João Henrique Chamorra Moura

Grau de Licenciatura em Ciências dos Materiais

Recuperação e separação das partículas de diamante para reutilização nas ferramentas de corte

Dissertação apresentada em cumprimento parcial dos requisitos para o grau de Mestre em Engenharia de Ciências dos Materiais

Orientador: Prof. Dr. Alexandre Velhinho, Professor titular, Faculdade de Ciências e Tecnologias, Universidade NOVA de Lisboa

Co - orientador: Engenheiro Nuno Duarte, DJDIN, Indústria e Comércio, Lda.

Conselho de avaliação:

Presidente: Prof. João Pedro Botelho Veiga, Departamento de Ciências dos Materiais, FCT-UNL

Arguente: Prof. Rui Jorge Cordeiro Silva, Departamento de Ciências dos Materiais, FCT-UNL

Vogal: Eng. Nuno Duarte, DJDin, Industria e Comércio Lda.

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Recovery and separation of diamond particle for reuse in cutting tools

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Resumo

No presente trabalho procuraram definir vários parâmetros para um posterior dimensionamento de um sistema de separação de desperdícios de ferramentas de corte diamantadas usadas na indústria de rochas ornamentais, em parceria com a empresa DJDin, sediada em Pêro pinheiro, em concreto, ferramentas à base de Liga Ferrosa e de Bronze. Como tal, várias formas de separação foram analisadas de modo a garantir um processo viavelmente sustentável a nível ambiental. As várias etapas de separação incluem a dissolução por lixiviação, com controlo de temperatura, aplicação de ultrassons e uma fase de neutralização de resíduos químicos. Todos os passos descritos, foram concretizados, obtendo-se melhores resultados na recuperação do diamante, utilizando ultrassons a 60º C, tendo sido observada uma maior taxa de separação de partículas de diamante, mantendo a sua integridade total, e uma menor libertação de vapores.

Palavras chave: Ferramentas de corte diamantadas, Lixiviação, Ultrassons, Sustentabilidade

Abstract

The present work aimed at defining several parameters for a further dimensioning of a waste separation system for diamond cutting tools, jointly with DJDin, settled in Pêro Pinheiro, based on Ferrous alloys or Bronzes and used in the ornamental stone industry and for cutting concrete. As such, several forms of separation have been analysed in order to ensure a viably sustainable process at the environmental level. The various separation stages include leaching dissolution under controlled temperature and ultrasonic stirring and a phase of chemical waste neutralization. Using ultrasounds at 60 ^{o} C, the sequence of processing steps led to satisfactory results in the recovery of the diamond, with a high rate of separation of the particles, maintaining its total integrity, with reduced corrosive vapour release.

Keywords: diamond cutting tools, leaching, ultrasounds, sustainability

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Acronyms

CENIMAT: Centro de Investigação de Materiais

CBC: Body Centred Cubic DCT: Diamond Cutting Tools

EDS: Energy Dispersive X-Ray Spectroscopy

FCC: Face Centered Cubic

SEM: Scanning Elletron Microscope

XRD: X-Ray Diffraction

ICDD: International Centre for Diffraction Data

Motivation and Objectives

We live in a world where an engineer has few considerations when it comes by choosing the materials and techniques to operate because we can cause huge impact in society and especially on the environment in a negative way, not giving the proper attention to these aspects. Nowadays, efforts have been made to upset this tendency by recycling, reducing or reutilizing raw materials to a better environmental and social behaviour to correspond to the current needs.

The aim of this master thesis focuses precisely on the survey of several critical parameters that enable the design of a separation system capable of recovering diamond particles from the wasted cutting tools used in ornamental industry by crushing, dissolving in *acqua regia* under controlled temperature and promoting faster dissolution of the metallic matrix though the use of ultrasonic stirring, and finally neutralization with the of reducing the ecological footprint by limiting the liberation of corrosive effluents at the end of the process.

The objectives of this master thesis are:

- Determine and define critical parameters for a subsequent scaling of wasted diamond cutting tools;
- Separate diamonds from the cutting tools scrap;
- Reduce costs, raw material and be able to replace manufacturing process currently used.

1. Introduction

1.1. Diamond cutting tools (DCT)

Diamond cutting tools (DCT) usually correspond to a diamond abrasive embedded in a metallic matrix. Such tools are commonly used in ornamental stone cutting industry and other related fields. These industries operate sawblades, consisting of a metal disk or core and possessing teeth around the periphery, upon which the diamond-containing abrasive segments are mounted via brazing or laser welding [1], [2]. A typical segment contains cobalt and several other alloying elements as the binding agent, reinforced up to 20% of diamond particles (approximately 35 carat) [3], the exact amount depending on geometry and dimensions of the tool.

Nowadays, DCT are processed by two main powder metallurgical techniques such as hot pressing or in some cases by cold pressing and sintering, where the diamond particles are embedded in the metal matrix by means of a combination between chemical and physical interactions [4]. Currently, at the end of their useful lifetime the cutting segments are turned into scrap without practically any commercial value and since the diamond cutting tools have been more requested for two main reasons: input of new materials and the necessity of new cutting tools for high precision and high productivity. Two of many enough reasons to explore more options to contribute for a sustainable practice in this matter.

1.2. Diamond

The word diamond originates from the Greek "adamao" and the adjective was used to describe it as the hardest substance known to man. The first knowledge of diamond started in India; were it was first mined. Before the 1870s diamonds were still rare and used by aristocracy. From the Portuguese discoveries in the late 15th century, diamond was brought to Europe and the demand increased in the 18th century, becoming ever more abundant. Substantial quantities of diamonds arrived from South America, but today diamonds are mined in about 25 countries, on every continent except Europe. So, it is a modern misconception that the world's diamonds came primarily from Africa: as they are a worldwide resource [6].

Scientifically, diamond is an allotrope of carbon, with a Face Centred Cubic (FCC) crystal structure, and the second most chemically stable form of carbon after graphite with various general properties described in Table 1.1. The circumstance of being the hardest material known to mankind dictates many of its uses for cutting, grinding and polishing operations. It can be used in natural or synthetic form, thought the present work deals with the second case, which is deemed as more appropriate for cutting tools [1].

Table 1.1 General properties of diamond [7].

General properties	Density		3.44e3 - 3.58e3 kg/m^3	
Mechanical properties	Young's modulus [GPa]	1.05×10^3 - 1.21×10^3	Shear modulus [GPa]	440 - 470
	Yield strength (elastic limit) [MPa]	2.8×10^3 - 2.93×10^3	Bulk modulus [GPa]	530 – 548
	Tensile strength [MPa]	2.8×10^3 - 2.93×10^3	Poisson's ratio	0.18 - 0.22
	Elongation [%]	0.23 - 0.28	Hardness – Vickers [HV]	4.2×10^3 - 4.9×10^3
	Compressive strength [MPa]	10×10^3 - 20×10^3	Fatigue strength at 10^7 cycles [MPa]	2.3×10^3 - 2.5×10^3
	Flexural modulus [GPa]	1.05×10^3 - 1.21×10^3	Mechanical loss coefficient (tan □)	2×10^{-6} - 4×10^{-6}
	Flexural strength (modulus of rupture) [MPa]	2.6×10^3 - 3×10^3	-	-
Impact & fracture properties	Fracture toughness [MPa.m$^{1/2}$]		7.8 - 9.5	
Thermal properties	Melting point [°C]	3.72×10^3 - 3.91×10^3	Specific heat capacity [J kg^{-1} °C^{-1}]	500 – 520
	Maximum service temperature [°C]	1.5×10^3 - 1.7×10^3	Thermal expansion coefficient [°C^{-1}]	0.8×10^{-3} - 1.2×10^{-3}
	Minimum service temperature [°C]	-273	Latent heat of fusion [kJ kg^{-1}]	5.2×10^3 - 5.3×10^3
	Thermal conductivity [W m^{-1} °C^{-1}]	900 - 2.32×10^3	-	-
Electrical properties	Electrical resistivity [µohm cm]	10×10^9 - 100×10^{18}	Dissipation factor (dielectric loss tangent)	200×10^{-6} - 300×10^{-6}
	Dielectric constant (relative permittivity)	5.5 - 5.7	Dielectric strength (dielectric breakdown) [MV m^{-1}]	10 – 20
Optical properties	Colour	Clear	Transparency	Optical quality
	Refractive index	2.4 - 2.43	-	-
Magnetic properties	Magnetic type		Non-magnetic	
Durability	Water (fresh)	Excellent	Organic solvents	Excellent
	Water (salt)	Excellent	Oxidation at 500 ºC	Excellent
	Weak acids	Excellent	UV radiation (sunlight)	Excellent
	Strong acids	Excellent	Halogens	Acceptable
	Weak alkalis	Excellent	Metals	Acceptable
	Strong alkalis	Acceptable	Flammability	Non-flammable
Primary production energy, CO$_2$ and water	Embodied energy, primary production [MJ kg^{-1}]	2.15×10^6 - 2.37×10^6	Water usage [l kg^{-1}]	7.03 - 7.77
	CO$_2$ footprint, primary production [kg kg^{-1}]	225×10^3 - 248×10^3	-	-

Processing energy, CO_2 footprint & water	Grinding energy (per unit weight removed) [MJ kg^{-1}]	766 – 847	Grinding CO_2 (per unit weight removed) [kg kg^{-1}]	57.5 - 63.5
Recycling and end of life	Recycle	False	Combust for energy recovery	False
	Recycle fraction in current supply [%]	0.465 - 0.51	Landfill	True
	Downcycle	True	Biodegrade	False
Price	Price [€ kg^{-1}]		233×10^3 - 466×10^3	

The diamond particles are the most important part of the cutting tools since they are responsible for the abrasiveness. As the sawblade cuts, due to the abrasive wear of the metal matrix, fresh diamond particles are continuously being exposed, and these will penetrate the material being cut (e.g. stone) [4].

