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MELTING AND UPGRADING OF TITANIUM POWDERS BY MEANS OF A HIGH FREQUENCY INDUCTIVELY COUPLED PLASMA

EXTRAMET is an indipendent Company whose main aim is applied research in extractive metallurgy; its principal fields of expertise are:

- Molten Salts Technology;
- Metallothermy;
- Hydrometallurgy;
- Oxides chlorination;
- Inductively coupled plasma technology

As far as inductively coupled plasma technology is concerned EXTRAMET is studying its applications to metals melting and refining and to metallic and ceramic powders elaboration.

The object of this presentation is to show some of the results obtained on melting and upgrading of titanium powders and thus the interest of the inductively coupled plasma in titanium metallurgy.

The process developed is included in a new route of production titanium (ingots or powders) from titanium tetrachloride;

The first stage consists of reduction of tetrachloride by a reactive metal in a molten salt bath. It results in a powder which undergoes a plasma treatment in order to meet the specifications.

The choice of inductively coupled plasma technology with this object is obvious because of its peculiar thermodynamical, energy transfer, chemical and hydrodynamical properties.
In the case of this application, the plasma is a thermal plasma obtained at atmospheric pressure.
Let us consider the most important properties of this type of plasma.

Figure 1 represents the enthalpy as a function of temperature for various plasma gases at atmosphere pressure. The steep variations of the enthalpy are essentially due to the heats of dissociation and ionization.

The very high enthalpy (and temperature) of the plasma and the possibility of transferring a large amount of energy to the plasma, independently in a large range of its nature, makes it very attractive for thermal treatments of refractory materials; thus, it is much more interesting than a flame, for example, because it permits storage and restitution, with a higher yield, of a large and controlled amount of energy.

The macroscopic transport of matter (diffusion), of charge (electrical conductivity) of momentum (viscosity) and of energy (thermal conductivity), in the plasma have to be considered in order to adapt the properties of plasma to the process.

Figure 2 represents the viscosity of argon, nitrogen, hydrogen and helium as a function of temperature. The viscosity of plasmas near 10.000 K lies in the range of 1×10^{-4} to 4×10^{-4} kg/m.s; these values are about 10 times higher than for the same gases at room temperature. One has to mention, as consequences, the difficulty of mixing gases or of introducing solid particles into some plasma areas and the importance of transfer between plasma and for example liquid metals.

The figure also shows the thermal conductivity of the same gases as a function of temperature. Its value, which depends strongly on the nature of the gas, is high; it is in the same order of magnitude as some metals.

Thus it is possible to produce plasmas with high values of viscosity and thermal conductivity and, therefore, to obtain very efficient thermal transfers between the plasma and the material.

Let us consider the peculiar properties of inductively coupled plasma (Fig. 3). These figures represent isovelocities and isotherms in a plasma generated in the torch schematized on the left. We observe the plasma peculiar configuration and the relatively low velocity of gas (comprised between 5 and 24 m/s). (In arc plasmas, velocities are in the range of several hundred m/s).

Therefore, the residence time of powders injected in this type of plasma is long.
Inductive plasmas are generated without electrodes which makes possible the use of reactive gases, and ultrapure material elaboration.

Let us say, for instance, the industrial application of this technology to the production of ultra-pure silica for optical fibres from technical tetrachloride.

These peculiar properties i.e. work at atmosphere pressure, low thermal inertia, its easy automation ... make of inductive plasma a choice tool for metallic and ceramic powders elaboration and transformation.

On Fig. 4 a 60 kW reactor is shown. The coil generates in that case an argon plasma.

In Fig. 5 we see the scheme of the setup used for titanium discontinuous melting. In this setup the material is placed in a water cooled crucible under the plasma.

The continuous treatment of titanium powder is realized in the setup of Fig. 6. In this case, the torch is composed of 3 quartz tubes.

An important purifying effect of the plasma has been observed in all our experiments. For example, analysis of a sample of titanium elaborated in the discontinuous reactor with an Argon-Helium plasma has given these results (Fig. 7). They show the effectiveness of the process to eliminate completely volatile impurities such as chlorine and sodium and reduce sensibly the amount of other impurities.

The process key parameters have been determined and classified. We have (Fig. 8), inter alia, studied the influence of plasma gas nature, raw materials quality, and the effect of a flux added to the raw materials.

For the study of the influence of raw materials quality on the process efficiency (Fig. 9), three kinds of materials have been used: microsponge, powder and turnings.
For instance, pellets composed of titanium powders and microsponge have been treated with an argon helium plasma.
These curves (Fig. 10) represent the eliminated % of a considered element as a function of microsponge % in pellets. Three dilution zones can be distinguished.
The first one (up to 30% microsponge in pellets) corresponds to a melted product, the second one (between 30 and 80 %) corresponds to a spongious product and the last one (from 80 to 100%) to a sintered product.
We clearly see that the maximum purifying effect is obtained at about 30% for a melted product.

We have compared the effect of two plasma gases on the purification of titanium, in identical thermal transfer conditions (Fig. 11).
In both cases a comparable quantity of impurities has been eliminated. In the case of Argon Hydrogen plasma the contents of H2 in the product is 99 ppm (lower than the tolerated quantity). Therefore an Ar-H_2 plasma can possibly be used.

We also studied the fluxes nature and quantity effect on titanium purification (Fig. 12). The fluxes tested have been fluorides of Li, Na, K, Ca, and Mg.
We see the interest of adding 1% of calcium fluoride and 0,5% of sodium fluoride to the raw materials for the elimination of impurities such as iron.

