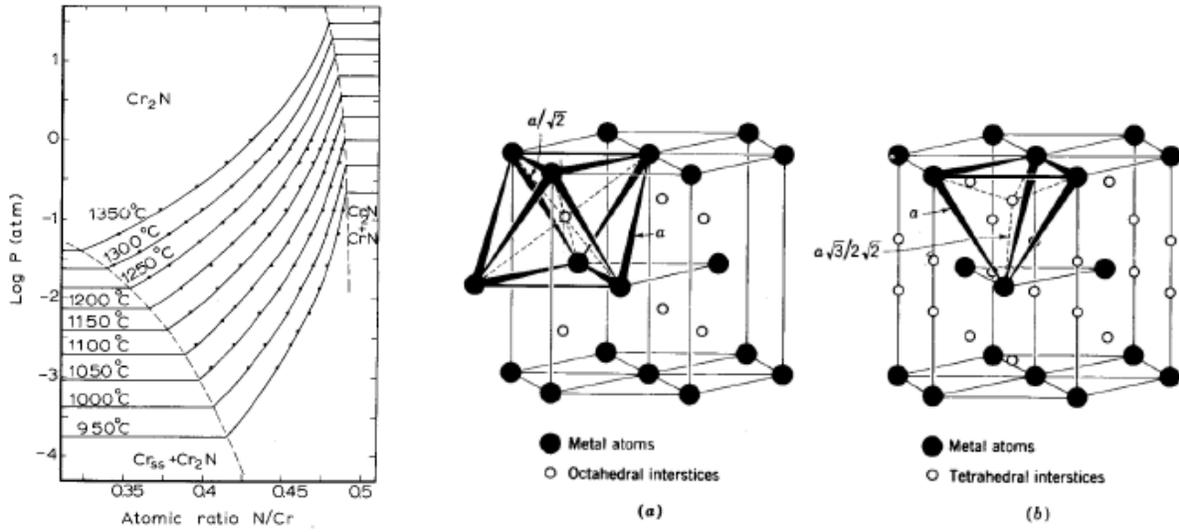
Our significant contributions to statistical thermodynamic analysis procedure for interstitial non-stoichiometric solid solutions  $MX_x$  in general demonstrated in this work [6] include

i) proposing simplifying standardized equation (3) for analysis of  $MX_x$  in equilibrium with  $X_2$  gas with partial pressure  $p(X_2)$  at temperature  $T$ ,

ii) proposing method for determining value for the parameter  $\theta$  a priori referring to number of interstitial sites per M atom available for occupation by X atoms in  $MX_x$  at the onset of statistical thermodynamic analysis in a way to yield constant  $E(X-X)$  over homogeneity range of  $MX_x$  at any given  $T$ .

In case of analysis of  $P$ - $T$ - $C$  relationships for hypo-stoichiometric sub-nitride  $CrN_x$  referring to isothermal  $P$ - $C$  relationships reported by Mills [9] as reproduced in Fig. 1,  $\theta$  was primarily assumed to be 1 noting that, in *hcp* lattice, if all the geometrically available O-sites are available for random occupation of N atoms (cf. Fig. 2 for schematic presentation of *hcp* lattice structure with O-sites (a) and with T-sites (b)),  $\theta$  must be 1. As reproduced in Fig. 3, with the choice of  $\theta = 1.0$ , isothermal  $A$  vs.  $x$  plots according to Eq.(3) showed change in slope in high range of  $x$  and low range of  $x$  demonstrating trend of increasing

repulsive N-N interaction in the higher range of  $x$  than in the lower range of  $x$ . Some authors in those days appeared to consider such trend of change in  $E(X-X)$  with composition  $x$  in  $MX_x$  acceptable interpreting the detected trend rational because the elastic repulsion between neighbouring X-X atoms would tend to rise with increasing occupation of interstitial sites but we did not because, even on phase changes of element between solid state and liquid state, change in enthalpy term is merely about 10 kJ/mol or so [11,12] and, if drastic  $E(N-N)$  change as depicted in Fig. 3 occurs, there would be no chance to keep the same crystal structure when  $E(X-X)$  changes drastically at certain  $x$ .



**Fig. 1.** Isothermal equilibrium pressure-composition (P-C) relationships for interstitial hypo-stoichiometric  $Cr_2N$  phase (reproduced from Fig. 1 in Mills [9]).

**Fig. 2.** Atomic configuration of *hcp* (hexagonal close packed) crystal lattice and two types of interstitial sites, octahedral interstitial sites (O-sites) and tetrahedral interstitial sites (T-sites) (reproduced from Fig. 10 in Barrett and Massalski [10]).

(a) O-sites, (b) T-sites.