1.3. Sustainability and Recycling of abrasive tools

Global trends on raw material pricing and availability drive tool manufacturers and raw material suppliers to strive for new materials and tool designs but also to achieve a sustainable world. With that in mind, sustainability can contemplate four main dimensions: Economy, Environment, Society and Technology For the particular case of abrasive tools, Economy is viewed in terms of main production and costs; Environment is represented by energy and material input, waste, recyclability, emissions and so on; Society corresponds to worker safety, health and labour education; while Technology translates into feasibility, workpiece quality, best practices and process and product performance. Product life is defined by several physical, functional, economical and legal constraints. The end of a cutting tool's life is either defined by the tool wear down to a pre-defined abrasive layer minimum thickness. Options for end of life are landfill, combustion, recycling, reengineering or reuse [8].

Nowadays, an inability to reuse the raw materials, particularly those contained in the abrasive elements of damaged sawblades, represents the waste of an economically valuable source, given that a significant amount of diamond particles could still remain in a damaged/scrapped sawblade, as indicated by *Sheed et al.*[4]. There are estimates in the literature [1] that about 10% of the diamond remains in the teeth of scrapped DCT. This fact provides an important motivation for the present work, which investigates methods for separating the diamond contained within scrapped sawblades for subsequent recycling.

1.4. Hydrometallurgical Processes

Even though few research works are reported in the literature, some separation methods were tested on DCT to recover diamond particles from a cobalt-based matrix also containing tungsten carbide reinforcements. The diamond was separated using a hydrometallurgical process, like lixiviation, where the segments were leached by *acqua regia*, a mixed solution containing HCl and HNO_3 [4]. Thus, diamonds could be recovered undamaged from the waste sawblades. During that study, the leaching rate was found to depend heavily on temperature: higher temperatures result in faster leaching kinetics, in accordance with Arrhenius equation.

1.5. Ultrasound technology

The use of ultrasonic vibration to aid in hydrometallurgical separation of diamond particles from a metallic matrix has also been studied [9], preference being accorded in the industry to high-frequency ultrasounds, due to a lower energy consumption level.

As said, even though there is not much information in recovery diamond from the cutting tools, efforts are being made to achieve better results providing a better society, economic and environmentally.

2. Methods and Materials

2.1. Characterization Techniques

2.1.1.DCT mass determination

In the present work, it was first determined the base materials, in concrete, alloy and brass based tools (Figure 2.1) in terms of weight, geometry and approximate crystallographic composition. The weight of the ferrous alloy and brass based materials were measured in a digital scale (Figure 2.2) having respectively 48.2 g and 6.7 g.

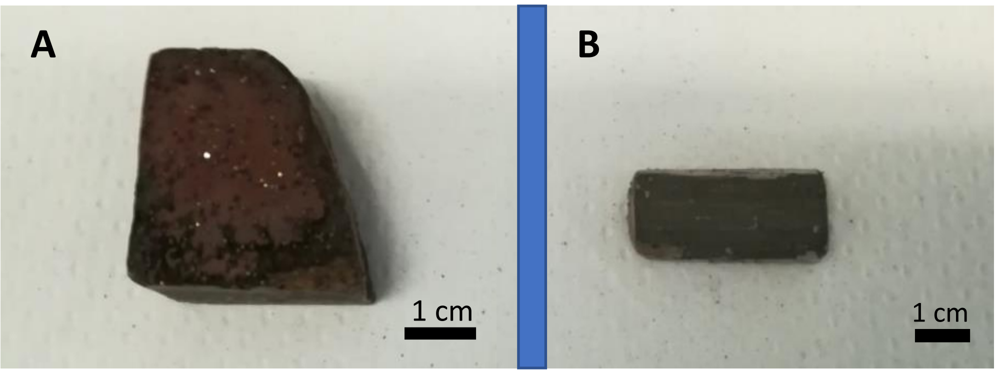


Figure 2.1 Samples: A- ferrous alloy; B - brass abrasive.

Figure 2.2 Digital scale.

2.1.2.Particle geometry determination

As for their geometry, Java-based image processing and analysing software (Image J, National Institutes of Health, USA) was used for the same based material in order to identify the mean size particle distribution.

2.1.3.Reflected Light (Optical) Microscope

An observation was performed, before and after the entire process being complete in order to see if the diamonds were damaged or not, using a Leica S9i with optical low magnification stereoscope (Figure 2.3) and a Leica DMI 5000 M inverted reflected light microscope incorporating a motorized stage and controlled by Leica application Suite (**LAS)** software, allowing the acquisition of depth field images (MultiFocus) and the grouping of sequential images (Multistep) Brightfield imaging contrast mode.

Figure 2.3 Optical magnifier used to observe the diamond particles samples.

2.1.4. Chemical identification

2.1.4.1. Energy Dispersive X-Ray Spectroscopy (EDS)

The diamond reinforced tools were analysed/imaged before and after the separation process by Energy Dispersive X-Ray Spectroscopy (EDS) (SEM Zeiss DSM 962 (Conventional SEM)), (Figure 2.4), at an accelerating voltage of 20 kV and a Back Scattered Electrons (BSE) and Secondary Electrons (SE) mixing signal. The samples were coated in a sputtering device (AGAR Sputtering Coater), with gold (Au) at 0.1 mA/mbar to ensure a better conductivity to the samples (Figure 2.5) and it was obtained images in top-view configuration.

Figure 2.4 Zeiss DSM 962 SEM microscope.

Figure 2.5 AGAR Sputtering Coater used on cutting tool samples.

2.1.4.2. X-Ray Diffraction (XRD)

X-Ray diffractometry (Rigaku DMAX IIIC) (Figure 2.6) was used to study the crystallographic structure of the ferrous alloy and brass based tools before entering in the process established in order to know with what kind of materials are going to be studied and tested. Each analysis was performed with a monochromatic Cu k-α radiation (40 kV and 30 mA) and every scan was recorded in the range of $2\theta = 20 - 85°$ at a total time scan of 13 minutes.

Figure 2.6 Rigaku DMAX IIIC diffractometer.

2.2. DCT Separation Process

2.2.1 Surface Preparation

In this first step, before doing dissolution, it was applied a commercial varnish used in cosmetic nail polish in all the surface of the samples except on the top surface (Figure 2.1) considering this last as an exposed area to evaluate the reaction and the speed rate of residual loss due to dissolution.

2.2.2 Leaching Dissolution

After the varnish, or crushing, being applied, the next step is to dissolve the samples emerging in a solution of *acqua regia* (three parts of chloridric acid and one part of nitric acid), based in [1]. It was prepared a solution of *acqua regia* for each samples of different binding metals. For the ferrous alloy sample it was prepared a 250mL solution containing 150 mL of distilled water, 75 mL of HCl and 25 mL of HNO_3 and for the brass sample a 100 mL solution containing 60 mL of distilled water, 30 mL of HCl and 10 mL of HNO_3, both reagents saturated. The concentration prepared for both cases were configured to the exposed area of the samples in study. The samples were emerged in the *acqua regia* solution measuring the weight of the same over a period. The set time of dissolution was established in two parts, first measuring periodically every thirty minutes for two hours and periodically every hour until six hours are completed, repeating the same procedure for five days. The other set was measuring the samples for 48h straight using the same measuring method as in the first set. Then it was established other parameters

Ultrasonic-controlled leaching (Figure 2.7) and Temperature-controlled leaching dissolution were added to this separation process, being tested at 25 ºC and 60 ºC temperature, together with

Ultrasonic, for the samples in study. The time set was for 5 days, measuring periodically every hour.

Figure 2.7 SONICA 3200EP S3.

2.2.3 Neutralization

In this work, the neutralization method was done by titration, being the titrant Sodium Hydroxide (NaOH 1M) and the titrated *acqua regia*, initially with a 50 mL of NaOH solution, titrating 50 mL of *acqua regia* solution. Before starting this experience, it was necessary to perform a centrifugation process to *acqua regia* in order to separate the solid phase from the liquid phase giving better performance for neutralization (Figure 2.8).

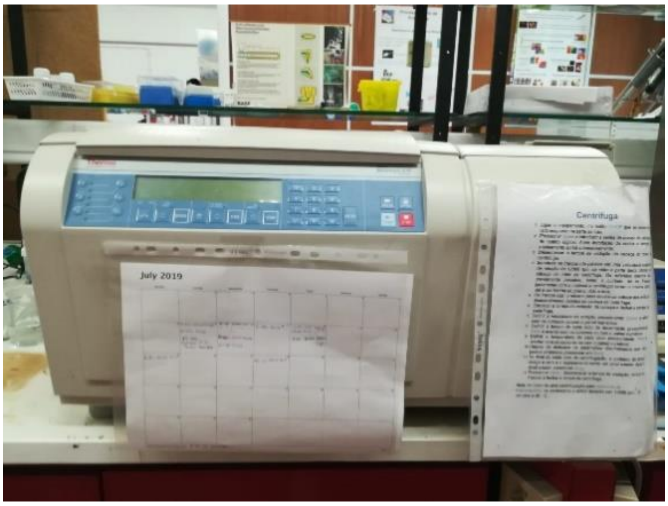


Figure 2.8 Heraeus Multifuge X1R Centrifuge.

The neutralization process was performed in an ice bath under vigorous stirring pouring the basic solution dropwise due to the fact of the reaction being extremely exothermic. The temperature was controlled with a mercury thermometer and the pH level was measured and controlled with a paper pH indicator (Figure 2.9).

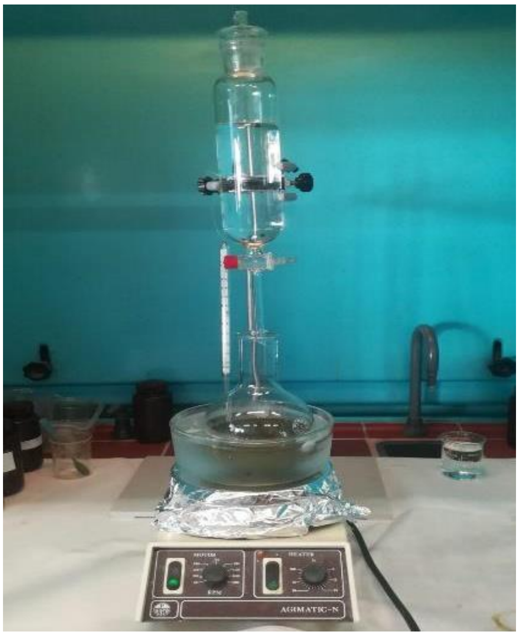


Figure 2.9 Assembly for neutralization.

