Pamukkale Univ Muh Bilim Derg, 29(5), 553-559, 2023

Pamukkale Üniversitesi Mühendislik Bilimleri Dergisi

Pamukkale University Journal of Engineering Sciences

Effect of various mineral acids during the hydrothermal leaching process of NiTi Alloy

NiTi alaşımının hidrotermal liç işlemi sırasında farklı mineral asitlerin etkisi

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Received/Geliş Tarihi: 17.08.2022
Revision/Düzeltme Tarihi: 25.10.2022
doi: 10.5505/pajes.2022.88021
Accepted/Kabul Tarihi: 01.11.2022
Research Article/Araştırma Makalesi

Abstract

Nickel and titanium-based alloys are commonly used for engineering or medical applications. NiTi alloys are recycled as additive materials at the end of their lifetime. Separate recovery of metals present in NiTi alloy is possible via hydrometallurgical methods; however, NiTi alloys are highly resistant to corrosion. Various mineral acids (H_2SO_4, HCl, HNO_3, H_3PO_4) have been investigated, and the effect of H_2O_2 in the leaching medium has also been explored. Different leaching yields have been observed, and correlations between them according to acid treatment conditions have been established. SEM, XRF, and EDS techniques characterized alloys' microstructure and chemical properties. Among mineral acids, H_2SO_4 and HCl illustrated the highest extraction efficiencies. However, the addition of hydrogen peroxide decreased this efficiency severely. The kinetics of dissolution was obtained through decreased leaching efficiency with the addition of hydrogen peroxide.

Keywords: High-Pressure acid leaching, Hydrogen peroxide, Mineral acids, NiTi file, Recycling.

Öz

Nikel ve titanyum bazlı alaşımlar genellikle mühendislik veya tıbbi uygulamalar için kullanılır. NiTi alaşımları kullanım ömürlerinin sonunda katkı malzemesi olarak geri dönüştürülür. NiTi alaşımında bulunan metallerin hidrometalurjik yöntemlerle ayrı olarak geri kazanılması mümkündür; ancak NiTi alaşımları korozyona karşı oldukça dirençlidir. Çeşitli mineral asitler (H_2SO_4, HCl, HNO_3, H_3PO_4) incelenmiş ve H_2O_2'nin liç ortamındaki etkisi de araştırılmıştır. Farklı liç verimleri gözlemlenmiş ve asit işleme koşullarına göre bunlar arasında korelasyonlar kurulmuştur. SEM, XRF ve EDS teknikleri alaşımların mikroyapısını ve kimyasal özelliklerini karakterize etmiştir. Mineral asitler arasında H_2SO_4 ve HCl en yüksek ekstraksiyon verimliliğini göstermiştir. Ancak, hidrojen peroksit ilavesi bu verimi ciddi şekilde düşürmüştür. Çözünme kinetiği, hidrojen peroksit ilavesiyle liç veriminin azalmasıyla elde edilmiştir.

Anahtar Kelimeler: Yüksek basınçli asit liçi, Hidrojen peroksit, Mineral asitler, NiTi diş eğesi, Geri dönüşüm.

1 Introduction

Metal-based materials are produced either the primary way from ore or secondary, which is recycled. The former is preferred due to its ecological and economic advantages [1]. Nickel-Titanium (NiTi) alloys are highly resistant to corrosion and shape memory behavior involving their typical applications in advanced dental treatment. Native compact NiTiO3 oxide layer creates a bioinert surface resistant to abrasion and corrosion induced by the body fluids. Thus, NiTi-based rotary files are used for root canal treatments in endodontics, mainly due to their biocompatibility and hardness, which are enough to erode tooth enamel [2]. After treatment, the re-use of NiTi files requires adequate sterilization, negatively affecting their mechanical properties with the risk of file fracture within the root canal during the subsequent treatment. Therefore, endodontic authorities consider NiTi alloy dental files to be disposable [3]-[5]. Hydrometallurgical recycling is suggested for these highly pure alloys, but the NiTiO3 oxide layer makes the alloy leaching difficult in acidic media [6-7]. Effects of strong mineral acids such as H_2SO_4, HCl, and HNO_3 were primarily investigated in recycling via hydrometallurgical leaching processes of materials containing Ni and/or Ti metals. In literature, various mineral acids such as H_2SO_4, HCl, and HNO_3 were used in leaching processes, of which the prominent use acid was [8]-[12]. For example, in a study on the leaching of NiMH batteries, 80% dissolution efficiency was obtained in experiments in which a 2 M H_2SO_4 solution 1/20 solid/liquid ratio was applied under stirring for 4 hours at 90 °C [9].

