Engineering and Technology Journal
Journal homepage: engtechjournal.org

Effect of Adding TiO_2 on Some Mechanical Properties of Galloy

Osamah A. Khadhair [a], Rana A. Anaee [b*], Kadhum M. Shabeeb [c]

[a] Al-Furat Al-Awsat Technical University, Kufa, Iraq, okudair@atu.edu.iq

[b] Materials Engineering Depart., University of Technology, Baghdad, Iraq, 130033@uotechnology.edu.iq

[c] Materials Engineering Depart., University of Technology, Baghdad, Iraq, 130121@uotechnology.edu.iq

* Corresponding author.

Submitted: 29/11/2019 Accepted: 08/01/2020 Published: 25/05/2021

K E Y W O R D S

Galloy; Amalgam; Dental alloy; TiO_2; Corrosion behavior; Mechanical properties.

A B S T R A C T

Because of importance the Ga alloys in dental applications, many attempts were done to improve the properties of this alloy. The current work involves addition of TiO_2 nanotube powder to Galloy to improve some mechanical properties. These properties included hardness, compression, and creep. The characterization of prepared TiO_2/Galloys with five wt% of TiO_2 (1, 2, 3, 4, and 5 wt%) was done by XRD and SEM/EDS. The results showed that the hardness, compression, were increased with increasing percentage of added TiO_2, while creep decrease. Some phases such as β-Sn, Ag_2Ga and Ag_9In_4 were contributed to improve the properties of new TiO_2/Galloy composites.

How to cite this article: O. A. Khadhair, R. A. Anaee, and K. M. Shabeeb, "Effect of adding TiO_2 on some mechanical properties of galloy", Engineering and Technology Journal, Vol. 39, No. 05, pp. 695-702, 2021.
DOI: https://doi.org/10.30684/etj.v39i5A.1395
This is an open access article under the CC BY 4.0 license http://creativecommons.org/licenses/by/4.0

1. INTRODUCTION

Dental amalgam fillings are widely used all over the world, and they consist of a silver alloy and mercury. The Ag alloy contains a fine powder of Ag, Cu, Sn and sometimes Pd, Zn or In [1,2]. Mercury is a liquid metal at room temperature and has a toxicity which concerned regarding the use of dental amalgam. Amalgam is still a preferred material where strength is the requirement for material selection. Hence, a need for metallic alternative for amalgam led to the development of Gallium alloy [3]. As a result, introduction of Gallium based alloys have been occurred as mercury free amalgam which was suggested by Puttkamer as long ago as 1928 [4,5], through mixing Ga liquid instead of Hg in amalgam alloy powder. Many authors highlighted on Ga alloy for dental applications [6,7], but Galloy had some defects such as surface roughness, marked discoloration and marginal breakdown, in addition to defects associated with corrosion, the setting expansion which was much greater than that exhibited by silver amalgam[8,9]. Also, high frequency of cracking of teeth restored with this alloy[10,11]. Therefore, and many attempts have been done to improve this alloy by adding some additives and surface treatments.
The present work aims to improve some mechanical properties of Galloy by adding TiO_2 nanopowder with five percent (1, 2, 3, 4 and 5 wt%) to investigate the hardness, compression, and creep.

2. EXPERIMENTAL WORK

I. Materials

The elements and materials used in this work are Gallium, Indium, Tin, and TiO_2. Ga, In and Sn used for the preparation of the liquid alloy. A standard amalgam alloy composed of (Ag, Cu, and Sn) used as powder alloy that mixed with liquid alloy. All elements used in this work with high purity obtained from different origins as shown in Table I.

Liquid alloy was prepared by alloying Gallium, Indium and Tin together at 230 ^oC until all the elements be liquid and let it cool down to room temperature, the weight percentages of Ga, In and Sn were (64, 24, and 12 wt.%) respectively and the melting point of obtained eutectic alloy is -19 ^oC.

Table I: Materials used in this work.