3. Results and Discussion

In this chapter, the different steps involved in the separation process are presented and discussed. The characterization of the provided DCTs before processing is treated in section **3.1,** followed by all the steps involved in dissolution in section **3.2**. Section **3.3** shows the neutralization performed after the previously discussed steps and finally in section **3.4** it is characterized the diamond particles separated and recovered from the provided DCT.

3.1. DCT Characterization

Before the separation process begins, the diamond particles were observed in the optical microscope (Figure 3.1) and measured with ImageJ software to obtain size particle distribution.

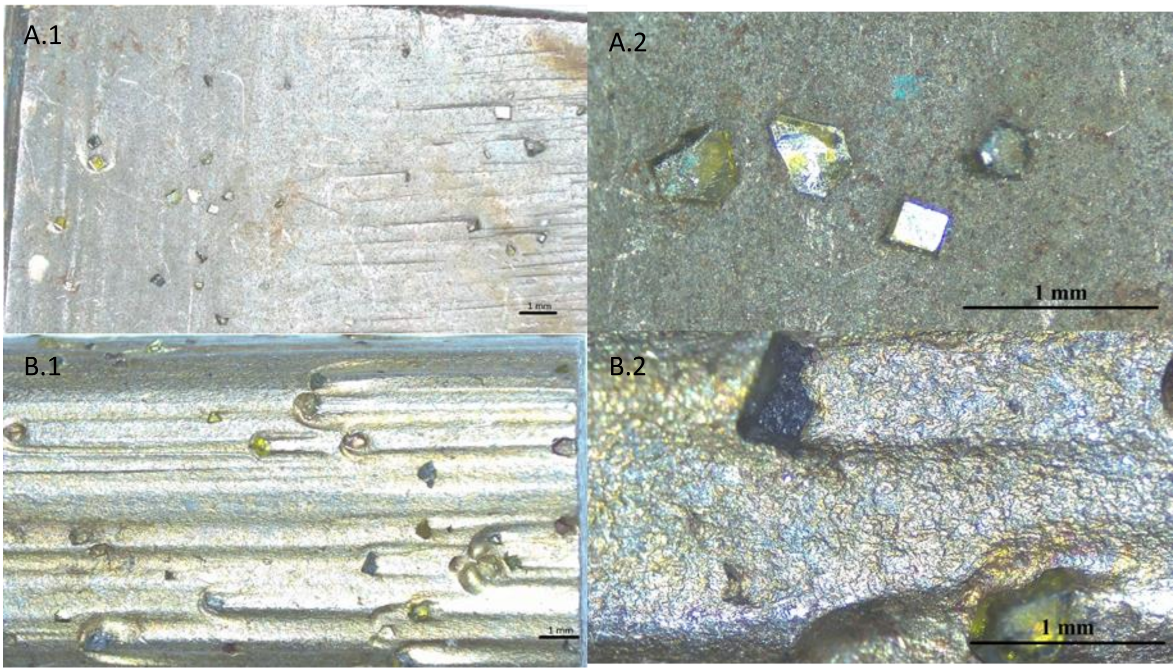


Figure 3.1 Optical Microscope observation with image A.2 and B.2 having a magnification five times greater than A.1 and B.1.

3.1.1. EDS characterization

After observing in the optical microscope, the samples were characterized with SEM/EDS as shown in Figure 3.2 and the identified materials are presented in Figure 3.3 and Annex 1.

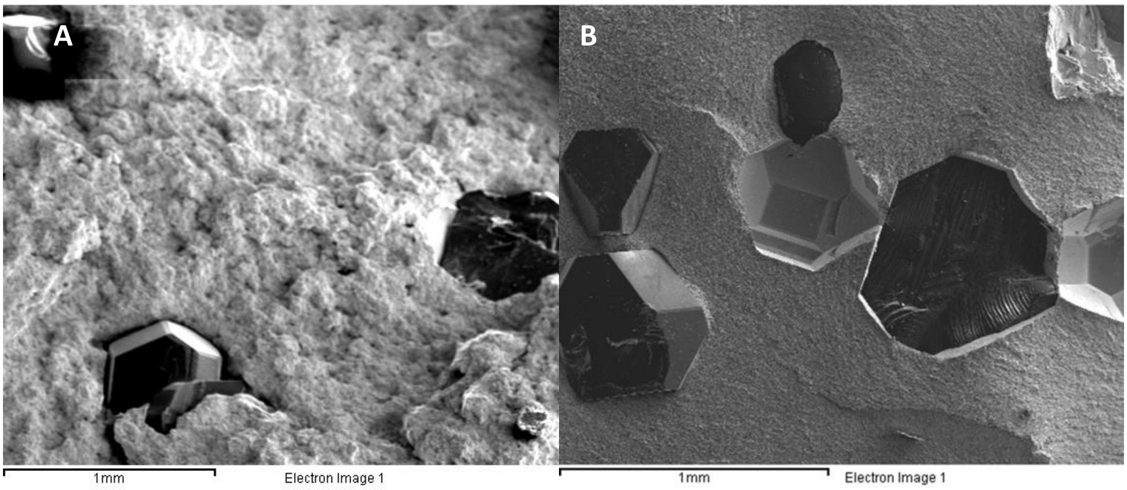


Figure 3.2 Top view (SE) of a brass sample (A) and ferrous alloy sample (B).

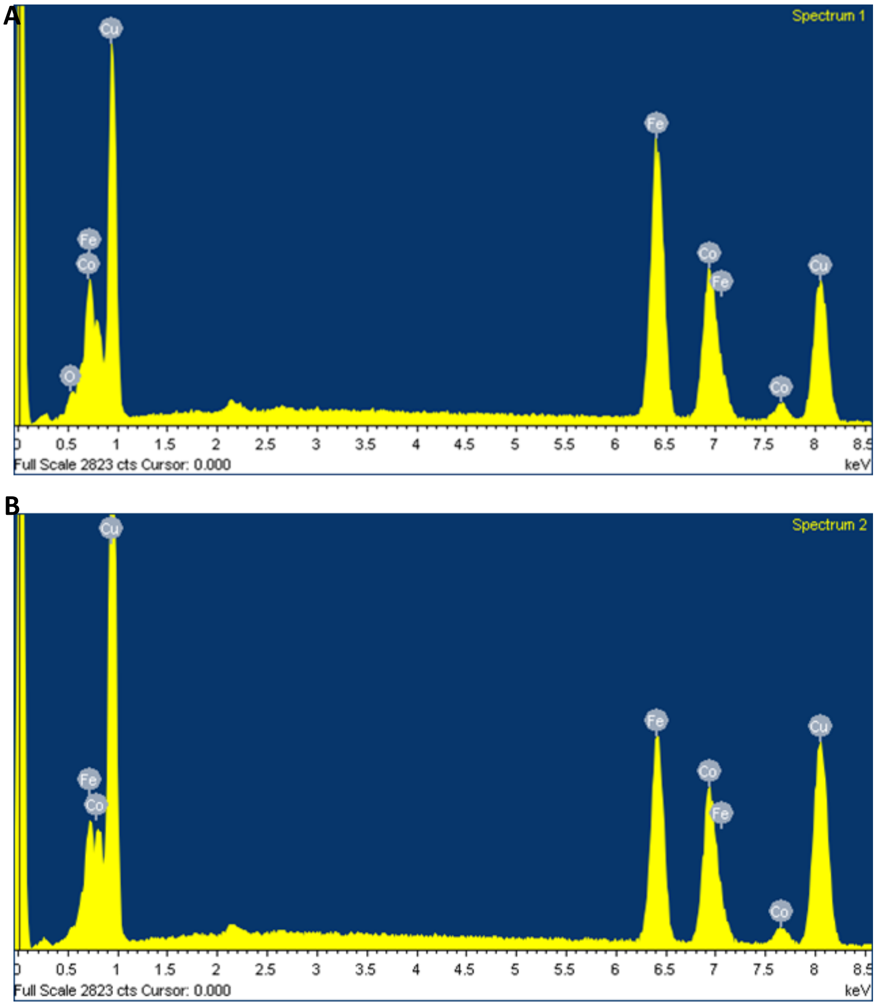


Figure 3.3 Spectra of ferrous alloy (A) and Brass (B).

3.1.2. XRD characterization

The XDR shows the crystallographic composition of the identified compounds contained in the samples (Figure 3.4 and Figure 3.5). It is noticeable a synthetic copper, Face Centred Cubic (FCC) specimen, assured by ICDD (International Centre for Diffraction Data 004-0836) and a synthetic iron specimen, Body Centred Cubic(BCC) (ICDD 006-0696) for ferrous alloy sample. For the brass sample, it is assured a synthetic iron, BCC (ICDD 087-0722) and synthetic copper, FCC (ICDD 004-0836). The diamond peak is in the 2Θ range, between 43,9 - 75º(ICDD database).

