ISSN : 0974 - 7486 Volume 9 Issue 7

Materials Science

Trade Science Inc.

An Indian Journal

Full Paper

MSAIJ, 9(7), 2013 [266-271]

Melting ranges of selected parent and solder dental alloys used for fixed partial dentures

Pascal De March[1], Aude Vallata[1], Birsena Dervisevic[1], Patrice Berthod[2]*

[1]Faculty of Dentistry, Department of Prostheses, University of Lorraine, 96 avenue de Lattre De Tassigny, B.P. 50208, 54000 Nancy, (FRANCE)

[2]Institut Jean Lamour (UMR 7198), Team 206 "Surface and Interface, Chemical Reactivity of Materials" Faculty of Science and Technologies, University of Lorraine, B.P. 70239, 54506 Vandoeuvre-lès-Nancy, (FRANCE)

E-mail: patrice.berthod@univ-lorraine.fr

ABSTRACT

The metallic frameworks strengthening prostheses are composed of successive alloys joined to one another and the temperature melting ranges of which need to be known to well operate the foundry operation as well as the two types of soldering usually realized. In this work eight parent alloys, four pre-solder alloys and four post-solder alloys were subjected to differential thermal analysis in order to know the real solidus and liquidus temperatures. Some of the alloys obviously solidify in one time (the single –phased alloys and the alloys containing a major phase) and other in two times (the bi-phased alloys with similar fractions for the two constituents). In all cases the temperatures of fusion's start and end, and the temperatures of solidification's start and end, were successfully determined. This led to several refractoriness classes (post-solder < pre-solder < parent alloys), an order in good agreement with the conditions of soldering needed all along the prosthesis fabrication. A simple criterion based on the separation of the contents in elements more refractory than the base element and the contents in elements less refractory than the base element, has been established for the prevision of the solidus temperatures and of the liquidus temperatures of the alloys based on gold and containing, with not too far contents, the same elements as the alloys studied in this work.

KEYWORDS

Dental alloys;
Refractoriness;
Differential thermal analysis;
Melting range.

INTRODUCTION

Metallic frameworks reinforcing fixed partial dentures are generally fabricated by assembling successive pieces of different alloys. In term of quantity present in the framework the most important alloy is called "Parent alloy" and the pieces made of this main alloy are joined together using first a pre-solder alloy, before the realization of the ceramic covering (the artificial teeth), and second a post-solder alloy (to join together the prosthesis elements previously realized)[1,2]. Using such procedure allows correcting the framework's distortion during the foundry process[3], improving the seating accuracy[4] and correcting the movement of teeth which possibly occurs before the prosthesis cementation is performed[5]. The mechanical resistance of the metallic framework, which can be at the origin of the failure of fixed partial denture is influenced by the mechanical properties of the main alloy present in the reinforcing metallic framework (the pieces of parent alloys), but also by the ones of the solder joint generally considered as the weakest part of the framework[6,7]. This is the reason why the mechanical behavior of the different solder joints are often subjects of investigations[8-10], notably concerning the microstructures of both parent alloy and of its solder joints which are, as well as the defects possibly present, rather important for the mechanical resistance of fixed partial dentures[11,12]. After placement of the prosthesis in mouth, other problems may occur, such as corrosion of the not-entirely covered parts (post-solder joints, eventually parts of the parent alloy) by the buccal milieu (saliva, more or less aerated), which can also be source of mechanical failure after long times. In this work it is wished to complete for several selected parent, pre-solder and post-solder alloys, earlier results obtained concerning both microstructures, defects states and micro-hardness[13], the metallurgical data about these different alloys, in this first part by measuring the melting range, which may be of importance for the joining procedure and thereafter for the metallurgical health of the metallic assemblage.

EXPERIMENTAL DETAILS

The studied alloys

Eight parent alloys were considered in this study: five "High Noble" ones rich in noble elements, a "Noble" one displaying lower contents in noble elements and two "Predominantly Base" ones based on nickel and chromium (chemical compositions given in TABLE 1). Four pre-solder alloys and four post-solder alloys (chemical compositions given in TABLE 2) were also considered.

The parent alloys were realized by investment casting: a pattern in resin was injected in a metallic mould to obtain the models which are thereafter used for giving the internal shape of the final mould in which the liquid parent alloy will be injected using a casting apparatus equipped with a centrifugal arm (Minicast®, Uger) and a gas-oxygen torch. If the main part of the solidified alloy was used to metallographic purpose a small part was kept to be machined, in order to obtain a parallelepiped of about $2 \times 2 \times 3$ mm^3 sample for the melting range measurements.

TABLE 1 : Chemical compositions of the studied parent alloys (all contents in wt.%; manufacturer's data).