Material	Purity %	Origin
Ga	100	Changing galaxy international trade., LTD
TiO_2	100	Changing galaxy international trade., LTD
In	100	Changing galaxy international trade., LTD
Sn	100	Changing galaxy international trade., LTD
ardent	A mixture of irregular (atomized)and lathe cut particles (44.5%Ag, 30%Sn, and 25.5%Cu)	Arlandastad, Sweden

II. Preparation of Base Alloy

The preparation of specimens were done according to the ADA specification No.1 [12] by trituration 1:0.5 g of powder alloy and liquid alloy respectively for preparation fills by amalgamator type (YDM-Pro), the trituration time is 8 seconds. Specimen dimensions were 6mm in diameter and 12mm in height as cylindrical shape. For specimen preparation, a Teflon mold was used and after the trituration, the fill paste was immediately put in the hole of the die by using a special instrument with the diameter 2.5mm called condenser, and then it was compressed into the die by 14 MPa for 85 seconds according to ADA specification No.1 [13-15]. Figure 1 illustrate the used mold and prepared specimens.

Figure 1: The used mold and prepared specimens

III. Characterization

The characterization of prepared specimens was done by:

1. X - Ray Diffraction

The X - ray diffraction analysis was performed on amalgam powder, base Galloy, 5% TiO_2/Galloy with X-ray machine (SHIMADZU LabX XRD-6000,) with copper Kα radiation at λ = 1.5406 Ao and a nickel filter. The range of the diffraction angle 2θº was (20º-90º).

2. Scanning Electron Microscopy (SEM)

SEM with high energy beam generated a verity of singles at the surface of solid specimen was used. This test was carried out using SEM type MIRA3 TESCAN. This test was done for base alloy and 5% TiO_2/Galloy.

IV. Mechanical Properties

1. Hardness test

Vickers microhardness test was done by a digital microhardness tester (Type TH715, Beijing, Time High Technology Ltd) with a static load of 200 g for 10 seconds at two different time intervals (1 day) and (7 days) after the trituration. Three recorders were measured at diagonal distribution across the specimen. The dimensions of the indentation are measured by the measuring microscope at 200× magnification.

2. Compressive Strength

The compressive strength was carried out using Instron machine, type Universal testing machine/WDW 200, with the speed of 0.5 mm/min. The specimen was vertically put between the jaws. The test was done after (1 day) and (7 days) after the trituration at temperature of 37±1 ºC.

3. Creep

This test was done at 37±1 ºC after (2 hours) and (45 min.) of trituration. And then the specimen was subjected to a constant axial pressure of 10 MPa and maintained for 21 hours. After that the shortening was obtained after measuring the length with micrometer caliper to calculate the percentage of creep according to A.D.A. Specification No.1 which allows the maximum of 3% creep[12]. The creep percent is calculated by the following formula [12]:

$$\text{Creep } (\%) = \frac{L_o - L}{L_o} \times 100 \qquad (1)$$

where: Lo is original length (mm) and L is final length (mm).

3. RESULTS AND DISCUSSION

I. Characterization

Figure 2 shows the XRD pattern of powder alloy which identify the phase exist in the standard amalgam powder. The Cu_3Sn phase and the Ag_3Sn phase at 2θ indicated in the Figure 2.

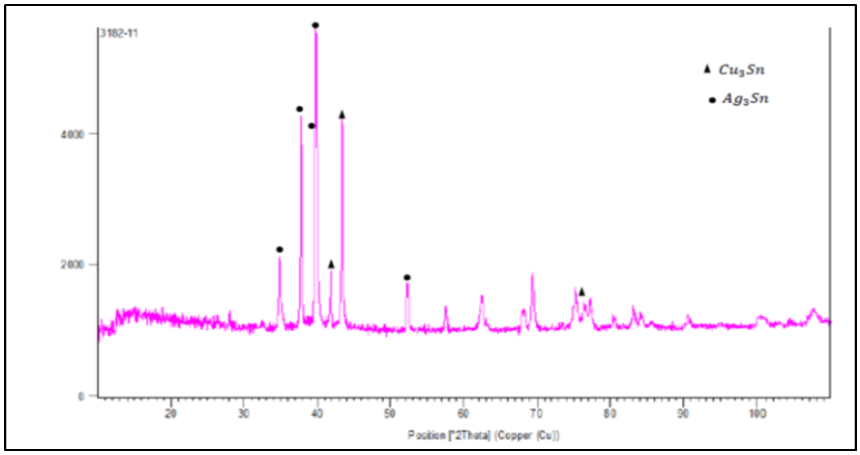

Figure 2: XRD analysis of standard amalgam powder.