Since NiTi alloys (around wt.% 50-50) have a high melting temperature, melting and reshaping a scrap of the alloy increases energy consumption. Different manufacturing techniques can produce NiTi alloys. The joint production method, vacuum induction melting, starts with pure metals. The reason is that a slight change in the chemical composition of these alloys can change their physical properties. The chemical composition can be significantly affected due to the accumulation of trace elements in the structure. A different manufacturing process, powder metallurgy, grinding, and sintering scrap, is unsuitable for NiTi files' physical and

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chemical properties. For example, NiTi alloys are super elastic and have a tight oxide layer on their surface [7].

No known leaching method for NiTi alloys has been described in the literature. Since a successful leaching efficiency could not be obtained in low and high-concentration mineral acids, a hydrothermal leaching process was used [8].

Studies demonstrated hydrothermal leaching methods under pressure in an autoclave are the most suitable recovery process [13]-[15]. Furthermore, other metals' and alloys' leaching efficiency was improved by adding oxidative chemicals like H2O2 within hydrometallurgical media. Several parameters were investigated, such as acid type concentration or H_2O_2 rate-oxidation mechanism. Thus, the complete dissolution of platinum was achieved by adding up to 2% H_2O_2 with HCl during recovery from platinum-containing catalysts [16]. Similarly, different concentrations of H_2O_2 were added to determine the leaching kinetics of copper converter slags in the leaching process with H_2SO_4. Increasing H_2SO_4 concentration and adding an amount of H_2O_2 enhanced the solution efficiency of Cu, Zn, and Fe metals in copper converter slag [17]. Ni, Co, Cu, and Mn could also be leached more effectively from used Li-ion batteries at 3.0 M H_2SO_4 concentration, 1 to 7 solid: liquid ratio, and the addition of 1.6 ml H_2O_2. Cobalt leaching maximum efficiency with the addition of 1.6 % H_2O_2 was reached [18]. Adding a number of H_2O_2 up to 2 mL within the leaching media of Ti ore in the Langkawi black sand structure and 2M H_2SO_4 concentration with a low solid: liquid ratio (1:30) increased leaching efficiency by 20% [19]. Finally, vanadium recovery from spent catalysts using 1 M H_2O_2 with 0.5 M H_2SO_4 provided more than 90% efficiency increase during vanadium leaching [20].

This study investigated the effect of mineral acids (H_2SO_4, HCl, HNO_3, H_3PO_4) on the hydrothermal leaching efficiency of NiTi alloy files. As a result of our previous studies, the solid to acid ratio was determined as 1:7 [8]. In order to monitor extraction efficiency, different volumes of H_2O_2 were added to both the H_2SO_4 1:1 solid: acid ratio mixture and also the HCl 1:1 solid: acid solid: acid ratio mixture. Based on the literature review, the leaching mechanism of NiTi was investigated, and a model was suggested for each proper acidic media.

2 Material and methods

2.1 Sample preparation

Waste NiTi files used in this research were obtained from Konya Necmettin Erbakan University Faculty of Dentistry in Turkey and separated with the help of a cutter in Figure 1.

Figure 1. Waste endodontic NiTi files.

Before high-pressure acid leaching, NiTi files were washed in ethanol solution for 30 minutes. Afterward, NiTi files were left to dry in the air for an hour. NiTi files have not been subjected to any mechanical treatment, such as grinding, and have only been cut in half to fit in the autoclave teflon chamber. HCl, H_2SO_4, H_3PO_4, and HNO_3 acids were used in this study. For dissolution efficiency of HCl and H_2SO_4, NiTi files were weighed with different solid/acid ratios such as 1:1, 1:3, 1:5, 1:7, and 1:9. After the first results (Figure2) solid/acid ratio was chosen 1:7 and investigated the efficiency of HCl, H_2SO_4, H_3PO_4, and HNO_3 acids.

This is comparable with previous studies and easy to prepare [15]. In addition, the effect of H_2O_2 was investigated with HCl and H_2SO_4 media. Acid concentrations were changed; thus, autoclave volume and sample:acid ratio was kept the same.