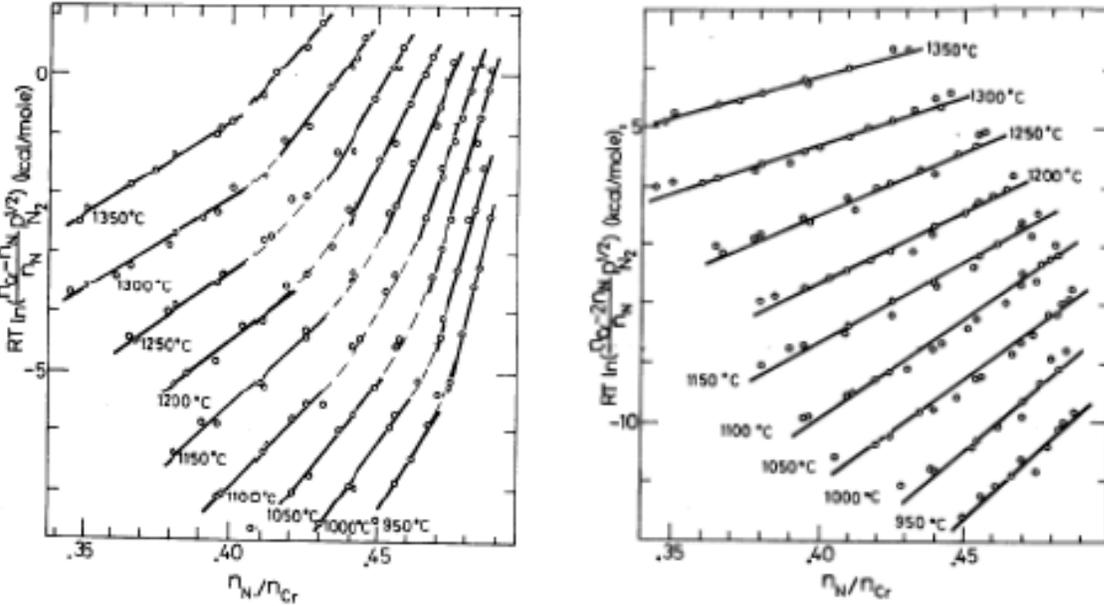
Number of M atoms in the unit cell = 6; Radius  $R$  of M atom =  $(2^{1/2}/4)a$ .

Number of O-sites in the unit cell = 6; radius  $r_O$  of O-site =  $0.414R = 0.146a$ .

Number of T-sites in the unit cell = 12; radius  $r_T$  of T-site =  $0.225R = 0.0795a$ .

$c = (8/3)^{1/2}a$  in an ideal *hcp* lattice.

In fact, when  $\theta$  was taken to be 0.50 close to the solubility limit of N in  $Cr_2N$  (i.e. N atoms are distributed randomly over half the number of geometrically available O-sites in *hcp* lattice of Cr),  $E(N-N)$  became constant over entire homogeneity composition range at any  $T$  as presented in Fig. 4. Thus, we judged this situation is more rational and, in all the later works on statistical thermodynamic analysis of non-stoichiometric interstitial compounds  $MX_x$ , starting point of the analysis was set to choose  $\theta$  parameter value in a way to yield constant  $E(X-X)$  over entire composition range at any given  $T$ .



**Fig. 3.** Isothermal  $RT \ln \left\{ \left[ \frac{(1-x)/x}{p_N} \cdot p(N_2) \right]^{1/2} \right\}$  vs.  $x (= n_N/n_{Cr})$  plots for  $CrN_x$  phase (reproduced from Fig. 1 in Ref.[6]).

**Fig. 4.** Isothermal  $RT \ln \left\{ \left[ \frac{2(0.5-x)/x}{p_N} \cdot p(N_2) \right]^{1/2} \right\}$  vs.  $x$  plots for  $CrN_x$  phase (reproduced from Fig. 2 in Ref.[6]).

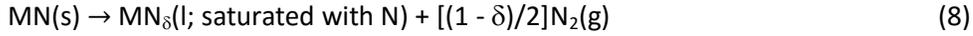
### 2.1.2. Decomposition pressure measurement of CeN

After a bit of struggling experimental efforts, number of data points sufficient to summarize a manuscript for publication were acquired from decomposition pressure measurement for CeN ( $T$  up to 2500°C,  $p(N_2)$  down to  $10^{-4}$  atm). Being quite satisfied, I started summarizing manuscript intending to submit it to *Journal of the Less-Common Metals* or some other Elsevier journal. One day, I was casually browsing through newly arrived journals at a library in Department of Nuclear Engineering and encountered a paper by O'Dell and Hensley [13] reporting decomposition pressure measurement results for CeN up to congruent melting temperature 2850 K (under  $p(N_2) > 3$  bar) and  $p(N_2)$  range down to  $10^{-2}$  atm. It was a shocking blow for me to know that similar experimental data acquired over a few months were already reported by other researcher. I felt miserable and could not set up my mind to work in the laboratory for a few days.

But, when I reviewed carefully together with Dr. M. Katsura the contents of the paper published by O'Dell and Hensley [13], we noticed that they did not measure the decomposition pressure at  $p(N_2)$  lower than  $10^{-2}$  atm due to coating of view window by evaporated substance at  $p(N_2)$  lower than  $10^{-2}$  atm. In fact, we suffered from the same trouble of window coating by evaporated substance (certainly, Ce metal thin film) and, to solve this problem, we integrated movable shutter beneath the quartz glass view window and we opened it instantaneously only on pyrometric temperature measurement.

Thus, we decided to publish our experimental data on Technology Reports of Osaka University [14]. As reproduced in Fig. 5, continuity is smooth between our data and data reported by O'Dell and Hensley. In Fig. 5, thermodynamically evaluated  $\log p(N_2)$  vs.  $1/T$  relationship for CeN by Kelley [15] is also presented. This thermodynamic  $p(N_2)$  vs.  $1/T$  relationship drawn by broken line deviated from the decomposition pressure measurement results. This is due to the reality that idealized reaction (1)