A strategy of characterization has been defined. All the methods used give information a posteriori, even if some of them allow appreciation the material properties and of the importance of the transfers during the treatment. In order to follow up the melting and purification of the metal in situ, a method which uses emission spectroscopy of elements has been carried out. The experimental setup (Fig. 13) is comprised of an optical fibre, a spectrometer and an optical multichannel analyser.

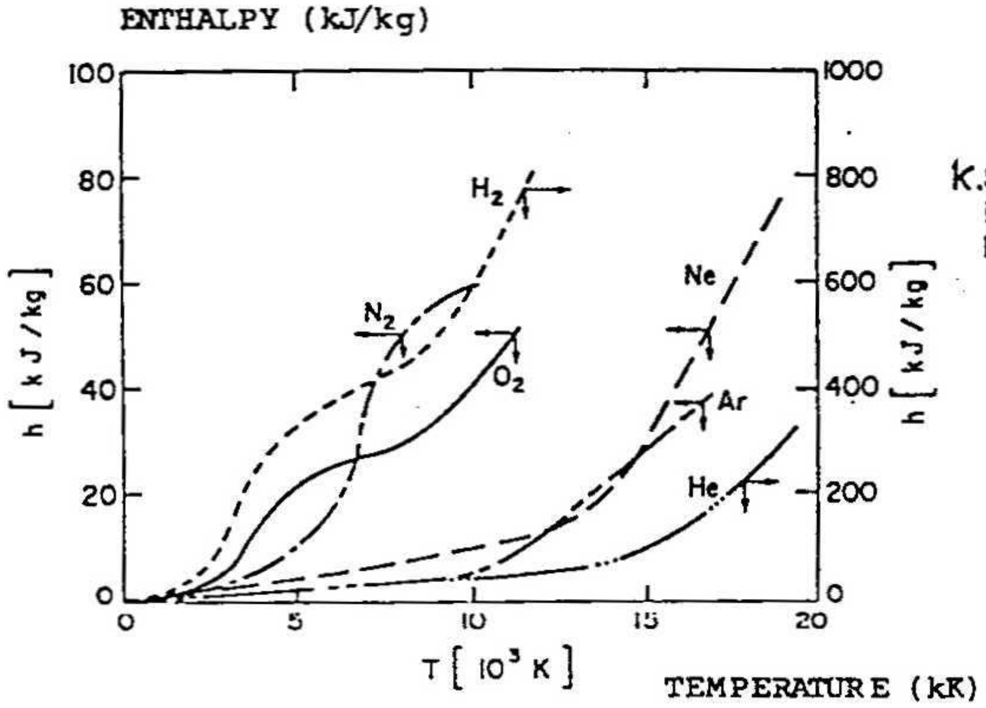
We have shown that the main purification phenomenon is evaporation of impurities in elementary or molecular form according to their physical and chemical properties.

A correlation of the impurities eliminated percentage (determined by analysis) and the surface under the curve of their emission intensity in the plasma as a function of time has been established (Fig. 14). As a result, the control of the process can be achieved. We also verify the best effect of potassium fluoride on titanium purification.

Thus, we have studied:

- the key parameters influence on process efficiency
- the chemical transfers at plasma-material interface
- the thermal transfers
- the process control.

The objective of future development of this process includes its optimization and its scale up to industrial production.
Production capacities of about 70 t/y are considered a first development step.



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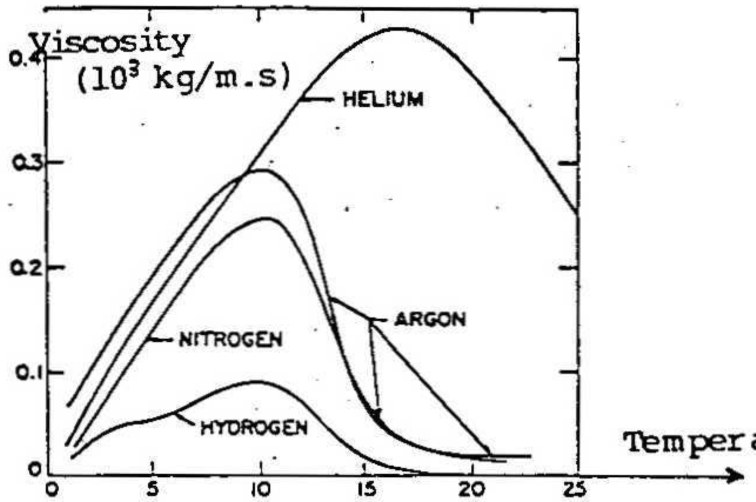
- Very High Enthalpy

- Enthalpy obtained from an outer source of energy

-> Transfer to materials of a very large and controlled amount of energy with a high yield

Fig. 1 – Enthalpy of a thermal plasma

TRANSPORT OF
- Matter (Diffusion)
- Charge (Electrical Conductivity)
- Momentum (viscosity)
- Energy (Thermal Conductivity)