Figure 3 shows the XRD pattern for base alloy (Ga alloy) where the formed phase are β-Sn, $CuGa_2$, $Ag_{72}Ga_{28}$, In_4Ag_9, Ag_3Sn and Cu_3Sn. All phases were interpreted according to the standard cards.

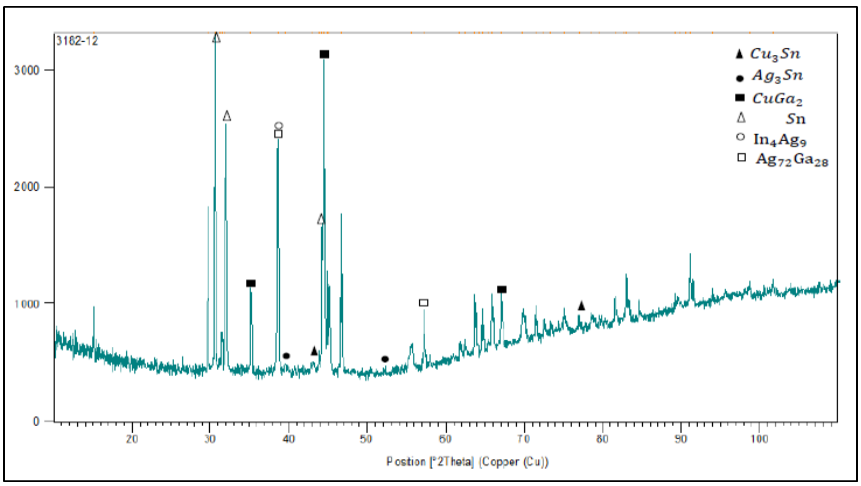

Figure 3: XRD analysis of base Galloy.

Figure 4 shows the XRD pattern of TiO_2 nanotube powder where the main peaks were at 2θ (10, 24.278, 28.382 and 48.441). This result is closely matched with observation of Odair P. Ferreira et al. where TiO_2 nanotube is prepared using different processing [18].

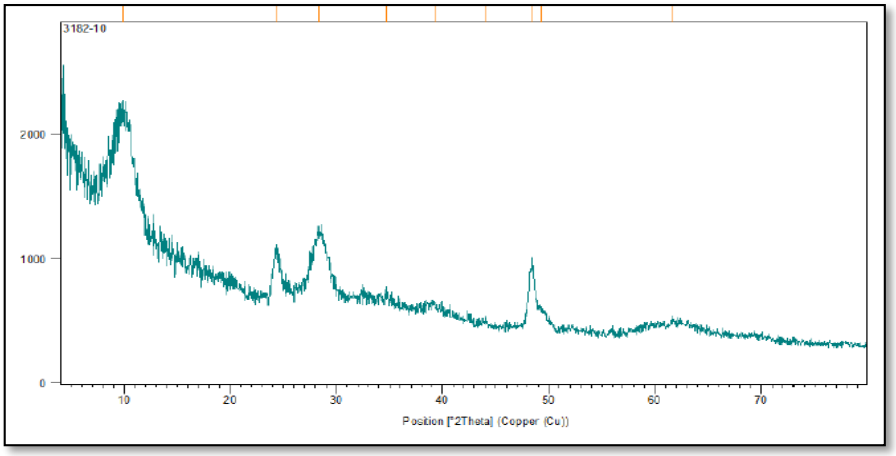

Figure 4: XRD analysis of TiO_2 nanotubes.

Figure 5 shows the XRD pattern of 5% TiO_2/Galloy. All the phases are the same in the based alloy in addition to presence of TiO_2 nanotube peaks that denoted in figure which has the main peaks located at 2θ (42.27, 82.382, and 48.441).

