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Journal of Scientific Reports-B, Number 9, April 2024

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Journal of Scientific Reports-B, Number 9, April 2024

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JSR B
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Journal of Scientific Reports-B, Sayı 9, Nisan 2024
Journal of Scientific Reports-B, Number 9, April 2024

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İÇİNDEKİLER / CONTENTS

ARAŞTIRMA MAKALELERİ / RESEARCH ARTICLES

DERLEME MAKALELERİ / REVIEW ARTICLES

Contents lists available at *Dergipark*

Journal of Scientific Reports-B

journal homepage: *https://dergipark.org.tr/en/pub/jsrb*

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ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

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Mekanik alaşımlama ile üretilen Al-Cu-Ni-Ti alaşımının yapısal ve termal karakterizasyonu

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Öz

Bu çalışmada $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımı, yüksek enerjili bilyeli öğütme cihazı kullanılarak üretilmiştir. Farklı öğütme süreleri sonrasında elde edilen toz karışımların mikroyapıları ve termal davranışları X-ışını kırınımı (XRD), taramalı elektron mikroskobu-enerji dağılımlı X-ışını spektroskopisi (SEM-EDX) ve diferansiyel termal analiz (DTA) ile karakterize edilmiştir. Öğütme süresinin artmasıyla alaşımın yapısında başlangıç fazlarıyla beraber AlNi ve Al_3Cu_2 intermetalik fazlarının oluştuğu belirlenmiştir. Bununla birlikte toz karışımın artan öğütme süresiyle parçacık boyutunun küçüldüğü ve daha homojen bir yapıya dönüştüğü görülmüştür. 30 saatlik öğütme sonrası elde edilen nihai alaşımın DTA analizinde kristallenme sıcaklıkları belirlenerek Kissinger metoduyla aktivasyon enerjileri hesaplanmıştır.
Anahtar Kelimeler: Al-esaslı alaşımlar, mikroyapı, termal özellikler, mekanik alaşımlama;

Structural and thermal characterization of Al-Cu-Ni-Ti alloy produced by mechanical alloying

Abstract

In this study, $Al_{60}Cu_{20}Ni_{18}Ti_2$ alloy was produced by using a high energy ball milling equipment. The microstructures and thermal behaviours of the powder mixtures obtained after different milling times were characterised by X-ray diffraction (XRD), scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX) and differential thermal analysis (DTA). It was determined that AlNi and Al_3Cu_2 intermetallic phases were formed in the structure of the alloy together with the initial phases with increasing milling time. However, it was observed that the particle size of the powder mixture decreased with increasing milling time and turned into a more homogeneous structure. After 30 hours of milling, the crystallisation temperatures were determined by DTA analysis of the final alloy and activation energies were calculated by Kissinger method.

Keywords: Al-based alloys, microstructure, thermal properties, mechanical alloying;

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1. Giriş

Alüminyum (Al) alaşımları, oda sıcaklığında karakteristik ve mekanik özelliklerinden dolayı çeşitli uygulamalarda yaygın olarak kullanılmaktadır. Al-esaslı alaşımların karakteristik özgül mukavemeti, havacılık ve otomotiv endüstrisinde kullanımı için onları ideal bir malzeme haline getirir [1], [2], [3], [4], [5]. Ancak, günümüzde kullanılan Al-esaslı alaşımların bazı durumlarda yüksek sıcaklıklarda mukavemetini kaybetme eğiliminde olduklarından düşük sıcaklıklarda kullanılan ürünlerde tercih edilmektedir. Sıcaklık değişimi ile Al-esaslı alaşımlarında görülen mukavemet değişimi, yüksek sıcaklıklarda meydana gelen aşırı tane büyümesinin neden olduğu mikroyapısal kararsızlığa atfedilebilir [6].

Al-esaslı alaşımların mukavemetine etki eden tane boyutunun performansı, Hall-Petch etkisi ile ilişkilendirilebilir. Nitekim tane boyutu, malzemenin mukavemeti ile ters orantılı olabilmektedir. Böylece tane boyutu küçüldüğünde alaşımların mukavemeti artmaktadır [7]. Bununla birlikte alaşımlar, aşırı yüksek sıcaklıklara maruz kaldığında nanokristal saf alüminyumda ortaya çıkan mikroyapısal kararsızlıklar nedeniyle kararlılığını yitirmektedir. Nanokristal alüminyumdaki mikroyapısal kararsızlık, tane sınırları tarafından sağlanan toplam serbest enerjideki önemli artış nedeniyle meydana gelmektedir. Mevcut serbest enerjiyi azaltmak için tane büyüme mekanizmasını artırma eğiliminde olan ve böylece nanokristal malzemelerin tane sınır alanını azaltan büyük bir itici güç vardır [8]. Bununla birlikte, yüksek sıcaklıklarda tane sınırı sabitleme kuvveti, tane büyüme sürecini engellemeye yetecek kadar yeterli olmadığı düşünülmektedir. Bunun aksine, termodinamik kararlılıkta tane sınırı enerjisindeki azalma, tane sınırlarında ayrışma eğiliminde olan ve çözünen atomların ilave edilmesiyle elde edilmektedir.

Bu nedenle saf alüminyumun tane boyutu üzerindeki olumsuz etkisini azaltacak Al-esaslı kompleks alaşımların üretilmesi olası çözümlerden sadece biri olarak gözükmektedir. Bu alaşımların yüksek sıcaklıklarda mukavemetinin artması, yapıda aşırı doymuş katı çözelti ve ikincil faz olan sert intermetaliklerin oluşmasıyla mümkündür. Katı çözelti oluşumu ve intermetaliklerin çökelmesi alaşımın mikroyapısal kararlılığını arttırmaktadır. Son yıllarda, daha yüksek performanslı malzemeleri elde etmek amacıyla Al-esaslı metal matrisli kompozitler veya nanokristal dağılmış amorf alaşımlar gibi malzemeler üzerine araştırmalar yapılmıştır [9], [10], [11], [12], [13]. Amorf, nanokristal ve intermetalik malzemeler gelişen teknolojiyle birlikte farklı uygulama alanlarına sahip olmasından dolayı araştırmacıların ilgisini çekmektedir [14], [15]. Çok fazlı alaşımların mikroyapısını daha iyi kavramak ve endüstride uygulanabilir hale getirmek oldukça önemlidir. Bu nedenle, kompleks Al-esaslı alaşımlar araştırılmaya değer en potansiyel adaylar olmaya devam etmektedir [16]. Bu kapsamda bu çalışmada, kompleks Al-Cu-Ni-Ti alaşımının üretilmesi ve karakterize edilmesi amaçlanmaktadır.

Çeşitli yöntemlerle üretilebilen Al-esaslı alaşımları, oda sıcaklığında ve toz metalurjisiyle üretmek istenildiği zaman uygulanabilecek en avantajlı yöntem mekanik alaşımlama yöntemi olarak karşımıza çıkar. Bu yöntem sayesinde pratik uygulamalarda kullanılabilecek toz malzemeleri, oda sıcaklığında ve arzu edilen parçacık boyutunda elde etmek mümkündür[17], [18]Böylece mekanik alaşımlama yöntemi kullanılarak nanokristal, kuazikristal ve amorf yapıya sahip alaşımların üretilmesi ve karakterizasyonu konusunda literatürde Al-Cu-Ti [19] ve Al-Cu-Fe [20], [21] gibi Al-Cu esaslı alaşımların olduğu birçok çalışma yer almaktadır. Bununla birlikte intermetalik faz oluşumunun incelendiği Al-Fe-Ti ve Al-Cu-Ni-Ti gibi alaşım tozları karakterize edilmiştir [22].

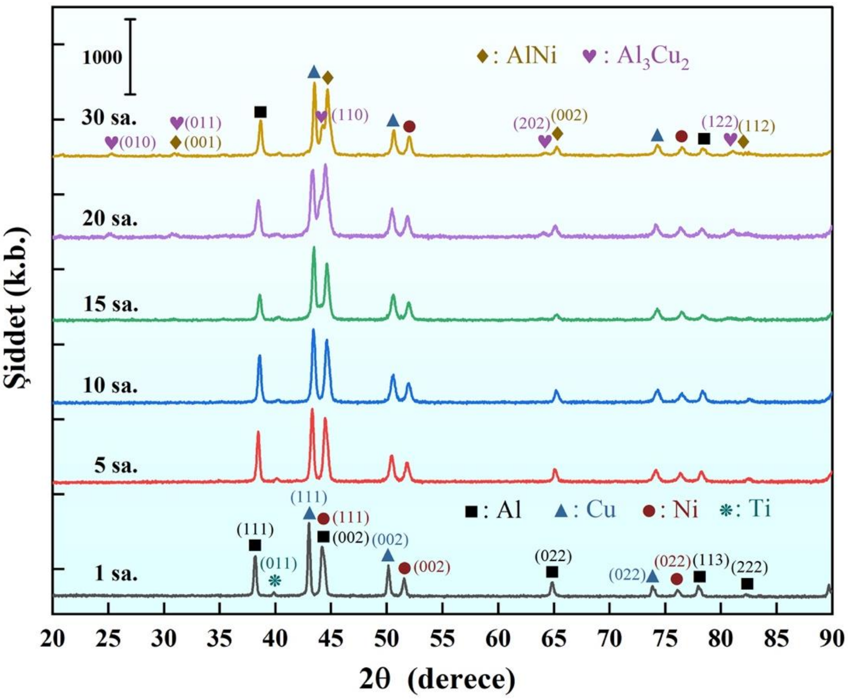
Alüminyum alaşımları gibi, titanyum ve alaşımlarının otomotiv ve havacılık uygulamalarında tercih edilmesi üzerine oldukça fazla çalışma yapılmasının temel sebebi mukavemet/ağırlık oranın oldukça yüksek olması ve yüksek sıcaklıklarda bu iyi özelliklerini muhafaza edebilmesinden kaynaklanmaktadır. Özellikle Ti elementi, Al-Ni alaşımlarıyla birlikte kullanıldığında üretilen malzemenin sürünme direnci oldukça iyi seviyelere ulaşmaktadır [23]. Bu nedenle, mekanik alaşımlama yöntemiyle üretilen Al-Cu-Ni-Ti tozlarının mükemmel aşınma direnci, yüksek mukavemet, yüksek sertlik, yüksek termal kararlılık, düşük yoğunluk gibi özelliklerinden dolayı teknolojik uygulamalar için oldukça uygun olduğu düşünülmektedir [24], [25], [26], [27]. Bu kapsamda, bu çalışmada sünek (Al ve Cu) ve gevrek (Ni ve Ti) metal tozları, $Al_{60}Cu_{20}Ni_{18}Ti_2$ (at.%) kompozisyonunu oluşturacak Şek.de mekanik alaşımlama işlemine tabi tutulmuştur. Farklı öğütme süreleri sonucunda elde edilen toz alaşımların faz değişimi X-ışını difraksiyonuyla (XRD), parçacık morfolojisindeki değişim taramalı elektron mikroskobu ve enerji dağılımlı X-ışını ışını spektroskopisi (SEM/EDX) ile analiz edilmiştir. Alaşımların termal kararlılığı ise diferansiyel termal analiz (DTA) ile belirlenmiştir.

2. Materyal ve Yöntem

Bu çalışmada $Al_{60}Cu_{20}Ni_{18}Ti_2$ (at.%) alaşımı, XQM-2 model yüksek enerjili bilyeli öğütme cihazı kullanılarak üretilmiştir. Alaşımı oluşturan başlangıç elementel tozları %99 saflıkta Aldrich firmasından temin edilmiştir. Başlangıç tozlarının toz boyut aralıkları tedarikçi firmadan sağlanan değerlerdir. Al toz parçacıkları 50–120 µm, Cu toz parçacıkları 5–8 µm, Ni toz parçacıkları 1–10 µm ve Ti toz parçacıkları 100–200 µm arasındadır. Alaşımı oluşturan başlangıç elementel tozları %99 saflıkta Aldrich firmasından temin edilmiştir. Öğütme işlemi, argon atmosferi altında sertleştirilmiş paslanmaz çelik hazne ve bilyelerle 10:1 bilye/toz ağırlık oranında 350 rpm öğütme hızında belirli öğütme sürelerine kadar (1, 5, 10, 15, 20 ve 30 saat) gerçekleştirilmiştir. Bu çalışmada öğütme hızı, mekanik alaşımlama işlemi sonucunda elde edilen $Al_{66}Co_{20}Cu_{14}$ alaşımı hakkındaki çalışma esas alınarak 350 rpm olarak belirlenmiştir[28]. Öğütme işlemi ne kadar hızlı gerçekleşirse toz parçacıklarına aktarılan enerji de o kadar yüksek olacaktır. Ancak belirli bir öğütme hızının üzerinde bilyeler, haznenin iç duvarlarında hareket ederek toz parçacıklarına herhangi bir çarpma kuvveti uygulamak için haznenin aşağısına düşemez. Bununla beraber yüksek öğütme hızlarda haznenin sıcaklığı yüksek bir değere ulaştığında tozlardaki yarı-kararlı fazların bozunmasına neden olur. Ayrıca öğütme haznesinin aşırı ısınması, daha yüksek plastik deformasyon sonucunda soğuk kaynaklanmada artışa neden olur ve toz parçacıkları öğütme haznesinin iç duvarlarına yapışabilir ve elde edilecek olan nihai toz miktarı bu nedenle daha düşük olabilir. Artan öğütme hızının bir başka dezavantajı da öğütme haznesi ve bilyelerin çok fazla aşınmasıdır ve bu da tozlarda kirliliğinin artmasına neden olabilir. Öğütme işlemi sonrası elde edilen toz alaşımların faz analizleri, Philips X'Pert PRO XRD cihazında CuKα radyasyonu ($\lambda = 0.15406$ nm) ile $2\theta = 20^o - 90^o$ aralığında yapılmıştır. Öğütme işlemi süresince toz parçacıkları kaynaklanma, kırılma ve yeniden kaynaklanma işlemleri nedeniyle yoğun gerinime maruz kalır [29]. Dolayısıyla parçacıkların morfolojisinde meydana gelen değişim, Zeiss EVO LS10 SEM ve Bruker EDX dedektörü ile 20 kV potansiyeli altında incelenmiştir. Mekanik alaşımlama yöntemiyle üretilen tozların termal analizleri, SII 6300 EXSTAR DTA cihazında 30-950 ℃ sıcaklık aralığında, 20 ml/dk. azot gazı akış hızı altında ve 30 °C/dk. ısıtma hızında gerçekleştirilmiştir. Mekanik alaşımlama yöntemiyle üretilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımlarının kristalit boyutu (D), XRD verileri kullanılarak Scherrer denklemi ile hesaplanmıştır.

3. Bulgular ve Tartışma

Uygun oranlarda tartılan başlangıç metal tozları, öğütücü bilyelerle birlikte öğütme haznesine konularak uygun süreler boyunca öğütülmüştür. Öğütme işlemine tabi tutulan toz karışımları, belirlenen sürelerde öğütme haznesinden çıkarılıp XRD, SEM-EDX ve DTA teknikleri kullanılarak karakterize edilmiştir. Farklı öğütme sürelerinden (1, 5, 10, 15, 20 ve 30 saat) sonra elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımının XRD sonuçları, Şek. 1'de görülmektedir. Mekanik alaşımlama işleminde; öğütücü tipi, öğütme haznesi ve bilyeleri, öğütme hızı, öğütme süresi, öğütme atmosferi, bilye-toz ağırlık oranı, işlem kontrol malzemesi ve öğütme sıcaklığı gibi toz yapısını etkiyen birçok parametre vardır. Dolayısıyla, bu çok sayıdaki işlem parametrelerini optimize ederek istenen toz yapısını elde etmek mümkündür. Geleneksel toz alaşımlarda bu değişkenlerin öğütülmüş tozların yapısı üzerindeki etkisine dair detaylı çalışmalar yapılmış olsa da yeni alaşım sistemleri üzerinde detaylı çalışmalar mevcut değildir. Bu çalışmada, diğer parametreler sabit tutulup yalnızca öğütme süresi değiştirilerek öğütme süresinin $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımında yapısal ve termal özelliklerine olan etkisi incelenmiştir. Şek. 1'deki XRD grafiği incelendiğinde öğütme işleminin 1, 5, 10 ve 15 saatlik sürelerinde alaşımı oluşturan başlangıç elementlerine ait piklerin yer aldığı görülmektedir. Bununla birlikte, öğütme süresinin artması Al (kübik, ICDD ref. no: 98-015-0692), Cu (kübik, ICDD ref. no: 98-018-0109), Ni (kübik, ICDD ref. no: 98-016-2415) ve Ti (hekzagonal, ICDD ref. no: 98-005-3784) fazlarına ait piklerin şiddetinde azalmaya ve genişlemeye neden olduğu anlaşılmaktadır. Öğütme işlemi ilerledikçe, ortaya çıkan yüksek enerji miktarı ve toz parçacıklarında oluşan kristalografik kusurların (nokta, çizgi ve düzlemsel kusurlar) artması nedeniyle pik genişlemesi artar. Öğütme işleminin 20 ve 30 saatlik sürelerinde ise alaşımın yapısında saf elementel piklerin yanı sıra, AlNi (kübik, ICDD ref. no: 98-060-4356) ve Al_3Cu_2 (hekzagonal, ICDD ref. no: 98-005-7668) AlNi (kübik, ICDD ref. no: 98-060-4356) ve Al_3Cu_2 (hekzagonal, ICDD ref. no: 98-060-4356) intermetalik fazlarına ait yeni piklerin oluştuğu görülmektedir. Bununla birlikte, yapıda Ti elementini içeren bir bileşiğe ait fazın görülmemesi, diğerlerine kıyasla toz karışımındaki küçük ağırlık fraksiyonundan ve yüksek kafes gerilimi ile parçacık ve kristalit boyutun azalmasından kaynaklandığı düşünülmektedir [29]. Bu çalışmadaki toz karışımlarının öğütülmesiyle meydana gelen faz oluşumu, şu Şek.de özetlenebilir: Başlangıç toz karışımı → elementel fazlar → elementel fazlar + intermetalik fazlar.



Şek. 1. Farklı öğütme süreleri (1, 5, 10, 15, 20 ve 30 saat) sonrası elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının XRD desenleri.

$Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının mekanik alaşımlama süreleri ile ortalama kristalit boyutu ve örgü gerinimi arasındaki ilişki Şek. 2'de yer almaktadır. Şek. 2'deki grafikten toz alaşımların kristalit boyutunun belirgin bir Şek.de azaldığı ve örgü gerinimi değerlerinin arttığı görülmektedir. Bu durum, öğütme işlemi süresinin artmasıyla toz parçacıklarında aşırı plastik deformasyon ve dislokasyonların meydana geldiğini belirtmektedir [29]. Mekanik alaşımlama yöntemiyle üretilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımlarının kristalit boyutu (D), XRD verileri kullanılarak Scherrer denklemi ile hesaplanmıştır [30].