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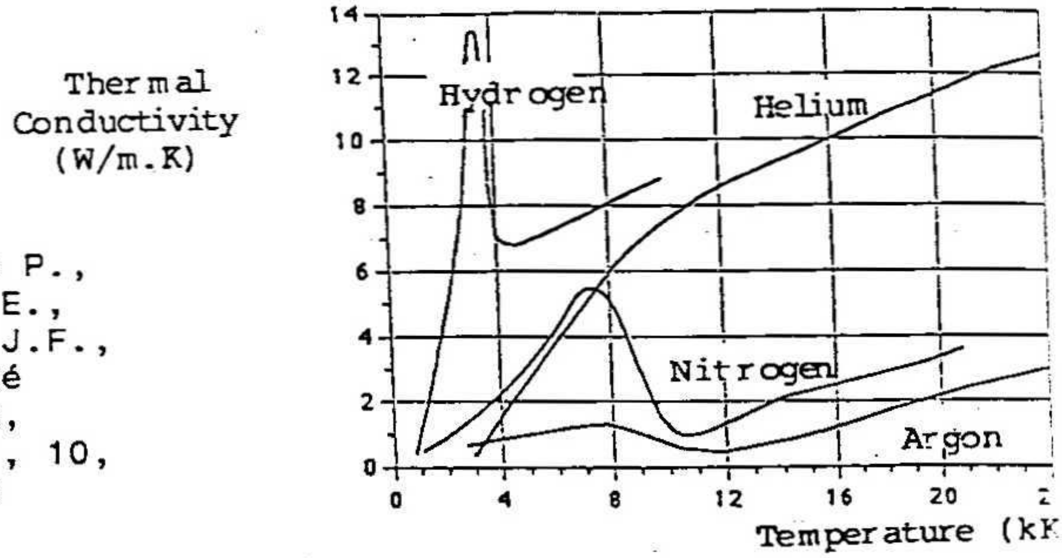

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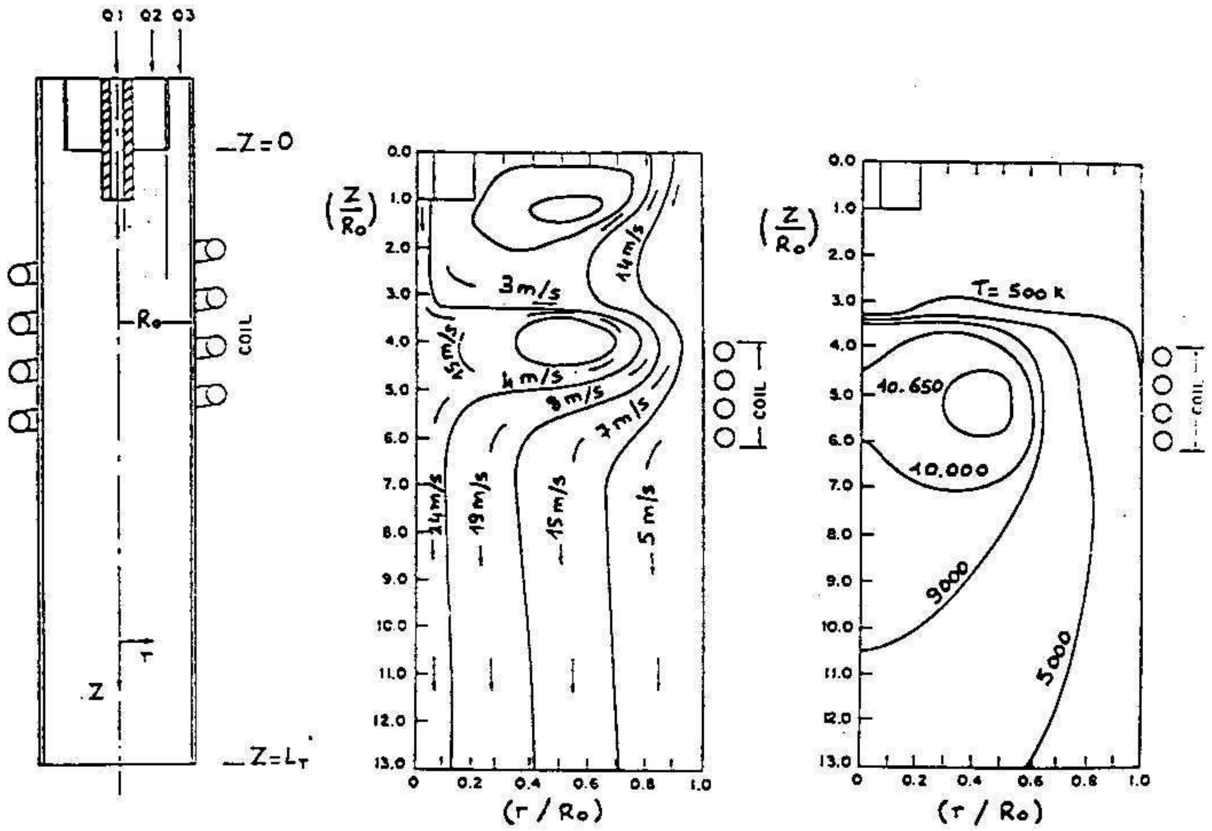
High Viscosity → Efficient Plasma-Material Thermal Transfer

High Thermal Conductivity → Efficient Plasma-Material Thermal Transfer

Fig. 2 - Transport properties of thermal plasma

FLOW AND TEMPERATURE FIELDS IN THE DISCHARGE REGIONS



(Q1;Q2;Q3 = 0.4;2.0;16 l/mn - LT = 18.2 cm
Ro = 1.4 cm - f = 3 MHz - P = 3.77 kW)