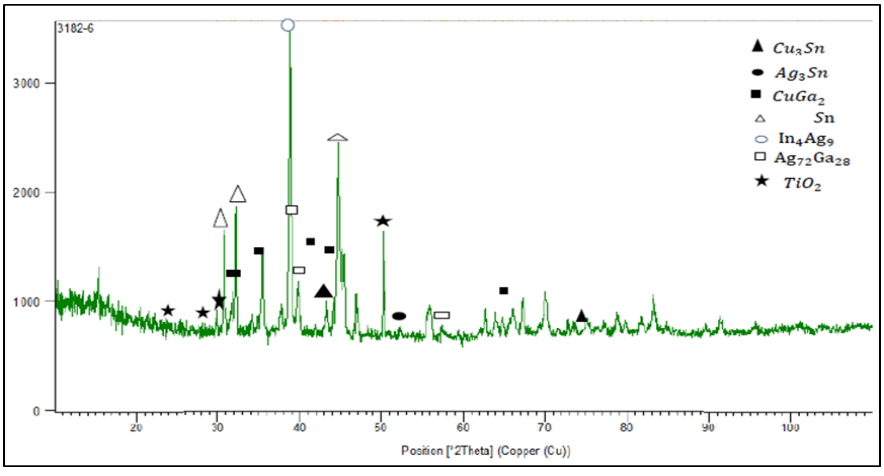

Figure 5: XRD analysis of 5% TiO_2/Ga alloy

The nanotube powder of TiO_2 have been examine by field emission scanning electron microscope (FESEM) to indicate the nanotube structure of the used powder as shown in Figure 6.

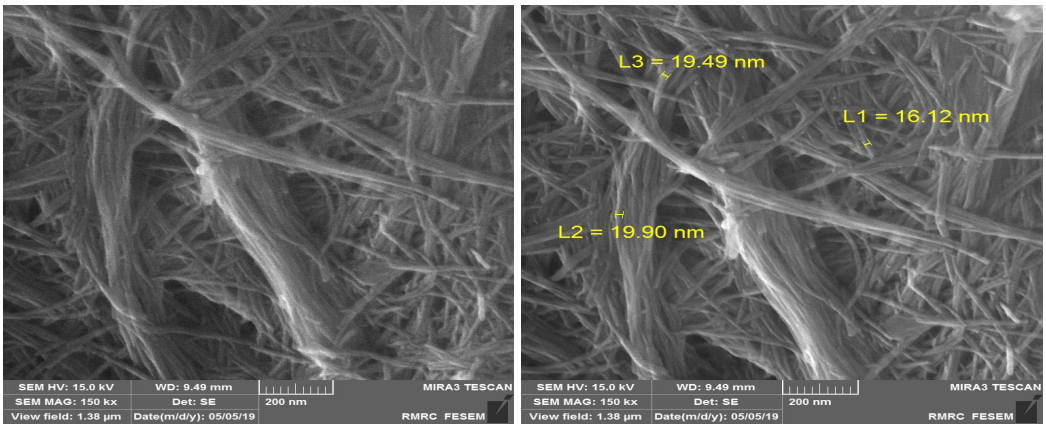

Figure 6: TiO_2 Nanotube structure.

The microstructure of the base alloy is observed in the Figure 7, the figure shows the unreacted cores of powder particles which consist of Cu + Sn + Ag surrounded by embedded zone within a complex matrix to produce $CuGa_2$. The core and the surrounding area denoted as A and C respectively and corresponding to the EDS test of the both region. The region B is referring to the matrix where it is consist of β-Sn and Ag_2Ga and Ag_9In_4, and the formed β-Sn is due to the following equation [19]:

$$Cu_3Sn + 6\ Ga \rightarrow 3\ CuGa_2 + \beta\text{-}Sn \qquad (2)$$

While the D region is consist of $CuGa_2$ phase, all the regions (A, B, C and D) are analyzed by EDS (Figure 8) which indicates the presented elements and their distribution in base alloy.

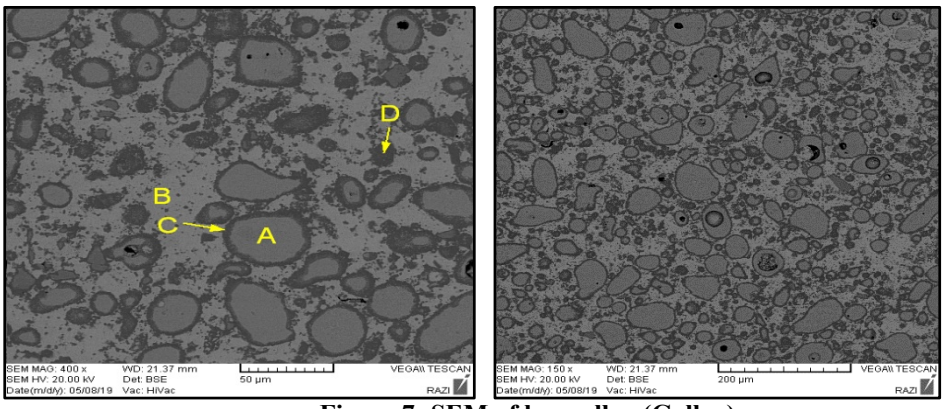

Figure 7: SEM of base alloy (Galloy).