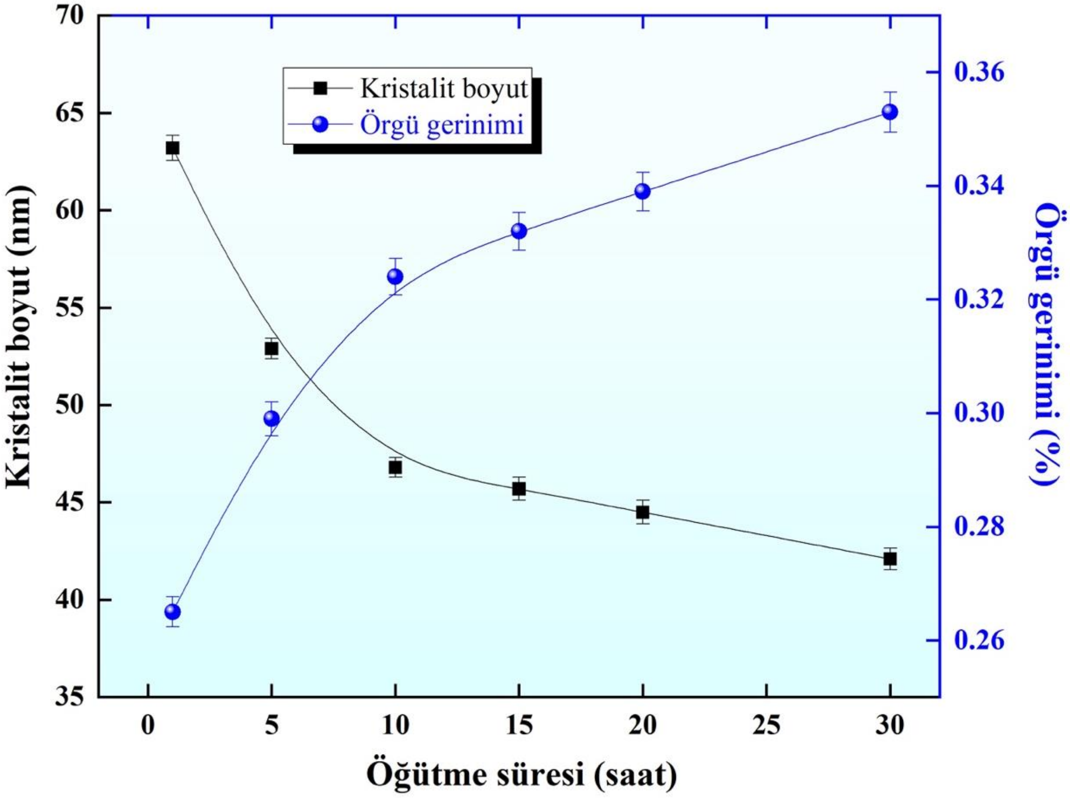
$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

Toz numunelerin örgü gerinimi (ε) değerleri, aynı XRD verileri için aşağıdaki denklemden hesaplanmıştır.

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{2}$$

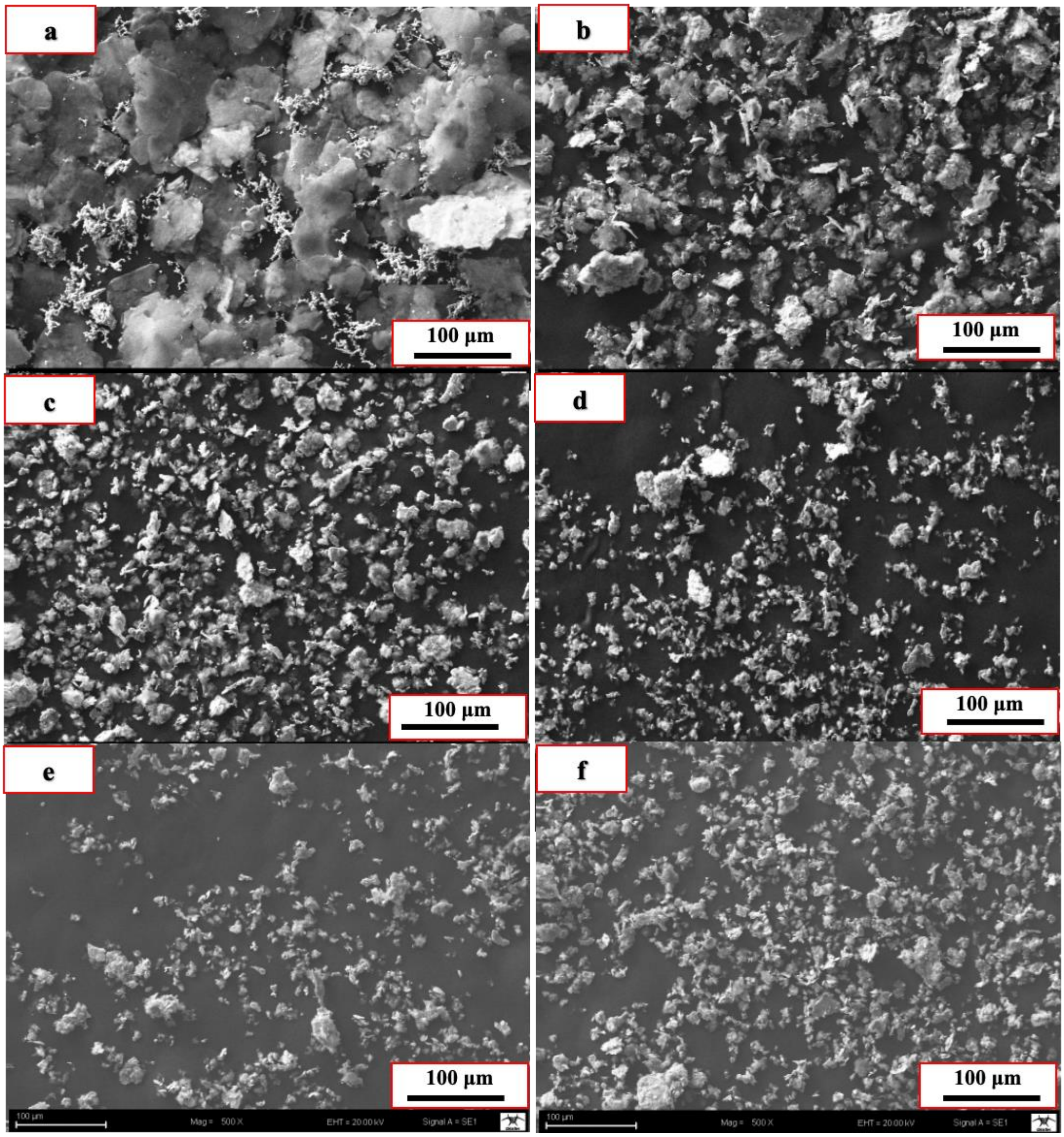
Burada; K = Scherrer sabiti, β = FWHM (piklerin yüksekliğinin yarısındaki tam genişlik), λ = X-ışını dalga boyu ve θ = radyan cinsinden pik yansıma açısıdır. Scherrer sabiti (K), partikül geometrisine ve numunedeki partikül boyutlarının dağılımına bağlıdır [31]. Bu durumda ise, K sabiti 0,94 olarak alınmıştır. Nihai olarak hesaplanan ortalama kristalit boyutu (D) ve örgü gerinimi (ε) değerleri tahmini bir hesaplamayı içermektedir. Ayrıca farklı bir yaklaşımla sonuçlar değerlendirilmek istense de bazı piklerin üst üste gelmesi sonucunda FWHM değerlerininin net olarak tespit edilememesinden elde edilen değerlerin birbirinden çok farklı olması nedeniyle Williamson-Hall yaklaşımı uygulanamamıştır.

$Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının 1 saatlik öğütme işlemi sonrası hesaplanan ortalama kristalit boyutu 63,2 nm olarak bulunurken, öğütme süresinin etkisiyle birlikte kristalit boyutta yaklaşık olarak %34'lük bir azalma meydana gelerek 30 saatlik öğütme işlemi sonrası tozların kristalit boyutunun 42,1 nm'ye düştüğü belirlenmiştir. Bununla birlikte, 1 saatlik öğütme sonrasındaki toz karışımların örgü gerinimi %0,265 iken, 30 saatlik öğütme sonrasında bu oranın %0,353'e arttığı hesaplanmıştır. Mekanik alaşımlama işlemi sırasında $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozları, yüksek enerjili çarpışmalardan ağır mekanik deformasyona maruz kaldığından, öğütme süresi arttıkça kristalit boyutları azalır ve artan dislokasyon yoğunluğu nedeniyle ortalama örgü gerinimleri artar. Dislokasyon yoğunluğu kritik bir değere yaklaştıkça, taneler düşük açılı alt sınırlardan ayrılarak daha küçük taneciklere ayrılmaktadır. Şiddetli plastik deformasyon nedeniyle alt taneler arasındaki hatalı yönelimler artar ve düşük açılı tane sınırlarının yerini yüksek açılı tane sınırları alarak nanokristal tanelerin oluşmasına neden olur. Öğütme süresince metal tozlarında görülen bu durum daha önce bildirilen sonuçlarla uyum içindedir [32], [33].



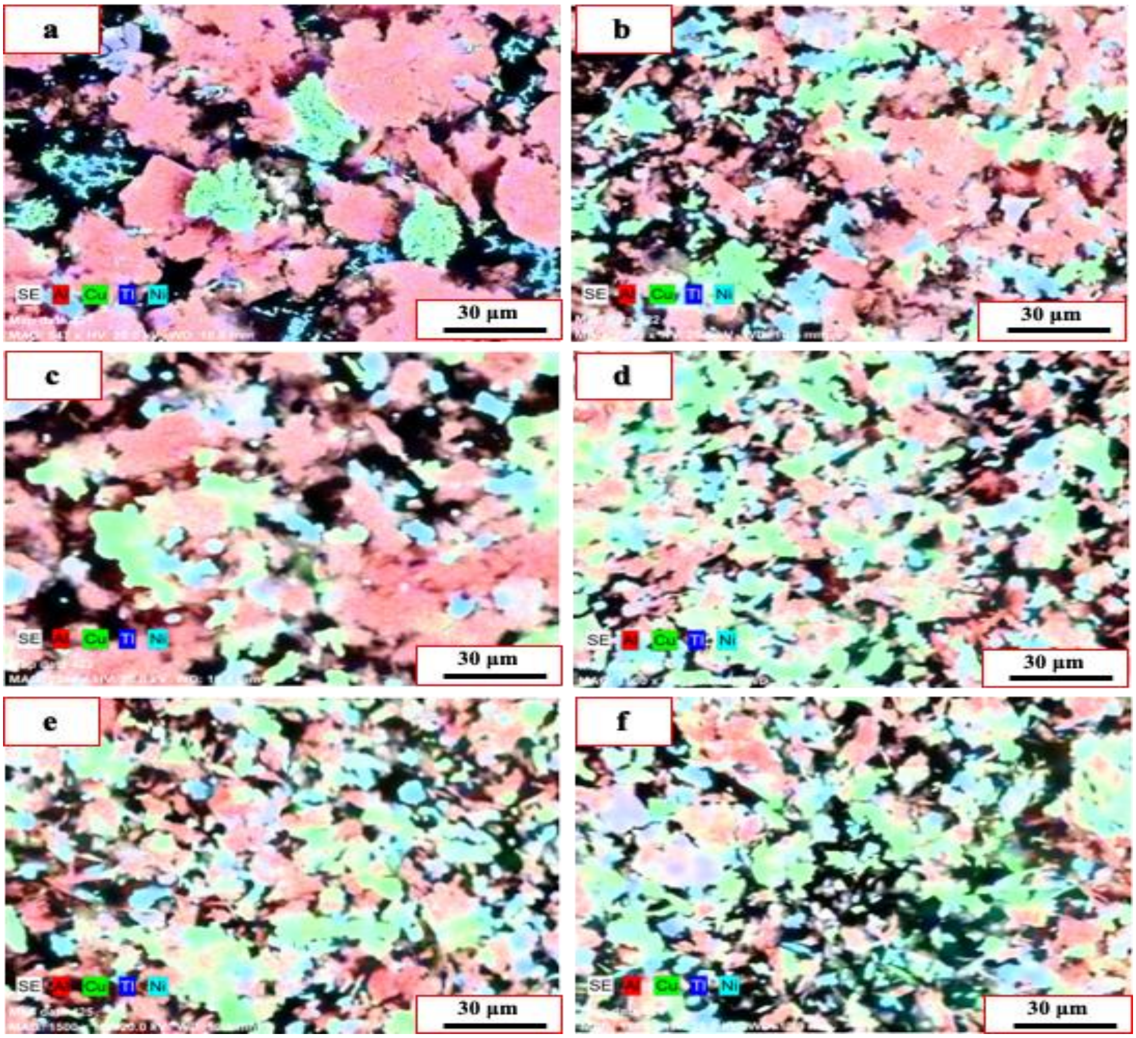
Şek. 2. $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımının öğütme süresince ortalama kristalit boyut ve örgü gerinimindeki değişim.

Mekanik alaşımlama yöntemiyle farklı sürelerde öğütülen $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının homojenliği, parçacık boyutu ve mikroyapısal değişimleri tespit edebilmek amacıyla SEM ile morfolojik inceleme yapılmıştır. Değişen alaşımlama sürelerine (1-30 saat) bağlı olarak elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının SEM fotoğrafları Şek. 3'te verilmiştir. Şek. 3a'da görüldüğü gibi, 1 saat öğütülen toz parçacıklarının her biri farklı Şek. ve boyutlardadır. Şek. 3b'de görüldüğü üzere 5 saatlik öğütme işleminden sonra başlangıç toz parçacıkları, soğuk kaynaklanmayla birlikte birleşip tekrar kırılmaya maruz kaldıkça tozun morfolojisinde gözle görülebilir bir fark ortaya çıkmıştır. Şek. 3c'de ise toz parçacıklarının boyutları tekrarlı soğuk kaynaklanma ve kırılma işlemi sonrasında giderek küçülerek ve daha homojen hale gelmeye başlamıştır. Bu aşamada, parçacıkların deformasyonla birlikte mikroyapısındaki değişim bilye/toz arasında meydana gelen çarpma kuvvetiyle meydana gelmektedir. Şek. 3d ve 3e'de ise artan öğütme süresine bağlı olarak toz parçacıklarının boyutlarında az bir artış gözlemlenmiştir. Parçacık boyutlarında görülen nispeten bu artışaa, yeni fazların oluşumunun etkisi olduğu düşünülmektedir. SEM fotoğrafları, XRD kırınım desenleriyle birlikte değerlendirildiğinde 15 saatlik öğütme işleminden sonra Ni ve Al metallerinin birleşerek AlNi fazını oluştuğu görülmektedir. Bunun bir sonucu olarak parçacıkların birleşmesiyle toz boyutunda bir artış meydana geldiği düşünülmektedir. Şek. 3f'de görüldüğü gibi, $Al_{60}Cu_{20}Ni_{18}Ti_2$ toz parçacıklarına etki eden çarpışma kuvveti 30 saat boyunca devam ettiğinde ise alaşımın mikroyapısı daha homojen hale gelmiş ve buna bağlı olarak tane boyutunda azalma meydana gelmiştir. Ancak, öğütme süresi arttıkça mikroyapı içerisinde topaklanmalar artmış, bunun bir sonucu olarak yapı içeresinde yer yer daha büyük boyutlu parçacıklar oluşmuştur. Bu durum ise Cu, Ni ve Ti tozlarının Al içinde çözünmesi olarak nitelendirilebilir. Dolayısıyla, toz parçacıklarında istenilen mikroyapıyı elde etmek için mekanik alaşımlama yönteminde temel prensip olan soğuk kaynaklanma ve tekrar kırılma mekanizmasının doğru bir Şek.de tekrarlanması gerekmektedir.

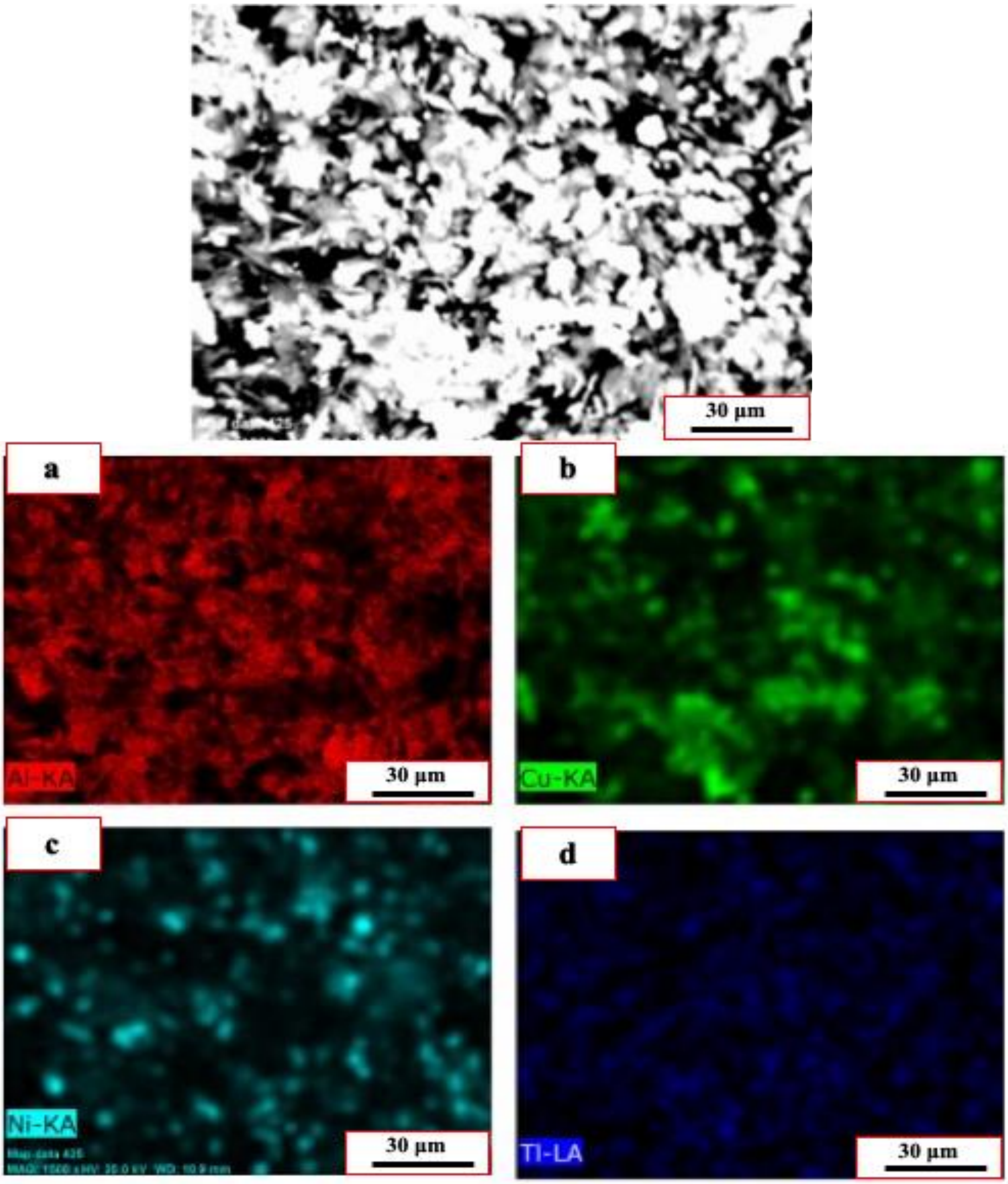


Şek. 3. Farklı öğütme süreleri; a) 1 sa., b) 5 sa., c) 10 sa., d) 15 sa., e) 20 sa., ve f) 30 sa., sonrası elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_{2}$ tozların SEM fotoğrafları.

Farklı sürelerde (1, 5, 10, 15, 20, ve 30 saat) öğütülmüş olan $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının değişen mikroyapı ve elementel dağılımını incelemek amacıyla EDX analizleri gerçekleştirilmiştir. Değişen alaşımlama sürelerine (1-30 saat) bağlı olarak elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının EDX elementel haritalama görüntüleri Şek. 4'te yer almaktadır. Şek. 4a'da öğütme işleminin ilk 1 saatlik süresinde elde edilen tozların EDX analizinde sırasıyla kırmızı renk Al elementini, yeşil renk Cu elementini, mavi renk Ti elementini ve turkuaz rengi Ni elementini belirtmektedirler. Şek. 4(b ve c)'deki görüntülerde başlangıç elementlerinin birbiri ile karışmadığı ve genel olarak heterojen bir yapıya sahip olduğu görülmektedir. Bununla birlikte, Al toz parçacıklarının oldukça büyük olduğu ve yapı içerisinde kümelendiği, ancak Cu, Ni ve Ti toz parçacıklarının ise kendi aralarında nispeten homojen olduğu ve Ni tozlarının bazı küçük koloniler oluşturduğu anlaşılmaktadır. Şek. 4d'deki EDX analizinde parçacık boyutlarında azalma ve buna bağlı olarak mikroyapıda homojenleşme eğiliminin olduğu görülmektedir. Ayrıca, XRD ve SEM sonuçları dikkate alındığında AlNi fazının oluştuğu ve Ni elementinin Al matrisi içerisinde çözündüğü düşünülmektedir. Dolayıyla yapıda oluşan intermetalik fazların parçacık boyutunu artırdığı anlaşılmaktadır. Şek. 4e ve 4f'deki görüntülerde parçacık boyutunun tekrar küçüldüğü ve daha homojen bir yapının oluştuğu görülmektedir. Şek. 5'teki 30 saatlik öğütme işlemi sonrası elde edilen tozların EDX elementel haritalama görüntüleri bu durumu desteklemektedir. Elde edilen bu sonuçlar, Al-Si alaşımı için bildirilenlerle uyum içindedir [34].