Ref.: M.I. Boulos; IEEE, Trans, Pl. Sc., PS-6, 93, 1978

- Peculiar Configuration
- Low Velocity Gas

ELECTRODELESS PLASMA

- Possibility of Using Reactive Gas
- High Purity Level

Fig. 3 - Characteristics of inductively coupled thermal plasma

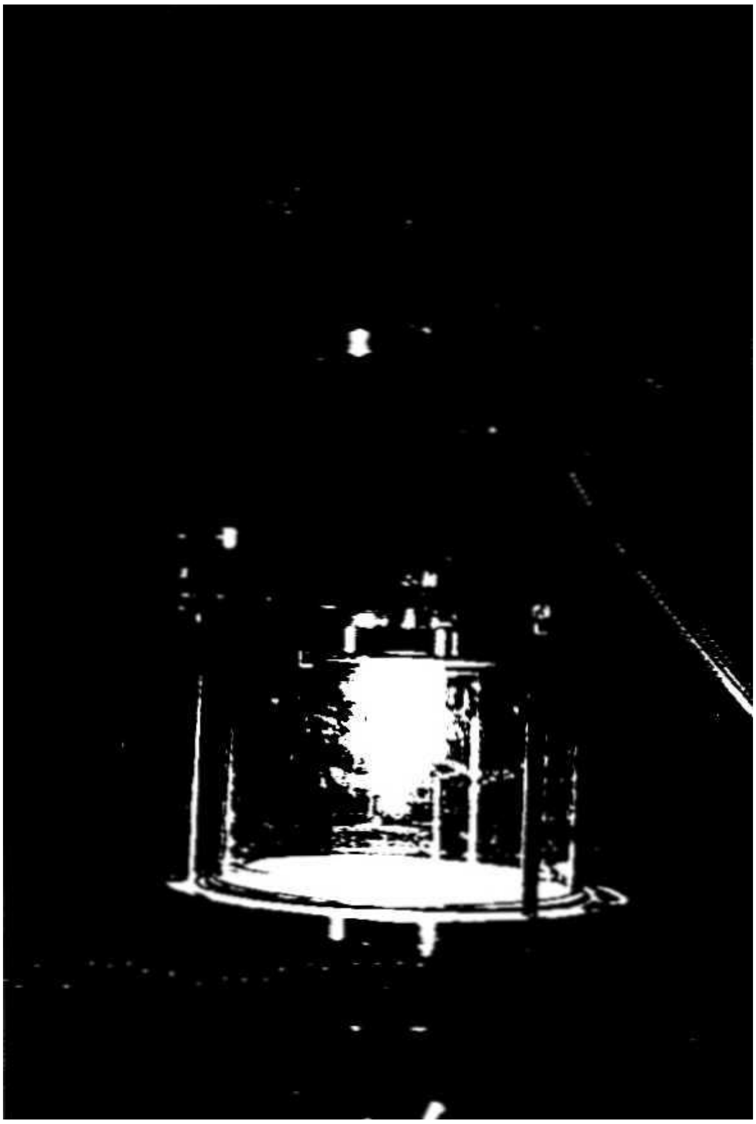


Fig. 4 - The 60 kW plasma reactor

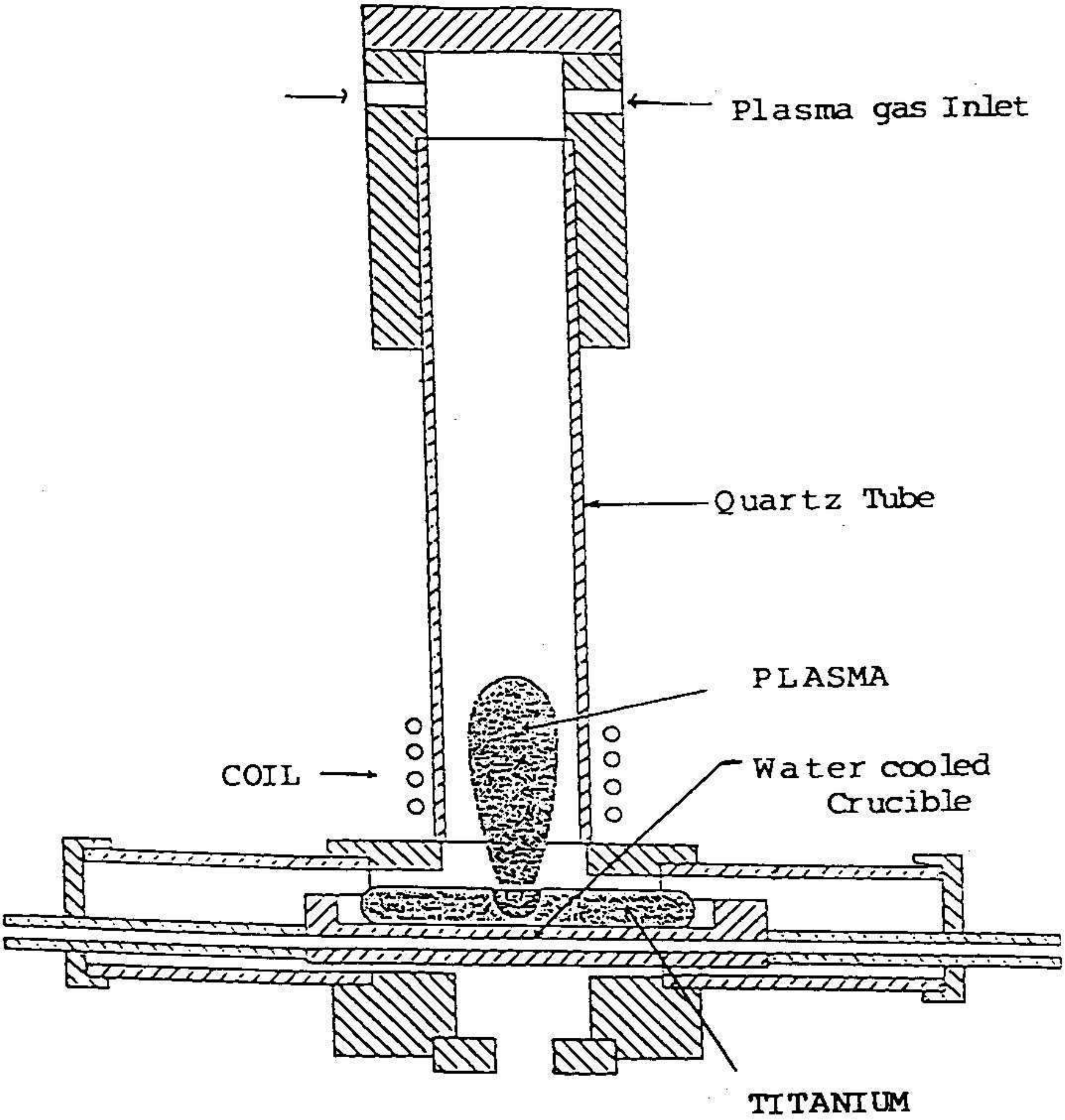