2.2 Leaching

NiTi endodontic files were dissolved with mineral acids such as TEKKIM HCl-30-32%, TEKKIM HNO_3-65%, MERCK H_3PO_4-85%, and MERCK H_2SO_4-95-98% by using 40 mL PTFE, Teflon-lined stainless steel autoclave to determine the most efficient one. Autoclave pressure values in prepared experiments are given in Table 1.

Table 1. Autoclave pressure values in prepared experiments with 1/7 sample acid ratio.

Acid Type	Molarity (M)	ΔH_b (kj/ mol)	Boiling Point (⁰C)	Autoclave Pressure (atm)
H_2SO_4	~7	40.567*	398 K (125 ⁰C)	~17 atm
HCl**	~7	16.2	378 K (105 ⁰C)	~39 atm

*: Water vaporization enthalpy at 473 K.

**: Vapor pressure values are calculated over partial mass.

The Clausius-Clapeyron equation calculated autoclave internal pressures according to acid types. Since the mixture-heating medium is below the boiling temperature of sulfuric acid, the vapor pressure of water has been taken into account. Leaching efficiencies of NiTi endodontic files were compared by using 7 times the weight of mineral acids specified via a high-pressure leaching process. While preparing an acid solution in an autoclave medium, obtained amounts of acids were weighed, and a fixed-volume solution was prepared by adding ultrapure water to 10 mL volume. The prepared mixture was placed in a Teflon chamber in the autoclave, and it was sealed. It was kept at 200 ⁰C for 2 hours and then left to cool in the air for 15 hours. 200⁰C was chosen as the leaching temperature, since 92%, 97%, and 100% efficiencies were obtained in experiments performed at 150 ⁰C, 170 ⁰C, and 200 ⁰C, respectively. It was chosen because of temperature and other parameters that maximum used products can withstand. Different volumes of H_2O_2 (MERCK-30%) were added to leaching acids (HCl and H_2SO_4) for the high-pressure acid leaching process, where high dissolution efficiency was observed. H_2O_2 was prepared for leaching in volumes of 0.1, 0.5, 0.7, and 1.0 mL, which was added to 10 mL acid solution.

2.3 Characterization

NiTi file's chemical composition was analyzed with the X-ray fluorescence spectrometer (Rigaku™, NEX-CG Energy Dispersive). XRF results are given the weight percentage (wt.%) of the elements present within the NiTi-based files. In addition, the dissolution tendency of elements dissolved from the surface (cross-sectional area) was investigated by using the elemental mapping method via Energy Dispersive Spectrum (EDS) with Scanning Electron Microscope (SEM) images (HITACHI™- SU1510).

3 Results and discussions

3.1 Properties of starting materials

Elemental analysis of starting files obtained by XRF confirms major presence of Ni and Ti, as well as minor elements such as Al, Ca, and Mg (Table 2). These results are specific to NiTi50 endodontic files with high purity; therefore, leaching performances in this work are considered specific to NiTi alloys.

Table 2. XRF analysis of NiTi50 endodontic files.

Element	% Mass	Statistical Error
Nickel	51.2482	-
Titanium	47.0476	0.0141
Others (Al, Ca, Mg, Fe)	1.7042	0.0149

Used acids for hydrothermal can be classified according to their pK_a values which relate to their dissociation abilities and their leaching power in water.

The pK_a is calculated via species concentration in solution after dissociation [21], the strongest acid has the lowest pK_a value. For example, HCl and H_2SO_4 are the strongest acids since their pK_a values are respectively -8 and -3 (Table 3) [22].

Table 3. Acid Types and pKa values [22].

Acid Types	pKa values
HCl	-8.0
H_2SO_4	-3.0
HNO_3	-1.3
H_3PO_4	2.12-7.2-12.7

3.2 Leaching of NiTi alloy using different mineral acids

NiTi alloys were hydrothermally leached with various concentrated mineral acids in solid: acid (1:7) ratio. Optimum leaching was obtained at this ratio in previous work. The previous study used NiTi60 type files with a different elemental composition. It has shown that varying the amount of composition changes the dissolving power of acids [8]. The dissolution is complete with treatment involving the strongest concentrated acids HCl and H_2SO_4 solutions (Figure 2). Nevertheless, dissolution efficiency is not respecting the acid power related to pK_a values. In fact, there is an increase of 1.7% by mass for HNO_3, while the amount of dissolution for a weaker acid, H_3PO_4, is around 40%. Known oxidative properties of nitric acid are suspected to be at the source of this difference by involving an increase of $NiTiO_3$ oxide layer at the alloy surface [23].