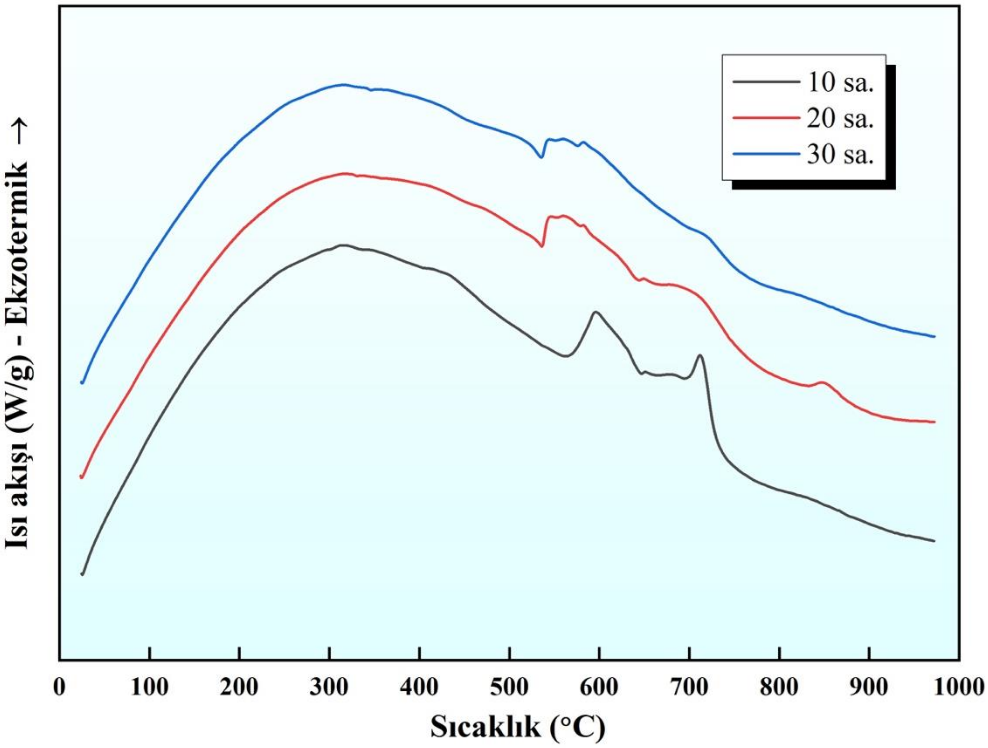


Şek. 4. Farklı öğütme süreleri; a) 1 sa., b) 5 sa., c) 10 sa., d) 15 sa., e) 20 sa. ve f) 30 sa. sonrası elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozların EDX haritalama görüntüleri.



Şek. 5**.** 30 saatlik öğütme sonrası elde edilen toz karışımın EDX elementel haritalama görüntüleri.

Yarı kararlı yapıların tespiti ve tanımlanması amacıyla kullanılan termal analiz yöntemi, teknolojik ve endüstriyel uygulamalar için oldukça önemlidir [35], [36], [37], [38]. Bu nedenle, $Al_{60}Cu_{20}Ni_{18}Ti_2$ toz alaşımlarında oluşan fazların termal davranışlarını belirlemek için termal analizler yapılmıştır. DTA, bir numunenin sıcaklığını artırmak için gereken ısı girdisini ölçmektedir. Artan sıcaklığa bağlı olarak alaşımdaki faz dönüşümü veya kimyasal reaksiyon ile meydana gelen enerji değişimlerinin tespit edilmesinde kullanılan yöntemlerinden bir tanesidir. DTA yöntemi, ısıtma veya soğutma sırasında numunede meydana gelen değişimlerin standart bir referans malzemeyle arasındaki sıcaklık farkı ölçümü prensibine dayanmaktadır. Farklı sürelerde (10, 20 ve 30 saat) öğütülmüş olan $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının DTA analiz sonuçları Şek. 6'da yer almaktadır. 10, 20 ve 30 saatlik öğütmeler sonucunda elde edilen toz numunelerin termal davranışlarında 595 °C ve 650 °C civarında belirgin iki ekzotermik pikin olduğu görülmektedir. Bu durum, numunelerin XRD sonuçlarıyla kıyaslandığında 525-625 °C ve 690-710 °C aralığında oluşan ekzotermik piklerin sırasıyla AlNi ve Al_3Cu_2 fazlarının oluşumunu belirtmektedir. Artan öğütme süresiyle birlikte numunelerde görülen geniş pikler, yapısal deformasyon ve kafes geriniminden kaynaklanan iç gerilimin azalmasına işaret etmektedir.



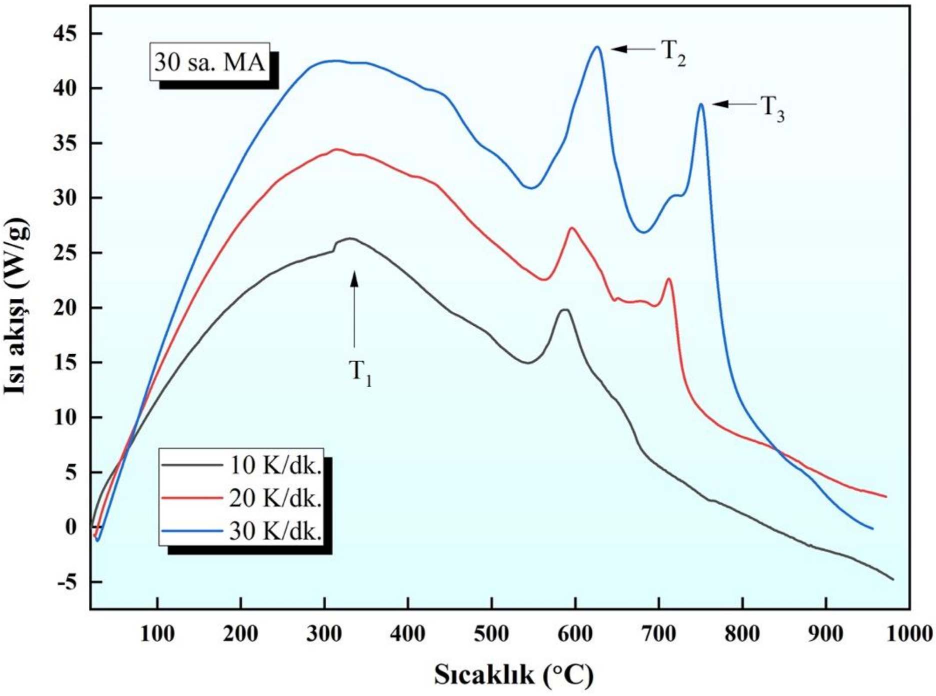
Şek. 6. Farklı öğütme süreleri (10, 20 ve 30 saat) sonrası elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ tozlarının DTA analizleri.

Mekanik alaşımlama yöntemiyle elde edilen nihai alaşımda görülen faz oluşumunun kristallenme davranışını inceleyebilmek için Şek. 7'de gösterildiği gibi sırasıyla 10, 20 ve 30 K/dk. gibi farklı ısıtma hızlarında DTA çalışması gerçekleştirilmiştir. 30 saatlik alaşımda görülen üç ekzotermik pikin varlığı T_1, T_2 ve T_3 ile belirtilen üç aşamalı bir kristallenme sürecini işaret etmektedir. Bununla birlikte, ısıtma oranlarındaki artışla DTA eğrilerindeki termal pik değerlerinin arttığı görülebilir, bu da alaşımın termal olarak yarı kararlı bir davranış gösterdiğini belirtmektedir. Bir kristallenme sürecini tanımlayan en karakteristik parametrelerden biri aktivasyon enerjisidir.

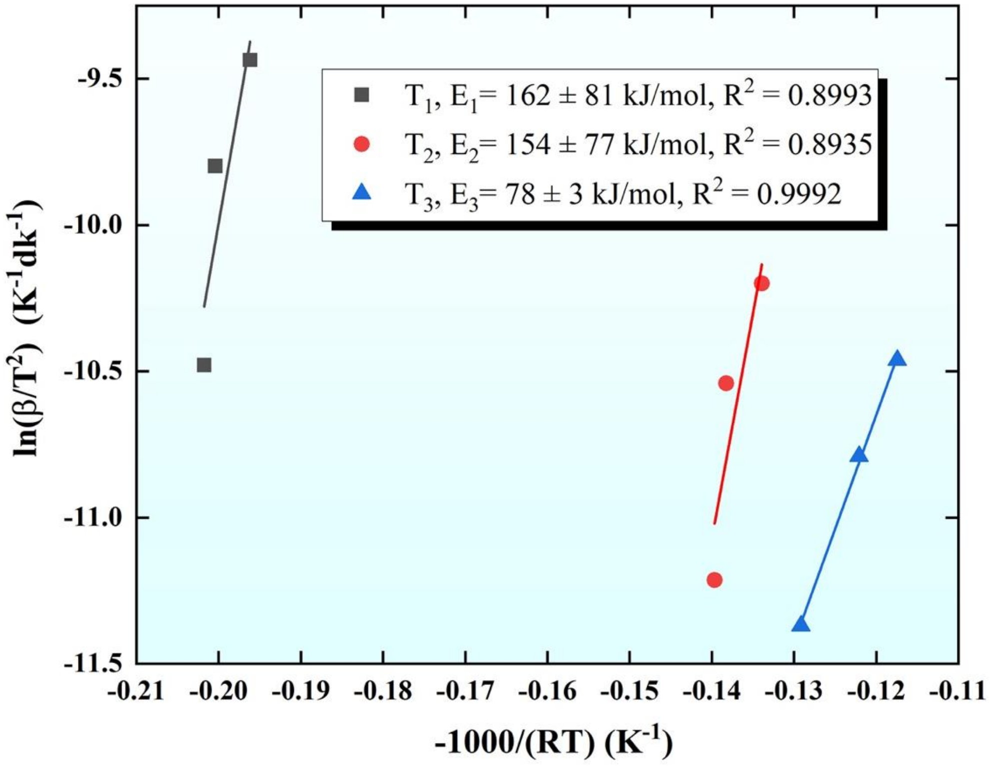
Aktivasyon enerjisi, bir kimyasal tepkimenin başlayabilmesi için aşılması gereken enerji bariyeridir. Tepkime başlamadan önce reaktiflerin bu enerji eşiğini aşmaları gerekmektedir. Aktivasyon enerjisi, tepkimenin hızını ve oranına önemli derecede etki eden önemli bir faktördür ve tepkimelerin başlaması için kritik öneme sahiptir. 30 saatlik öğütme işlemi sonrası elde edilen alaşımda meydana gelen kristallenme sürecinin aktivasyon enerjisi (E_k), Şek. 8'de gösterilen Kissinger yöntemi uygulanarak hesaplanmıştır [39].

$$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E_k}{RT} + sabit \tag{3}$$

Burada; β = ısıtma oranı (10, 20 ve 30 K/dk.), R = gaz sabiti (8,314 J/mol.K), T = pik sıcaklığı (T_1, T_2, T_3), E_k = aktivasyon enerjisidir. Şek. 8'de görülen doğruların eğimi, aktivasyon enerjisi değerlerini elde etmek için kullanılmıştır. Eğimin değeri, doğru bir çizgi ile verilerin uyumunu temsil eder ve aktivasyon enerjisini ifade eden E_k değerini hesaplamak için kullanılmaktadır. Alaşımın DTA analizinde elde edilen pik sıcaklıkları (T_1, T_2, T_3) kullanılarak hesaplanan aktivasyon enerjileri sırasıyla E_1= 162 ± 81 kJ/mol, E_2 = 154 ± 77 kJ/mol ve E_3 = 78 ± 3 kJ/mol olarak bulunmuştur. Elde edilen değerler, literatürde aynı kompozisyon ile ilgili çalışmalar olmadığı için Al-Cu alaşımlarıyla ilgili yapılan bazı çalışmalar ile kıyaslandığında ortalama E_k değerlerinin daha yüksek, ancak Ni-Ti alaşımlarına göre ise daha düşük olduğu görülmektedir. Genel olarak, yarı kararlı alaşımların aktivasyon enerjisi arttıkça alaşım daha kararlı hale gelmektedir. Alaşımların aktivasyon enerjilerindeki bu değişim, farklı kompozisyon ve mikroyapı ile ilişkili olabilir [40], [41].



Şek. 7. 30 saatlik öğütme sonrası elde edilen toz karışımın farklı ısıtma hızlarında elde edilen DTA grafikleri



Şek. 8. 30 saatlik öğütme işlemi sonrası elde edilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımın pik sıcaklıkları (T_1, T_2, T_3) için çizilen Kissinger doğruları.

4. Sonuçlar

Mekanik alaşımlama yöntemiyle üretilen $Al_{60}Cu_{20}Ni_{18}Ti_2$ alaşımı, farklı öğütme süreleri (1, 5, 10, 15, 20 ve 30 saat) sonrasında XRD, SEM-EDX ve DTA çalışmaları ile incelenmiştir. XRD sonuçları, öğütme süresinin artmasıyla alaşımın yapısında başlangıç fazlarıyla beraber AlNi ve Al_3Cu_2 intermetalik fazlarının yer aldığını göstermiştir. Ayrıca, devam eden öğütme işlemi süresince toz numunelere ait kırınım piklerinin genişlemesi ve şiddetlerinin azalması, örgü gerinimindeki artış ve kristalit boyutundaki azalma ile ilişkili olduğunu belirtmiştir. SEM-EDX sonuçlarından, öğütme işleminin başlangıcında büyük boyutlu olan toz parçacıklarının soğuk kaynaklanma ve tekrar kırılma mekanizmalarının tekrarlanması sonucunda daha küçük boyutlu ve homojen yapıya dönüştüğü görülmüştür. Alaşımların termal kararlılığı DTA ile incelenmiş, nihai alaşımın aktivasyon enerjisi ilk üç kristallenme pikleri için sırasıyla 162 ± 81, 154 ± 77 ve 78 ± 3 kJ/mol olarak bulunmuştur. Öğütme işlemi sonrasında elde edilen tozların daha sonra mekanik ve fiziksel özelliklerinin değerlendirmesini yapabilmek için sıcak izostatik presleme, geleneksel sinterleme, mikrodalga sinterleme ve kıvılcım plazma sinterleme (SPS) gibi yöntemlerle iri hacimli hale getirilebilir.

Teşekkür

Yazarların özellikle teşekkür edecekleri kimse bulunmamaktadır.

Kaynakça

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Small particles, big changes; synthesis, characterization of nanomaterials and an overview of their application areas

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Abstract

In the age of advanced technology, nanomaterials, their chemical and physical properties, characterization methods and synthesis methods have become very interesting in the scientific world. Considering the size, shape, and synthesis conditions of nanomaterials, and physical structure, the related materials are synthesized at the nanoscale. Nanomaterials have electrical, magnetic, optical, mechanical, and catalytic properties superior to micro materials and have the potential to create new and advanced products. For this reason, nanomaterials are widely used in the healthcare sector, textile industry, automotive technology, energy systems, science, and education. In general, this review covers the synthesis of nanomaterials, characterization methods, and their approaches to application today. In particular, nanomaterials have been obtained from top to bottom or from bottom to top with different specific approaches, and the structures of nanomaterials have been elucidated by explaining the relevant characterization methods. Finally, by giving an overview of the applications of the synthesized and

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characterized materials in daily life, the study was completed with the achievements of the nanoscale world.

Keywords: Characterization Methods; Nanomaterials; Nanobiotechnology; Nano world.

1. Introduction

The term nanometer (nm) is one billionth of a meter (10^{-9}), and a single strand of human hair is 60,000 nanometers. For example, it can be assumed that the size of atoms is about 0.1 nanometers [1]–[3]. The term nano was first used in the scientific world by Richard Feynman in 1914. American physicist and Nobel Prize winner Richard Feynman was invited to the annual meeting of the California Institute of Technology of the American Physical Society in 1956 with a speech entitled “There is a Lot of Room at the Bottom” [4]. In this speech, he took his place in the scientific world with the definition of the specific concept of nanotechnology and the related studies he has done. The American Journal of Physics came up with the following concept immediately after this speech: “Why can't we write the entire 24-volume Encyclopedia Britannica on one pin?”. Along with Richard Feynman's speech and related conclusions, he emphasized that the laws of nature do not limit studies in the field of nanotechnology at the atomic and molecular level, the main deficiency is in terms of relevant equipment and technical knowledge. As can be deduced from this conversation, nanostructures help to illuminate the unknowns of the scientific world with scientific and technological approaches. For the general definition of nanotechnology, in addition to the aforementioned work of Richard Feynman, in 1974, Norio Taniguchi became the second person to use the concept of nanotechnology and said the following sentences: “Nanotechnology mainly consists of the processing, decomposition, combination and deformation of materials by an atom or a molecule.”[5]. Nanotechnology deals with the physical, chemical, and biological properties of structures and atoms at the nanoscale, as well as materials and systems that are renewed. This branch of science, which is groundbreaking in various fields today, can also be characterized as the new industrial revolution or the age of advanced technology. In this context, nanotechnology has become a branch of science that studies and researches the behaviour of matter in dimensions between 1-100 nm. With another approach, if the size of a usable nanostructure is considered to be 1-100 nanometers, it can be seen that the field of study of nanotechnology is atoms and structures at the molecular level. Together with this approach, the synthesis, characterization, and functionalization of nanoscale materials in a controlled manner, making them usable at the nanoscale, is the goal of nanoscience and nanobiotechnology [6]. Small research carried out at the micro level in the field of nanotechnology leads to radical innovations in various fields. In addition, the differences in nanoscale structures are not only related to the small size but also related to the fact that they reveal different physical properties at small sizes. The best example of this is that the quantum properties become obvious as the size of nanomaterials decreases, or the geometric arrangement of atoms affects the physical properties of matter. Carbon-based materials, bismuth crystals, and gold can be cited as a good example of this [7]. While the bismuth crystal is a macroscopic metal group element, it shows a semiconductor property in the form of a nanowire [8]. Gold, on the other hand, appears yellow in macroscopic size, while it appears red when examined at the nanoscale. In other words, it has been observed that materials with different geometric, electronic, and optical properties, although they are composed of the same atoms, have different characteristics and structural properties in nanoscale structures [9], [10]. However, reducing the size of the material by reducing its size reveals a different characteristic feature. The size of material at the nanoscale is related to the freedom of movement of the free electrons it holds in its structure in Oct (x, y, and z-axis). If the free electrons are moving in all three directions, then the material is called a "3D" (three-dimensional) structure. The solid materials we encounter in our daily lives are examples of 3D structures [11]. If free electrons can move in two directions, these are materials with a "2D" (two-dimensional) structure. 2D materials are observed in layered structures, one layer may consist of a single kind of atom, while the other layer may consist of another kind of atom. To give an example, group 4A elements such as Silicon (Si), and Germanium (Ge) are layered and belong to the 2D material class [12]. Materials whose free electrons have the property of moving only in one direction are called 1D (one-dimensional) structures. Carbon nanotubes, metal oxide nanotubes, or nanowire structures are examples of 1D materials [13]. On the other hand, 0D (zero dimension) is a nanostructure containing free electrons, but in the form of nanoball and nano-dispersion, which can isolate each other. For example, core nanoparticles, hollow nanoparticles, fullerenes, and quantum dots are zero-dimensional materials [14]–[16]. Although 0D materials do not seem to have a specific electronic function, they are indispensable dimensions in various fields, including nanoscience and quantum computing applications. To mention this, materials with different nano-dimensions can show various structural and characteristic properties. The 1D bismuth crystal shows three different structures and conformational properties. These are rod structure, tube structure, and atomic sequence. The inner part of the rod form of bismuth crystalline shows a crystal structure-property. The tube form is a hollow sphere, and the bismuth crystal, which is formed in the form of an atomic array, consists of atoms attached to the surface. All of these three-dimensional structures are evaluated as nanowires. The synthesis of these materials with different sizes has developed high-activity catalysts, optical applications, advanced technological devices, surfactants, drug carriers, superconductors, pharmacological drugs, and therapeutic products along with exhibiting extraordinary properties [17], [18]. That is why nanotechnology has led to the awarding of Nobel Prizes in various branches of science in the 21st century. At the same time, it has become a multidisciplinary branch of science where basic sciences and applied sciences intersect. In other words, the most obvious advantage of nanotechnology is that by using smaller devices, the performance increases exponentially along with the reduction of the material size [19]. Thanks to this, nanotechnology has a fairly wide field of study for basic disciplines such as engineering, materials science, chemistry, biochemistry, physics, and medicine [10], [20]–[25].