Fig. 5 - Set-up for titanium powders discontinuous melting

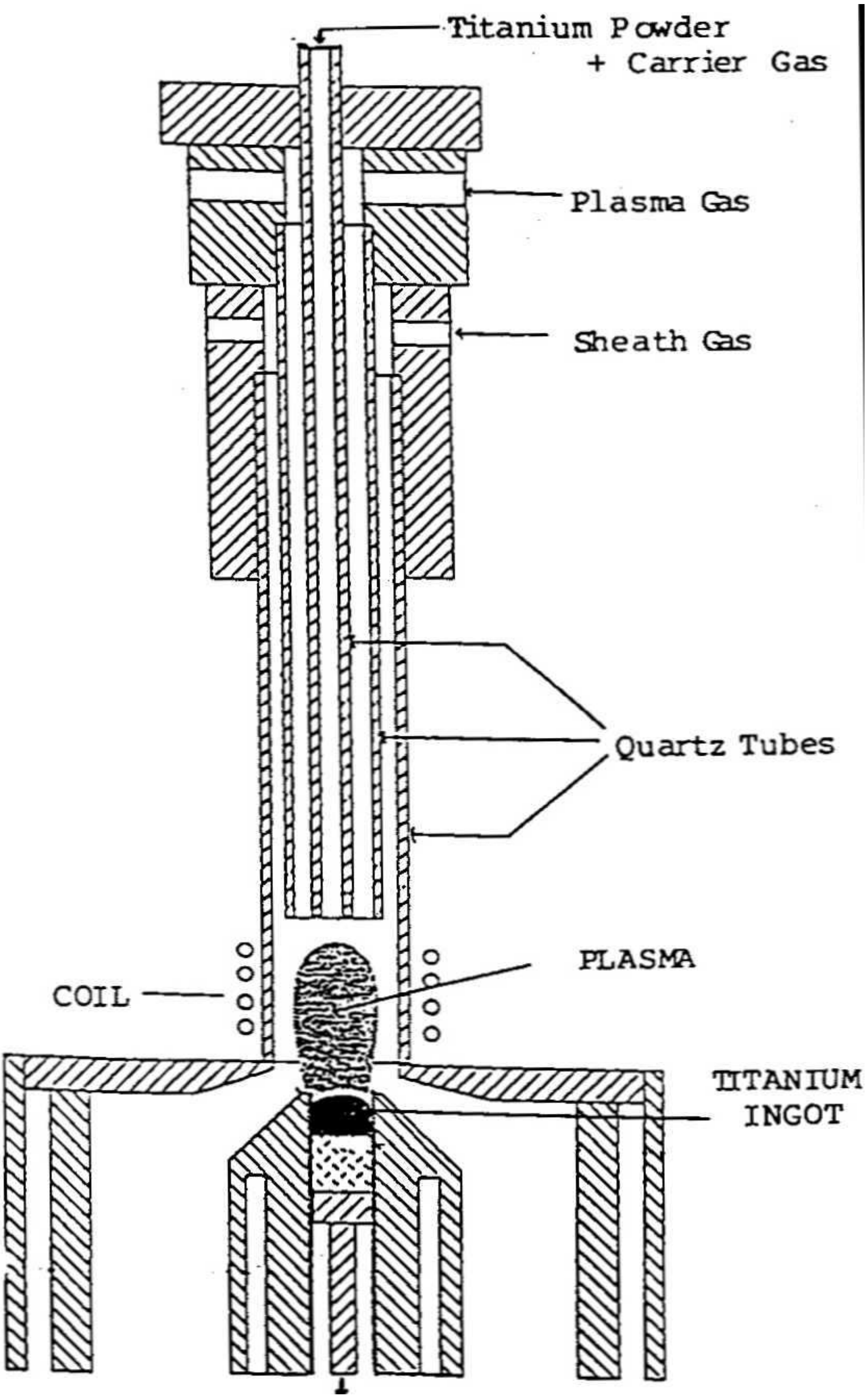


Fig. 6 – Set-up for titanium powders continuous melting

Discontinuous reactor - Operating conditions:

$P = 8$ kW - $Q_{Ar} = 30$ l/mn - $Q_{He} = 2.2$ l/mn

	Content (µg/g)	
Element	Starting Powder	Final Product
Cl	1122	Not detectable
Na	652	Not detectable
Fe	229	124
O	< 5000	1910
N	< 150	463
C	< 1500	110