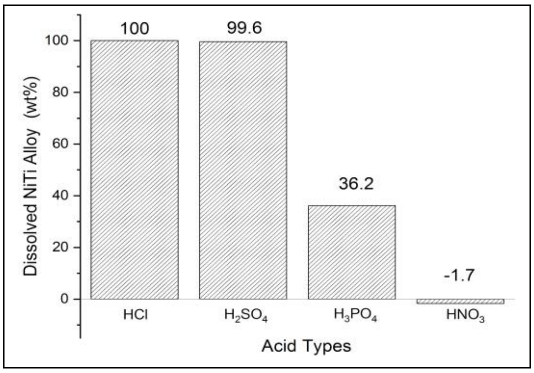

Figure 2. Weight mass dissolution of NiTi alloy with different acids (S:A ratio (1:7)).

Optimization of hydrothermal leaching with HCl and H_2SO_4 was investigated for a different solid: acid ratio from 1:1 to 1:9 (Figure 3). Hydrothermal leaching of NiTi alloy is considered as completed when acid rate is above solid: acid 1:3. On the other hand, for incomplete leaching conditions (solid: acid 1:1), dissolution performance is better for H_2SO_4 than HCl. This result does not conform with the acids pK_a as mentioned above. However, leaching efficiencies of NiTi files witness a slight decrease as the solid:acid ratio increases from 1:5 to 1:7. This phenomenon may be attributed to the salting-out effect during leaching in the presence of Ni^{2+}, Ti^{4+}, $SO4^{2-}$, and $HSO4^{-}$ ions as enhanced ionic potential due to increase of acid concentration [24]. After passing its maximum solubility (calculated concentration for crystallization is 68%) of 38.5% in HCl solution, the insoluble gaseous form is released either as HCl gas or Cl_2 gas [25]-[27].

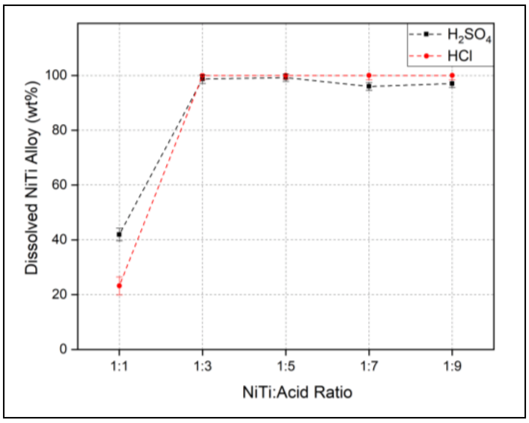

Figure 3. Weight mass dissolution of NiTi files with different S:A ratio for HCl and H_2SO_4 solutions.

3.3 Acid effect on the NiTi alloy

Effects of acidic treatments are visible at the surface of files; therefore morphological and chemical mapping of samples partially leached with solid:acid (1:1) conditions were characterized (Figure 4 & Figure 5). Solid: acid 1:1 ratio was chosen to see the development of the corrosive environment on the NiTi file. The surface state of NiTi alloys leached by H_2SO_4 and HCl solutions, which involve complete leaching above acids, are completely different. A compact layer with pitting is observed with H_2SO_4, while brittle layers are present with HCl Figure 4(a) & (4b). In comparison, the surface layer on NiTi alloys leached with H_3PO_4, and one with HNO3 are tightly in contact with the bimetallic core Figure 4(c) & 4(d).

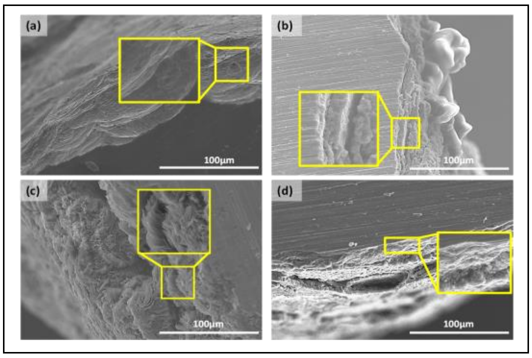

Figure 4. SEM micrographs of undissolved NiTi files remaining from leaching solutions prepared 1:1 S:A ratio. (a): H_2SO_4, (b): HCl, (c): H_3PO_4, (d): HNO_3.