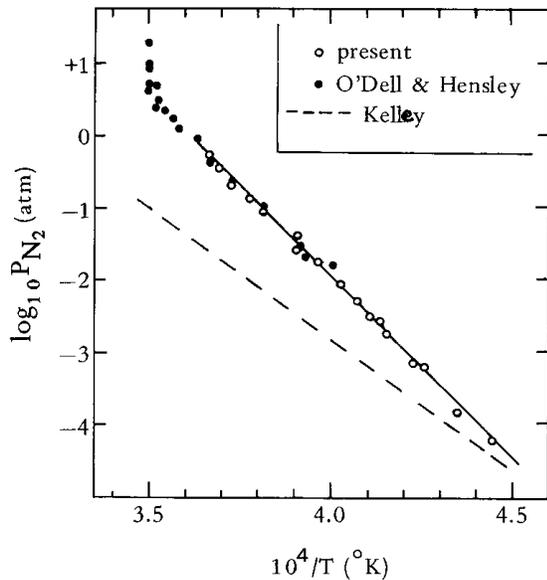
involving pure M(l) is assumed in thermodynamic evaluation whereas, in reality, molten M yielded from incongruent melting of MN(s) is saturated with N



and thence, rigorously speaking, thermodynamic expression for Gibbs' free energy of formation  $\Delta G_f(\text{MN})$  of MN would become

$$\Delta G_f(\text{MN}) = \Delta H_f(\text{MN}) - T\Delta S_f(\text{MN}) = (1/2) RT \ln p(\text{N}_2) + RT \ln a(\text{M}) \quad (9)$$

where  $\Delta H_f(\text{MN})$  refers to thermodynamic enthalpy of formation of MN,  $\Delta S_f(\text{MN})$  thermodynamic entropy of formation of MN and  $a(\text{M})$  chemical activity of M(l) saturated with N.



**Fig. 5.** Decomposition pressure  $p(\text{N}_2)$  of CeN plotted as a function of reciprocal temperature  $1/T(\text{K})$  (reproduced from Fig. 3 in Ref.[14]).

Solubility  $\delta$  of N in molten M would become greater with increasing  $p(\text{N}_2)$  (i.e., with increasing  $T$ ) and accordingly the discrepancy between the thermodynamic  $p(\text{N}_2)$  vs.  $1/T$  relationship estimated from  $\Delta G_f(\text{MN})$  and measured decomposition pressure temperature relationship for MN would become greater with increasing  $p(\text{N}_2)$  or rising  $T$  for any known MN including CeN.

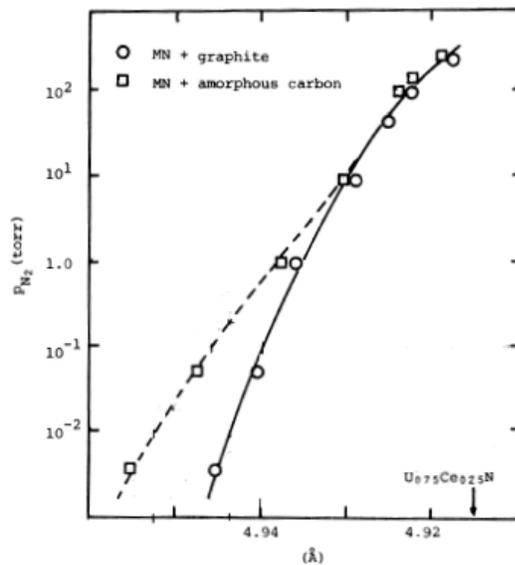
### 2.1.3. Synthesizing carbides, carbon-nitrides and nitrides

#### 2.1.3.1. Carburizing metal nitride MN using non-graphitic carbon with carbon activity $a(\text{C})$ greater than 1

When I entered in laboratory of Prof. T. Sano in April 1971, Dr. M. Katsura who was awarded Dr.Ing. degree in 1969 on the basis of his work undertaken at Kernforschungsanlage Jülich (KFA) with thesis entitled "Beitrag zum Uran - Kohlenstoff - Stickstoff - System" started working conscientiously to use non-graphitic carbon with chemical activity  $a(\text{C})$  of carbon higher than 1 (carbon activity of graphite being in reference state is 1) as carburizing medium after successfully demonstrating by X-ray diffraction

(XRD) that free carbon precipitated from reaction of  $UC_2$  [16] and UC [17] through reaction with  $N_2$  gas to form carbo-nitride  $UC_{1-x}N_x$  was not graphite but non-graphitic carbon with  $\alpha(C)$  higher than 1.

I was very fortunate to be involved in this line of work [18] that was presented at *Thermodynamics of Nuclear Materials 1974* meeting organized by IAEA (International Atomic Energy Agency) in Vienna in 1974. My contribution in this work was preparation of  $U_{0.75}Ce_{0.25}N$  solid solution through reaction between UN and CeN and to compare its reaction with graphite and with active carbon to get results as reproduced in Fig. 6 that demonstrates, when  $U_{0.75}Ce_{0.25}N$  being mixed with excess graphite or with excess active carbon was reacted with  $N_2$  at a given  $p(N_2)$ , carbon content in the synthesized carbo-nitride was higher with the active carbon than with the graphite.



**Fig. 6.** Equilibrium  $p(N_2)$  for  $U_{0.75}Ce_{0.25}C_xN_{1-x}$  synthesized from  $U_{0.75}Ce_{0.25}N$  with excess free C (amorphous carbon or graphite) at 1400°C plotted against lattice parameter (reproduced from Fig. 2 in Ref. [18]).

### 2.1.3.2. Nitriding metal and metal carbide in uncracked $NH_3$ gas possessing exceptionally high $\alpha(N)$

In 1930, two papers came out of Germany reporting nitriding of metals using flowing  $NH_3$  gas; one authored by Hägg [19] reporting synthesis of mono-nitride MoN of Mo that was not synthesized using  $N_2$  gas even at very high pressure up to a few hundreds of atm and another by Lehrer [20] reporting synthesis of hypo-stoichiometric sub-nitride  $\epsilon-Fe_2N$  of Fe that was also difficult to be synthesized in  $N_2$  gas. These two research works were published originally in German language but, on account of its pragmatic technical importance, flow conditions of  $NH_3$  gas reported in Lehrer's work were fully reproduced in classical textbook co-authored by Darken and Gurry [21] written in English.