Fig. 7 - Purification of a titanium powder melted by an argon-helium plasma

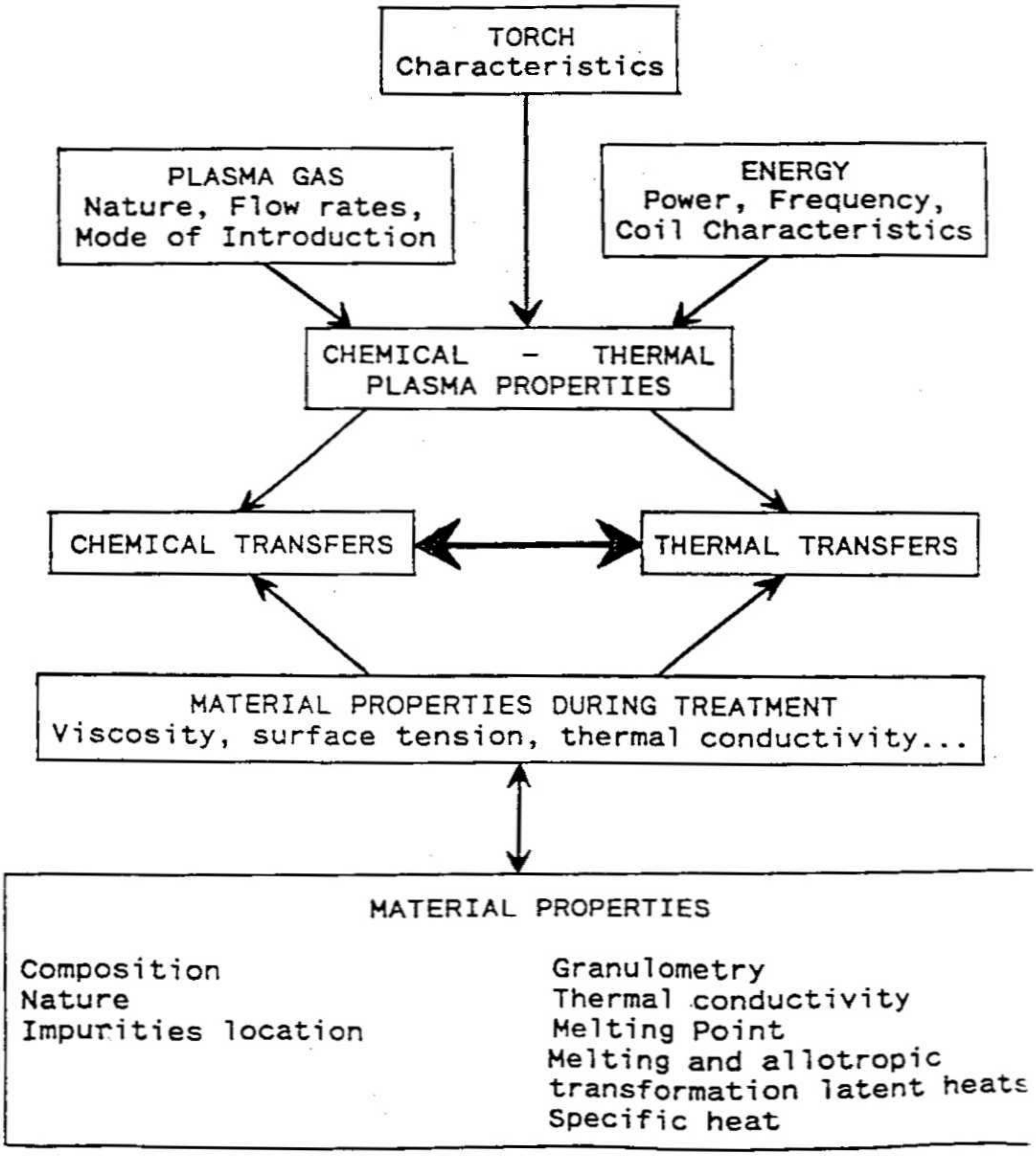


Fig. 8 - Key parameters for the plasma process

I. RAW MATERIAL PURITY LEVEL

	Contents in µg/g		
Material Element	Microsponge	Powder	Turnings
Cl	1971	689	<12
Cu	1617	78	17
Mn	391	6.0	14
Na	187	1008	7
Co	67	0.3	0.8
Cr	3100	31	89
Fe	30660	82	320

II. OPERATING CONDITIONS

Treatment of pellets composed of
Titanium powder and microsponge
$P = 8$ kW – $Q_{Ar} = 30$ l/mn – $Q_{He} = 2.2$ l/mn