Nevertheless, small crystalline structures are observed with H_3PO_4, while a compact layer is present after HNO_3 leaching. The reactivity of acids towards the alloy is estimated via the presence of alloy elements and elements of acid anions on the surface with EDS elemental mapping (Figure 5 & Table 3). Concerning Ni and Ti alloy elements three different situations are observed.

i. Strong presence of Ni and Ti with H_2SO_4,
ii. Strong presence of Ti but weak presence of Ni with HCl and HNO_3,
iii. Weak presence of Ni and Ti with H_3PO_4.

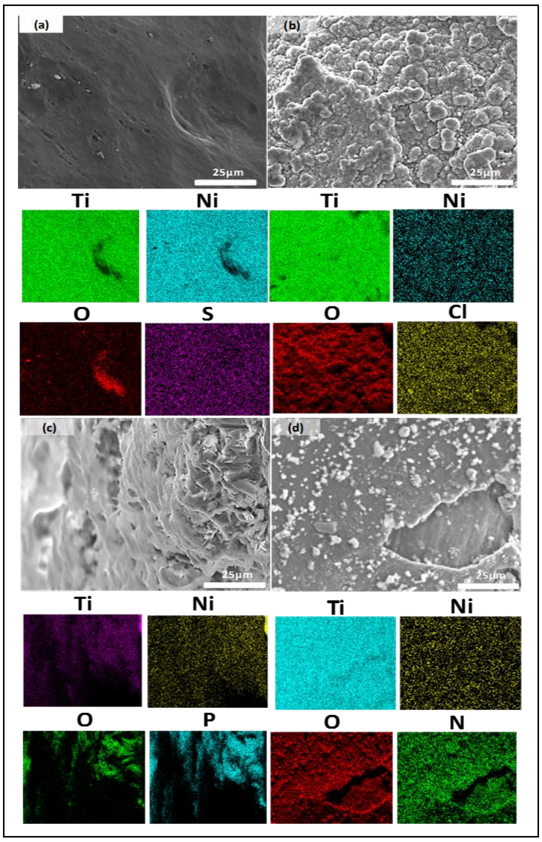

Figure 5. EDS mapping of undissolved NiTi files remaining from leaching solutions prepared 1:1 S:A ratio. (a): H_2SO_4, (b): HCl, (c): H_3PO_4, (d): HNO_3.

Surface atoms onto untreated NiTi files consist almost exclusively, and at equivalent levels with Ni and Ti, the level of other atoms is low (Table 4).

Table 4. EDS elemental ratio (at.%) on NiTi alloy surface after acidic treatment.

Media	HCl	H_2SO_4	HNO_3	H_3PO_4
Nickel	0.37	40.62	0.28	6.60
Titanium	24.16	41.82	26.53	10.24
Oxygen	75.18	17.48	73.19	70.49
Anionic Elements	(Cl) 0.29	(S) 0.08	(N) 0	(P) 12.66

After H_2SO_4 leaching, the level of Ni and Ti is still equivalent, but the atomic rate of O is more than 17% while the rate of S is too low. The leaching is probably triggered by the oxidative effect of H_2SO_4, followed by continuous acidic digestion of oxides. Concerning HCl and HNO_3, similar atomic rates are calculated with a very high concentration of oxygen (>73 at. %) and lower concentration of Ti (>24 at. %), while Ni and anionic elements (Cl & N) are almost null. These results suggest a formation of TiOx compounds at the surface. Nevertheless, mass loss is observed only with HCl while the mass of alloy increases within HNO_3 media. Thus, the oxidative effect is dominant with HNO_3 involving a passivation layer around the alloy.

Whereas the only oxide source in the HCl solution is solvent, the strong acid probably induces a decomposition of the water molecule, which can oxidize Ti. Finally, both Ni and TiOx are leached since a consequent mass loss is weighted at the end of the HCl process with a high rate of acid. The last results are relative to H_3PO_4 media in which the rate of an anionic element is much higher than other acids reaching 12.66 at.%. Conversely, Ni and Ti atomic weight ratios are a few percents where Ti is higher than Ni, while O ratio is more than 70 at.%. Due to moderate weight loss observed during leaching can be an efficient leaching process [28]. Moreover, Ti compounds contain twice more phosphate ions as Ni compounds which can explain the percentage difference.