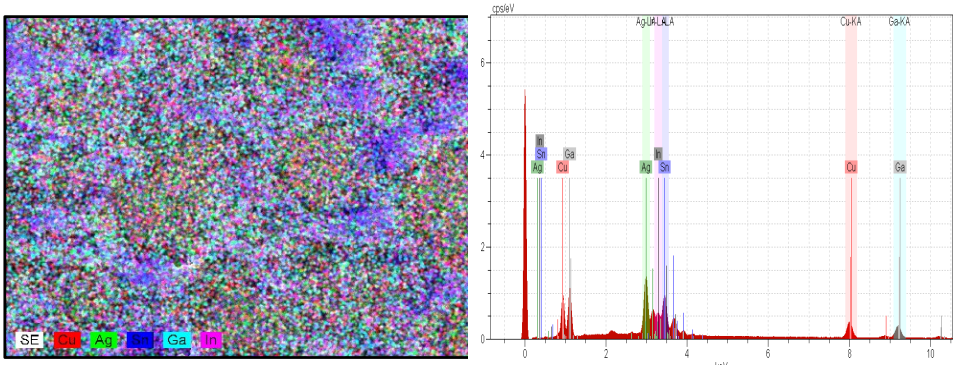

Figure 8: EDS of base alloy (Ga alloy).

Figure 9 shows the SEM images of 5% TiO_2/Ga alloy. The A region attributed to unreacted powder particles (Sn-Cu-Ag) and the surrounding area is the reaction zone consist of $CuGa_2$ phase of the base

alloy. The B region is consisting of TiO_2 nanotubes as it clear with EDS analysis Figure 10. The other phases are the same as that observed in the base alloy and that confirmed by XRD test result.

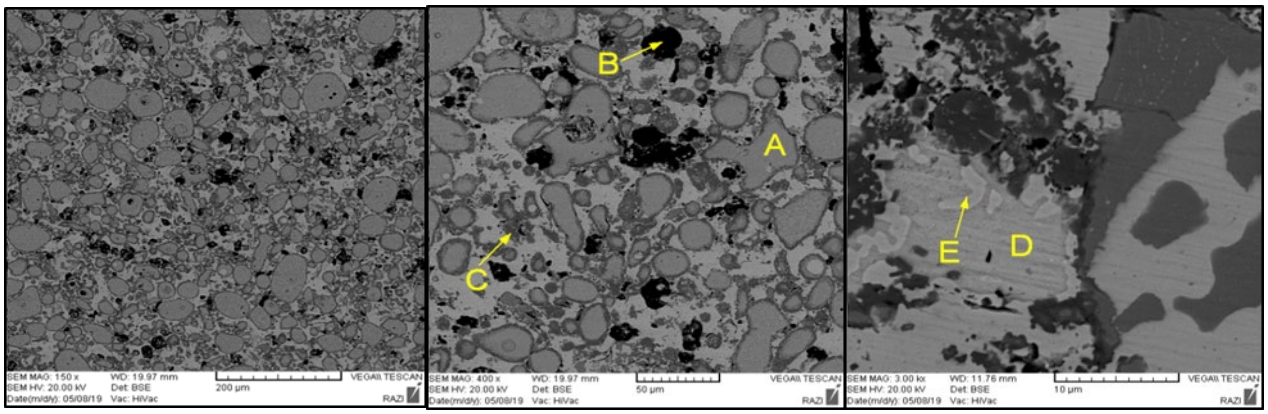

Figure 9: SEM images of 5% TiO2/Ga alloy.