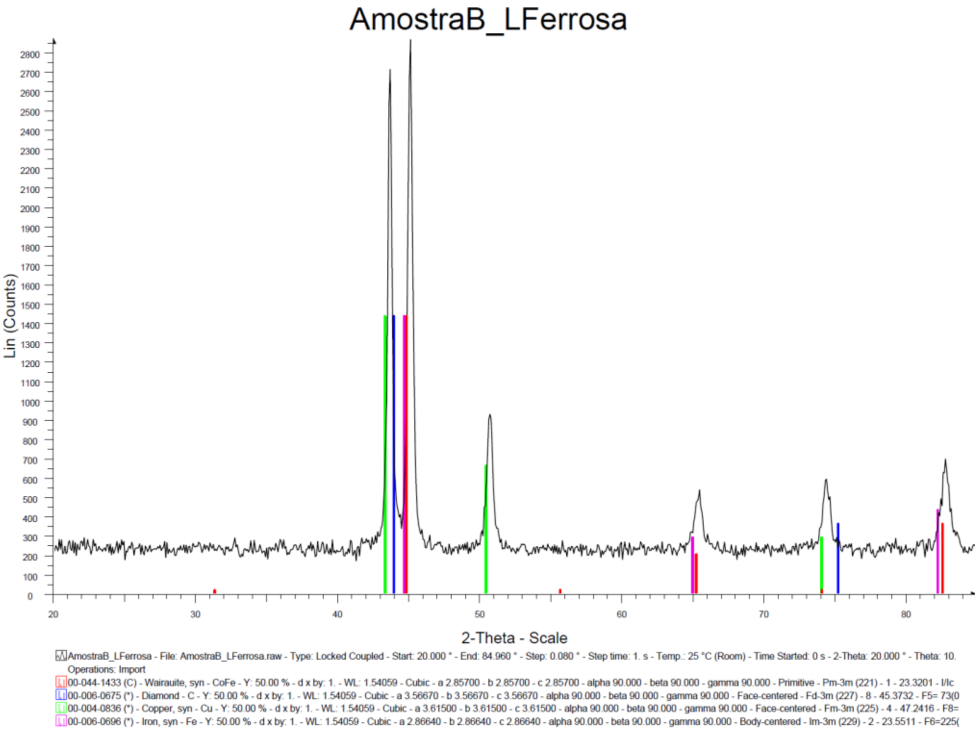


Figure 3.4 XRD spectrum of ferrous alloy sample.

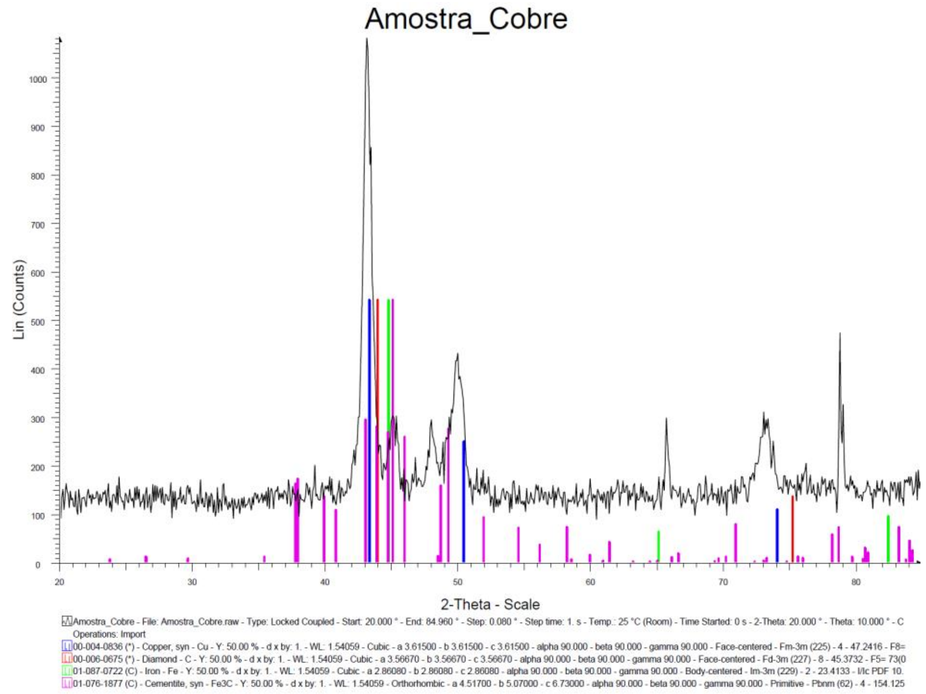


Figure 3.5 XRD spectrum of brass sample.

3.1.3. Image analysis

In order to determine the dissolution rate properly, it was necessary to define previously the surface area of the material exposed to the action of the solution, covering the remaining surface of the samples with a nail varnish (Figure 2.1). The values of the exposed area of each sample are 4.081 cm^2 and 1.080 cm^2, for ferrous alloy and brass respectively, both measured with ImageJ software. Also, it was studied the mean size particle distribution using the mentioned software.

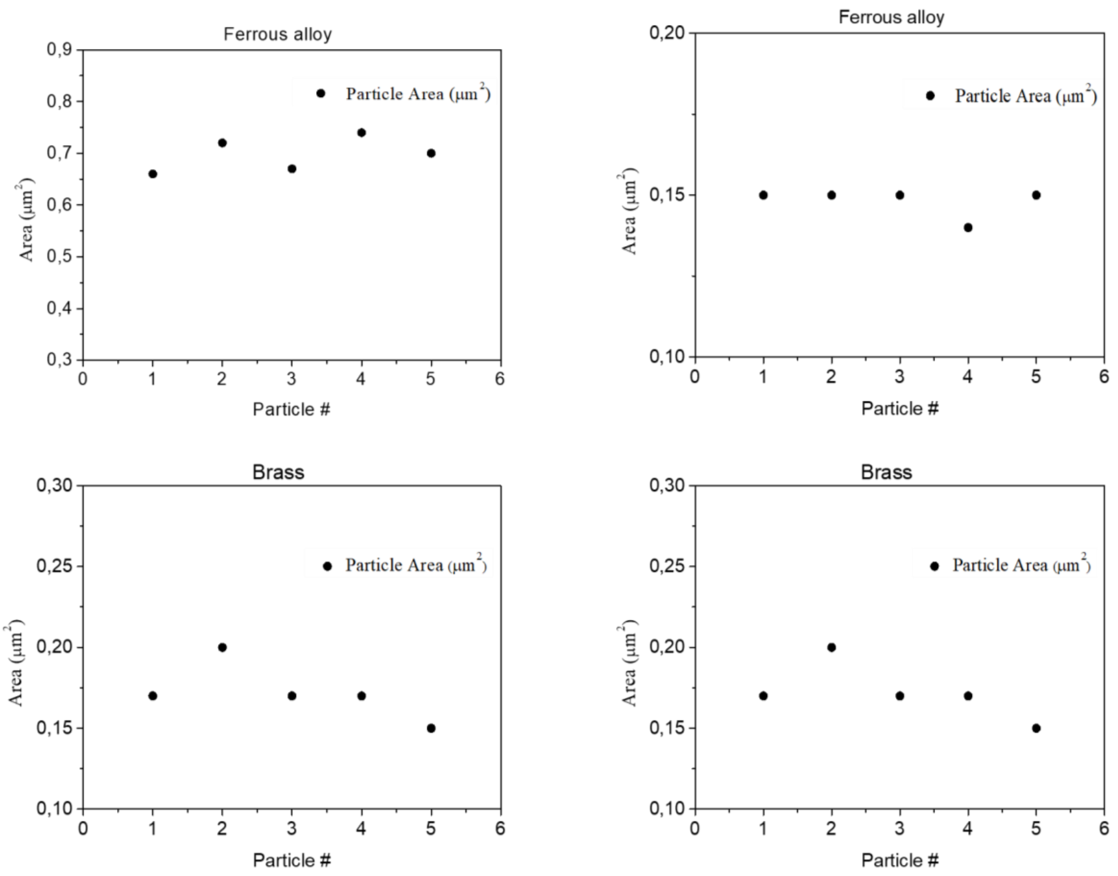


Figure 3.6 Mean particle size distribution of diamonds in the brass binder. The results shown in chart A.2 and B.2 were obtained using Image J software with a magnification 5 times greater than in chart A.1 and A.2.

3.2. DCT unassisted dissolution

It was put in practice the dissolution of DCT making a previous application of the nail varnish in all the area of the sample except in one side in order to control the dissolution rate by attacking only that side. Beside not having any concrete result that could say for sure that the dissolution rate was controlled, it is known that dissolving is a surface phenomenon since it depends on solvent molecules colliding with the outer surface of the solute and the same solute dissolves faster when it is grounded into small particles because it gives a bigger surface area to attack.

Acqua regia solution is composed by HCl and HNO_3 in the proportions of 3:1 respectively. Given that, the samples from the two DCT had significantly different dimensions, being different volumes of solution required in the two cases (Figure 2.1 and Table 3.1).

Table 3.1: Scale of the acqua regia solution for the samples in study

	Total Volume (mL)	HCl Volume (mL)	HNO_3 (mL)
Ferrous Alloy	250	75	25
Brass	100	30	10

The evolution of the dissolution process was accompanied in two different ways: periodically measuring during six hours for five days and measuring periodically when the samples are emerged in the solution for 48h straight. It was used, for both, ferrous alloy and brass, a varnish application, comparing the dissolution rate between them. For the ferrous alloy sample, it is possible to see that more than 75 wt.% of the exposed area was dissolved within 48 hours rather than only 6,5 wt. % of weight loss on a regular measure of six hours a day(Figure 3.7 and Figure 3.8), meaning that for the same exposed area, the weight loss was 8 times faster when the sample is emerged for 48 h. As for the brass , only 17% of the sample weight per exposed area was lost aside from a total dissolution of the sample emerged in less than 48h (approximately 42h).The selectivity of *acqua regia* (in particular chloridric acid) with brass is an important factor for the fact that a better dissolution occurs for the brass sample.