As a follow-up experiment of Hägg [19], we tried nitriding of Mo under flow of  $NH_3$  gas (uncracked  $NH_3$  with suppressed extent of dissociation from that in equilibrium state) and demonstrated that synthesis of MoN was indeed extremely difficult [22]. It took several tens of hours by reaction undertaken at 700°C for XRD peaks identifiable as MoN with weak intensity to emerge co-existed with strong XRD peaks identifiable as sub-nitride  $Mo_2N$  and then, by mere rise of the reaction temperature by 25°C to 725°C, XRD peaks of MoN immediately disappeared implying that temperature window for synthesizing MoN must be very narrow because the reaction rate would become unacceptably slow when reaction temperature was taken to be lower than 700°C but, when temperature was risen to 725°C, it would dissociate into  $Mo_2N$  instantaneously.

## 2.2. First post-doctoral experience at Kernforschungszentrum Karlsruhe (KfK) in Germany

Prof. T. Sano, boss professor in my laboratory at Osaka University, was personally acquainted with Prof. Fritz Thümmeler at IMF (Institut für Material- und Festkörperforschung) in KfK in Germany. So, before completing my Dr.Eng. degree work in March 1977, Prof. Sano contacted Prof. Thümmeler to ask arranging me a one-year post-doctoral position (Gastwissenschaftler) at IMF in KfK starting from September 1977. My direct supervisor at KfK was Dr. Helmut Holleck.

Nowadays, most of research students have chances to attend international conferences held in foreign countries to accumulate experiences in presenting their results in English. But, before taking the first paid position at KfK in Karlsruhe, I never travelled to any overseas country for conference presentation although, in Japan, most of learned societies have regular discussion meetings twice per year, one in spring and another in autumn, and it is almost a *must* for research students to present the progresses of their work at 6 months interval in such meetings.

My monthly salary at KfK was nominally about 3,000 DM (Deutsche Mark) and, after tax reduction, it was still about 2,000 DM which corresponded to 200,000 JPY (Japanese Yen) by the exchange rate in those days or 2,000 Euros in modern terms. It was quite a leap from monthly scholarship 50,000 JPY for Dr. course students in Japan in those days. So, I managed to purchase programmable scientific calculator TI-58 of Texas Instruments soon after arriving Karlsruhe that was extremely useful to carry out statistical thermodynamic calculations after moving to Lisboa (Portugal).

Another luxury at KfK was excellent library service. Every week, each researcher received regularly list of titles in newly arrived journals at the library and, if we want copy of any published work in the list, we simply mark with X and returned the list to the library through internal mail service. Then, next week, we receive the requested copy. I took full advantage of this library service system to collect as many equilibrium *P-T-C* data published for future analysis.

I was assigned to undertake evaluation of thermodynamic stability for UN-MN systems for extensive range of *M* including *f*-group transition metals as well as *d*-group ones under supervision of Dr. H. Holleck. Unfortunately, this ambitious attempt was not successful and even KfK internal report was not completed even after 4 months extension of the original 1 year contract to make my stay at KfK 16 months till December 1978. Anyway, this first European experience was invaluable for me to kick-off my career as a materials researcher.

One day towards the end of my 1 year contract as Gastwissenschaftler at KfK, I phoned Prof. T. Sano in Japan inquiring if there was any research position vacancy in university or research institute in Japan available. His answer was *no* but suggesting me to return to Japan to work at some industrial research laboratory. As I had no intention to work for industrial applied research, I decided to find some research job myself in some English speaking country. So, thereafter, I regularly dropped at KfK central library after lunch to look at job advertisement in *New Scientist* and other journals. When I encountered job advertisement in any material related research category, I enclosed a copy of my CV and dispatched immediately to the address of the institution of the job advertisement. I dispatched nearly 50 such applications. One day, I received an inquiring letter from Dentistry Department of Queen Mary College in London asking my motive to change research field from nuclear materials to dental materials stating that my application passed through the preliminary documentation review but the juries were puzzled because of my past research records as a matter of course. It was simply my mistake. I was so desperate to find some research job before terminating my contract at KfK and thence, when I saw any job advertisement with a key word *material*, I put my CV inside an envelope and posted to the address without carefully checking the details of the job description. I had to reply immediately to Dental School of Queen Mary College apologizing my carelessness stating that I had no intention to change my research area to dental materials.

In the end, I was accepted at Metallurgy Department of Sheffield University, UK, and moved from Karlsruhe by train through London to arrive Sheffield in the afternoon of 2nd February 1979 (Friday).

### **2.3. Second post-doctoral position at University of Sheffield in England**

When I arrived Sheffield, it was packed with heavy snow. At the Sheffield train station, Dr. David H. Warrington picked me up and brought me to the Metallurgy Department to introduce two other future collaborators, Dr. Hywel A. Davies (deceased in June 2015) and Dr. Howard Jones. After brief introduction to these future collaborators to work with intimately and a few other colleagues, Dr. Warrington took me to a university residence, Sorby Hall, where I was supposed to stay for a week or so temporarily before I found an adequate residence independently.

As I was a post-doctoral research staff, I was accepted as a member of Senior Common Room in the Sorby Hall. After dinner at Top Table in the dining room of the Sorby Hall, I went down to the Senior Common Room to watch TV and to have drinks. It was Friday evening and most of British residents went back home for week-end. So, the Senior Common Room that evening was quite empty. There I met first time Maria Cândida Barrinha Loia who came to Sheffield from the beginning of 1979 to carry out part of her Dr.Eng. degree work at IST under supervision of Prof. Neil Atherton at Chemistry Department of Sheffield University. We got married on 28th February 1981.

Tasks assigned at Sheffield University was totally new to me. It was to characterize refined micro structures of Ni-based super-alloys produced by rapid solidification processing by transmission electron microscope (TEM). I was not familiar with metallography, even with the classical metallography using optical microscope. Specimen material was prepared by chill block melt spinning (CBMS) process that would yield rate of cooling on solidification up to  $10^6$  K/s.