2. Synthesis of Nanomaterials

It is possible to synthesize and characterize nanomaterials by various methods. There are 2 approaches to the synthesis of nanomaterials. These approaches are top-down and bottom-up. The first group, called top-down, treats the material as a whole and starts processing, at the end of the process, the material is divided into small particles. This process allows the material to reduce the structural shapes of microscopic elements to the size of nanometers using chemical etching or surface shaping techniques. In top-down approaches; basic processes such as mechanical milling, electrospinning, lithography, spraying, arc discharge method, and laser ablation method are used. Bottom-up approaches explain the synthesizability of atoms, molecules, or compounds existing in the structure of the material as a result of dimensional growth and clustering as a result of chemical reactions. For this reason, nanomaterials of atomic or molecular size are brought together in clusters in such a way that organic decay, multi-molecular structures, and macro-molecules form structures. Chemical vapor deposition (CVD), solvothermal, and hydrothermal methods, sol-gel method, soft and hard decoupling and reverse micelle method are among the bottom-up methods that hold the nanomaterial together (Figure 1) [26], [27].

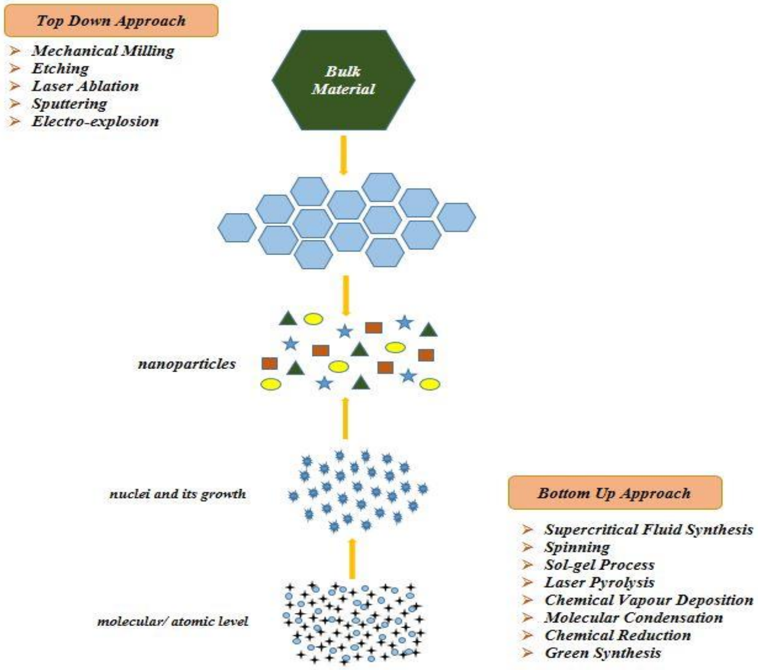


Fig. 1. Basic approach scheme for top-down or bottom-up synthesis of nanomaterials [16].

2.1. Top-Down Methods

- *Mechanical Grinding Method*

Mechanical grinding is a cost-effective method used to produce materials at the nanoscale. In this context, the ball grinding system, which is one of the mechanical grinding systems, is the most preferred method. The ball grinding system was developed by John Benjamin in 1970. It is performed by applying intense mechanical energy to the nanomaterial contained in the form of balls and dust particles in the grinding medium. This system is based on the energy transfer resulting from collisions between the Decaying medium and the sample. In the first stage, fine and irregular particles are formed as a result of the dust Decoupling or sliding between the balls. When the second stage is passed, the nanoparticles formed undergo deformation. At the last stage, fractures are observed in the sample that has undergone deformation and broken into pieces. At the end of these stages, the production of nanocomposite materials of various sizes is carried out. Among the advantages of the ball grinding system, it aims to produce a large amount of high-purity materials, increase the Decolonization of slightly soluble substances in water at affordable costs, and give new properties to the products formed. In addition to these advantages, there are also some disadvantages. The long production time, Decontamination of nanoparticles that will form steel balls in the mechanism, and very high energy requirements during material synthesis can be considered among the disadvantages. The materials produced in the ball grinding system synthesize nanomaterials, which provides the opportunity to meet innovative approaches [26], [28].

- *Electrospinning Method*

The process of producing nanofibers from polymers using electrostatic forces by Formhals in 1934 is called the electrospinning method [29]. With the electrospinning method, an electrical charge is applied to the polymer solution by applying a high potential voltage to the solution. After this step, a polymer gel is formed, which emerges from the fine jet and flows towards the grounded target placed opposite the assembly [30]. During this current, the polymer jet is scattered into very thin fibres, resulting in nano-sized fibres. Since electrospinning, the energy source, and one end of the collector (collector plate) are connected to the ground, it is important to enclose the system in a closed circuit. For this reason, one of the two electrodes in the circuit is placed correctly in the polymer solution, and the other is connected to the opposite collector. The pump placed in the back part of the electrospinning system creates a continuous pressure by pushing the polymer solution in the glass tube through the pipette towards the metal plate. Together with the given current, the polymer solution creates an electrical field in the glass tube. On the surface of the solution, an electrical charge occurs and exerts a force in the opposite direction to this surface tension. The electric current charged to the system can reach up to 30 kV, and when the intensity of the electric field gradually increases, it is observed that the hemispherical liquid in the layout forms a conical shape [31]. This conical shape is known as the Taylor Cone [32], [33]. In this conical way, as soon as the electrical force defeats the surface tension, the charged polymer jet is rapidly directed out of the pattern. As a result of nanoparticles with the same electrical charge repelling each other, the polymer jet is separated into very thin fibres, and collected on a metal plate. While the polymer jet accelerates under the influence of electrical force, the viscous resistance gradually increases. As soon as the viscous resistance is equal to the electrical force, the polymer jet begins to show an unstable distribution [34]. During this movement, even a slight air turbulence causes the material to oscillate. Generally, nanofibers with a diameter of 40-2000 nm (0.04-2 microns) can be produced by the electrospinning method [35]. Parameters such as the concentration of nano-sized fibres, the distance between the capillary tip and the metal collector, and the potential flow Deceleration at the extreme point affect the synthesis of the desired nanomaterial [36]. Polymeric materials produced by this method, carbon-based ceramic nanofibers, compared to other nanotubes, have various advantages in such matters as cost and single-stage material production [37], [38]. In addition, it is often used in the production of nano, and micro-sized medical purposes, ceramic coating, and flexible and fireproof materials based on their size [39]–[41].

- *Lithography*

Lithography is a printing technique in which painting and writing are combined side by side or intertwined on a flat surface sheet from the past to the present. If this technique is to be adapted to nanomaterial synthesis, it is a convenient, simple technique that improves the nano architecture using a focused light or electron beam [42]. The lithography technique is divided into two main groups in the form of masked lithography and unmasked lithography [43]. Masked lithography covers photolithography, nanoimprint lithography, and soft lithography techniques. Masked lithography nanopatterns perform processing on a large surface area using a specific pattern and template. It covers unmasked lithography, scanning probe lithography, focused ion beam lithography and electron beam lithography [44]. In mask-free lithography, on the other hand, random nano pattern making is performed without the need for any template [45]. the 3D free nano patterns are integrated by a focused ion beam in combination with wet chemical deposition. Lithography is an alternative method that is most often used in printing, pressing, and molding techniques instead of photons and electrons [46].

- *Spraying*

Spraying is a general method of producing nanomaterials by treating solid surfaces with high-energy particles (plasma or gas) (Figure 2). The spraying process can be carried out in different ways. Flamethrower pyrolysis and magnetron sputtering are examples of these methods. Magnetron sputtering is a method by which very thin metal coatings are obtained as a result of gas treatment in vacuum chambers emptied under a certain pressure. This method is based on the conversion of solid material into gas by breaking atoms from solid material as a result of high-speed treatment with high-energy ions. The sprayed ions are inert gases and argon gas is usually used as a spray source, while metal surfaces are used as a solid material. As a result of the collision of metal atoms and gas molecules, atoms scattered in the vacuum chamber are scattered. The spraying process allows the material to be atomized and deposited in a substrate to form a layer. Thanks to the inert gas used as a spray source, low-pressure plasma is produced. Another method, flame retardant pyrolysis, has been used in laboratory or industrial areas since twenty years ago to obtain nanoparticles quickly and in a single step. This spraying method involves mechanisms related to the liquid and gas phases of a large number of metal oxide nanoparticles. The metal-containing precursor is dissolved in a flammable carrier solution with the help of oxygen. Evaporation and transformation of the precursor substance are achieved thanks to the heat released into the environment after spray ignition. Nanomaterials produced in gas-to-solid transformations have crystal purity and single-mode size distribution. Since the nanoparticles obtained by this method have high purity, they are preferred in applications. Nanomaterials produced by flame spray pyrolysis are used in many fields such as catalysts, batteries, gas sensors, advanced pigments, biomaterials, food supplements, and nanotoxicology screening studies. In general, the spraying method is used to produce layered or thin nanofilms from nanomaterials. Nanomaterial production is achieved as a result of the collision of the inert gas sprayed at high speed with the metal melt [5], [26], [47].

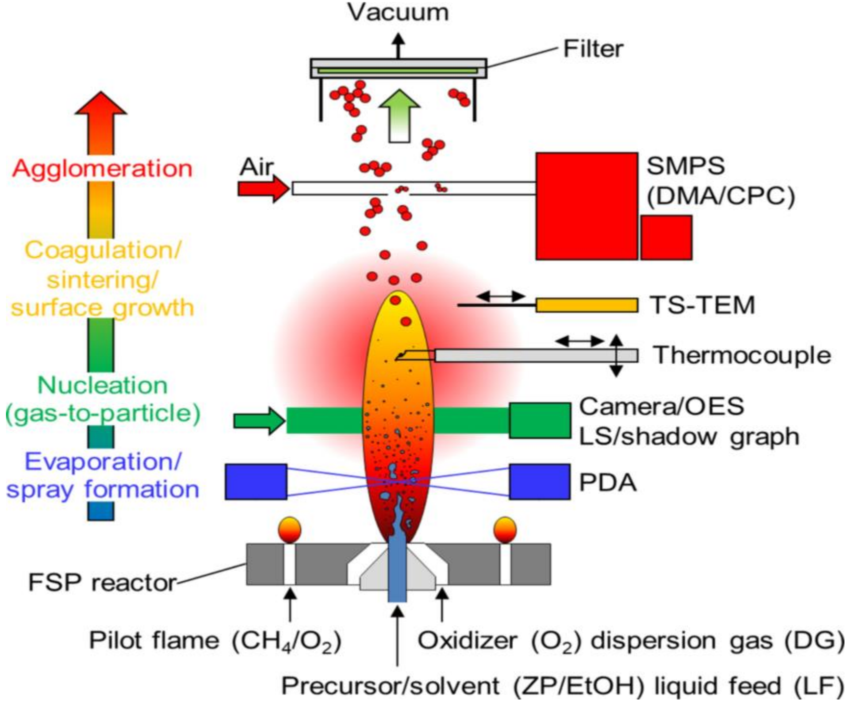


Fig. 2. Demonstration of the flame spraying method used for the analysis of nanoparticle production stages from metal oxide material. As the ignited gas, a mixture of zirconium n-prop-oxide and ethanol is distributed and ignited with the help of oxygen. Monitoring of the volume of liquid feed (LF) and dispersion gas (DG) and whether the nanoparticles have reached the desired size should be carried out (Reprinted with permission from [48], Copyright WILEY).

- *Arc Discharge Method*

The arc discharge method used for nanomaterial synthesis and nanoparticle production is mainly performed in an environment where noble gas and reactive components are present. The metal wire on the system essentially creates a current in the form of plasma and collects the material together with the formation of its magnetic field. Dec. For this reason, the electron source in the system creates high-energy sources with plasmas and electron beams in such a way as to form an arc. A fairly high temperature is applied to the reactive components and nanomaterials are synthesized by creating a high current on the metal wire in a short time [49]. In addition, as a by-product during the arc discharge method, a high electric current is needed, so heat is released. A current is applied between two graphite rods positioned at a close distance, one pole of which is the anode, and the other pole is the cathode, in such a way as to create electrical energy. Carbon accumulation occurs at the cathode pole, while graphite rods, which are considered a reference, are used at the anode pole [50], [51]. This synthesis method often produces fullerene, carbon nanotubes, multilayer graphene, and amorphous spherical carbon-based materials [52]. Among the given materials, the arc Decrement method is used most often in the production of fullerene. The production of fullerene is mainly based on the collection of nanomaterials formed on the electrode surfaces of two graphite rods under a certain helium pressure. Since the presence of moisture and oxygen in the environment will prevent the formation of fullerene, the presence of pure helium in the chamber is important. In addition, the arc discharge method is used to obtain graphene efficiently [53], [54]. It affects the nanomaterial formed under the current conditions in graphene synthesis. The nanomaterials that will be formed can be collected on the anode or cathode surface or on both electrode surfaces. In addition, collections can also be observed in the inner chamber, unlike the electrode surfaces [55]. The conditions under which material synthesis takes place in the arc discharge method lead to differences in the forms of the nanomaterial formed. The arc discharge method allows the synthesis of different material groups under changing electrode groups or ambient conditions [26], [47].

- *Laser Ablation*

Laser ablation synthesis is the process of removing matter from the surface using short and intense laser pulses that hit the target material. The laser beams sent to the target material are first transferred to the electrons contained in the solid, and with this high-energy transfer, the nanoparticles are vaporized. The process of material removal from the target surface is explained by the weakening of bonds due to the absorption of light by the substance. Depending on the intensity of the laser beam incident on the target surface, a plasma cloud is formed with ions, atoms, electrons, or larger particles that break off from the surface. The process of plucking metal atoms from this electron cloud has led to various methods and approaches. The laser ablation technique is a powerful method for processing brittle hard and heat-sensitive substances and for thin film production. Therefore, the efficiency of the ablation process is understood by the ablation rate. The ablation rate is determined based on the average ablation rate per single laser pulse and the thickness of the removed layer. The ablation rate varies depending on parameters such as photon energy, laser flux, beam width at the focal point of light, internal pressure, enthalpy of evaporation, optical processing depth, wavelength, photon repetition rate, pulse energy, pulse duration, energy density, etc. Accordingly, the reduction of the laser wavelength increases the ablation rate. The short wavelength laser beam causes small particles to break off from the target surface easily. The repetition rate is the number of pulses produced by the laser system in one second. Due to the accumulation of thermal energy depending on this period, it causes an incubation effect. The repetition rate increases and decreases in direct proportion to the amount of substance to be extracted from the target surface. Depending on these approaches, the property of the material to be synthesized varies depending on the reactions it will give to laser light. For example, in strong and intense pulsed laser systems, it does not matter whether the material has a metal or dielectric structure since dielectric ionization will occur very quickly. Based on these approaches, the laser ablation process is studied in three main groups: thermal, photochemical, and photophysical. The first method, material ablation in the thermal approach is based on a heating or evaporation process using laser light. The term photochemical laser ablation, on the other hand, occurs by directly separating molecules, indirectly breaking molecular bonds due to material impurity and stability. Finally, the third method, the photo physical ablation technique, non-thermal approaches determine the ablation intensity of the material. When these methods are also examined, the laser ablation process varies depending on the laser system used and the property of the target substance to which the laser beams are transmitted. The property of the laser system depends on the speed of ablation and the mechanism of its realization. For this reason, it is very important to determine and implement the appropriate experimental stages for the target substance laser system to be selected. Depending on these approaches, the laser ablation process is used in the synthesis of carbon-based nanomaterials, the production of oxide composites, and various nanomaterials synthesis in the ceramics industry [5], [26], [47], [56].

2.2 Bottom-Up Methods

- *CVD (Chemical Vapour Deposition)*

The CVD (Chemical Vapour Deposition) method is a very old nanomaterial synthesis method. The first practical application can be given as an example of coating the filaments with carbon or metals to make incandescent lamp filaments durable in the 1880s. In the same years, Ludwig Mond and other researchers developed the chemical vapour deposition method (CVD), the carbonyl process, to obtain pure nickel. The method, which has been developed over many years, has been used for the production of high-purity refractory metals such as titanium, tantalum, and zirconium. In addition, it has been a guiding device that has developed in various processes from material synthesis to purification. Among the application areas of CVD, the thin film coating process is used Decently on the surface. In this method, the reaction takes place while the raw materials, which are in the form of gas or vapour, are transported to the compartment called the hot substrate. Reactions occur on or near hot surfaces. Solid products are deposited on the surface as a thin film and various materials are synthesized by this mechanism (Figure 3). If we give an example of these materials; the use of carbides coated with CVD in the industrial field and diamond coatings can be made. CVD is a very good nanoparticle synthesis method in the production of carbon-based nanomaterials, metal deposition, solar cells, microelectronics, and insulating material production [57].

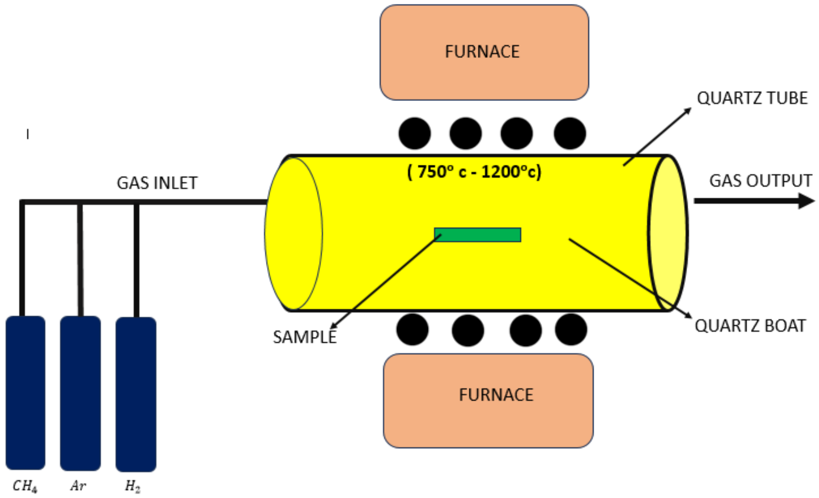


Fig. 3. The working mechanism of the CVD device, the gas inlet outlet, and the compartment where the sample is located [57], [58].

- *Solvothermal and Hydrothermal Method*

The solvothermal method is a method used for the synthesis of oxidized and non-oxidized crystalline materials. For example, highly porous structures such as zeolite, silicate-based materials, crystalline solids, and nanoparticles are produced by this process. The non-oxidized nanomaterials that can be produced by this method can be given semiconductor structures, borides, carbon nanotubes, phosphides, diamonds, nitrides, carbides, and chalcogenides. In the solvothermal technique, it is a method based on the synthesis of nanomaterials with a solvent, that is, a solvent in a closed container, rising far above boiling points. Hydrothermal method, on the other hand, 19. It has emerged with the branch of geology that started in the middle of the century, studying certain mineral and rock formations, and simulating hydrothermal conditions. In hydrothermal synthesis, the formation of nanomaterials takes place at a temperature higher than room temperature. The reaction system is based on the principle that an aqueous solution reacts with a special sealed container by heating and applying vapour pressure. A substance that is insoluble or slightly soluble in the solvent is dissolved by the hydrothermal method and regains a crystalline structure. The reaction kinetics and crystal growth kinetics of the hydrothermal method occur when reactants dissolve in the hydrothermal environment, ions and molecules also enter the solution by forming a bulk. They are Decoupled according to the temperature differences between the two layers of the boiler at the top and bottom. Ions and molecules contained in groups are adsorbed in the form of vapour. It then decomposes and undergoes desorption. The adsorbed product is in motion at the intermediate level, and the Decayed substances crystallize at the end of the process (figure 4). The same crystals formed show different morphological properties under different hydrothermal conditions. In fact, this method has quite significant advantages over others. With the production of unstable nanomaterials at high temperatures and the method used, minimal material loss is observed. Solvothermal and hydrothermal methods are quite preferred methods in nanomaterial synthesis. The only feature that distinguishes the solvothermal method from the hydrothermal method is the synthesis of nanomaterials in a non-water environment. In addition, it takes place in closed systems in two methods. As for material synthesis, it is used in the production of various geometric structures such as nanowires, nanorods, nanotubes, and nanospheres [59], [60].