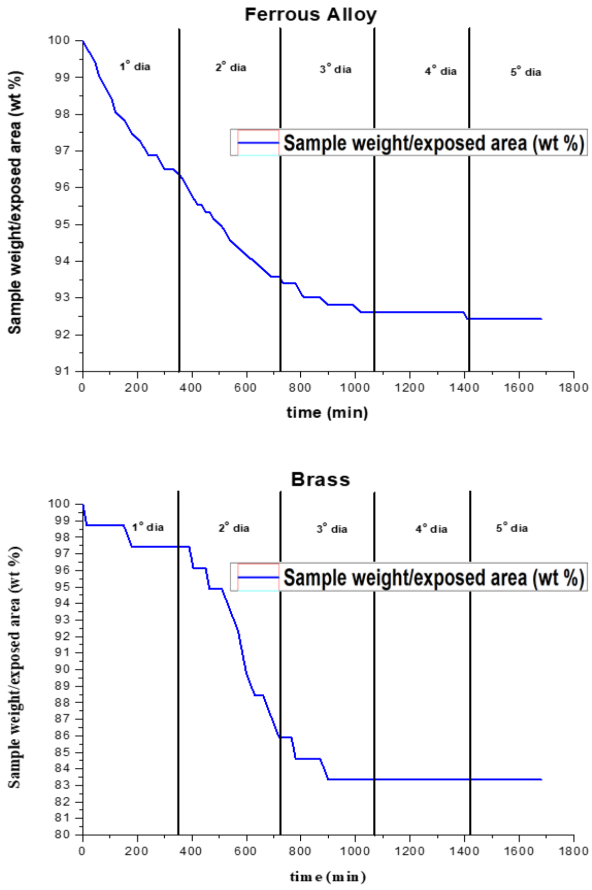


Figure 3.7 Evaluation of the dissolution rate of the samples emerged in acqua regia for 5 days.

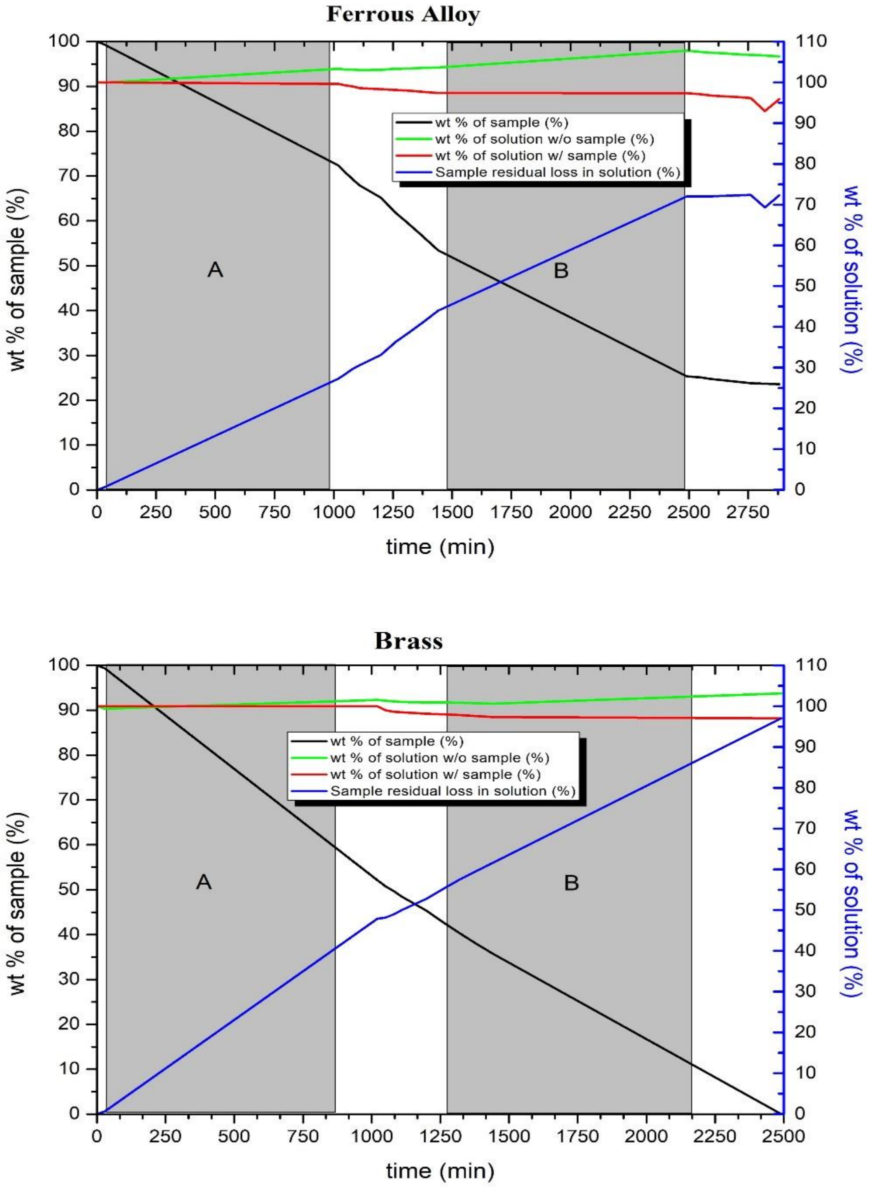


Figure 3.8 Evaluation of the dissolution rate with samples emerged in acqua regia during 48h straight.

3.2.1 Ultrasonic-assisted dissolution

So, to understand whether agitation of the solution could improve the dissolution of the metal binder and so accelerate the separation process of the diamond particles, a similar experiment was undertaken with the aid of an ultrasonic bath. Weight measurements of the ferrous and brass samples were performed in periods of 5 hours for 5 days, at room temperature (25°C). The results are shown in Figure 3.9, where the dissolution rate and the weight loss percentage are compared to those previously obtained for the unassisted dissolution experiments.

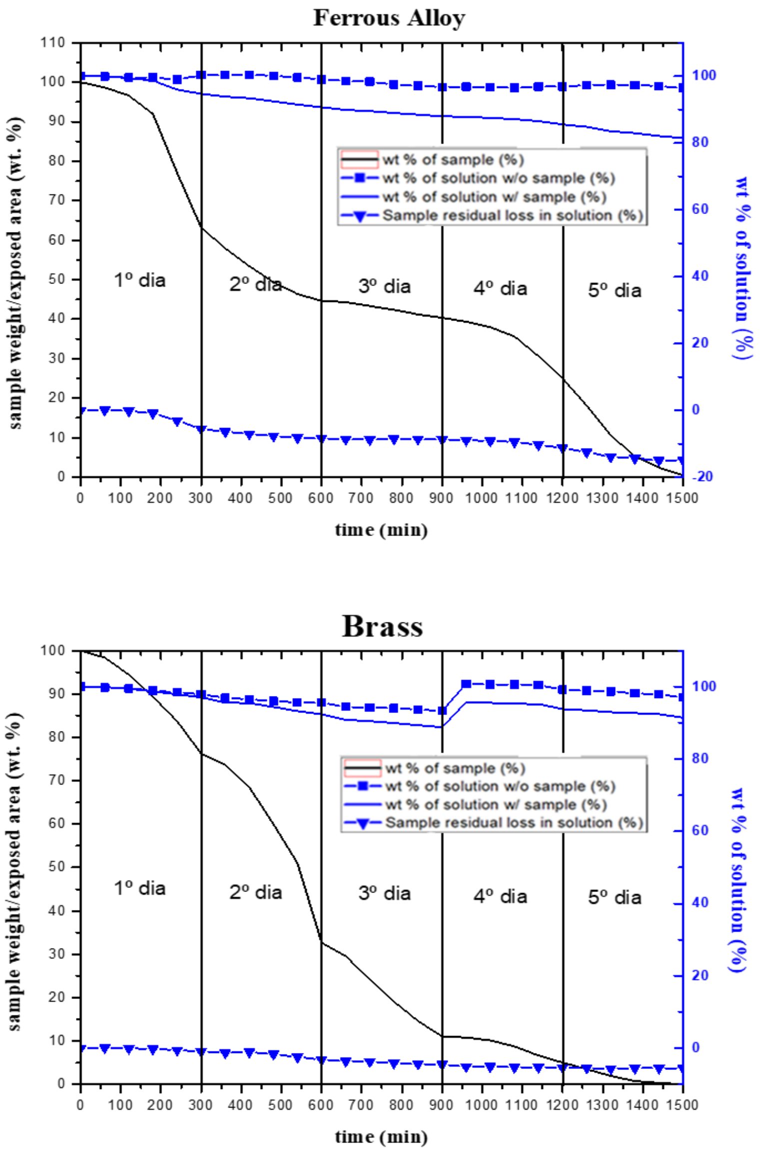


Figure 3.9 Dissolution rate @ 25º C Temperature.

It is possible to observe that, the application of ultrasounds leads to a higher dissolution rate per exposed area. Such an effect may be explained by the cavitation of ultrasound-generated high-pressure bubbles within the solution, which leads to a constant renovation of unsaturated solution near the exposed metallic surface and concomitant removal of dissolved metal ions, decreasing the local metal ion concentration and exacerbating the dissolutive reaction.

3.2.2 Temperature-assisted dissolution

A complementary approach was to study the evolution of the dissolution rate at higher temperature; the chosen value was 60 °C, based on a previous study by Celep *et al.* [4], which applied mechanical stirring to a solution where waste sawblade material was immersed at temperatures ranging from 20 °C to 65 °C. The results obtained during the current work, using ultrasound agitation, are shown in Figure 3.10.