In Sheffield, my monthly salary was nearly half the salary at KfK that raised my concern before moving from Karlsruhe to Sheffield but I managed to survive quite all right in Sheffield.

Cândida and myself departed Sheffield at the end of May 1982 towards Lisboa driving Mini. We took a ferry boat at Portsmouth to Santander to cross Spain through Salamanca to reach Portuguese border at Vilar Formoso at around 9 o'clock in the night. Cândida proposed to sleep some hotel around Vilar Formoso but, seeing that the distance to Lisboa was only around 300 km, I imagined we might arrive Lisboa within 5 h and insisted to continue driving to Lisboa straightforwardly. I did not know there was no motorway network like now in Portugal. So, we arrived to Lisboa only around 6 o'clock in the morning. This was the starting point of my life in Portugal.

## **3. In Portugal as an Independent Researcher**

I assumed that I could start working at LNETI in the beginning of June 1982 but, apparently due to delayed procedure of administrative paper works, I had to wait till the beginning of July to start working at LNETI. Contract was temporary and the monthly salary was 50,000 Escudos (or 50 Contos) that corresponded to about 50,000 JPY which was comparable to my scholarship as Dr. course student in Japan and half the salary at Sheffield University. So, I felt a bit uneasy about my future prospect of life as a materials researcher noting the sequence of experiences that, on each move from one institution to another, my salary was reduced by half but I did not care much about financial aspect of my life simply hoping to carry out good scientific work somehow.

### **3.1. Period in Sacavém; 1982 - 1983**

When I started working at LNETI in July 1982, our section (Departamento de Metalurgia e Metalomecânica (DMM)) was in Sacavém Campus outside Lisboa but with prospect of soon moving to newly constructed Lumiar Campus. So it was recommended not to start any experimental work at

Sacavém. I found it was a convenient situation for me to start analyzing *P-T-C* data compiled since the KfK period. I was given a desk in an office room to share with Eng<sup>o</sup> Carlos Pacheco da Silva and Eng<sup>o</sup> Paulo Carreira. There I concentrated on calculating a series of *P-T-C* data using programmable TI-58 calculator I purchased in Karlsruhe. The first 2 publications in 1983 with affiliation LNETI [23,24] were made with address of Sacavém Campus.

Head of DMM/LNETI, Dr. Henrique Carvalinhos, was one of founders of *SPMater.* and I became a member of *SPMater.* (Socio No. 187). soon after started working at LNETI.

### 3.2. Period in Lumiar: 1983 to date

One of first events taking place at Lumiar Campus of LNETI was 1. Encontro Nacional da Sociedade Portuguesa de Materiais (Materiais 83) to which I submitted 3 communications [25-27]; one reported preliminary analysis results of metal-hydrogen (M-H) systems on the basis of statistical thermodynamics [25], another on aspects of nitriding steel using flowing NH<sub>3</sub> gas as a nitriding medium [26] and one more co-authored with Dr. David H. Warrington was summary of work carried out in Sheffield University [27]. The last one [27] was presented orally by Dr. David H. Warrington because he as well as Prof. Robert W. Cahn was one of invited speakers to Materiais 83.

#### 3.2.1. Statistical thermodynamic analysis of non-stoichiometric interstitial compounds (X = H, C,N,P,S)

Next 2 publication with affiliation LNETI [28,29] were made with new address of Lumiar Campus although the calculations were done at Sacavém. Since then, there are more than 40 papers regarding statistical thermodynamic analysis of non-stoichiometric interstitial compounds published on peer-reviewed journals. Comprehensive review of this line of work was published in 2013 as a monograph entitled "Interstitial Non-stoichiometric Compounds" from LAP (Lambert Academic Publishing) [30].

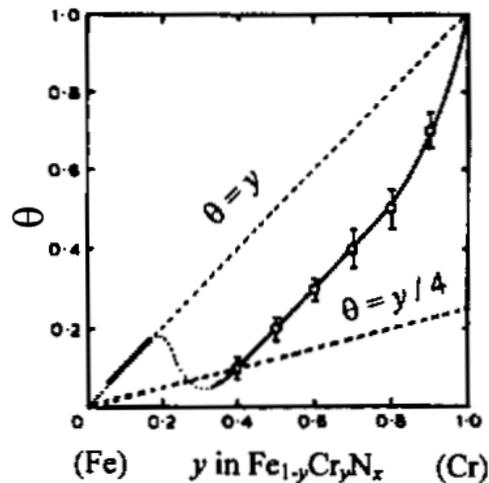
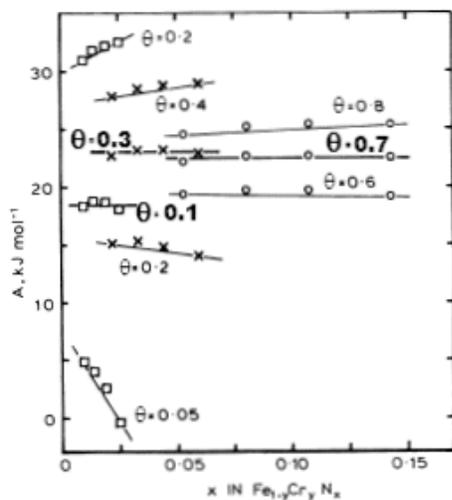
One of significant conclusions drawn from this line of work was formation of two types of atom clusters around N atom in molten Fe<sub>1-y</sub>M<sub>y</sub>N<sub>x</sub> depending on composition *y* of metal M whose affinity to N is stronger than affinity of Fe to N (M = Cr,Ti,V,Mn,Al).