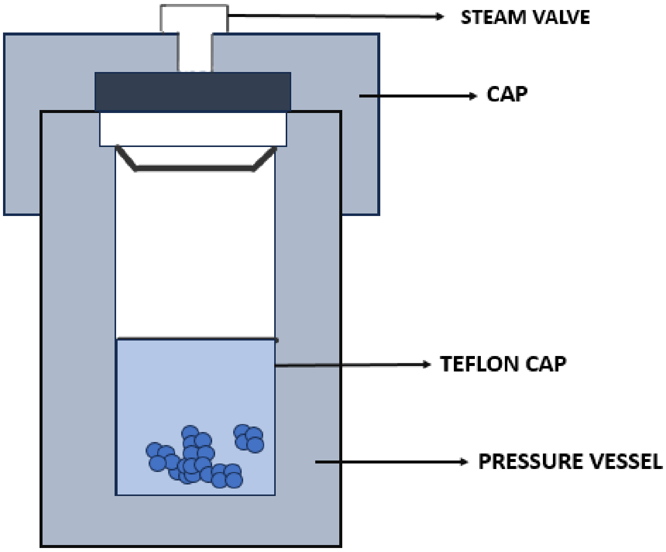


Fig. 4. Diagram of typical hydrothermal method equipment [61].

- *Sol Gel Method*

It is a wet chemical technique used to produce colloidal nanoparticles from the liquid phase. Metal oxides are at the beginning of the nanomaterials produced using this method. The metal oxide synthesis process is completed in several steps At the first stage, the metal oxides are dissolved in water or alcohol, heated by hydrolysis/alcoholises, and converted into a gel consistency by mixing [62]. Then condensation occurs. During the condensation phase, oxo-(M-O-M) or hydroxo-(M-OH-M) bridges are formed. It causes the formation of metal-hydroxo- or metal-oxo-polymer in solution. As a result of the condensation process, the solvent viscosity increases and is allowed to age, and porous structures are formed. During the aging stage, the pore structure decreases, and the distances between colloidal particles increase. At the end of the aging process, water and organic solvents are removed from the gel and the drying process takes place. The calcination process is required for the production of nanoparticles. With the calcination process, the formation of dust or biofilm occurs in the material. The product obtained and the influencing factors are the nature of the material taken from the guide, the hydrolysis rate, aging time, pH the amount of water, and the molar ratio of the material in the guide. Advantages such as the cheapness of the material produced by the sol gel method, homogeneous distribution, and low processing temperature facilitate nanomaterial synthesis. Due to the interest in energy conversion and storage applications in the last few years, extensive studies have been conducted on lithium-sodium ion batteries, fuel cells, photocatalytic applications, sol gel syntheses of 2D nanolayers, ceramic and glass production, metal oxide-based aerogels, hierarchically porous monoliths sol gel synthesis [5].

- *Soft/Hard Templates*

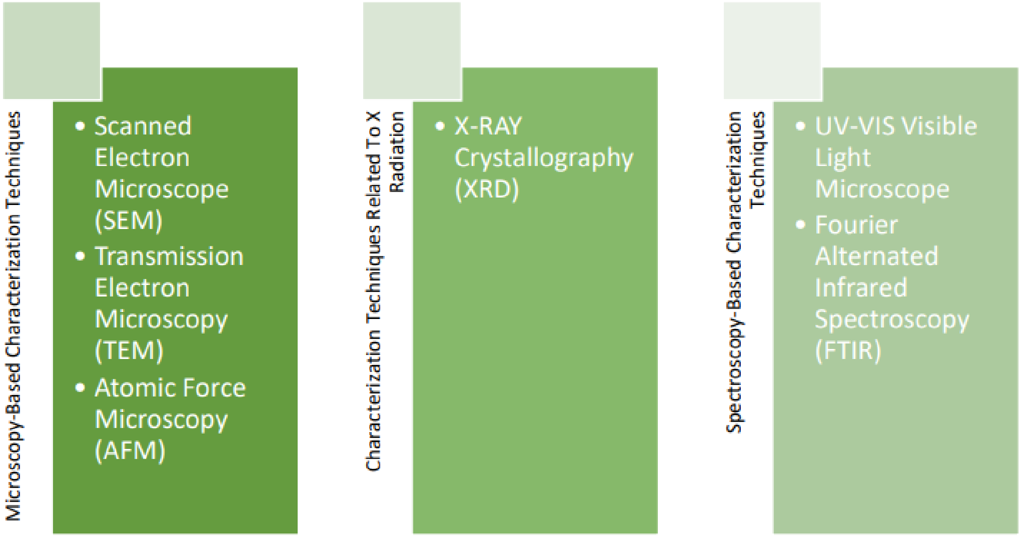
They are simple traditional methods that are widely used in the production of nanoporous materials. The application of soft templating provides an advantage in the development of materials with simple, relatively moderate conditions and various morphologies. A large number of nanoporous materials, block copolymers, flexible organic molecules, and anionic, cationic, and non-ionic surfactants are being produced. In the substance to be synthesized, a nano-sized material is obtained through hydrogen bonds, Van Der Waals interactions, and electrostatic forces. Examples of this are nanomaterials such as mesoporous polymeric carbon nanoparticles, single crystal nanoparticles, porous alumina, and N-doped graphene. Another method, hard stencilling, is also called nano casting. The use of solid materials as templates is the process of filling solid template pores with precursor molecules to obtain nanostructures. In rigid templates, it is desired to maintain the porous structure during the pioneering transformation process and to ensure that the nanostructure produced can be easily removed without deterioration. For this reason, the choice of a rigid template is important. A few of the materials used are; carbon black, carbon nanotubes, colloidal crystals, and silica-based materials. These templating methods take place in three main steps on the synthetic path. The first step is the selection or development of the appropriate original template. Then, the desired precursor is filled into these template pores and converted into an inorganic solid. It is removed with the template for the desired porous copy to be obtained. With the use of these mesoporous templates, nanowires, nanostructured materials with 3D nanostructures- metal oxides, and various nanoparticles are produced [5].

- *Reverse Micelle (RM) Method*

Reverse micelles are called nanometer-sized surfactant clusters containing water molecules encapsulated in a non-polar solvent [63], [64]. For the first time in 1982, the synthesis of a nano material was performed by Boutonnet et al. using the reverse micellar method [65]. In water, the oil emulsion is hydrophobic, the tails are directed towards the core, which traps the oil droplets in it, resulting in normal micelles. However, the condition of a water emulsion of hydrophilic tips in oil in a core containing water results in the formation of reverse micelles [3]. Reverse micelles are evenly coated with a single layer of surfactant and in an oil phase, isotropically distributed nano droplet structures are seen [50]. The activity and conformation of enzymes in the reverse micelle method are an example of the formation of droplet structures. In this method, three methods are considered to switch enzymes to the fat phase [66]. The first and simplest of these methods is the injection method. A hydrocarbon solution is prepared for the injection method, and a small amount of concentrated aqueous protein solution is added to the solution. Another second method is the dissolution of proteins in a hydrocarbon micellar solution. The last method is the preferred phase transfer method for proteins that are slightly or not soluble in water at all [67]. However, the reverse micellar method, along with biotechnology and bioorganic approaches, addresses a large number of application areas, including transformations of water-insoluble substrates [68].

3. Characterization of Nanomaterials

The characterization process examines the relationship between the structure, performance, and production of a nano-sized material Decently. Various analytical techniques are used to detect and measure nanoparticles. In these analytical techniques; various parameters such as optical, morphological, electrical, magnetic, physical, and chemical are the decisive elements for material characterization. Nanomaterial characterization studies the size, shape, porous structure, solubility, chemical composition, crystal structures, charge potential and surface area of molecules. SEM (Scanning electron microscope), TEM (Permeable electron microscope), AFM (Atomic force microscope), XRD (X-ray crystallography), UV-VIS (Visible light microscope), FTIR (Fourier transform infrared spectroscopy) devices are used for the characterization of nanomaterials (Scheme 1) [69]. These nanostructures are materials that function in many other fields such as the cosmetics and pharmaceutical industry, catalysis reactions, biomedical applications, chemical sensor systems and medical imaging devices [70]. It is possible to study the characterization of nanomaterials using microscopic, spectroscopic, and spectrophotometric-based devices with various parameters.



Scheme 1. Schematic representation of microscopic, spectroscopic, and spectrophotometric analyses of methods used in the characterization of nanomaterials.

3.1. Microscopy-Based Characterization Techniques

- *Scanning Electron Microscopy (SEM)*

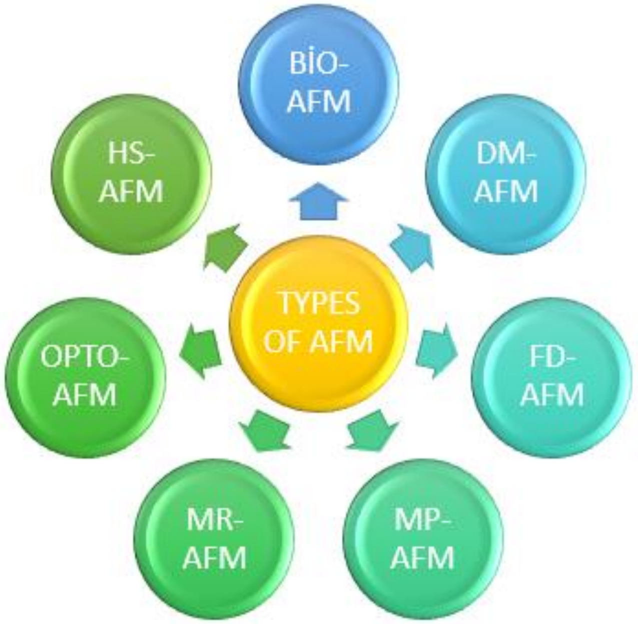
It is a measurement made using electrons in motion on highly magnified images of nano-sized materials. This system is based on bombarding the sample by focusing it with an arc that produces electrons. It is a microscopic analysis used to image nanoparticles of very small sizes [71]. The Decrement rate of SEM is used in the analysis of organic and inorganic materials at the nanoscale between 300,000-1,000,000. When working with SEM, the sample to be studied first needs to undergo a detailed examination and preparation phase before entering the microscope. First of all, the sample should not exceed 100 nanometers in size. In scanning electron microscopy, only conductive ions are studied. Non-conductive samples are made conductive with special layers such as gold, platinum, or carbon [72]. At the same time, an electrostatic charge occurs when working with conductive ions. Due to the magnetic field, a grounding process must be applied before the samples enter the microscope. After the sample has been examined and passed through the preparation stage, it is glued to the holder with epoxy adhesive or carbon adhesive tapes. A hole is located where the sample was found. Through this hole, an argon beam is sent to the sample, and images are taken by dropping on the material. In these images, grayscale is heavier, and the material can be clearly distinguished. SEM device equipment, maintenance, and workmanship is a device that needs to be taken care of [73]. When SEM is used together with other disciplines, innovative approaches are seen in the imaging of the material and device performance. Scanning electron microscopy gives better results about the composition, elemental analysis, location, and shapes of samples when worked together with an X-ray detector (EDX) [74]. SEM is widely used worldwide, not only in the characterization of nanomaterials but also in in-situ materials engineering. In addition, secondary electron (SE) and backscatter electron (BSE) are being studied together and this technology is also needed in imaging. When working with conductive materials in the SEM device, the secondary electrons (SE) are first thrown to the surface quickly to form an image. This image is visible with a small diameter electron beam. Backscatter, that is, the primary electron beams do not have a good resolution; it does not prevent the determination and information about image concentrations and atomic numbers [75]. As mentioned above, SEM is one of the few devices that is highly preferred and used in many disciplines around the world because it offers more different imaging techniques.

- *Transmission Electron Microscopy (TEM)*

Permeable electron microscopy is a type of microscope that emerged in the 1990s as a result of demand, requirements, and research. It allows us to study atomic-scale structures and the chemical environment in which the material is located at the nanoscale. Permeable electron microscopy consists of two parts. These are; resin and hardening bases. In these yellow sections, it is first mixed with a toothpick in a petri dish and the sample is added to it. The sample is glued in aluminium foil on small weights with a hot plate and epoxy adhesive is poured on it. After the sample preparation stages, it is possible to take an image easily on the device. TEM is a tool that allows us to get clearer images by interacting with high-energy electron beams thanks to the ability to see the sample at ultra-high resolution [76]. In characterization with permeable electron microscopy, nanomaterial structures such as nano tubes or nano-sized particles, and powders ground by the mechanical method are studied. In TEM analysis, two different types of products are prepared according to the sample to be studied. The first of these is the preparation of nanoparticles with a non-magnetic structure and the other is the preparation of nanoparticles with a magnetic structure using methods and methods suitable for the device. The nanoparticle, which does not have a magnetic structure, is subjected to ultrasonication for five minutes. This process is the process of distributing the material in solution by applying ultrasound at a low temperature. It is very important for this process that the solution used does not clump. Therefore, attention should be paid to the interest of the solution, it should not leave carbon and evaporate when it remains at room temperature for 10-20 minutes [77]. Since the samples are mostly carbon-based, it is very important that they leave residues in the environment. To determine whether there is a residue, a few drops of the solution should be dropped into a clean glass and evaporated TEM [78]. In addition, if it becomes transparent in water, it means that there is no carbon residue in that sample. When the desired properties are achieved, the flat grid or C perforated grid in the microscope is slowly and horizontally emptied into the beaker with the help of forceps. The grill is dried on filter paper under an infrared lamp. If there is no grid or it is not desired to be used for this process, a substrate with a thickness of 100 nm can be used. In addition, the sample is thinned before it is given to the device, this process allows you to get a clearer and better resolution image of the material from the device. Nanoparticles that have a magnetic structure, i.e. magnetic powders, are more difficult to prepare than powders that do not have a magnetic structure [79]. The reason for this is the agglomeration of magnetic powders, that is, the clustering of materials with larger particle sizes. Although they are easily Decayed by ultrasonication, they come together and cluster together again as soon as sonication stops [80], [81]. Therefore, the sample is placed between the pole parts of the device on the objective lens Dec. Since polarization in the material is an undesirable event, it is recommended to use TEM by going through certain stages for particles that have a magnetic structure. Permeable electron microscopy (TEM) is more often preferred than other types of microscopes because it helps us to elucidate the fibre, nanoparticle, and internal emission structure of many particles and nano-sized materials.

- *Atomic Force Microscopy (AFM)*

It is studied with atomic force microscopy on various surfaces such as polymer membranes, tissues, cells, proteins, nucleic acids, and functional materials. Morphological and physical properties of high-resolution research, it is possible to characterize various biological and synthetic bio-interfaces, that is, microorganisms or biomolecules are in communication with natural and synthetic structures with the AFM device. There are probes on the atomic force microscope that scan the molecule and allow us to obtain three-dimensional images. The feature that distinguishes these probes from other types of microscopes is that they obtain imaging in both solid and liquid media. The probe surface mimics it by changing the chemistry of the molecule under study. This makes it possible to investigate the mechanical, chemical, conductive, electrostatic, and biological properties of more surface interactions in the environment [82], [83]. Atomic force microscopy is very important because it can map the structures of bio aerosols with high resolution with a signal-to-noise ratio from the microscopic scale to the sub-nanometer scale [83]. The molecule to be examined in this device goes through a preparation stage. Then, whichever material is being worked with at the tip of the microscope, the adjusted needle and the molecule surface interact in contact. Thus, the desired image can be provided on the device without damaging the molecule. Since the AFM device allows us to study different molecular structures, structures that support this microscopy have been invented to study and investigate in various fields (Scheme 2). The optical detection system of AFM and its derivative Bio-AFM, which allows it to work in aqueous solutions that detect liquid cells, is Bio-AFM. When shaping the sample to be studied, its derivative, which shakes the probe tip to reduce friction and has a dynamic mode, is DM-AFM. It is the FD-AFM that shapes the surface of the biological system based on the force and distance curve. MR-AFM is a type of multi-parameter microscope that maps the contours of the sample being studied by looking at its physical and chemical properties. While drawing the lines of the sample, its derivative, which maps multi-frequency in its physical parameters, is MF-AFM. OPTO-AFM is a microscope that shows better by providing advanced optical imaging for complex images. The AFM derivative, which is mapped at a high speed by accelerating the image 1000 times and showing the biological sample accordingly, is called HS-AFM [83]. The atomic force microscope is mapped according to the concentration and atomic resolution of the sample to be examined. The images are obtained with constant altitude mode and typical atomic resolution, i.e. based on the Pauli principle. Fixed-height AFM images make the sample appear brighter. In addition to the types and variety of microscopes with AFM, the chemical bonds of the atom are observed [84], [85]. This feature distinguishes atomic force microscopy and its derivatives from other microscopes.



Scheme 2. Derivatives of atomic force microscopy in various types and characterization analysis.

3.2. Characterization Techniques Related to X-Radiation

- *X-Ray Crystallography (XRD)*

XRD is a device that displays diffraction axes that reflect the physicochemical properties of the material when it collides with a wide-ranging and crystalline nanomaterial. The three-dimensional materials that make up the crystal structure are crystalline. Various microscopic and spectroscopic methods have been tried to study and understand the phases of crystalline materials. These methods worked in the characterization of nanomaterials, but the XRD device was invented because the desired result could not be achieved. X-ray crystallography studies the physicochemical properties and crystal structure of materials in detail. The voltage arc formed during the characterization stage provides information on the structure of nanoparticles, electron density, and many other topics [86]. It allows the characterization and research of nanomaterials and nanostructures in this direction. When analysing materials at the nanoscale, powder diffraction X-rays are used. Powder diffraction, also known as the Debye and Scherer method, is one of the methods that require the least material. These methods can be performed quickly, and qualitative analyses easily without damaging pure and multi-component mixtures. If there is a very small amount of samples for nanoparticles or nanomaterials to be studied, it is easier to work with X-ray crystallography than other analysis methods. Therefore, he works with XDR devices in nanomaterial and nanoparticle characterization, nanomaterial extraction, catalysis reactions, geochemical materials, and forensic medicine [87].

3.3. Spectroscopy-Based Characterization Techniques

- *Ultraviolet-Visible Region (UV-VIS) Spectrophotometer*

Ultraviolet-visible region (UV-VIS) light spectroscopy is a technique used to measure the absorption of absorbed and emitted light and sample in the UV-visible region. UV provides visibility between 200 and 400 nm, while UV-VIS visible region device increases this visibility range up to 400-800 nm thanks to light microscopy. With the development of technology, UV-VIS microscopy provides visibility between 1 nm and 1100 nm wavelength today. The device is a device consisting of a light source, a wavelength selector, detectors, and lenses, respectively. In this device, which provides high resolution, measurement is taken by placing the material being studied between the light source and the detector. The light beam it absorbs is measured before and after the measurement is taken. Accordingly, the lights used in the device are Deuterium and Tungsten lamps. It is a characterization technique used to evaluate the size, concentration, and degree of aggregation of nanoparticles and nanoparticles and to monitor stability. It is a frequently preferred analytical method because it is economical and easy to use. UV-VIS visible light microscopy is also used to determine the number of activated carbon iodine, as well as to prove the accuracy of the amount of material [88]. Since it is sensitive to the near-surface refractive index of nanoparticles and nanoparticles, it is very preferred at the characterization stage. UV-VIS is a device that is often used for the measurement of molecules or inorganic ions in a sample solution. UV-VIS visible zone light microscopy is very useful because it gives easy and accurate results in a short time [89].