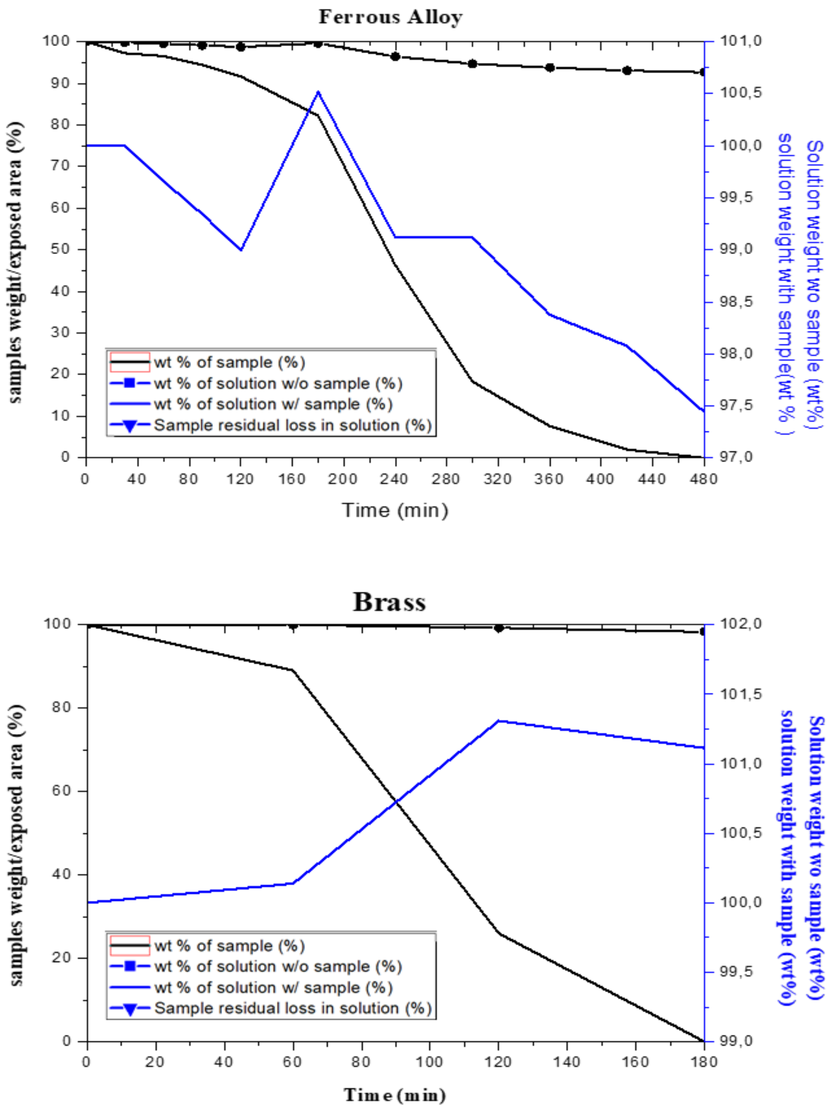
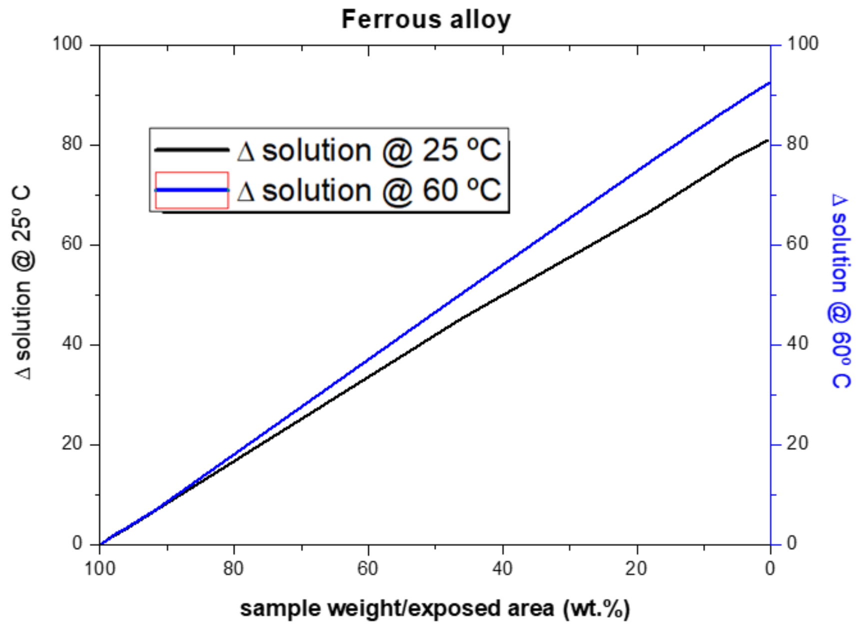


Figure 3.10 Dissolution rate @60 °C Temperature.

Comparing these results with those shown in Figure 3.9, when the temperature is raised the leaching rate also increases, in accordance with the indications from the literature. While complete dissolution of a brass sample required 25 h at 25ºC, the same material was totally dissolved in just 3 h at 60ºC. Concerning the release of corrosive vapours from the solutions, the effect of the elevated temperature should not be noticeable, but as it can been seen in Figure 3.11 there is a difference in the slopes between dissolution made from different temperatures.



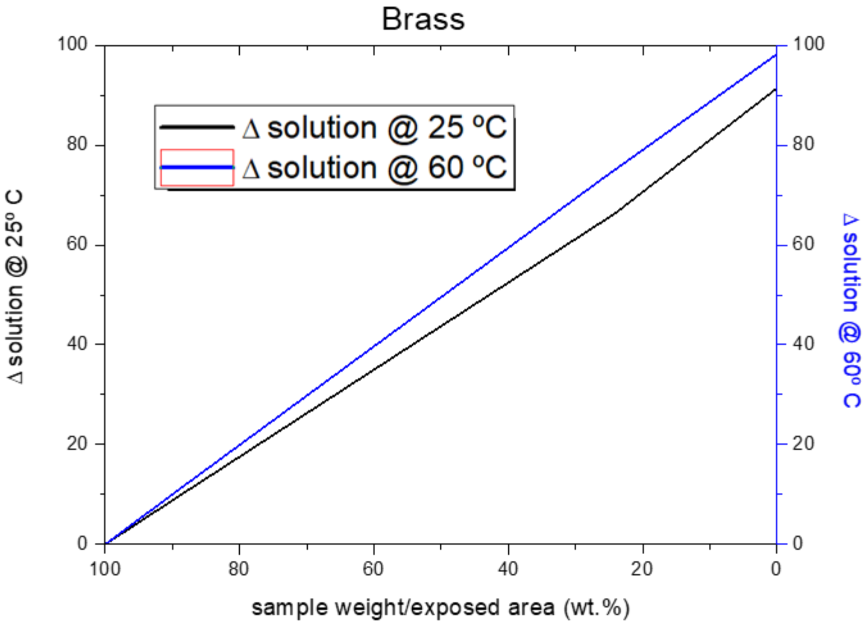


Figure 3.11 Behaviour of corrosive vapours release at different temperatures.

3.3. Solution neutralization and diamond particles separation

An obvious consequence of the leaching approach to diamond particle removal is the generation of an *acqua regia* waste effluent, which places evident environmental difficulties and prevents easy recovery of the diamond particles that may have been released from the metallic binder.

Thus, neutralization of the resulting solution is warranted. To that effect, a titration method was implemented in the present work, giving rise to stable salt compounds.

An alkaline solution was prepared from 26g of sodium hydroxide (NaOH) dissolved in 100 ml of distilled water under an ice water bath – rendered necessary by the high exothermic nature of the reaction – being stirred until complete homogenization. 50 mL of this solution were then added dropwise into 50 mL *acqua regia* solution, also under stirring.

The result consisted of a slurry whose pH level was difficult to measure accurately. This required a centrifugation operation to be performed, in order to separate the solid (containing diamond particles and precipitated metal) and the liquid phases, before effectively performing the neutralization. The centrifugation was performed for 5 minutes at 12000 rpm, under a 22º C temperature. The resulting separated phases are shown in Figure 3.12.

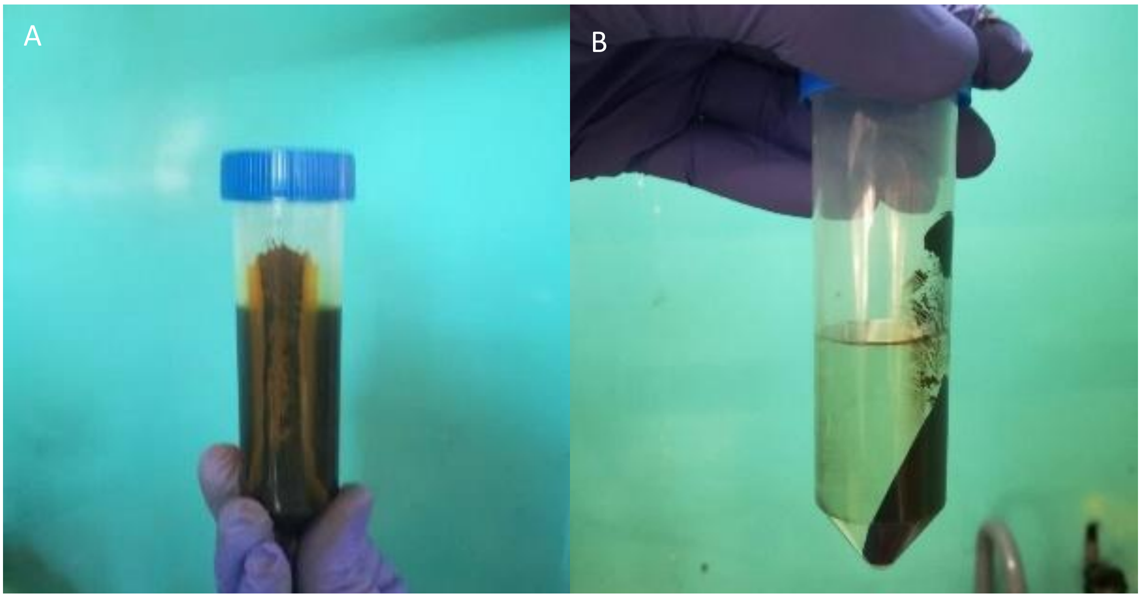


Figure 3.12 Acqua Regia solution after centrifugation: A- Ferrous alloy; B- Brass.

Neutralization was performed afterwards, and the results obtained were as expected (Figure 3.13). In order to understand the evolution of pH levels, titration curves were determined for both solutions (containing brass or ferrous residue). The data experiment was obtained by measuring the solutions with a pH indicator paper and for that reason it was not possible to define a specific measurement. It should be necessary another method to characterize the titration curve, as well. Although, it was possible to verify a good evolution of the pH level. It was also determined the equivalence point for both solutions, as presented in Figure 3.14.