Example case of estimating atom clustering in molten Fe<sub>1-y</sub>Cr<sub>y</sub>N<sub>x</sub> on the basis of thermodynamic analysis is reviewed in the following. This analysis was done in late 1980s [31,32] using *P-T-C* data reported for molten Fe<sub>1-y</sub>Cr<sub>y</sub>N<sub>x</sub> by Ishii *et al*[33]. As the range of temperature concerned was just above the liquidus temperature, Fe<sub>1-y</sub>Cr<sub>y</sub> lattice was assumed to hold face centered cubic (*fcc*) configuration of the solid phase. As always practiced in the proposed standardized statistical thermodynamic analysis procedures, starting point of the analysis was to assign  $\theta$  parameter value. Solubility *x* of N in the molten Fe<sub>1-y</sub>Cr<sub>y</sub>N<sub>x</sub> was comparatively small being no higher than 0.15 even at *y* = 0.90. In such very low range of *x*, nearest neighbour interaction between N atoms was proposed to be taken as 0 because of lacking neighboring N atom around any given N atom occupying O-site. Thus, determination of  $\theta$  for given *y* in Fe<sub>1-y</sub>Cr<sub>y</sub>N<sub>x</sub> was done to find  $\theta$  value to fulfill condition [34]

$$E(N-N) = 0 \quad (10)$$

As shown in Fig. 7 [32],  $\theta$  was determined to be 0.10 for *y* = 0.40, 0.30 for *y* = 0.60 and 0.70 for *y* = 0.90, for example. The  $\theta$  vs. *y* relationship for molten Fe<sub>1-y</sub>Cr<sub>y</sub>N<sub>x</sub> determined as such is plotted in Fig. 8 [30]. Up to *y* = 0.20,

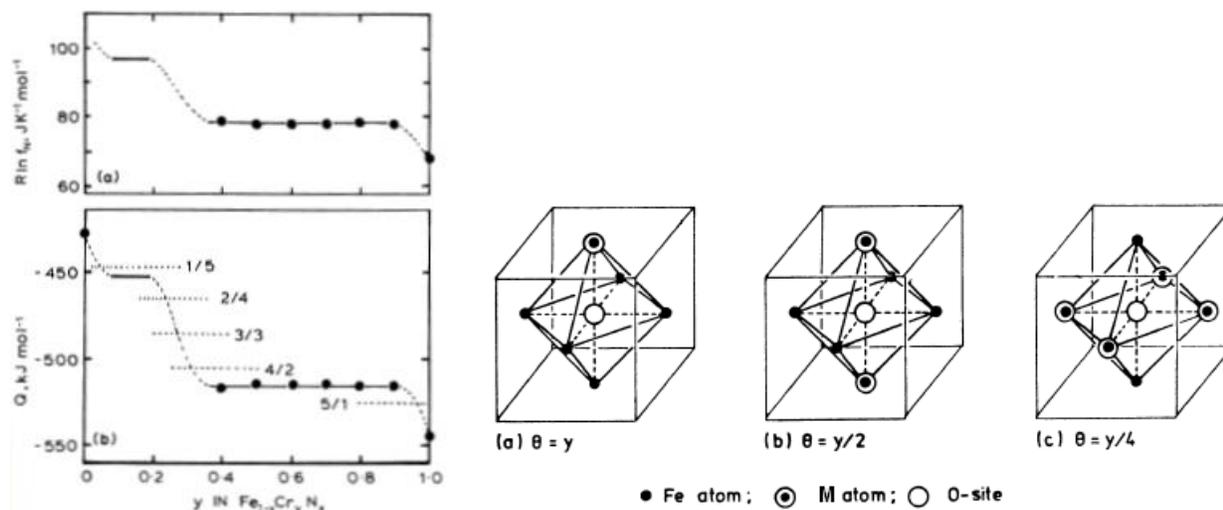
$$\theta = y \quad (11)$$



**Fig. 7.** Plots of  $A \equiv RT \ln \{[\theta - x]/x\} p(N_2)^{1/2}$  vs.  $x$  for molten  $Fe_{1-y}Cr_yN_x$  at  $T = 2023$  K with various choices of  $\theta$  values (reproduced from Fig. 3 in Ref.[32]).

○ :  $y = 0.90$ , × :  $x : y = 0.60$ , □ :  $y = 0.40$ .

**Fig. 8.** Values of  $\theta$  vs.  $y$  in molten  $Fe_{1-y}Cr_yN_x$  (reproduced from Fig. 3.57 in Ref.[30]).



**Fig. 9.** Values of  $R \ln Zf_N$  (a) and  $Q$  (b) in molten  $Fe_{1-y}Cr_yN_x$  as a function of  $y$ ; horizontal dotted lines in (b) show positions of values of  $Q$  estimated from sum of  $E(N-Fe)^0 = -71$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $E(N-Cr)^0 = -90$   $\text{kJ}\cdot\text{mol}^{-1}$  [31] at various ratios of Cr to Fe (reproduced from Fig. 5 in Ref.[32]).

**Fig. 10.** Possible atom clusters formed in *fcc*  $Fe_{1-y}M_yN_x$  lattice in which affinity of M to N is stronger than affinity of Fe to N.

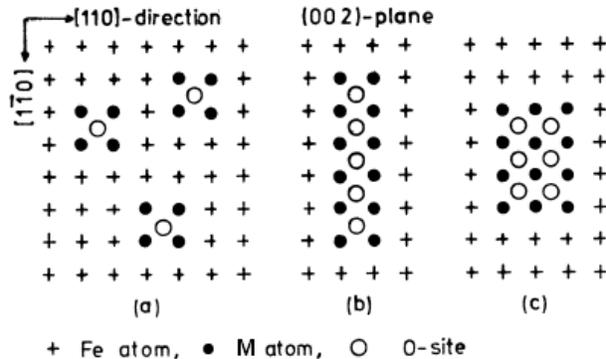
(a) **1 M/5 Fe** cluster (or **M-N dipole**; composed of one M atom and five Fe atoms);  $\theta = y$ ,

(b) **2 M/4 Fe** cluster;  $\theta = y/2$ ,

(c) **4 M/2 Fe** cluster;  $\theta = y/4$ .