3.4 Dissolution efficiency

When they are in excess and have high concentrations, HCl and H_2SO_4 are the most efficient acids for leaching. For both acids, an increase in the oxygen ratio is unavoidable with partial process conditions. In order to facilitate this oxidation step and to accelerate leaching, the oxidative agent H_2O_2 was added to the Teflon jacket at a different ratio from 1 to 10% (0.1 to 10 ml) (Figure 6).

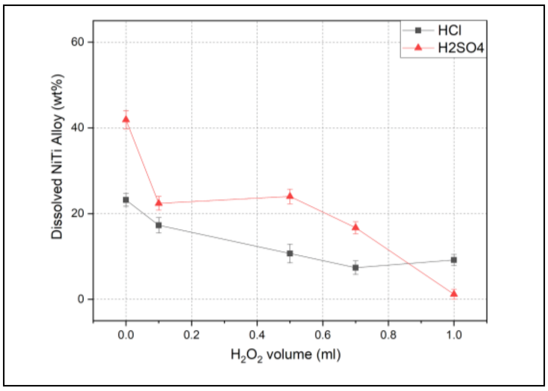

Figure 6. Weight mass dissolution of NiTi files with different addition of H_2O_2 volume in H_2SO_4 and HCl solutions (S:A=1:1).

The expected higher leaching ratio by increasing the oxidative power of the media was not reached. With the addition of the oxidative agent into H_2SO_4, mass loss decreases from 42% to 2%, while with H_2O_2 into HCl, loss changes from 24% to 9%. In other words, by increasing their oxidation, NiTi alloys become more resistant to acid attacks, and the development of more stable oxide at their surface might be the reason.

The addition of H_2O_2 affects the reactivity of acidic media involving the evolution of the surface morphology of NiTi files (Figure 7). In comparison with the surface morphology of simple acidic treatment Figure 7(a) & 7(b), the surface of samples treated in highly oxidative acid is smoother and more compact Figure 7(c) & 7(d). The pittings observed after the H_2SO_4 treatment and the brittle layers resulting from the HCl treatment are no more visible. The enhanced oxidative power leads to the formation of a highly passivated surface [29].

The oxide layer on the alloy surface is too thin to be characterized by XRD, while the EDS cannot describe crystallographic structure. Nevertheless, the surface atomic ratio is calculated by EDS analysis (Table 5), and oxygen reactivity of both Ni and Ti transition metals and oxide stability are largely studied in the literature [30].

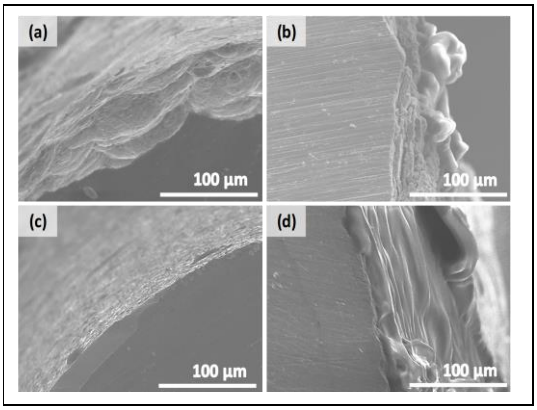

Figure 7. SEM micrographs of undissolved Ni-Ti files remaining from leaching solutions prepared 1:1 S:A ratio. (a): H_2SO_4, (b) HCl, (c): H_2SO_4-1ml H_2O_2, (d): HCl-1ml H_2O_2.

Table 5. EDS elemental ratio on NiTi alloy surface after acid+H_2O_2 treatment.

Acid Types	Element (wt%)	without H_2O_2	1 ml H_2O_2
HCl	Ni	0.37	11.78
	Ti	24.16	26.04
	O	75.18	62.18
H_2SO_4	Ni	40.62	9.98
	Ti	41.82	22.55
	O	17.48	67.47

Ti is more sensitive to oxygen; thus, its oxide is more stable than Ni. When the oxidation mechanism is only due to the HCl effect, the Ni element is completely dissolved, and oxidized Ti is on the surface. The formation of TiOx cannot prevent the dissolution of Ni.

Whereas, Ni is partially dissolved, and the weight mass dissolution is reduced by more than 50% when adding H_2O_2 to leaching media. In other words, the formation of highly oxidized Ni_2O_3 and/or TiO_2 structures increases the stability of NiTi alloy within the HCl solution. Similarly, adding H_2O_2 in H_2SO_4 changes the surface chemistry of alloys completely. The bulk Ni/Ti rate (1:1) and the mild oxidation state turn into a high oxidation state with two times more Ti than Ni on the surface. Increasing the rate of Ti, which bonds more oxygen than Ni in its higher oxidation state (2.0 for 1 Ti vs 1.5 O for 1 Ni), suggests the increase of the stability by the addition of H_2O_2 accelerates the formation of highly stable TiO_2 in both acidic media.