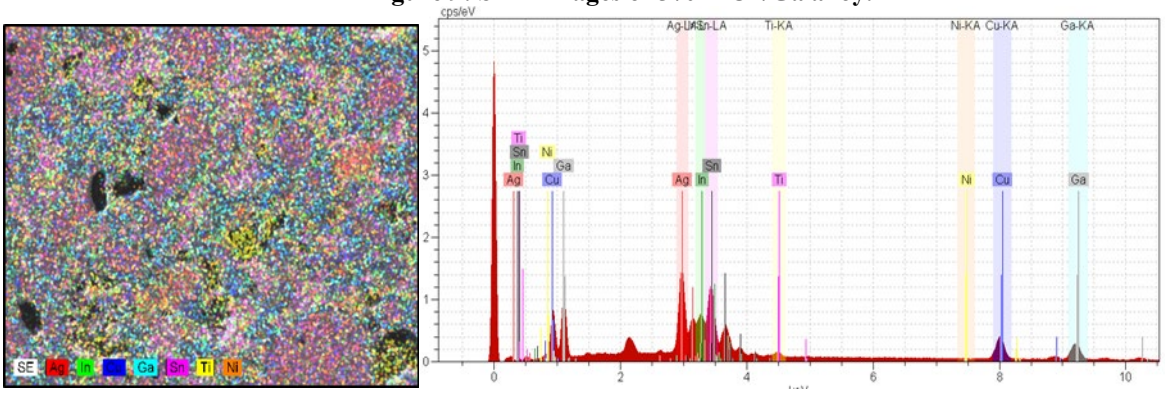

Figure 10: EDS images of 5% TiO_2/Ga alloy.

II. Microhardness

The microhardness test has been done for prepared specimens of Galloy with additions of different percentages of TiO_2. The microhardness was determined after 1 and 7 days as shown in Figure 11. The behavior shown in this figure indicates that the microhardness increased with increasing weight percent of additive compared with the base alloy without addition due to their structure as nanotube through the filling of the vacancies and increases the coherent and bounding between the components [20]. Generally, addition of metal oxides increases the hardness as shown by Neorhana et al. who used Al_2O_3 and ZnO nanoparticles to enhance hardness and other mechanical properties of dental filling [21].

The data of microhardness indicate that the hardness increased after 7 days compared with the values after 1 day because of the setting reaction doesn't complete immediately and some liquid alloy found and that will weaken the alloy, so after 7 days the setting reaction is complete and the alloy reach to its final strength.

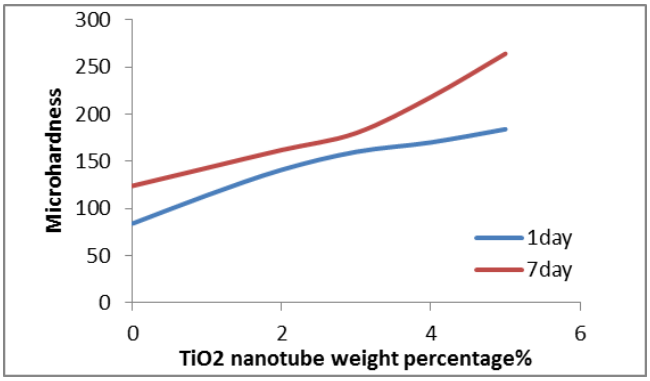

Figure 11: Microhardness of Galloy reinforced by TiO_2 nanotube

III. Compressive Strength

The strength of a dental filling restoration must be high enough to resist the biting force especially compressive force. The produced specimens were tested after (1 day) and (7 days) and there is a high increase in the compressive strength after 7 days in the comparison with 1 day because the setting reaction is not complete at 1 day as shown in Figure 12. The TiO_2 led to increasing compressive strength of base alloy and the strength increases with increasing weight percent from 1 to 5 wt%. The increased compression after adding TiO_2 nanotube of dental amalgam has been reported in previous studies, for instance, the researchers found that dental amalgams containing admixed or noble metals have higher compressive strength [21]. Also the good reinforcement with TiO_2 nanotube attributed to the good interfacial bonding between nanotubes and Galloy as well as the uniform distribution of TiO_2 nanotube.