(reproduced from Fig. 3 in Ref.[35]).

However, in the range of  $y \geq 0.40$ , variation pattern of  $\theta$  with respect to  $y$  looks somewhat strange. Anyway, plots of the estimated values of  $Q$  and  $R \ln Zf_N$  using  $\theta$  values determined as such as a function of  $y$  would yield plateaus in the range  $0 < y < 0.2$  and in the range  $0.4 \leq y \leq 0.9$  as reproduced in Fig. 9 implying that the surrounding of  $N$  atom occupying  $O$ -site would hold constant in the range of  $0 < y < 0.2$  as well as in the range  $0.4 \leq y \leq 0.9$ . Judging from the level of the plateau of  $Q$ , it was concluded rational to assume that, in the range of  $0 < y < 0.2$ , cluster must be most likely composed of 1 Cr atom and 5 Fe atoms (**1 Cr/5 Fe cluster** or **Cr-N dipole**) and, in the range  $0.4 \leq y \leq 0.9$ , **4 Cr/2 Fe cluster** as depicted schematically in Fig. 10.



**Fig. 11.** Some possible ways of planar extension of the **4 M/2 Fe** cluster depicted in Fig. 10 (c) over the (002)-plane of *fcc* lattice leading to different values of  $\theta$  with a fixed number of 12 M atoms.

- (a) isolated clusters;  $\theta = y/4$ ,  
 (b) planar extension leading to  $\theta = (5/12)y$ ,  
 (c) planar extension leading to  $\theta = (6/12)y = y/2$ .  
 (reproduced from Fig. 4 in Ref.[35]).

Then, possible cause for deviation of  $\theta$  from the relationship in the range of  $y > 0.40$

$$\theta = y/4 \quad (12)$$

as seen in Fig. 8 was considered and, as depicted in Fig. 11, planar extension of the **4 M/2 Fe** cluster depicted in Fig. 10 (c) over the (002)-plane of *fcc* lattice leading to different values of  $\theta$  with a fixed number of 12 M atoms was presented as the acceptable explanation.

These results were reported also at **Materials 91** meeting of *SPMater* [36].

### 3.2.2. Nitriding in flowing $\text{NH}_3$ gas environment

After moving to the new Lumiar Campus of the institute in spring of 1983, setup of experimental apparatus to carry out nitriding in flowing  $\text{NH}_3$  gas (i.e. uncracked  $\text{NH}_3$  gas) was started with dedicated assistance of Eng<sup>a</sup> Teresa Marcelo. It was not at all an easy task to negotiate with a glass blower to compose a system with configuration we demanded but, thanks to patience and highly diplomatic communication skill of Eng<sup>a</sup> Teresa Marcelo, the glass blower composed the experimental apparatus within acceptable waiting time.

Experimental results obtained using this apparatus was first presented at a conference in San Sebastian (Spain) in 1986 [37] and then integrated in more comprehensive article published in 1990 [38]. Significant novelty in the published article [38] was the first demonstration of hydriding power of uncracked  $\text{NH}_3$  gas ( $\text{NH}_3$  gas with suppressed extent of dissociation from the equilibrium level by

flowing) at relatively low temperature while its high nitriding power at relatively high temperature exceeding 700°C was well established before [19-22].

Theoretical validation to possession of hydriding power by uncracked NH<sub>3</sub> gas was soon presented by Katsura in his publication in 1992 [39].

### 3.2.3. Water atomisation

Water atomizer D5 designed and composed by Davy McKee Ltd. of Sheffield (later, this division of Davy McKee became independent to ASL - Atomising Systems Ltd.) was already purchased at DMM in LNETI and waiting for setup when I entered to LNETI in 1982. As I had been working on rapid solidification processing in Sheffield University before moving to LNETI, I was assigned to be responsible to the D5 water atomiser operation. Rate of cooling on solidification achieved by water atomisation process (probably around 10<sup>3</sup> K/s or so) is not so high as the one achieved by CBMS (up to 10<sup>6</sup> K/s) but advantage of water atomisation is the product morphology, powders with refined grains of irregular shape, that can be consolidated using conventional powder metallurgical (PM) processing techniques while CBMS produces thin ribbon.

Davy McKee sent a technician, Mr. John Palmer, for 1 week to install the atomiser and to instruct us basics of the atomiser operation. I accompanied with Mr. John Palmer for one full week trying to learn as much as I could during the limited time.

When Dr. José Brito Correia moved from IST/UTL to DMM/LNETI in 1986, we started together test operations of the D5 atomiser by varying systematically the operational parameters of the atomiser and the results were published on *Powder Metallurgy* [40]. When Portugal was integrated in EC (European Community) in 1987, special privilege was given for Portuguese researchers to participate in Stimulation Project. We joined two EC Stimulation Projects in sequence using D5 water atomiser as the tool to produce raw material powders.

Although rate of cooling on solidification by water atomisation was modest, satisfactory extent of super-saturation of alloying constituent was realized for water atomised alloy powders and this characteristic was used to produce consolidated component with enhanced mechanical strength from water atomised alloy powders through conventional extrusion process.