- *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR is a spectroscopic analysis method using Fourier transform infrared photons used in nanomaterial characterization. FTIR is a characterization technique that examines the bonds between molecules of a material, intramolecular bonds, absorbance or emulsion value [89]. In this technique, it provides information about the functional groups in molecules and the vibrational frequencies of bonds. In this method, which uses infrared rays, the photons sent interact with the conducting material. Fourier transform infrared spectroscopy provides a resolution of 5 microns. It is faster than other methods because the working and measurement time is about 30 minutes. Infrared light is used to determine changes in carbon bonds between carbon-structured nanomaterials and polymers [90]. As mentioned above, the main purpose is to show different absorption and emulsion properties of organic or inorganic materials at different wavelengths using infrared light. While this is being studied in spectroscopy, first of all, nanomaterials in the device, radiation passes through the interferometer and is detected by the detector, creating a signal. This signal is transferred to the computer and the Fourier transform is performed to find samples whose elemental and molecular weight are unknown. Fourier transform infrared spectroscopy is a spectroscopy-based device that is often used in nanomaterial characterization, as it provides a good resolution view in a short time and provides information about molecular bonds.

4. Overview of the Application Areas of Nanobiotechnology

The synthesis, characterization, and material acquisition of nanomaterials bring about a lot of innovations in nanotechnological applications. Today, nanotechnology is considered to be the revolution of the modern scientific era. For this reason, it continues to progress with the studies carried out every day. Nanotechnology is used in most of the items we use in our daily lives, from the clothes we wear, sunglasses, medicines we use, ready-made food packages, technological tools, and hard drives. The reason why nanotechnology is widely used is that it brings advantages such as being cheap, easy to transport, certain content and not taking up much space. In addition, it can be shown as an example that the materials produced can be used repeatedly, the products are quite small, light, and robust [91]. Today, nanobiotechnology is widely used in the food industry, textile industry, automotive industry, science and education, energy production, and healthcare sector [92], [93].

- *Nanobiotechnology in The Healthcare Sector*

All studies used nanotechnologically in the field of health are collected under the name nanomedicine. Nanoscale materials and nanoelectronic biosensors have been developed to diagnose, develop treatments, and stop diseases. Currently, the most important approach for the applicability of the correct treatment process in various diseases such as diabetes, cancer, pneumonia, COPD, and Alzheimer's is to make the correct diagnosis [94], [95]. To make an accurate and accurate diagnosis, the importance of nano sensors and nano particles at the nanoscale level is great [96]. For this reason, the main purpose of nano medicine is to support patients whose treatment has not been found with today's technology with nano biotechnology [93]. For this reason, drug release is one of the most common studies in nanomedicine, and a lot of research is being done on this topic. For example, when drugs loaded with nanoparticles are injected into the patient's body, the drug they are carrying is directed toward diseased cells. On the other hand, they pass to healthy cells without harming them and destroy diseased cells. With the acquisition of more information thanks to the delivery of drugs to nanoparticles, the field of nano vaccines has also been developed through many research and development stages. Chemotherapy drugs loaded into nanoparticles are one of the most important application areas [97]. Nano carrier-based application systems enhance cellular and humoral immunity and also have an important value in vaccine treatment [98]. No specially developed treatment has been found for the Covid-19 virus, which has taken the whole world captive in recent years. Instead, nanotechnology and nanomedicine developments have been used to reduce the course of the disease and reduce the mortality rate. It will continue to be an important tool for improving human health and quality of life in future generations as well. The innovations brought by nanotechnology enable the realization of more effective and personalized treatments in the medical world. These structures have many advantages, such as increasing the solubility of drugs, protecting against degradation, reducing toxic effects, extending the duration of activity, improving bioavailability, regulating pharmacokinetic and distribution properties, targeting cells and tissues. The progress of nanotechnology in the field of healthcare brings with it the development of treatments in medicine, while promising an exciting future about the limits of potential future applications. Nanotechnology continues to play an important role in the field of protecting and improving human health [99].

- *Nanobiotechnology in The Food Industry*

The main goal in the food industry is to increase the number of products that are of high quality, natural, preservative-free, and additive-free, but have a long shelf life for consumers. In line with these requests, nano biotechnology and nanomaterials have also entered the business in the food industry. The primary goal of Nano Food is to make food additives, nutritional supplements, and product packaging. With the use of nanoparticles, products can be produced in packages that are more resistant to environmental conditions and have protective properties against light and gases in the atmosphere. In this way, spoilage-resistant, high-quality, and microbiologically safe foods can be consumed. Another application is that the production, demand and need for recyclable packaging are increasing day by day. These packages are nanomaterial additive products because, in addition to protecting their nutritional content, plastic packaging destroys the carcinogenic effects on nature. Nano-technological materials in the food industry are very important for environmental sustainability by reducing the waste problem [100]. Thanks to the production of foods using nanotechnology techniques, food processing, and nano-material-based sensors, it contributes to all application areas such as spoilage, loss of consistency, and intelligent packaging.

- *Nanobiotechnology in Textile Industry*

The textile industry is one of the sectors where nanotechnological materials are used the most. With the integration of molecular-scale sensors, electronic devices, and computers into fabrics, fabric production has become possible in the “Interactive Electronic Textile” sector. Fabrics used in the textile industry have been given different properties in the nanometric dimension. As an example of these applications, silver particles have been added to sock yarn to prevent bacteria and bad smell/odors [101]. The production of various types of fabrics that do not wrinkle, do not stain, do not burn, do not tear exists today. In the future, it is aimed to use these fabrics in various fields from medicine to textiles by supporting them with nano materials that change color with sensor mechanisms, are affected by ambient gas, or do not burn. For example, the shirts we wear in everyday life will detect what is happening around us, will be affected by sound, and will record data. Fabrics produced based on nanomaterials are expected to have properties that will store energy, self-clean, and protect against external factors when necessary. The deficiency of smart textile fabrics is that the clothing comfort of the garment is not at the desired level and the need for a power battery is among the problems. If we look at the advantages, the clothing user will be able to receive warnings about dangers and track health information instantly. Nanobiotechnology has a great potential to meet these needs. Promising nano materials are the most useful technological tools to be used in the textile industry in terms of their size, structure, and morphology [102], [103].

- *Nanobiotechnology in the Automotive Sector*

With globalization, competition in the automotive sector is also increasing over time. The interest in vehicles that run on less fuel are durable, long-lasting, use renewable energy sources, and do not harm the environment has increased day by day. The applications offered by nanotechnology show promise in this regard. It has been seen that the motors designed by integrating into nanomaterials have a longer service life and are more powerful. In addition, vehicle parts manufactured with nanomaterials are more robust and lightweight in structure. These nanomaterials introduced to the automotive sector offer as little fuel use as possible and great comfort from a material point of view. In addition, another problem that exists in the automotive sector is that there are very few environmentally friendly, cheap, comfortable-to-use, durable fuel cell alternatives. Fuel cells are systems that convert chemical energy into electrical energy [104], [105]. Nanotechnology supports the production of materials that contribute to the development of fuel cell technology and lead to more efficient sustainable energy production. The advantages that nanotechnology will provide, from hydrogen gas in the atmosphere to energy storage, to vehicle parts in fuel cell manufacturing, have led to major changes in the automotive sector [106], [107].

- *Nanobiotechnology in Science and Education*

With the increasing processing speeds and capacity of computers day by day, three-dimensional virtual reality applications have started to be used a lot. With the development of augmented reality technology, the online education environment offers people the opportunity to study as if in a natural classroom environment. This situation creates a cost-effective educational environment that can reduce the financial expenses spent on education, the cost of travel, and food. In addition, with virtual reality, people will be able to Decouple together in the virtual world and increase their social interactions. Another approach is that artists and creative staff will design three-dimensional works of art using virtual reality tools. Engineers and designers have made virtual reality useful for creating product prototypes and conducting simulations. This is why nanotechnology is of great importance in the field of science and education. Because it accelerates innovations, molecular-level investigations, product development, and progress in science and education and offers a better future [108]–[110].

- *Nanobiotechnology in Energy Production*

Each country aims to obtain nanomaterials that are risk-free, low-cost, and have renewable energy sources. Department of nanobiotechnology, the importance of efficient production, storage, and transportation of energy is quite great [111]. For this reason, the main energy source of nanobiotechnology is provided from hydrogen gas. The reason for this is that hydrogen is very light and flammable. Hydrogen gas has the potential to produce high energy when burned, and as a result, Decontamination of the environment is among the desirable properties. As a result of this, electrical energy is generated when hydrogen gas is burned. Therefore, hydrogen is the candidate that is considered the most suitable for replacing fossil fuels in terms of energy production with its physical structure and chemical reactions [112], [113]. In addition, since hydrogen gas is nanoparticle-based, it is the main energy source that meets the energy conversion, demands and requirements. Studies on energy sources, nano-sized materials, and more efficient, high amounts of energy obtained sustainable, reliable, and easy-to-transport products are increasing day by day. In addition, energy production has a lot of applications in fuel cells, portable computers, electric vehicles, and mobile phones. With nanobiotechnology, the material size is quite small, safe, cost-effective, easy-to-transport products are being used today and alternative energy sources are being developed [2], [114], [123]–[129], [115]–[122].

5. Conclusion

Nanoparticles, which have gained a different dimension with the technology that has developed since Richard Feynman used the term nano in 1914, are carbon-based materials. Rapidly developing nanomaterials are synthesized using physical and chemical methods. When the material is considered as a whole, it is a top-down approach technique that explains its structural shapes by reducing them to nanometer size using physical methods. Examples of top-down approaches are mechanical milling, electrospinning, lithography, spraying, arc discharge method, and laser ablation method. The method that explains the molecules that exist inside nanomaterials, their dimensional growth, clustering, and synthesis by creating macro molecules, is a bottom-up approach. Chemical vapour deposition (CVD), solvothermal and hydrothermal methods, sol-gel methods, and soft and hard Decoupling are bottom-up approaches that hold and combine by forming macro molecules with the reverse micellar method. After the nanomaterials are synthesized, various analytical techniques are used to detect and measure the nanoparticles. Together with these approaches, the characterization process of materials is carried out based on their optical, morphological, electrical, magnetic, physical, and chemical properties. The characterization of nanomaterials is carried out using microscopic, spectroscopic, and spectrophotometric-based devices. Scanning electron microscopy (SEM), permeable electron microscopy (TEM), and atomic force microscopy (AFM) are used in microscopy-based techniques. In the spectroscopic-based characterization of nanomaterials, various methods such as X-ray crystallography (XRD) are used. In spectrophotometry-based methods, UV-VIS is used for the characterization of nanomaterials in visible light microscopy and Fourier transform infrared spectroscopy (FTIR). Nanomaterials, which have been synthesized and characterized, are currently active in various fields from the textile and food industry, automotive and health sector, science, and education to energy production. From the clothes we wear to the technological tools we use, the nanomaterials that exist in our lives are still being studied by the scientific world and research groups. With these activities, it is aimed to develop existing products or produce new products. With the development of technology, nanomaterials have led to revolutionary changes in our lives.

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Journey to the sweet world of beekeeping: historical development, honey harvesting and overview of bee products

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Abstract

Beekeeping started in ancient times when the first humans naturally killed the swarms nesting in tree and stone hollows and utilized their honey. Beekeeping, which was practiced with primitive methods until a few years ago, has developed up to today's modern beekeeping in the light of scientific discoveries and developments. There are approximately 56 million beehives worldwide and 1.2 million tons of honey is produced from these hives. For this reason, honey is seen as a foodstuff that the first people meet their need for sugar, easy to digest, and quickly mixed into the blood. In addition, materials such as pollen, propolis, bee venom, and beeswax obtained from beekeeping have a very important place in health and industrial fields. However, there are not enough resources to guide today's beekeepers both for beekeeping and for bees and bee products in our country and in the world. Within the scope of this study, the historical development of beekeeping, beekeeper's calendar, hive types and sizes, honey harvesting and hive care, bee products, etc. It aims to give an overview to people interested in beekeeping.

Keywords: Beekeeping, Bee products, Bee venom, Pollen, Propolis

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1. Introduction

The earliest evidence of true beekeeping dates back to ancient Egypt in 2450 BC. It is also possible to find reliefs of hives and bees in the Sun Temple of the Fifth Dynasty pharaoh, Newossere Any, discovered south of the Great Pyramid of Giza in 1898. Early humans naturally killed the bees that settled in tree hollows and rock cavities and benefited from their honey. The history of beekeeping, paintings drawn in caves dating back to 7000 BC, bee fossils, and similar historical finds from very old years confirm this view [1]. In historical development, tree hives were used as hives until the Stone Age, then earthen and clay containers were used as hives and developed until the beehives used today. Real beekeeping started with people taking some honey without killing the bees nesting in the tree hives and leaving some honey to the bees. [2]. Although global stocks of managed honey bee colonies appear to be increasing, significant declines in wild and domesticated bees and colony losses have been reported in many parts of the world. Beekeeping, which is seen as one of the important branches of modern agriculture, can be successfully practiced almost everywhere in our country. The climate, vegetation, rainfall regime, and topographical and geological features of the geography we live in allow for high yields in beekeeping [3]. Beekeeping is an occupation where good results can be obtained with little capital, labor, and a conscious approach. Anyone who wants can easily take care of 2-3 hives in the garden of his/her house, or it can be increased to 20-30 hives by adding a commercial dimension to the business. Therefore, it can be the main occupation for a family's livelihood. In addition to this, it can also be easily done as an auxiliary activity that provides additional income besides the main profession [4]. Various products obtained from beehives such as honey, beeswax, pollen, bee venom, and propolis provide important inputs to the national economy. The frequent use of these products in the food and health sector and their consumption as food are of great importance for healthy living and balanced nutrition. The greatest importance of beekeeping in terms of agriculture is that it helps the pollination of plants. Many orchard owners around the world rent beehives for their orchards during the pollination period. According to research, this natural function of the bee in the pollination factor provides a 40% increase in yield. The bee travels from flower to flower to collect pollen and provides a great advantage in fertilizing plants with natural methods [5]–[7].

Traditional beekeeping is a type of beekeeping that has been going on for centuries, in the traditional system everything continues in its natural course. In our country, it is done in hives called black hives. The type and dimensions of black hives vary from region to region. There are those made by hand such as wooden crates, as well as those made by knitting in the form of baskets or plastered with mud, slime, and animal excrement. Bee colonies are not under the control of the beekeeper. At this point, the only thing the beekeeper can do is to protect the hive against negative external factors. In traditional beekeeping, it is not possible to feed the bees when necessary, diagnose and treat diseases, intervene in hive problems, replace the queen with a more efficient queen, etc. [8]. In the traditional system, the honeycomb and honey must have completely natural ingredients. For this reason, honey produced by traditional methods is more preferred in the market than honey produced by modern methods [9].

Modern beekeeping is a type of beekeeping that started in the 1850s with the discovery of frame hives. 3 main features distinguish modern beekeeping from the traditional system. First of all, the frame inside the hive, the ready-made combs, and the machines for extracting honey from the combs differ. For 1 kilogram of honey, the honeybee visits about 5.5 million flowers to collect nectar and transforms it into honey in the hive. If a single bee produced a 500-gram jar of honey, it would be able to fill it in 2,000 days. This corresponds to approximately 5.5 years. Honey bees, on the other hand, live for a maximum of 45 days and spend a great deal of labor to produce a jar of honey. Ready-made honeycomb makes the bee's work much easier [10]. The bee frame quickly fluffs up the finished comb and starts to store honey in the comb chambers. Thus, she is freed from the process of building the foundation of the hive and spends most of her time storing honey. In addition, the beeswax in the honeycombs emptied of honey in the honey extractor can be used again and again by the bees [11]. The main advantages that distinguish the modern system from traditional beekeeping can be listed as follows:

- Since a ready-made comb is used, the bee spends its performance on honey storage, so honey production is higher than expected.
- Hives can be opened easily, and diseases and in-hive problems can be detected.

- Honey harvesting is quite easy.
- Queen change can be made for breed breeding.
- It is under the control of the beekeeper to swarm or not to swarm weak hives.
- Artificial swarming is possible.
- Bee products such as pollen, bee venom, and royal jelly can be taken easily.
- New developments and techniques in beekeeping can be applied.
- It is much easier in modern hives to prevent the winter and spring extinction of bees when honey is scarce.

The disadvantage of modern beekeeping is the suspicion of the substances used in the production of artificial comb on the bee. Due to the lack of standards and weak controls on artificial honeycombs, beekeepers are skeptical. The way to avoid this suspicion is not to consume the artificial part in the middle of the purchased artificial honeycomb [12].

In this study, it is aimed to create the literature necessary for beekeeping to be done with the right methods and techniques. From the historical development of beekeeping to honey harvesting, bee calendar, bee care, and bee products, it is aimed to give a general perspective to people interested in beekeeping. As a result, it is envisaged to ensure the sustainability of beekeeping.

2. How to start beekeeping?

Before starting beekeeping, you should start beekeeping after learning basic theoretical information from the right books, magazines, and related institutions. The biggest factor that leads new beekeepers to failure is relying on hearsay information. For this reason, it is the healthiest to contact people who are successfully practicing modern beekeeping around you and learn the right starting information. It is possible to start beekeeping with modern methods by adding swarms to an empty hive that we buy, by hiving stray bees that we find in the field, or by buying a hive with bees. The best of these methods is to start by buying a hive with a strong bee population and a young queen. With this method, it is possible to approach the hive and the bee with more accurate techniques. For beginners, 3 hives are ideal, after learning the techniques, the number of hives can be increased over time and commercialized [9], [13].

The first thing the beekeeper needs to learn is undoubtedly the rules to be considered when entering the apiary. To do beekeeping safely, it is necessary to know what behaviors annoy bees and take precautions. For example, opening the hive door in windy, rainy, and harsh weather; approaching the apiary by applying pungent odors such as essence, perfume, and cologne; blowing on the bee ball, breathing directly on the bee; also, when hive maintenance is to be done, it is necessary to move calmly and quickly and not to stop on the flight paths of bees [14]. The second thing to learn is the method of opening the beehive and checking the frames. When the beekeeper looks at a frame, he should be able to recognize which cell contains honey, which cell contains brood, or which contains pollen. He should also be able to recognize the female bee, drone, and queen at first glance. From time to time, the beekeeper will be confronted with various problems in the hive and must learn to deal with them [15]. They should feed the bees when necessary, harvest the products at the end of the period, and learn the methods of bringing the apiary to the wintering position. Therefore, the beekeeper who wants to be successful should constantly research and try to follow and learn the current methods of beekeeping [16].

3. Hive types and dimensions

The technical characteristics, location, and types of hives in which bee colonies spend their entire lives are directly related to the efficiency of beekeeping. Various hive models are used around the world, but the most widely used are Langstroth and Dadant-type hives. Although Langstroth-type hives are mostly used in our country, intermediate models close to the Dadant type are the majority because the hive dimensions are made differently. A Dadant-type hive consists of 5 parts (Fig. 1.). These are; the bottom board, body or brood box, honey box, cover board, and cover [7].

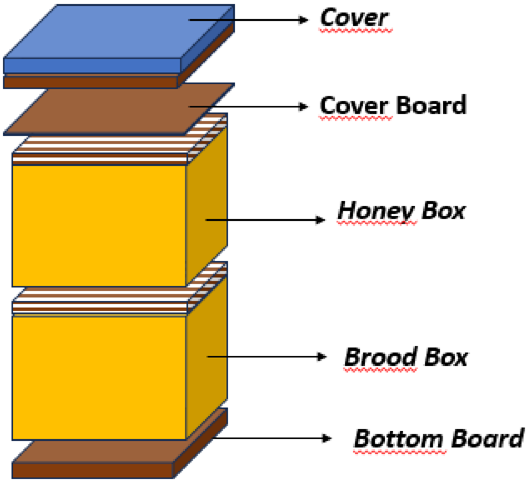

Fig. 1. Dadant-type hive consists of a cover, cover board, honey box, brood box, and bottom board.