Fig. 9 - Influence of raw material quality on the process efficiency

III. RESULTS

P : Eliminated % of Element X
pm : Microsponge % in pellets

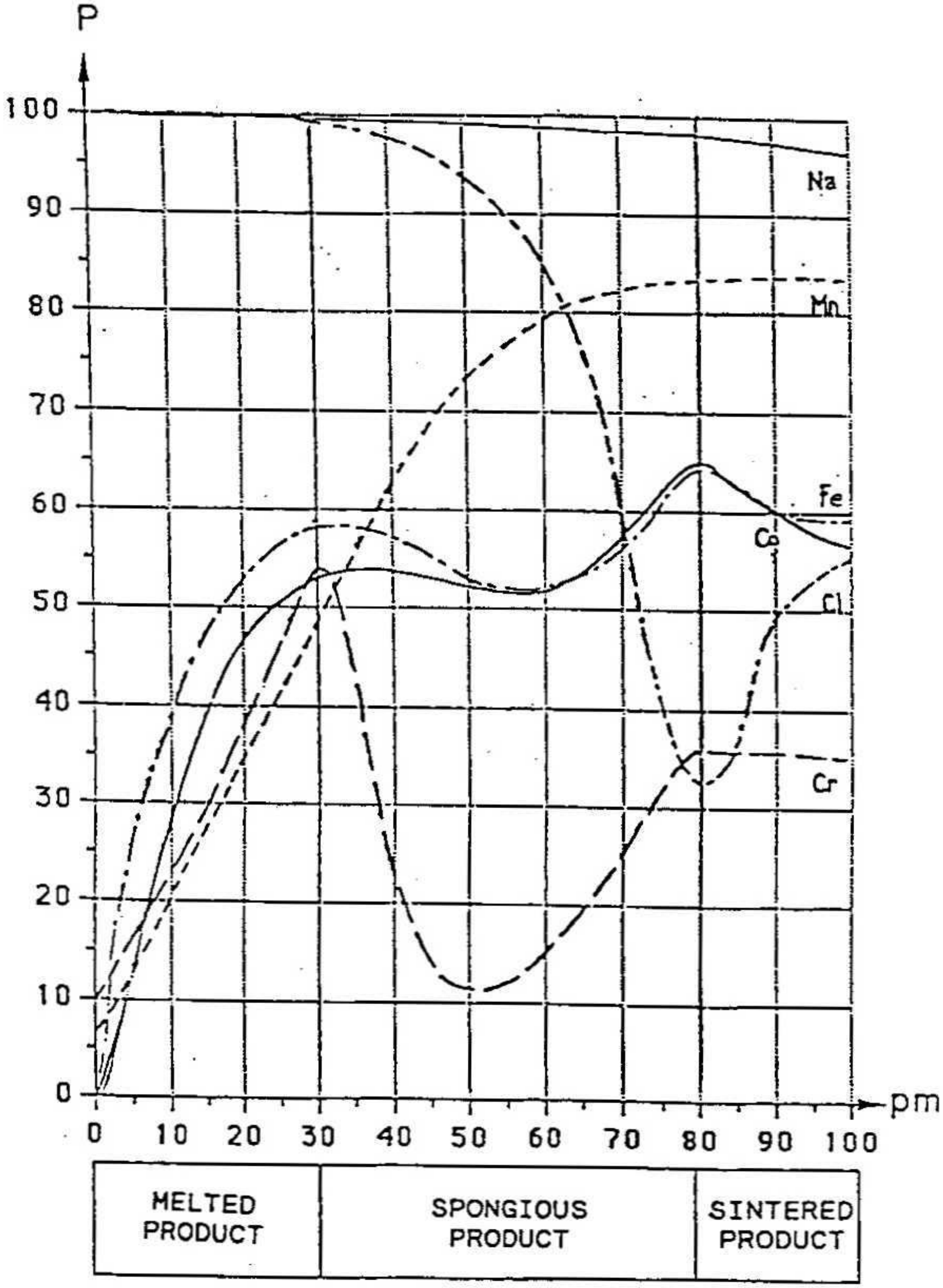


Fig. 10 - Eliminated % of impurities as a function of microsponge % in pellets

I. OPERATING CONDITIONS

Gas	Flow Rates Ar l/mn	Flow Rates l/mn	Power kW
Ar - He	30	He: 2.2	8
Ar - H_2	30	H_2: 0.30	7

II. RESULTS

Microsponge % in Microsponge-Turning Mixtures		34 %	36 %
Plasma Gas Nature		Ar - He	Ar - H_2
Impurities Contents in Raw Material (µg/g)	Cl	1128	1190
	Cu	21.4	21.7
	Mn	58	61
	Na	9	9
Impurities Contents in Product (µg/g)	H	2	99
	Cl	128	118
	Cu	9.7	6.8
	Mn	4.3	2.7
	Na	0.4	0.65
Impurities Eliminated %	Cl	88	90
	Cu	54	69
	Mn	92	95
	Na	95	93

Fig. 11 - Influence of gas plasma composition on titanium purification

OPERATING CONDITIONS:

$P = 8$ kW − $Q_{Ar} = 30$ l/mn − $Q_{He} = 2.2$ l/mn

	Contents in µg/g			
Element	Raw Material	Product		
		Without Flux	With 1% CaF_2	With 0.5% NaF
Cl	1074	49	136	133
Mn	121.5	82	66.6	59.5
Na	762	<0.03	0.53	1.64
Cr	952	830	541	711
Fe	9255	4750	2600	3620