### 3.2.4. Synthesizing carbide, carbon-nitride and carbide using concentrated solar beam

One day in 1997, Prof. Luís Guerra Rosa of IST/UTL visited me at INETI informing me that he had got beam time of solar furnace at PSA (Plataforma Solar de Almería) in Tabernas (Spain) and if I would like to take advantage of the opportunity. I immediately replied YES proposing to try synthesizing carbides of *d*-group transition metals using concentrated solar radiation as the reaction heat source simply because synthesizing carbide of U and other transition metals using laboratory electric furnace was my familiar experimental routine at Osaka University and I thought it would be very convenient to heat the starting material, carbon / metal (C/M) mixture, instantaneously from ambient temperature to the reaction temperature of about 1500°C merely in view of saving processing time to cut quite long slow-heating duration in laboratory electric furnace.

Although I proposed this line of carbide synthesis using solar furnace, I became quite skeptical about the outcome after knowing that unit experimental duration in solar furnace is mere 30 min because I knew well with reference to my past experiences that it would take some tens of hours to synthesize carbide with high crystallinity to yield sharp XRD peaks in electric furnace and situation would be the same in solar furnace. However, to my great surprise, when the reaction chamber was opened after the 1st trial, typical smell of carbide came out. In fact, XRD verified the M/C powder mixtures were indeed converted to carbides with satisfactorily high degree of crystallinity yielding sharp XRD peaks in spite of relatively short reaction period of mere 30 min.

Exact reason for this favourable result of synthesizing metal carbides in such short period remains unknown to date although it might be ascribable to either presence of wide spectrum of visible light wave components in solar radiation besides infrared (IR) heat radiation alone in "dark" electric furnace environment or extremely rapid heating rate from ambient temperature to reaction temperature at the onset of the irradiation with concentrated solar beam.

Irrespective of the true cause leading to the formation of carbide of high crystallinity in such short reaction duration under concentrated solar radiation, solar carbide synthesis was proved to be a very convenient carbide powder production route saving conventional electric power.

In collaboration with PSA, more than 10 publications came out.

After 2005, collaboration with another solar energy research institute, PROMES-CNRS (Laboratoire Procédé, Matériaux, Energie Solaire - Centre Nacional de la Recherche Scientifique) in Odeillo, France, started. In this collaboration with PROMES-CNRS, more than 10 publications arose as well including ones demonstrating effect of colour filtering of solar beam on reaction product [41,42].

In these collaborations with PSA in Spain and PROMES-CNRS in France using concentrated solar beam as reaction heat source, Dr. Fernando Almeida Costa Oliveira joined us since 2001 with 1st joint publication came in 2002 [43].

More recently, we started to try using  $\text{NH}_3$  gas flow as a nitriding medium under heating with concentrated solar beam in vertical type furnace SF5 at PSA. From this line of work two publications were made [44,45] and the most recent analysis result was presented at ***Materials 2015*** held in Porto [46].

#### 4. Concluding Remarks

As reviewed above, more than 90% of my professional life as a materials researcher in Europe was spent in Portugal and correspondingly more than 90% of journal publications and conference presentations were made with affiliation of National Industrial Research Institute although with occasionally changing names from *LNETI* through *INETIndustrial* and *INETInovação* to current *LNEG*. Therefore, I feel it a gratifying recognition for me to be awarded with the SPMater Prize.

Recently, Prof. Constantin Politis (a former colleague of mine at KfK; now at Patras University, Greece, after long years in USA) gave me a chance to present a review article [47] on *Journal of Surface and Interfaces of Materials*, for which he is a founder Editor-in-Chief, summarizing my past works using active carbon as a carburizing medium with high  $\alpha(\text{C})$  and uncracked  $\text{NH}_3$  as a nitriding medium with high  $\alpha(\text{N})$  together with the works using processing routes being away from equilibrium state including rapid solidification processing and solar radiation heating in which heating from ambient temperature to reaction temperature around  $1500^\circ\text{C}$  is done instantaneously in unified view point of influence of unstable chemical species and non-equilibrium processing route on reaction product. It was a unique opportunity for me to review these lines of works in integrated view point.

There are still several tasks undone.

For example, in case of statistical thermodynamic analysis, the proposed method worked all right for compounds holding metallic nature but, for non-stoichiometric ionic crystals, the proposed procedure failed to work. In the early 1980s, I attempted to analyze  $\text{UO}_{2\pm x}$  according to this approach but no rational conclusion was drawn. I hope some standardized statistical thermodynamic analysis procedure applicable to ionic non-stoichiometric compounds is found by somebody.

Solar synthesis of higher nitride of Mo and Fe in uncracked  $\text{NH}_3$  gas is still in infantry stage and the results demonstrate potentiality of the process certainly but with lacking quantitative rigorosity. Thus, it is hoped that, one day, more rigorous quantitative relationship between N content in the produced non-stoichiometric compound and  $\alpha(\text{N})$  varying constantly along the flow path as

demonstrated by Katsura and collaborators in the laboratory electric furnace [48] is somehow established under solar irradiation heating condition.

### Acknowledgements

My sincere thanks are due to Dr<sup>a</sup> M<sup>a</sup> Manuela Oliveira and Dr. Luis Gil who took great trouble of initiating the recommendation process for me to receive this award and also to Prof<sup>a</sup> Paula Vilarinho of Universidade de Aveiro (President of *SPMater*) and committee members to agree to award this prize to me. Taking advantage of this occasion, I would like to express my sincere gratitude to my wife, M<sup>a</sup> Cândida Barrinha Loia Shohoji, to take me to this very comfortable country with long intimate historic relation with my motherland, Japan. Without our encounter in 1979 in Sheffield, I would never have arrived to this beautiful country with people with warm broad heart. Our joint life in Sheffield started with my serious disease staying 1/4 of my time in cancer ward of the University Hospital but, fortunately, we managed to survive to date...

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