The bottom board of the hive should be made of a single piece; if it cannot be made of a single piece, gaps should not be left at the joints of the pieces. Because every gap and crack in the bottom board provides a habitat for fungi, bacteria, and insects that may come from the environment [17]. The moth butterfly is the most common example. The body, or brood box, is the main habitat of bees. This is where the bees enter the hive. The queen is located in this section and during the brood rearing period she is on the honeycomb in the brood box. In some periods, when the bees cannot fit in the hive body, they go upstairs. Since the bee colony is in the brood chamber during the winter season, the hive body must be strong and resistant to the harsh conditions of winter. In addition, sacks or sturdy pieces of cloth can be used as cover boards, many beekeepers prefer pieces of cloth. The advantage of rags is that they do not annoy the bees by making noise when the hive cover is opened and help to ventilate the inside of the hive in summer. This helps to get rid of moisture and dampness inside the hive. There must be ventilation holes in the hive cover and these holes must be opened in summer. The cover should be made in such a way that it fits the hive well and protects the hive in adverse weather conditions. As mentioned, if the hive is to be purchased ready-made, it should be purchased from companies that are especially engaged in beekeeping and know this subject. There are various technical errors in the hives prepared by local carpenters who are not engaged in beekeeping. Therefore, no matter which type of hive is preferred, there are common rules to be considered for a good hive [18], [19].

Rules to be considered in a good hive

1. The hive body, i.e., the brood box, should be at least 2.5-3 cm. The boards to be used for the hive body should be made of well-dried, knotless, and strong wood. Linden wood is highly preferred in hive construction, instead the most ideal is pine wood.

2. The hives must be made by people who are engaged in beekeeping or have knowledge in this field and their measurements must be precise. It should be ensured that all hives are the same size. If the dimensions are not taken into consideration, using frames and honey in different hives will cause various problems.

3. Particular attention should be paid to the joints of the hive body. It should not be perforated or hollow, and insulation should be paid attention to prevent moisture.

4. Hive models should be made according to previously tested and accepted measurements. The models that emerge at the end of long efforts enable the bees to live in the best way and produce products without disturbing their natural order.

5. Only the outward-facing sides of the hives should be painted white or beige.

6. Those who will do mobile beekeeping should prefer a flat hive cover, those who will do fixed beekeeping should prefer a cradle-shaped hive cover.

7. Hive bottom board should be made mobile if possible.

8. Necessary gaps should be left for the bees to move easily in the hive and for the hive to be ventilated on summer days. According to these measurements,

- 7.5 mm between the two frames on the sides and the inner surface of the shell,
- 10 mm between the frame head and the inner surface of the barrel,
- 25 mm between the bottom board and the bottom slat of the frame,
- The gap between the two frames is 36-38 mm,
- 12 mm between the top slats of the frame,
- There should be a 10 mm gap between the top slats of the frame and the cover board.

9. Langstroth type hive is highly preferred according to TSE 3409 standards which is the most suitable for the methods and dimensions in beekeeping (Fig. 2.).

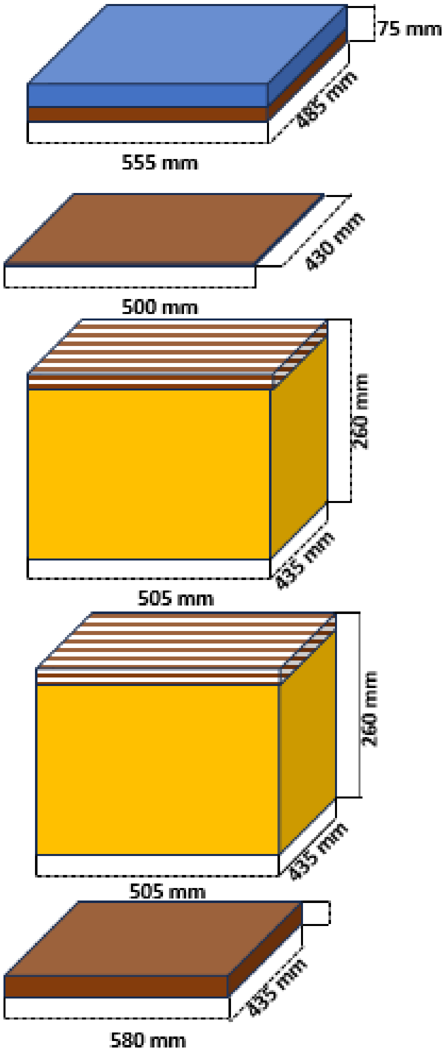

Fig. 2. Langstroth-type hive dimensions according to TSE 3409 standards.

4. Bee care

Beekeeping is one of the most common agricultural activities all over the world. The most important feature that distinguishes modern beekeeping from traditional beekeeping is that the bees can be easily fed when necessary. Feeding is done in the spring, when the bees start to come out of the hive, to encourage the queen to lay eggs. The queen laying as early and as many eggs as possible strengthens the colony. The queen's activity leads to an increase in yield during the honey collection season [20]. Autumn feeding is to complete the winter food of the bees and again to encourage the queen to lay eggs and to ensure that the bees enter the winter with young and healthy bees. For this reason, it is necessary to check the bee's care and nutrition status frequently. In the spring season, the sherbet is prepared in the form of water with sugar at a ratio of 1:1. In the fall season, sugar is increased in a ratio of 1:2. For example, it is prepared as a ratio of 1 kilogram of sugar to 1 kilogram of water or a glass of sugar to a glass of water. If a spoonful of honey is added to the mixture while preparing sherbet, the tendency of bees to sherbet increases. It is possible to prepare this mixture with various ingredients. Sherbet is prepared with clean water, so first boil the water, and wait for the boiled water to cool down a little. Add sugar or honey to the water that is warm enough not to burn the finger. Stir until the sugar is completely dissolved and do not boil again after this stage. Sherbet boiled again will cause digestive tract disorders in bees. The syrup should be given in the afternoon when the weather is warm and should not be too hot or cold. There are various feeders for giving sherbet, and the amount of sherbet prepared is adjusted depending on the consumption power of the bees. However, if the beekeeper does not have a feeder box at hand, the alternative is to make a few small holes in the lid of a jar. The syrup is poured into the jar and the lid is tightly closed and placed over the feeding hole drilled on the lid. Another method is to pour the prepared syrup into the cells of the swollen comb. Care should be taken not to chill the bees in the honeycomb taken out and sherbetted, and to feed them without harming them. If for some reason the feeding of bees is forgotten, or if it is necessary to feed the bees at a time when the weather is not suitable; bee cake is a very easy method instead of sugar syrup. Because giving syrup when the hive is not opened and the bees cannot go out for food increases the possibility of diarrhea, pathogenicity, and dysentery in the colony [21], [22]. There are commercially available bee cakes, but there is also an easy recipe that anyone can prepare at home. Strained honey and powdered sugar are kneaded in a bowl to make bee cake. The cake kneaded until it reaches the consistency of dough is wrapped in a bag. Depending on the consumption power of the bees in the hive, the prepared cake is opened and placed in the feeding area. Alternative techniques are used in cake preparation according to the nutritional content of the bees. If we formulate them: 3 kg honey, 1 kg pollen, and 6 kg powdered sugar; 3 kg honey, 1 kg skim milk powder, 6 kg powdered sugar; 3 kg honey, 6 kg powdered sugar, 400 g skim milk powder, 20 g pollen or bee vitamin. With these methods, the bee care and feeding period is realized very easily and efficiently in line with the possibilities available.

5. Beekeeper calendar

For people interested in bee care and breeding, 4 main periods are very important. These periods can be classified as spring care, honey harvesting period, fall care, and finally wintering period. Problems that follow each other during the period can be faced with problems that reduce yield, damage the hive, and negatively affect the fight against external factors. Therefore, the goal of the modern beekeeper is to make the queen bee more effective and increase the number of worker bees in the hive until the honey harvest period [23]. When the total number of bees in the harvest season reaches around 80,000-100,000, the beekeeper will have reached the desired amount of honey. During this period, the beekeeper must fulfill his/her duties with care and experience, because if the number of healthy bees in the hive increases, the amount of nectar will increase at the same rate [24].

5.1. Spring Care

In the spring period, the care that the beekeeper will do on the hives has a great impact on the honey yield that year. The first thing a conscious beekeeper should do is to maximize the honey yield that year without neglecting spring maintenance. This period, which is defined by taking the days when the vegetation on the land is dense, covers 10-30 days on average. During the spring season, vegetation, climate, and geographical conditions affect the amount of nectar. Bees store the honey left over from their daily nectar needs for the hive in the hive during this season. The second work to be done in the apiary during this season is the precautions taken for winter. Also, during this period, it is to remove the items that will prevent the bees' nectar search and flight. If the hives are placed side by side and covered, it is necessary to arrange the hive positions according to the appropriate intervals given. If the hive entrance holes are closed, they should be opened, and bee dead and waste that block the flight holes should be cleaned. When we divide the beekeeper's calendar into seasons, the all-important honey-harvesting season covers a very small period [7].

5.2. First Care and External Intervention to Hives

Bees do not miss the opportunity to go out for excretion, especially during the warm and fertile days of spring. During this period when the flower population increases in the environment, they start to carry pollen to the hive. However, the cold at night and the increase in temperature during the day cause the bees to get sick frequently and the brood to get cold. For this reason, it is not right to open the hive until the weather is completely warm. In addition, opening the hive in cold weather makes the bees panic and irritable, and the decrease in the hive temperature increases the honey consumption of the bees. It is the healthiest method to detect the problem by intervening from the outside of the hive and observing the movements of the bees until the weather warms up during the period [25]. The following are the conditions to be observed when externally inspecting the beekeeper:

5.2.1. Efficiency of the queen

The presence or absence of the queen, which is vital for a hive, is very important. If the bees enter and leave the hive quickly on favorable days and seasons and bring nectar, this indicates the efficiency of the queen. However, if the bees are not carrying nectar and are hovering on the outer surface of the hive, the queen is most likely dead for the winter [26].

5.2.2. Food status

Checking the nutritional status, it is possible to tell from the wax residue on the bottom board of the hive that the nectar is rapidly depleting and the bees are starving. Also, if the lavra sacs have started to be expelled, this may be because the brood is cold or hungry. If there are a lot of dead bees being thrown out, it is an indication of a disease in the hive or that the food supply has reached a critical level. When food becomes scarce in the hive, older bees begin to commit suicide for the sake of the young bees and the health of the hive. This suicide takes place by clamping their heads in the comb chamber and suffocating. In addition, it is not correct to give sherbet to hives with critical nutritional status because the weather has not warmed up completely. It would be more appropriate to give solid feed to hives that need nutritional support. As described in the bee cake recipe, a mixture of powdered sugar and strained honey should be prepared and given from the feeding area. However, if there is no material for bee cake, glazes are taken from the honey frame from previous periods and left on the brood frames [27].

5.2.3. Hive population

It is possible to determine this number by monitoring the number of bees entering and leaving the hive. If worker bees enter and leave the hive one or two at a time, it indicates that the bee population in the hive is low and insufficient. But if the worker bee enters and leaves the hive 3-5 times in a healthy and lively way, it shows that the hive is strong. At the same time, in the evening, after the bees enter their nests when the hive is tapped lightly, strong hives react very quickly, and a strong buzz is emitted. Weak hives have a very weak buzz [28].

5.2.4. Disease status

It is possible to estimate whether the bees in the hive are diseased by observing the number of bees entering and leaving the hive. If there are more dead bees on the bottom board of the hive than expected and we know that the amount of food inside is sufficient, it is first thought that the bees are diseased. Therefore, Varroa disease is seen if wingless bees are hovering at the bottom of the hive or on the floor; Nosema disease is seen if there are small groups of bees on the floor and around the flight tray and the bees are not flying [29]. If the bees are carrying pupal-looking dead brood from the hive to the flight tray, they have Lime or Stone disease. In cases of various diseases like this, it is normal for the bees to have diarrhea for the first few days they are outside. However, if this period is prolonged and lasts for weeks, dysentery should be suspected if the flight tray and the front of the apiary are dirty [10]. During the external inspection, hives that are likely to be diseased or problematic should be marked, and when it is time for internal inspection, those hives should be serviced first. When the weather gets warmer and the temperature difference between day and night decreases, it is time for internal maintenance and inspection of the hives. It should be started in the early hours of a calm and sunny day that will not move the bees during maintenance [30]. During internal maintenance, it is necessary to perform the following operations first in order:

a) If the bees are irritable during the first maintenance, the bellows are lit and smoke is given appropriately without suffocating the hive. If the smoke is not given properly, it has the opposite effect on the bees and they become irritable and flighty. In the spring period, the insufficient amount of nectar in the field and the critical level of nutrients in the hive is also a state of stress for bees. Therefore, it is possible to see the bees irritable in the first phase of the internal examination. The bellows are lit and smoke is given 2-3 times in slow waves through the flying hole and after waiting for about 2 minutes, the noise starts to decrease. The condition of the bees is checked by opening the top cover, if necessary, smoke is given slowly several times from the edges of the cover. The top cover is not opened completely to prevent the brood from getting cold. However, if the top cover of the hive is in one piece, the maintenance should be completed as soon as possible and the top of the hive should not be left open. In addition, the top of the hive should be covered with a cloth opened as much as necessary, and move quickly [31].

b) The hive frames are checked one by one to check their condition. The frames should be kept in the hive to avoid the risk of the queen falling out and being damaged or destroyed. During this check, the number of eggs and lavra, the condition of the worker bees, and the amount of honey and pollen are reviewed. If there is a mix of lavra in different stages of growth in a frame, with occasional empty eyes, this indicates that the queen is aging and inefficient in the hive. It is normal to have brood in different lavra stages in the same frame. But a fertile queen lays eggs without any gaps between cells and it is possible to see the areas with brood in a strip. The appearance of the lavra in the different stages is uniform, not jumbled together. Bees stand in clusters, especially on cold winter days. For this reason, in the first days of the spring season, brood can be seen in the frames inside the hive where the bees are concentrated, and the number of bees and brood decreases as you move toward the edges. As the weather gets warmer and the bees start to spread in and around the hive, the number of broods starts to increase towards the frame [32].

To keep the temperature of the brood chamber constant, the frames that are not occupied by bees are taken out and the internal volume is reduced by placing a hive partition board. In the section without a partition board, straw, grass, rags, newspapers, etc. are filled with easily accessible, clean parts to provide insulation. At the same time, the top cover of the hive should be overhauled in such a way that the young do not catch cold. Honey frames left over from the previous period may have occupied too much space, leaving no space for the queen to lay eggs. These frames are removed and replaced by frames with fluffed and ready-made honeycomb. Because of the abundant nectar in the field, the bees store a lot of honey in the hive, so there may be no space left in the hive for the queen to lay eggs. In this case, the drone cells in the brood box should also be removed, and a fluffed honeycomb or ready-made honeycomb with female cells should be placed in that area [33], [34].

c) The condition of the queen in the hive should be reviewed. If the queen is present or not, if her wings are worn out, if she is old, if she is sick, or if her ability to lay eggs has decreased for some reason, she must be replaced with a new queen [35].

d) The honeycomb cell or hive is checked for diseases such as mold, honeycomb moth, foulbrood, and bee lice. Necessary measures must be taken for diseases that show symptoms in the hive. There are alternative treatment methods for all bee diseases in our country. Before using these medicines, it should be ensured that they are licensed and produced only for bees. It is necessary to use some protective medicines, vitamins, and support mixtures against disease during this period. It is necessary to make the relevant preventive and therapeutic medicines against diseases in the early spring when the bee population is low. because the risk of finding drug residue in the honey stored in the hive is minimized because the honey harvest has not yet started [36].

e) The physical structure of the hive should be reviewed. If there is a situation that will prevent the development of bees or offspring, the hive should be replaced. Hives that are thought to have problems should be removed from the apiary and necessary maintenance should be done. In addition, moldy, moth-eaten, and rusty hives are dried by placing them in the sun. Holes, cracks, and dismantled places on the hive should be repaired with new pieces of wood. Bee wastes on the surface of the hive should be scraped and cleaned completely and then disinfected with a blowtorch or by holding it over a burning fire at regular intervals. Hive painting should be repeated without neglect during this period [37].

f) In a hive with 10 frames during the brooding period, if 2 frames have a lot of bees, this family is weak. If the number of frames is 3-4 and the queen is old and sick, this is also effective in the weakness of the hive. However, if the hive has 3-4 frames and the queen is healthy, her activity in the hive is moderate. If the number of frames in the hive is more than 4 and the queen is hardworking, it can improve itself until the honey harvest season which is an indication that it will be a strong hive. If the number of bees and brood in the hive is low, this hive should be combined with another hive. 1 strong hive produces more honey than 10 weak hives. In hives with 3-4 frames and hard-working queens, it is necessary to supplement the young comb in other strong hives. In the hives, the frame with closed eyes should be removed from its place and the cells on it should be cleaned and placed in the place to be strengthened [38].

g) For hives whose nutritional status has reached a critical level, supplements should be fed from outside. This process can also be repeated to encourage the queen to lay eggs. On days when the weather is cold and opening a hive is risky, it can be supported with various products, but after the weather warms up, sherbet can be given easily. Bees usually prepare themselves for the cold winter settings and start to die out in the spring when the weather starts to warm up. This is because bees are dormant during winter and consume very little food. But as the weather warms up, the bees become active and their food consumption is very fast. Since the flower population is high in the field, the hive that is left without food during this period is doomed to die. To prevent this situation, the nutritional status of the hives should be checked and bee activity should be increased [39]. If there are honeyed and glazed frames in the hive, it is necessary to encourage the bees by scratching over the glaze to make it easier for the bees to feed. If there is not enough food for the bees and they are weak from hunger, they will probably not eat the prepared syrup. In such cases, warm syrup is immediately prepared and sprayed into the hive without harming the bees and without getting them wet. This process saves the hive from extinction by directing the bees, which are revived during the period, towards more sherbet [40].

h) If there is no natural water source close to the apiary, the water source for the bees must be clean, clear, and changed daily [41].

6. Swarm of bees

A population of bees living in colonies can reproduce again in colonies by splitting into hives with the queen. This division of hives is called swarming. The new population that leaves the hive is called swarming bees. The swarming season is one of the most busy periods for the beekeeper. During this season, the hives should be well maintained and the apiary should be monitored and kept under control at certain times of the day [42]. This phenomenon is very common when the season and the flower population are very diverse. In the spring, the bees, whose numbers are increasing and no longer fit in the hive, begin to prepare for swarming. The swarming season covers the period from the beginning of May to mid-June. The beginning and end of the swarming period varies according to climate, vegetation, and geographical conditions. The swarming season ends with the start of the major honey collection season when pollen levels are at their highest. The most obvious indication that the colony is ready for swarming is the appearance of queen udders on the hive frames. Normally there is only one queen in each hive and when a second queen is encountered, war between colonies begins. The queen in the hive cannot even tolerate the new queen udders carried by the worker bees and tries to damage them. However, during the swarming season, the queen is needed for the new hive. In this case, the worker bees place queen cells in the form of thimbles on the bottom of the combs to produce new queens and prevent the queen from damaging the cells [43]. When the queen meets the young queen, the worker bees do not allow them to fight. Angered by this, the queen stops laying eggs and feeding and becomes weak and ready to fly. One day when the weather is favorable, she leaves the hive with a few worker bees. The queen settles on a suitable tree branch in the vicinity and puts the worker bees on top of each other to form a cluster. The swarm-shaped swarm bees are duly removed by the beekeeper and placed in the new hive [44]. In this way, when the season is favorable, swarming can occur up to the second, third, or even sixth hive. However, each swarm means that the hive population decreases and hive strength decreases. The beekeeper who wants to keep the honey yield high has to prevent natural bee emergence or should not allow swarming after the first swarm. Because as the number of swarming hives increases, the swarm population leaving decreases. The last swarms cannot prepare themselves for winter and the beekeeper has to take care of them. Since the mother of the first swarm to leave the hive is fertilized, she can start laying eggs immediately. However, in later swarms, the young queen is not fertilized and leaves the hive 5-6 days after birth to be fertilized [45]. Although modern beekeeping techniques are contrary to natural methods of swarming, sometimes this cannot be avoided. Swarming bees usually leave the hive between 9 and 12 o'clock. The first swarms to leave the hive cannot fly very far because the queen is old, so they land near the apiary and in low places. The second, third, and later swarms tend to fly farther and land in high places because the queen is young. Sometimes these swarms do not even land near the hive but tend to nest further away directly. Various methods are possible to get the bees to land when swarming starts. It is therefore necessary to prepare the hive where you intend to place the swarm in advance so that the bees can live in it in a healthy way [46]. If possible, 1-2 frames should be preferred in the hive. A gap of 2 cm should be left between the raised combs, and if honey or sugar syrup is applied to the comb, it will be easier for the bee to enter the hive and accept the hive as a nest. The swarming hive should always be kept high above the ground, and if possible, it should be covered to keep it cool. In addition, when the bees leave the hive to swarm, their guts are full of honey, so swarming bees are calm and not easily harmed [47].