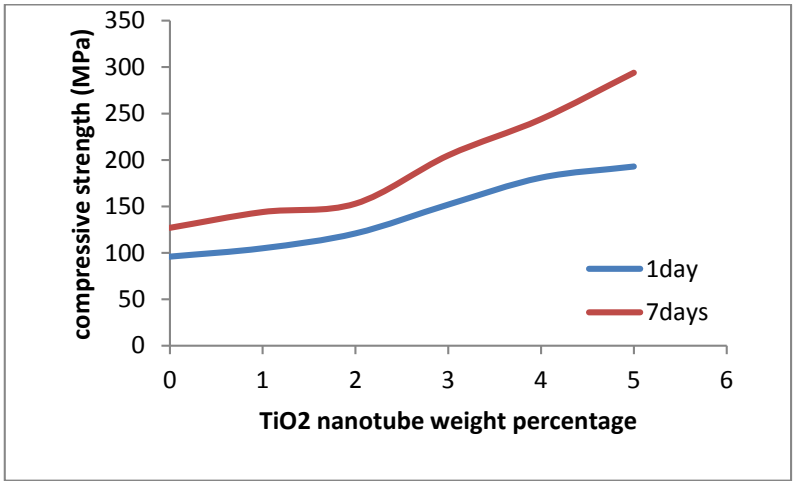

Figure 12: Compression of TiO_2/Galloy after different period.

IV. Creep Test

Figure 13 shows the creep for TiO_2/Galloys with different percentages (1, 2, 3, 4, and 5 wt%). The addition of TiO_2 nanotube powder works to increase creep resistance (decrease creep percent) with good interfacial bonding and distribution that inhibit dislocation movement, so increase the creep resistance, also the TiO_2 nanotube obstacles the movement of the dislocation and grain boundary sliding which represent the main source of creep.

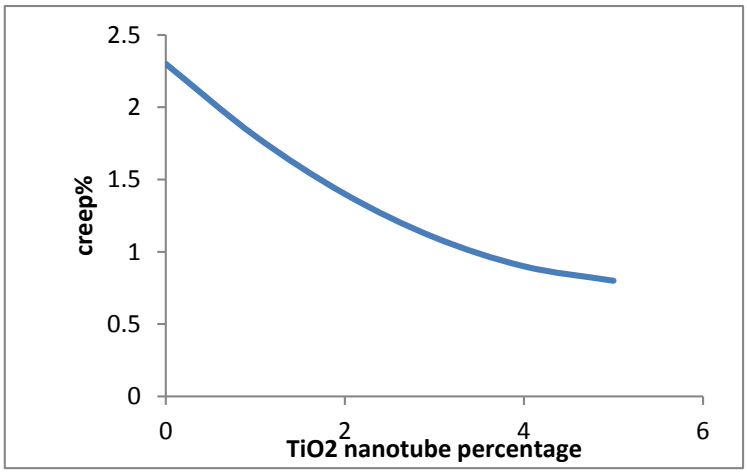

Figure 13: Creep of Galloys with additives.

4. CONCLUSIONS

The addition of TiO_2 nanotubes to Galloy led to improvement of some mechanical properties of this alloy through the formation of obstacles to dislocations movement and increasing the strength within the alloy and then increases the hardness, compression and tensile strength in addition enhance creep resistance. The characterization techniques of TiO_2/Galloys confirm the presence of TiO_2 nanotube within the main phases such as β-Sn, Ag_2Ga and Ag_9In_4.

References

[1] H. H. Jaber, Improvement of mechanical and corrosion properties of Dental amalgam alloys, Ph.D. Thesis, University of Technology, Baghdad, Iraq, 2007.

[2] A. Akbal, H.Yilmaz, E. Tutkun , D. Mehmet Kos, Aggravated neuromuscular symptoms of mercury exposure from dental amalgam fillings, J. Trace Elem. Med. Biol., 28 (2014)32–34. https://doi.org/10.1016/j.jtemb.2013.09.005

[3] R. Singh, S. Tandon, M. Rakhee, Comparative evaluation of clinical efficacy of gallium and amalgam alloys in primary molars, J. Indian Soc. Pedo. Prev. Dent., 22(2004)68 – 72.

[4] F. J. Shaini, F. K. Wahaba, G.P. Flemingb, P. M. Marquisb , A. C. Shortallb, A palladium-free gallium-based alloy: analysis of composition and microstructure, Dent Mater ., 19 (2003) 653–661. https://doi.org/10.1016/s0109-5641(03)00009-5

[5] S. M. Dunne , R. Abraham, A study into the performance of a gallium-based restorative material, British Dental J. 189 (2000) 310-313.