Fig. 12 - Flux effect on titanium purification

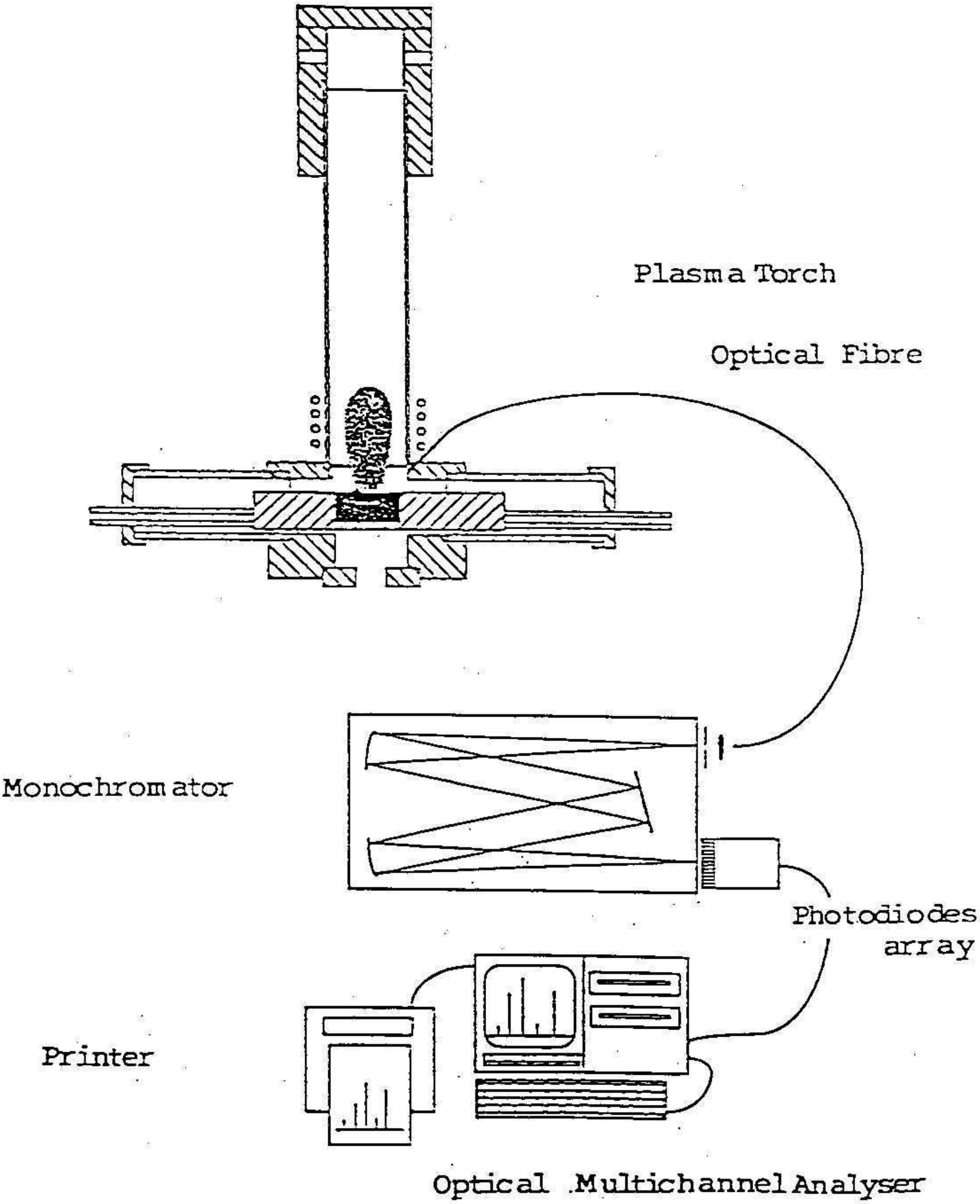


Fig. 13 - Experimental set-up for the purification follow-up

OPERATING CONDITIONS:

- Plasma : Q_{Ar} = 30 l/mn - Q_{He} = 2.2 l/mn
- Raw Material : Microsponge-Powder Mixtures (40% - 60%)
- Flux : LiF, NaF, KF, MgF_2

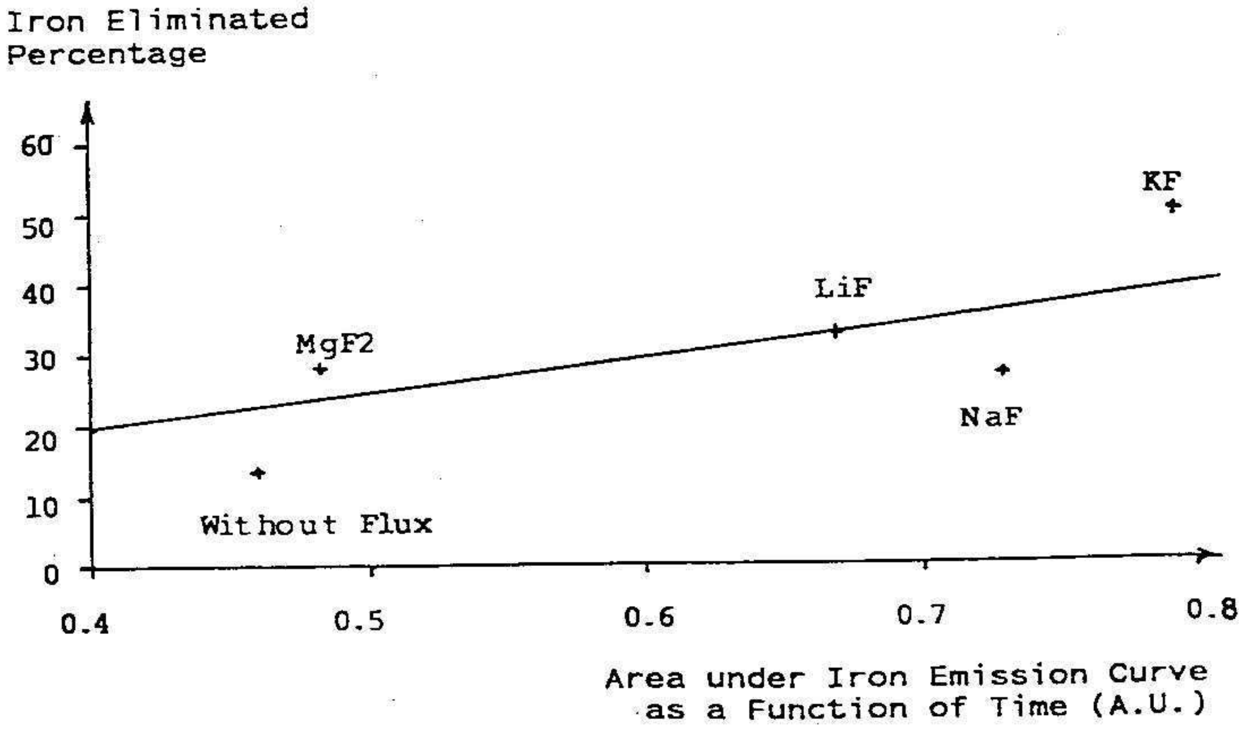


Fig. 14 - Titanium purification follow-up