7. Honey period and harvest

Honey is 'the collection by honey bees of the sweet substances found in plant flowers, flower essences or living parts of plants and secreted by insects in the flower. The collected nectar is separated into its components in the digestive systems of the bees and stored in the honeycomb cells and is defined as a matured, sweet product with consistency [48]. Honey contains about 200 different components. The chemistry of honey and the amount of nectar varies depending on the botanical source. But honey is mainly composed of 82% carbohydrates, 17% water, 0.7% minerals, 0.3% protein, vitamins, organic acids, and free amino acids [49]. The amount of water in honey varies according to the maturity of the honey. Normally, mature honey should contain 17% water content. The high-water content in honey causes it to spoil more easily. Honey contains approximately 15 types of sugars depending on the source from which it is obtained, and the enzyme activities secreted by the glands of the bees to convert the honeydew into honey. However, fructose (levulose) and glucose (dextrose) constitute the majority of these 15 types of sugar. The total sugar content of honey is approximately 80% [50]. Besides sugar and water, honey contains valuable minerals such as iron, copper, potassium, calcium, magnesium, phosphorus, silicon, aluminum, chromium, nickel, and cobalt. Secretory honeys are richer in mineral content. They can be used for therapeutic purposes due to their high mineral content, but they may also be preferred by some consumers because they are not crystallized. In addition, honey may contain vitamins B, C, E, and K depending on the amount obtained and the amount and type of pollen it contains. Amino acids, which are the building blocks of proteins, are found in very low amounts in honey. However, 17 different amino acids have been identified in honey. Acids are the substance that gives honey its unique odor. It also ensures that honey has an acidic structure [51]. The pH value of honey varies between 3.4 and 6.1 depending on the ambient conditions, but the general average is 3.9. Some of the enzymes in honey are obtained from plants and some from glands. Enzymes are among the most valuable substances that play an active role in the formation and storage of honey. The amount of enzymes in natural and non-heat-treated honey is quite high, such honey meets quality standards [52]. There are losses in enzyme value in heat-treated honey. Honey is a very important food that is easy to digest, nutritious, and has protective and therapeutic properties against many disease-causing factors through vitamins, minerals, organic acids, amino acids, and enzymes. Honey is classified in three ways according to production, marketing, or source. It can be classified as strained and honeycombed according to its production and marketing method and as flower and secretion honey according to its source. Flower honey is a type of honey produced by bees by collecting the nectar secreted from the nectar glands in the flowers of plants and in some cases in the petioles and stems of cherries, broad beans, cotton, and peaches. Glandular honey is a honey derivative created by bees by collecting the secretions secreted by insects living on forest trees such as pine, oak, beech, spruce, etc. The type of honey produced in our country is pine honey [53], [54]. Honeycomb honey is a type of honey made by honeybees for incubation purposes, hexagonal in shape, produced only from beeswax, and stored on a frame. Strained honey is another type of honey obtained by separating the honey from the honeycomb using straining machines. Honey harvesting should be carried out towards the end of the honey collection season before the end of the summer period before the amount of nectar in the field is exhausted. In honey harvesting after the nectar flow has stopped, the bees become very angry and aggressive, this is due to the psychology of looting the hive. Before harvesting, the beekeeper must make all preparations to avoid problems [55]. The first preparation is to prepare the environment where the honey will be placed. This area should be an environment where the beekeeper can work comfortably. In addition, all precautions should be taken to prevent bees from entering the room. The second stage of preparation is the beekeeper's self-preparation. A mask and clean overalls suitable for the apiary should be worn. In particular, to prevent bees from entering the overalls, the feet should be tied with a bag and tied with a rubber band [56]. The beekeeper should review all his equipment. He should prepare gloves, brushes, hand irons, bellows, a stand where he can put honey supplements, and a large white cover in front of the hive to be used during shaking [57]. Honey harvesting is started early in the morning to avoid the danger of marauders. On cool and cloudy days, the bees will swarm in the brood and the number of bees in the honeycombs will be minimal [58]. Therefore, the bees must be removed from the frame, for which 4 methods are used.

7.1.1. Shaking and spraying method

It is a method frequently used by beekeepers who do not have many hives. The biggest disadvantage of the shaking method, which is clean, healthy, and additive-free, is that the bees become irritable and injured. A stand on which we will put the honey we separate from the hive body is placed next to the hive we will harvest. From the duly lit bellows, smoke should be given in slow waves 2-3 times on the edge of the hive cover board. The honey bees are separated from the brood with the help of a hand iron taken on the table and covered immediately. The brooder is also covered with the cover board. At this stage, it is divided into two shaking methods. The first one is to shake the bees in front of the hive, for this a white cover is laid in front of the hive to cover the flying board. The shaken bees are directed towards the hive by blowing smoke with a bellows. The second method of shaking is to cover the brood box with the cover board but leave a hole through which the bees are directed up and down. This prevents the bees in the brood from being disturbed during harvesting and becoming irritable. A framed honey pot with 4-5 empty combs is added to the brood box and covered with a wet cloth. Bees are prevented from flying by half-opening the top honeycomb cover, shaking it on the cover, and occasionally running a bellow over the honeycomb. Some beekeepers take the frames with honey directly without taking the honeycomb on the brood and try to shake the bees into the honeycomb. This is a very inconvenient method. Because the bee that is shaken into the honeycomb is shaken again with the second frame just when it is trying to be removed. If the bee is shaken more than once, it becomes irritable and quite aggressive, which makes harvesting difficult [59]. For this reason, the most accurate method in the shaking technique is to hold the frame by both ends and make a quick downward shaking motion, or to hold the frame by one side and hit hard on the hand holding the frame with the free hand to make the bees fall. The beekeeper sweeps away the few bees remaining on the frame with a brush. The beekeeper needs support at this stage. He hands the frame to the assistant, and it is placed in a box prepared for filtering and immediately covered with a wet cloth. In this way, the harvest is done quickly. During the process, the beekeeper must be careful not to smear the honey around and not to harm the bees. Contaminated honey will cause a marauding invasion in the hive. The harvested hive is quickly covered and the same process steps are repeated in the second hive [60].

7.1.2. Bee Escape Method

In this method, a bee-evading device is mounted in the center of the cover board and placed between the brood box and the honey pot. Bees can go down to the brood box with the bee-escaping device, but they cannot go up. Thus, within 2-3 days the bees leave the honeycomb, and the honey frames can be harvested easily. For this method to be applied in the hive healthily, there should be no brood in the honeycomb because the honeycomb will be full. After all, the keeper bees cannot go down. The disadvantage of this method is that in very hot weather the bees cannot go up to provide ventilation in the hive and the honey in the honeycomb starts to melt [61].

7.1.3. Chemical Substance Methot

With this method, very large commercial products are used in apiaries abroad. For products that bees do not like the smell of, it is applied to the hive with a special device under the lid. Bees leave the honeycomb at certain intervals and go down to the brood chamber. When the chemical materials used in this method pose a risk to human and bee health, it is necessary to pay attention to legal regulations for the use of appropriate techniques [62].

7.1.4. Air Blowing Method

This method is based on the principle of removing the bees from the frames by blowing air with pressure. A stand with an open bottom is placed in front of the hive. A wide cloth is stretched between the hive flying table and the stand or a ramp is placed in the flying hole for the bees to climb easily. The honey pot is placed on the stand and pressurized air is sprayed into the frame gaps. The bees falling on the cover with the pressure of the air are guided away from the frame by the bellow's smoke. The honey pot emptied from the hive is removed from the apiary very quickly by covering the top and bottom. Various models of air-blowing tools developed for this process are available for sale [63].

7.2. Straining honey

For honey straining, the temperature should be 25-30 °C to ensure the fluidity of the honey, ease of straining, and room temperature. The glazes on the honeycombs of the frame to be filtered should be removed with a glaze knife or glaze comb. The glazed frame is placed in a centrifuge (honey filtering) machine rotated manually or electrically and the honey is filtered. To clean the remaining honey contaminants from the combs, the frames with the drained honey are placed in the brooder in the evening and cleaned by the bees. This cleaning process must be done early in the day to avoid marauding bees. The clean and usable frames can be placed back into the hive in the spring [64]. Against the honeycomb moth, honeycombs can be suspended and fumigated by burning powdered sulfur in a fire, charcoal, or electric stove. However, the moth eggs in the combs may not die during this application, so the process can be repeated several times at intervals of 2-3 weeks. If the combs are to be used again, the risk of disease can be high. This is why in some countries honeycombs are only allowed to be used for one year. For this reason, mothballs should never be used to preserve frames. Naphthalene, a petroleum product, is a carcinogenic substance and its residues in honey and beeswax are very dangerous for human health. If too many chemicals are used, the honeycombs should be melted into wax and removed. In addition, the honey removed from the filtering machine is passed through a multilayer sieve to remove wax crumbs and foreign substances. However, small particles and air bubbles in the honey will cloud the color of the honey [65]. For this reason, the honey is placed in a resting tank and allowed to rest. The small wax residues and air bubbles are collected at the top in the form of foam. The foamy part is stored separately as feed for the bees or for making vinegar and liqueur. When the honey has settled and clarified in the resting tank, it is packaged. As honey contains different building materials, it undergoes constant structural changes even during packaging. These changes are usually due to crystallization, darkening of color, increase in acidity, and increase or decrease in the types of sugars in the honey. In addition, increasing the storage time of honey or heating increases the HMF (hydroxymethyl furfural) value [66]. It is important to know that crystallization of honey starts at 5-7°C and deterioration starts at 10°C, so strained honey should be stored below 5°C if it is not heated. For crystallized honey to return to its original state, the honey pot should be dissolved in a container of hot water to dissolve the honey [67]. The honey pot should never be melted directly over a fire. Honey dissolved in this way will crystallize again. The beekeeper should therefore safely filter the honey from the hive through the frame and store it according to the information he has learned [59].

8. Bee products

8.1. Pollen

Pollen is the name given to the plant dust sac in the head of the male reproductive organs of plants, which contains the genetic characteristics of the plant [64]. In addition to containing high amounts of protein and carbohydrate sources, it is a rich source of vitamins and minerals. Vitamins contained in pollen; It contains vitamins such as provitamin A, vitamin B1, vitamin B2, vitamin B3, vitamin B5, vitamin B5, vitamin B6, vitamin B12, vitamin C-D, and vitamin E. As minerals, they contain calcium, phosphorus, iron, copper, potassium, magnesium, sulfur, sodium, and iodine minerals [65]**.** Pollen is collected by pollen trapping, which is an important part of the hive. Pollen traps, which are located at the entrance of the hive and are only large enough for bees to pass through, collect the pollen carried by the bees during the passage of each bee and allow it to accumulate in the pollen trap chamber. The pollen accumulated in the hopper is collected at 1-2 day intervals. It is dried in drying tanks at a temperature not exceeding 42◦C. This method reduces the water content of pollen by 7%-8 [66]. Pollen with reduced water content is cleaned by sieving, packaged in an airtight container, and stored in a cold environment. Pollen that has been cleaned and needs to be stored for a long time can be fumigated with CO2 gas. In addition to honey production, pollen can also be used for colony feeding when necessary. Pollen can technically be dried in drying cabinets, but it can also be simply dried in an airy and shady place out of direct sunlight. As mentioned before, pollen is a natural nutrient that contains amino acids, vitamins, and minerals that are important for the growth and development of living things [67]. Thanks to these substances, it is of great importance in human health and nutrition and in maintaining general body resistance. Pollen should be collected in the morning on an empty stomach, at least half an hour before breakfast, 4 hours after dinner, 4 hours after dinner, or before going to bed with warm milk, fruit juices, or plain. The daily dose of pollen in the human body is 15-40 g for adults, 10-15 g for children aged 6-12 years, and 5-15 g for children aged 3-5 years. In addition to being a very useful bee product, pollen plays an active role in increasing mental and physical activities, eliminating anemia, liver and prostate diseases as well as various diseases such as cancer [68], [69].

8.2. Beeswax

Beeswax is a liquid secreted by the wax glands in the last 4 pairs of abdominal rings of young worker bees. As it comes out of the rings, it solidifies after contact with air and is white at the moment of secretion, darkening as time passes [70]. Since beeswax is an apolar product, it is not soluble in water as it is soluble in various alcohols. The chemical structure of beeswax contains 72% alkali esters, 14% free fatty acids, 11% hydrocarbons, 1% free alcohol, and 2% unknown substances. The melting temperature of beeswax is between 62-65◦C and its density is 0.95. Since the density of beeswax is lower than the density of water, it does not dissolve in water and starts to dissolve in alcohol [66]. Beeswax can then be obtained by removing the wax layer that forms on the surface of the water when left to rest. In addition to this process, solar melting pots can also be used. In ancient times, beeswax was used in embalming, to prevent the sarcophagus lids from breathing, and as an adhesive agent [71]. Bees synthesize wax by eating honey and from the carbohydrates contained in the honey they eat. After consuming honey, bees secrete wax in the form of a chain-like cluster at 35◦C. The wax flake from the abdominal rings is transferred to the chin with the help of the feet. The wax transferred to the jaws is processed and used in honeycombing and honeycomb making. In addition to these, it is largely used in industrial areas, honeycomb making, cosmetics, decoration, the pharmaceutical industry, and the health sector [72].

8.3. Propolis

Propolis is a sticky substance collected from plants by bees. While propolis has a hard and brittle structure at 15 ◦C, it can turn into a soft, pliable structure at 30◦C. Depending on the source from which it is obtained, it has colors ranging from black to yellow. The components in the structure of raw propolis vary according to the source from which it is obtained. However, it usually contains 50%-55% resin and balsam, 20%-35% plant-derived waxes, 10%-15% ethereal and essential oils, 2%-5% pollen, and small amounts of organic and inorganic compounds. According to other sources, propolis contains 46% balsam, 27% wax of plant origin, and 15% flavones and flavonoids. In addition, flavones and flavonoids are substances that give propolis antifungal, antiviral, and antibacterial properties [73]. Honey bees therefore open and collect propolis, the protective resins of the plants, with their lower jaws. They soften it in their mouths, add various enzymes, and turn it into pellets for the hive. They carry the pellet using their front legs and place it in a pollen basket on their hind legs [74]. Bees accumulate propolis in parts of the hive such as the bottom board, frame edges, and behind the entrance hole. Since propolis is a sticky material, collection is done by scraping. After this process, propolis may not be clean and may contain various residues. After being cleaned from waste materials, the harvested raw propolis is brought to the laboratory, and 'Soft Propolis Extract' is produced. Propolis is used by bees to close cracks and open parts in the hive, to prevent the pests that enter the colony and cannot be thrown out of the colony from smelling by mummifying them through propolis, to polish and polish the honeycombs, to sterilize the hive, and as a raw material for medicine in various fields [75]. Propolis therefore has antibacterial, antifungal, antiviral, and anesthetic effects. It is used commercially to make medicines, lozenges, tablets, creams, and solutions. Propolis helps in the destruction of tumor and cancer cells, in the treatment of inflammation of the large intestine, in the treatment of wounds in the mouth caused by chemotherapy, in the treatment of asthma, and in the cleaning of cell wastes in the body thanks to its antioxidant properties [76], [77].

8.4. Bee Venom

Bee venom is a product produced by the venom glands of worker bees and stored in venom bags. Bees in the egg stage have very little ability to produce venom. Bees reach their peak venom production capacity at 12 days of age. A worker bee produces around 0.3 mg of bee venom in its lifetime. At 20 days of age, they lose their ability to produce venom [78]. Overwintering bees cannot produce bee venom. Bee venom is rich in the polypeptide chemicals mellitin, and apamindin. Phospholipases, which are enzymes, are also present in bee venom at around 12% [79]. Therefore, bee venom has a chemically highly efficient structure. It contains substances that are very important and actively used in the field of pharmacology. For this reason, various methods of collecting bee venom have been developed [80]. One of them is a glass plate apparatus placed in parallel with wires spaced 5-10 mm apart. This device is placed on the hive flight board or the bottom board of the hive. 12-volt current is applied to the porous plate, which creates a slight shock effect on the bees passing through contact. With the shock effect, the bees release their venom on the glass plate and do not die because they cannot pass through the glass plate by trying to prick their stingers. When the bees drop the liquid poison on the glass plate, it turns into crystalline, and the crystallized poison is collected with the help of a razor blade. Bee venom is used in the protection and defense of the colony against enemies and in the treatment of various diseases. The use of bee venom is more limited compared to other bee products, but it is sold as tablets in pharmacies in developed countries such as the USA and attracts great interest. Bee venom is a product that can be used in joint disorders such as rheumatism. This product is often used as an anti-inflammatory in flu infections, in the treatment of allergic diseases, and the treatment of diseases such as gout and asthma [81]. The American Apitherapy Association has reported that it is also used in eczema, tissue hardening, skin cancer, and scar removal. Bee venom is a highly preferred product in the treatment of epilepsy, some types of cancer, throat infections, migraines, cholesterol, sinusitis, and ulcers [82].

9. What to do with a bee sting and bee sting?

The stinger on the back of worker bees is the most effective weapon for self-defense. Although the bees' stinger is behind them, they can easily stab their enemy with their stinger in all kinds of defense. The bee stinger consists of two parts. The first part is the oval-shaped venom sac, which is connected to the intestines from the abdominal cavity. The second part is the stinger. On the stinger, 9 hook-shaped structures look like arrowheads. It is these hooks that prevent the bee from coming back out after sticking the stinger [83]. After stinging, the bees inject the venom stored in the venom sac into the enemy's body and the enemy feels great pain. In addition to the stinger, which it cannot remove because of the hooks, sometimes a part of its intestines also breaks off and remains where the stinger is stuck together with the venom sac. The life of the bee whose stinger remains stuck in the enemy's body ends within 1-2 days. For this reason, bees with the stinger stuck in the enemy become more aggressive and attack the enemy more. However, the bee with a stinger has no chance to sting again and after the bee stings, panic, and hand, arm, etc. movements should not be made. Such movements attract the attention of other bees and cause them to attack [84].

Bee venom has a distinctive odor, and the spread of this odor causes other bees to become irritable. Therefore, in case of a bee sting, the sting should be washed. When removing the bee stinger from the sting site, it should be removed by holding the venom sac. Because if the poison enters the body through the stinger, it causes increased pain. The danger of a bee sting depends on the person's constitution, allergies, or the number of stinging bees [85]. In the case of a bee sting where a person is allergic to bee stings; redness, itching, and swelling are seen throughout the body. In addition, there are symptoms such as breathing difficulties, abdominal pain, vomiting, and heart palpitations. In addition, as the throat muscles contract and the pharynx swells, breathing becomes increasingly difficult and the patient may suffocate [86]. The most effective alternative and fast medicine method against bee stings is cleaning with ammonia. It can be applied to the place where the bee stings, as well as 5-10 drops in a glass of water. It is not correct to rub or suck where the bee stings. Putting ice on the sting, applying yogurt, or drinking buttermilk contributes to the reduction of pain [87].

10. Conclusion

Beekeeping is a branch of agriculture where products such as honey, beeswax, pollen, propolis, and bee venom are produced with traditional and modern methods from the past to the present. It has become a very popular profession in our country and developed countries. Bees contribute not only to crop production but also to pollination and fertilization factors of plants in the ecosystem. For this reason, bees are one of the living groups that play an active role in natural selection and have a high risk of contamination. To prevent this risk of contamination and to approach the hive with the right techniques and methods, it is necessary to acquire basic information. It is not correct to learn basic information about beekeeping from hearsay and wrong sources, it is better to learn from people who have done this job and have experience or from current sources that have a command of the literature. Bee diseases in the hive, parasites, queen use, nutritional status, and colony management are the main causes of bee losses. Therefore, unconscious use of pesticides; hive sizes and spacing; location of the hive and care of the bees; water, air, and environmental pollution should be taken into consideration.

This study focuses on the importance of beekeeping in our lives, how to start beekeeping, and how to care for bees and bee products. While dealing with beekeeping, it is discussed how the correct bee breeding should be based on the literature. In this way, certain problems have been overcome. We believe that it will guide the way for future bee studies.

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