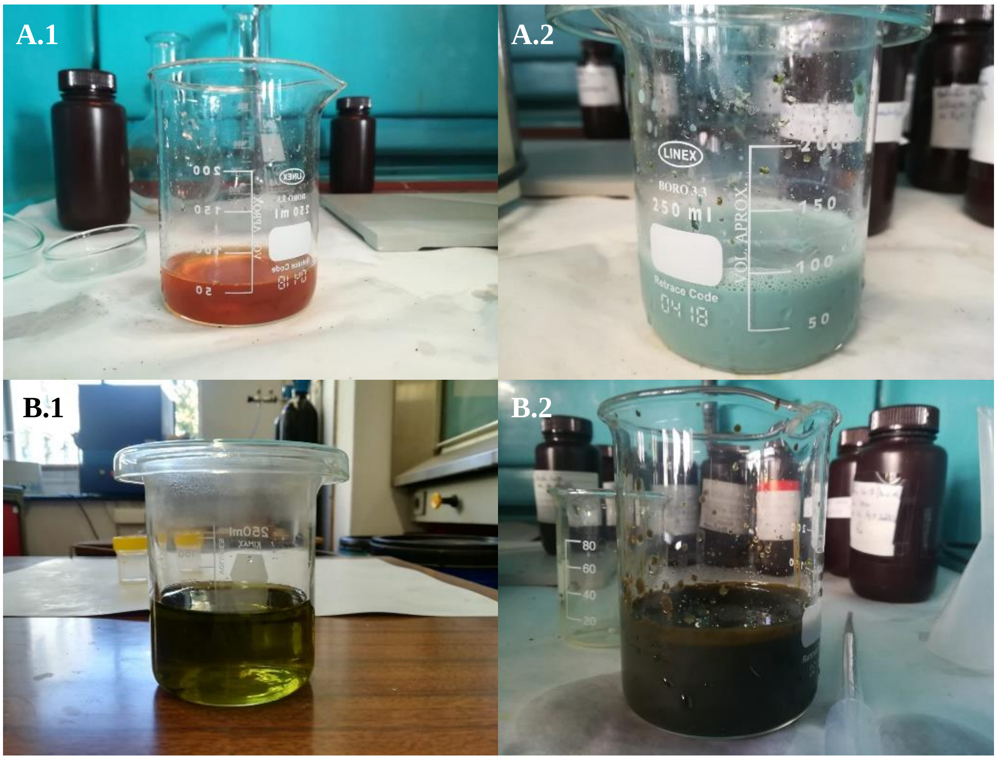


Figure 3.13 Neutralization: A.1 and B.1 respectively - Ferrous Alloy and brass before neutralization; A.2 and B.2 respectively - Ferrous Alloy and brass after neutralization.

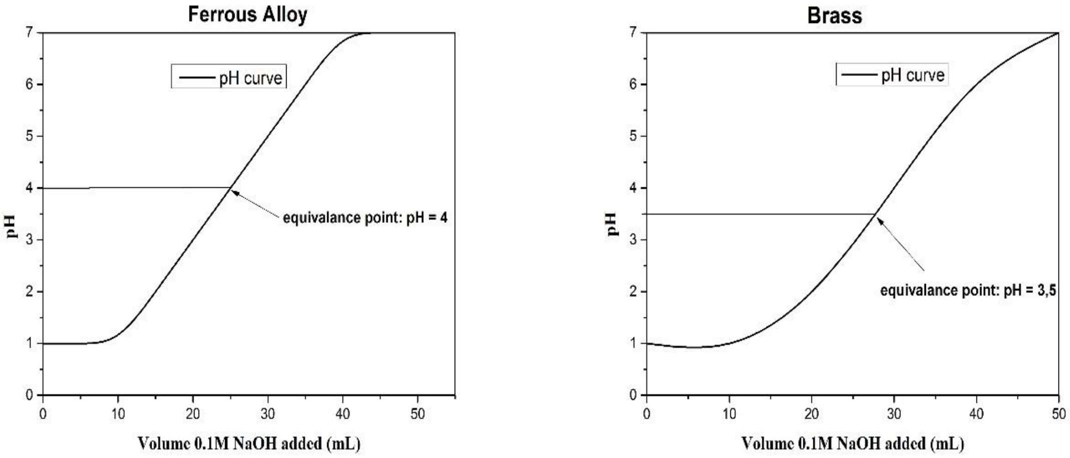


Figure 3.14 Titration curve for the titrated solutions with: A- Ferrous Alloy residues; B- Brass residues.

3.4. Characterization of the recovered diamond particles

3.4.1 Reflected Light (Optical) Microscope

After separating the diamond particles, it was finally observed in the optical microscope. The images obtained shows at a first glance that the diamonds have a different colour from usual, whereas brass dominant colour at naked eye is yellow, which could indicate that the same material could remain in the surface of diamond particles. (Figure 3.15 **A**). As it take a closer look, it is possible to see that some diamonds show no brightness properties (Figure 3.15 **B**) and so, for a better understanding, an EDS characterization was made to know what material residues remains in the diamond surface.

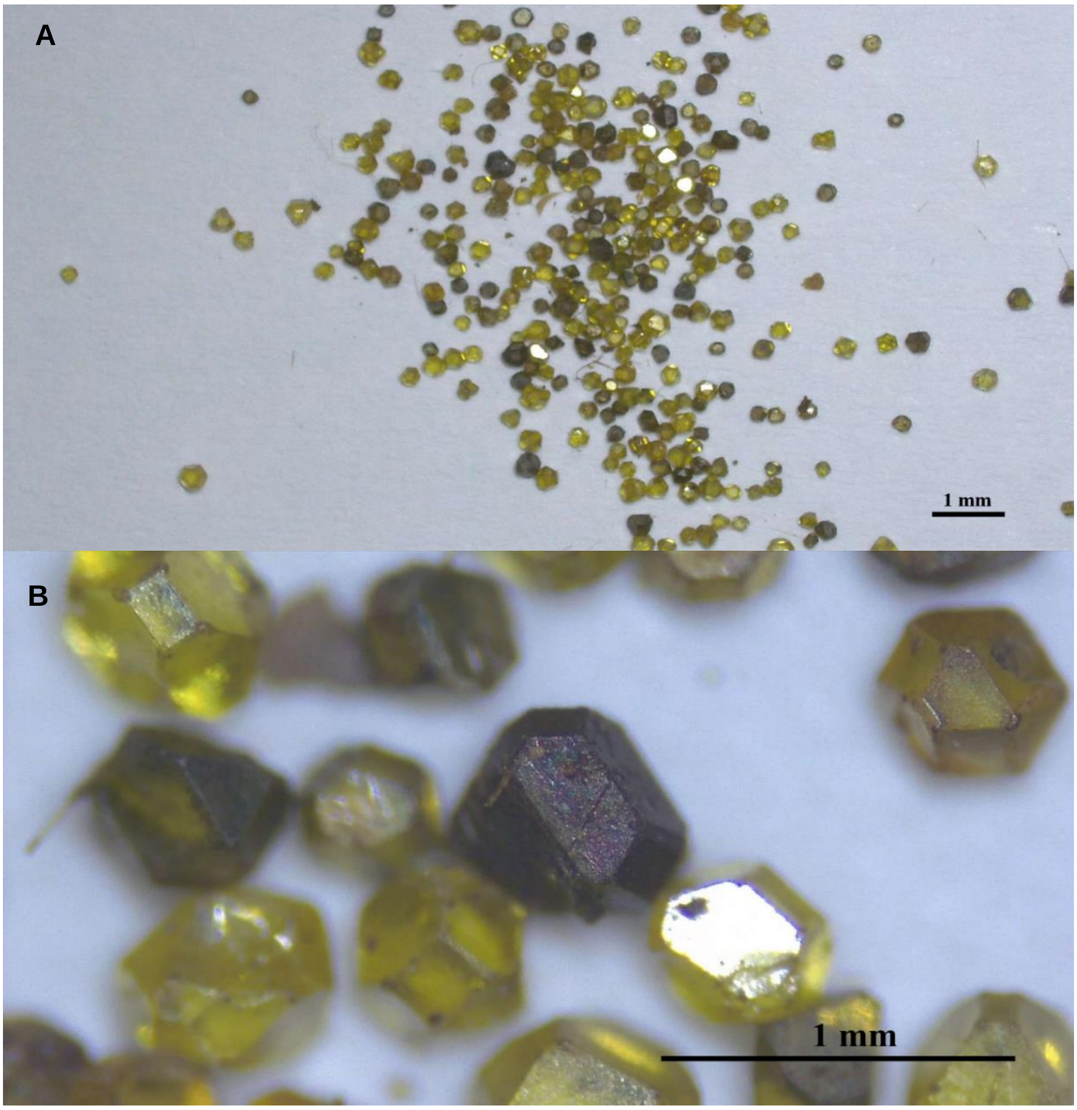


Figure 3.15 Optical Microscope observation: Image B has a magnification five times greater than Image A.

3.4.2 Energy Dispersive X-Ray Spectroscopy (EDS)

With the EDS characterization, it is shown in Figure 3.16, along with a table of the identified compounds in Figure 3.17 and Annex 2, that recovered diamonds do not present visible evidence of wear or fracture. The elements detected were Carbon, Iron and Copper, with new elements present after separation that we not in the virgin sample like Titanium and Silver. Those new elements may have appeared due to some contamination in the separation process.

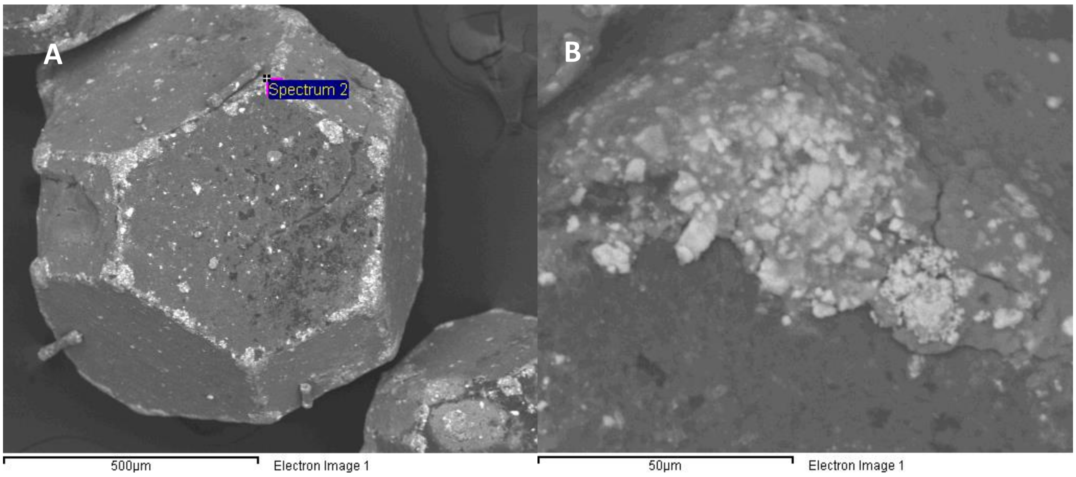


Figure 3.16 EDS images of the diamond particle from top view (A) and diamond crest from top view (B).