[6] J. C. Taggart, Handbook of Dental Care: Diagnostic, Preventive and Restorative Services, Nova Science Publishers, Inc., New York, Ch.3 (2009).

[7] R. M. Waterstrat , R. W. Longton ,Gallium-palladium alloys as dental filling material, Public Health Rep., 79 (1964)638-642. https://doi.org/10.2307/4592209

[8] M. A. Alher, Ni ion release of TiO_2 and TiO_2/Hydroxylapatite composite coatings formed on NiTi shape memory alloy produced by powder metallurgy, Ph.D. thesis, Production Engineering and Metallurgy Department, University of Technology, Baghdad-Iraq, 2013.

[9] D. A. Porter, Phase transformations in metals and alloys, 2nd edition, Chapman & Hall, 2-6 Boundary Row, London SEl 8HN, UK, 1992.

[10] H. Hero, T. Okabe, H. Wie, Trace elements in persons with dental amalgam, J. Mater. Sci., 8 (1997) 357-360.

[11] K. Moharamzadeh, I. M. Brook , R. V. Noort, Biocompatibility of Resin-based Dental Materials, Materials, 2(2009) 514-548. https://doi.org/10.3390/ma2020514

[12] A. D. A., Guide to dental materials and devices, American Dental Association Specification No.18 for alginate impression material, 7th (1992).

[13] A. C. Shortall , F. J. Shaini, A study into the performance of a gallium-based restorative material, British Dental J,189 (2000). https://doi.org/10.1038/sj.bdj.4800752

[14] R.E. Shaker, W.A. Brantley, Q. Wuc, B.M. Culbertson, Use of DSC for study of the complex setting reaction and microstructural stability of a gallium-based dental alloy, Thermochimica Acta, 367-368 (2001)393-400. https://doi.org/10.1016/S0040-6031(00)00660-2

[15] H. H. Jaber, Study of Gallium Based Restorative Alloy, J. of Babylon University/Pure and Appl. Sci., 22 (2014) 914-923.

[16] M. A. Meftah, Mechanical and corrosion improvement of dental amalgam using Zinc Oxide and Titanium Oxide particles, MSc. Thesis, University of Babylon, Iraq, 2014.

[17] C. P. Ju, Y. H. Chen, W. F. Ho, S.Ching, W.C. Chen, D. B. Shieh , J. Huey, Effect of heat treatment on structure and properties of dispersed-type dental amalgam, J. Mater. Sci. Mater. Med., 19(2008)83–93. https://doi.org/10.1007/s10856-007-3046-1

[18] O. P. Ferreira, A. G. Souza Filho, J. M. Filhob , O. L. Alves, Unveiling the Structure and Composition of Titanium Oxide Nanotubes through Ion Exchange Chemical Reactions and Thermal Decomposition Processes, J. Braz. Chem. Soc., 17(2006)393-402. https://doi.org/10.1590/S0103-50532006000200025

[19] V.A. Bykov, T.V. Kulikova, K. Yu. Shunyaev , A.B. Shubin, Thermal Expansion of Cu-Ga-Sn Alloys, Trans. Tech. Publications, Switzerland, 353 (2014)137-142. https://doi.org/10.4028/www.scientific.net/DDF.353.137

[20] N. A. Almuslet, H. J. Elamin, B. O. Elbashir, Hardness Enhancement of Amalgam Teeth Fillings Using Diode Laser (675 nm), J. Anal. Sci. Technol., 2 (2011) 64-68. https://doi.org/10.5355/JAST.2011.64

[21] Y. Xia, F. Zhang, H. Xie, N. Gu, Nanoparticle-reinforced resin-based dental composites, J. Dent., 36(2008)450-455. https://doi.org/10.1016/j.jdent.2008.03.001

[22] A. I. Ancharov, T. F. Grigorieva, S. V. Tsybulya, V. V. Boldyrev, Chemical interaction of Cu–In, Cu–Sn, and Cu–Bi solid solutions with liquid Ga–In and Ga–Sn eutectics, Inorg. Mater., 42 (2006) 1058–1064. https://doi.org/10.1134/S0020168506100025