Despite high corrosion resistance properties, NiTi alloys were almost completely leached in HCl and H_2SO_4 media via a high acid ratio (1:7) and high molarity under pressure. The investigations by adding H_2O_2 in acidic solutions suggest the formation of a compact surface based on highly oxidized Ni and Ti compounds. The alloy surface is passivated, and its stability in acidic media is improved via probably the TiO_2 formation. These results also explain the mass uptake of NiTi when the alloy was only subjected to HNO_3, which is a highly oxidative strong acid. Although, HNO_3 forms an oxide layer on the surface, it is not as stable as the H_2O_2 layer, but in a brittle structure. Concerning the pressurized leaching with H_3PO_4, partial dissolution cannot be prevented until a compact phosphatic structure is formed on the surface (Figure 8).

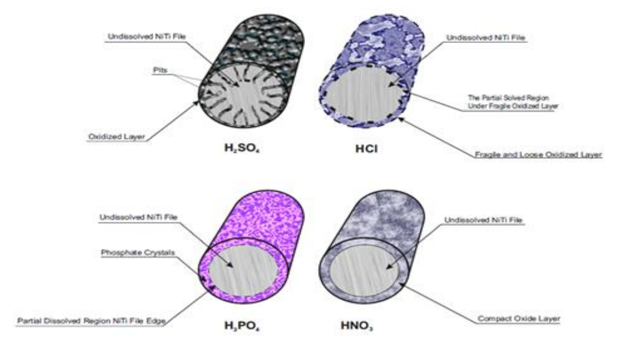

Figure 8. Dissolving mechanism of mineral acid solutions of NiTi files at cross- section area by autoclave leaching

In the study of Ozgun et al., H_2SO_4 was chosen among several mineral acids because its high leaching efficiency at room temperature under preheated optimum leaching conditions was determined as a result of experiments with many parameters. However, the pressure effect, which was absent in Ozgun et al., was made more comprehensive in this study [8].

4 Conclusion

Different dissolution mechanisms were observed in leaching studies with various mineral acid types while aiming for complete dissolution efficiencies. The dissolution in H_2SO_4 is directly affected by the temperature increase and pressure change, but the pressure increases in the leaching process with HCl, played a more active role in increasing the leaching efficiency. A phosphate layer was formed in the leaching process with H_3PO_4, and full dissolution efficiency could not be achieved since the phosphate structure acted as a barrier between the acid solution and the alloy. A compact oxide layer was also formed in the HNO_3 leaching process. In addition, it was observed that the addition of H_2O_2 had a reducing effect on the dissolution efficiency of various mineral acid types. Adding H_2O_2 played an affirmative role in determining the dissolution kinetics of mineral acids with high dissolution efficiency. The formation of ceramic oxide layers is probably modifying the mechanical properties of the alloy surfaces and must be investigated in future works. The different mechanisms under the influence of varying mineral acids also showed differences in yields. For this reason, a working process was obtained by starting from acid types (HCl, H_2SO_4) where the active mechanism is present. As a result, the economic recovery of NiTi scrap with uncontrolled content and morphology (such as chips, files, dust, etc.) that cannot be used in technologies with advanced production methods (VAR, EBM, etc.) has been realized. These scraps are expected to contribute to the economy.

5 Acknowledgments

The authors would like to thank the Necmettin Erbakan University Scientific Research Projects Coordination Department under the Grant No. 201224004 for their support.

6 Author contribution statements

“In the scope of this study, Muhammed İhsan ÖZGÜN in the formation of the idea, the design and literature review, in the assessment of obtained results, supplying the materials used and examining the results; Ahmet Burçin BATIBAY in the formation of the idea, the design, in the assessment of obtained results, supplying the materials used and examining the results; Bayram ÜNAL literature review, in the assessment of obtained results, supplying the materials used and examining the results; Yasin Ramazan EKER the spelling and checking the article in terms of content; Arslan TERLEMEZ the spelling and checking the article in terms of content were contributed.”

7 Ethics committee approval and conflict of interest statement

There is no need to get ethical approval. Authors declares that they have no conflict of interests.

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