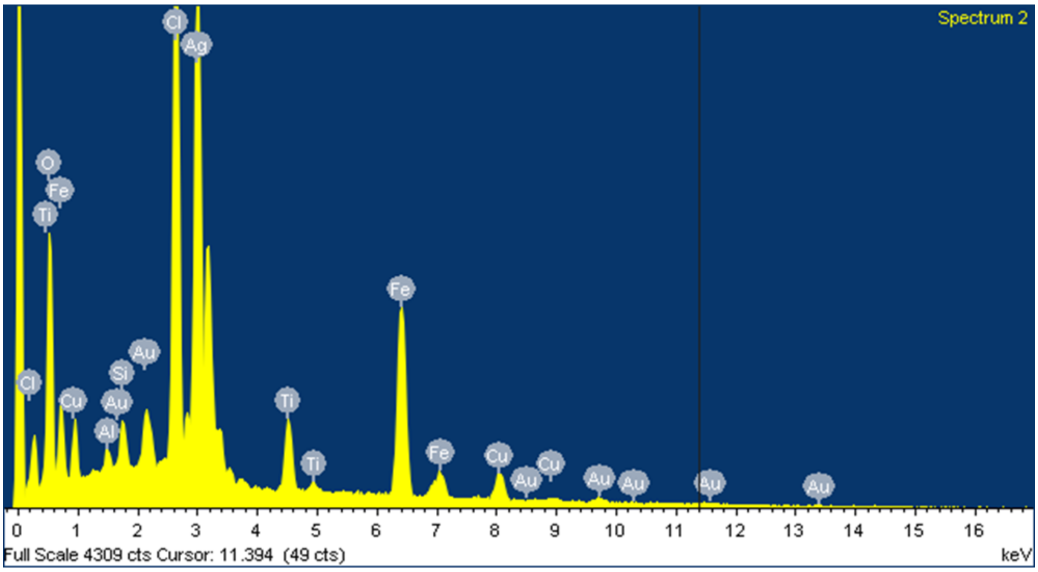


Figure 3.17 Spectrum of the diamond particles.

The Figure 3.18 shows the mean particle size distribution using a Java-based image processing and analysing software (Image J, National Institutes of Health, USA) of the images in Figure 3.18 **A** and Figure 3.18 **B**. It is possible to conclude that the remaining diamonds have approximately the same size, which it can't be taken for granted, but at a first analysis, the dissolution process does not have a great reaction against diamonds, being a very positive point in the separation process maintaining their integrity.

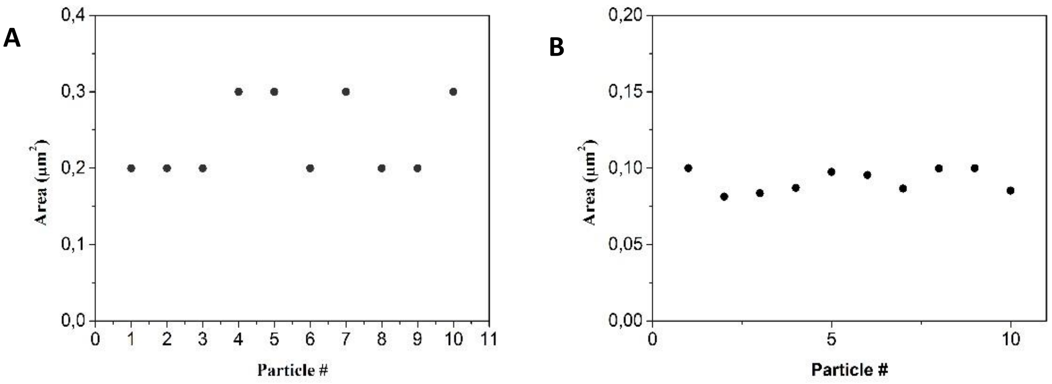


Figure 3.18 Mean particle size distribution of diamonds in the brass binder. The results shown in chart B were obtained using Image J software with a magnification 5 times greater than in chart A.

Finally, after the separation process been completed, it is now feasible to scale a waste separation system for the diamond cutting tools, including the proposed evaluated parameters as shows Figure 3.19, a schematic image of the system. It is also possible to conclude that the most efficient, as well sustainable, separation method performed was with an ultrasonic controlled dissolution at 60ºC of temperature.

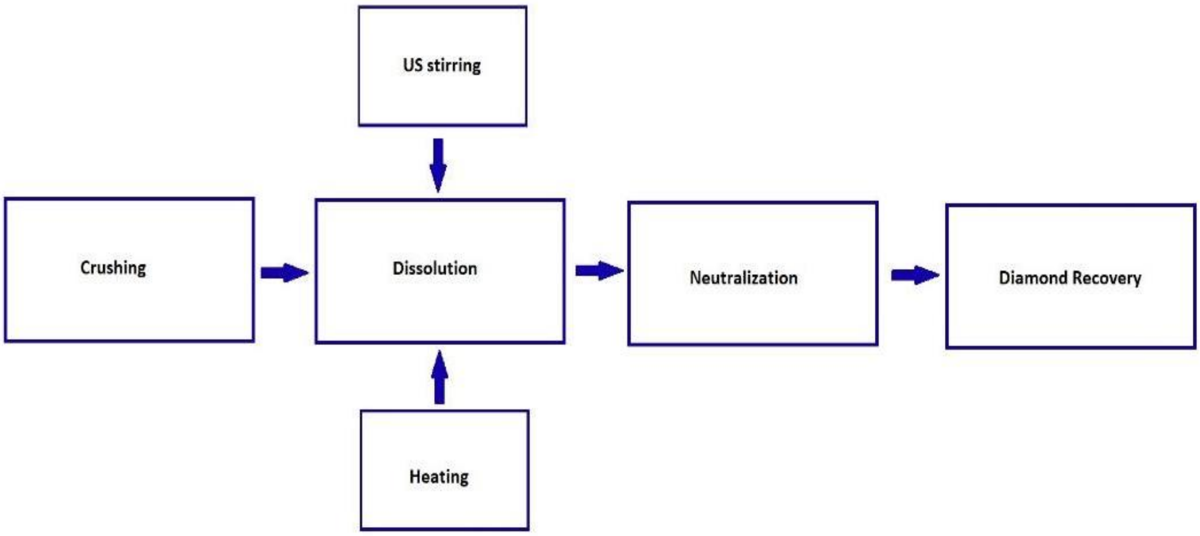


Figure 3.19 Schema of each step of the separation process.

4. Conclusion and Future Perspectives

A new process technique, based in general chemical and "green" technologies, has been presented in this present work to recover the undamaged diamonds from the cutting tool scrap pieces. This procedure may be applicable for mass production in an industrial level, being able to substitute the actual method played in research laboratories. In addition, the proposed process technique is flexible, being able for any engineer, especially for chemical engineers, to explore more about more effective methods to recover what is desired as changing production parameters as well.

In this work, two different materials were presented: A ferrous alloy and brass, both abrasive, with diamond embedded in the metal matrix, being the last recovered from the cutting tool scrap.

The tests performed on provided DCT scrap samples showed that the two samples are- in that order: ferrous alloy, composed essentially by Cu and Fe with a small amount of Co and the brass, composed by Sn and Cu with a small amount of Co too. The XDR presented the same peaks for both samples and provided the confirmation of synthetic diamond present in the samples.

The recovery process implemented showed us desirable results, as temperature being a fundamental parameter coupled with the use of ultrasonic technique for the best results with a 60ºC of process temperature with low frequency ultrasonic bath in an acidic *acqua regia* solution being the key for a faster dissolution rate with low release of chemical vapours and to use a greener technology that allow reducing at most the ecological footprint. The suggested cover up was confirmed with the results from dissolution tests.

As future perspectives it is interesting to study and discuss the implementation of chelating resins, as for his selectivity of taking up transition metals from solutions and as for environmental advantages[10-12]. Also, another method interesting to study the utilization of wetting agents already used in metallography to enhance the surface energy of a liquid or solid surface and thus to modify etching speed or selectivity of the based material [13].

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Annex

Annex 1

Table 4.1 Elementar composiotion for the ferrous alloy sample as recieved.

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	0.61	1.2909	2.19	0.23	7.69
Fe K	8.21	1.0507	36.09	0.34	36.25
Co K	5.24	1.0536	23.00	0.31	21.88
Cu K	7.65	0.9125	38.72	0.39	34.18
Totals			100.00		

Table 4.2 Elementary composition for the Brass alloy as received.

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
Fe K	5.91	1.0813	25.14	0.29	27.19
Co K	5.26	1.0951	22.07	0.30	22.62
Cu K	10.73	0.9339	52.79	0.37	50.19
Totals			100.00		

Annex 2

Table 4.3 Elentary composition of the diamond particles recoverd from the brass sample

Element	App	Intensity	Weight %	Weight %	Atomic %
O K	9.39	0.5085	31.62	0.40	65.51
Al K	0.16	0.6993	0.40	0.05	0.49
Si K	0.41	0.8223	0.86	0.05	1.01
Cl K	5.68	0.8647	11.24	0.12	10.51
Ti K	1.41	0.8232	2.93	0.08	2.03
Fe K	7.30	0.9076	13.77	0.16	8.17
Cu K	1.80	0.8883	3.47	0.13	1.81
Ag L	15.32	0.8182	32.06	0.28	9.85
Au M	1.69	0.7919	3.66	0.20	0.62
Totals			100.00		