HIGH NOBLE PARENT ALLOYS	
dSIGN98	86 Au - 12 Pt – 2.0 Zn
Aquarius Hard	86 Au - 8.5 Pt - 2.6 Pd - 1.4 In
dSIGN91	60 Au -31 Pd -1.0 Ga -8.4 In
Lodestar	52 Au - 39 Pd - 1.5 Ga - 8.5 In
W	54 Au - 26 Pd - 1.5 In - 16 Ag - 2.5 Sn
NOBLE PARENT ALLOY	
dSIGN59	59 Pd - 28 Ag - 8.2 Sn - 2.7 In - 1.3 Zn
PREDOMINANTLY BASE ALLOYS	
4ALL	61 Ni - 26 Cr - 11 Mo - 1.5 Si
Pisces Plus	62 Ni - 22 Cr - 11 W - 2.6 Si - 2.3 Al

TABLE 2 : Chemical compositions of the studied solder alloys (all contents in wt.%; manufacturer's data).

PRE-SOLDER ALLOYS	
HGPKF 1015 Y (for dSIGN98and Aquarius hard)	60 Au – 36.5 Ag
SHFWC (for dSIGN91 and dSIGN59)	47 Au –10.3 Pd –41 Ag – 1.4 In
HFWC (for Lodestar and W)	45 Au –12.4 Pd –41.5 Ag – 1 In
Supersolder (for Pisces Plus and 4ALL)	53.5 Pd– 7 Ag–35.6 Ni – 3.8 Sn
POST-SOLDER ALLOYS	
.650 (for dSIGN98)	65 Au – 13 Ag-20 Cu – 2 Ga
.615 (for dSIGN91, dSIGN59 and Lodestar)	61 Au – 13 Ag – 17 Cu – 7.6 In
.585 (for Aquarius Hard)	59 Au – 16 Ag – 18 Cu – 7 Ga
LFWG (for W, Pisces Plus and 4ALL)	56 Au – 27 Ag – 16 Zn

The pre-solder and post-solder alloys (part of ribbon with dimensions 30×2 mm^2) were melted in a borax-vitrified crucible using a butane-oxygen blow-torch. They solidified with the shape of half ball-like ingots and a mass of about 1 gram. Samples of about the same shape and dimensions as above were then obtained by cutting.

The differential thermal analysis runs

The Differential Thermal Analysis (DTA) runs were performed using a TG/ATD 92-16.18 Setaram device, in an atmosphere of pure Argon at a pressure of 1 bar and with a gas flow of 2 litres per hour. The thermal cycles applied were all composed of a first heating at +

Full Paper

20°C/min from ambient temperature and this until reaching 950°C, followed by a slower second heating at + 5°C/min until reaching 1450°C. The cooling was also realized in two times, a slow rate one (-5°C/min down to 950°C) and a faster rate one (-20°C/min) down to ambient temperature.

RESULTS AND DISCUSSION

General shape of the obtained DTA curves

The DTA results obtained can be classified in two main categories:

- one containing the curves displaying seemingly only one endothermic and one exothermic phenomena,
- one containing the curves for which two endothermic and two exothermic phenomena were distinguished (examples of the Supersolder pre-solder alloy and the LFWG post-solder alloy).

The two types of DTA curves, plotted as {thermal flow} versus {temperature} are presented for illustration of the first category (only one peak at heating as well as at cooling) in Figure 1 (examples of the two parent alloys dSIGN91 and W) and for illustration of the second category (two peaks at heating as well as cooling) in Figure 2 (examples of the two solder alloys: Supersolder used for pre-ceramic soldering and LFWG used for post-ceramic soldering).

By consulting the micrographs[13] illustrating the microstructures of the alloys the DTA curves of which contain only one endothermic peak in the heating part and one exothermic peak in the cooling part, it appears that these alloys are most of them either single-phased alloys (e.g. W) or bi-phased alloys with a small fraction of the second phase (e.g. dSIGN91). In contrast, the alloys having led to DTA curves presenting two endothermic peaks in the heating part and two exothermic peaks in the cooling part, are generally characterized by the presence of two phases or constituents in their microstructures with equivalent volume or mass fractions (at least fractions of the two phases/constituents not so far from one another).

Melting ranges and solidification ranges; comparisons with the manufacturer's data

All the temperature values determined for the beginning of fusion, the end of fusion, the beginning of solidification and the end of solidification are displayed in TABLE 3. Despite that there are several exceptions, it generally appears that the temperature of fusion start is slightly higher than the one of solidification's end. In the same way each temperature of fusion's end is slightly higher than the solidification's start one. This usual difference is due to the fact that the applied heating rate and cooling rate were not infinitely low.

TABLE 3 : Values of the limit temperatures of the fusion ranges and of the solidification ranges for all the studied alloys; comparison with the manufacturer's data.

Temperatures in °C		End of solidification	Solidus temp. (manuf.'s data)	Start of fusion	Start of solidification	Liquidus temp. (manuf.'s data)	End of fusion
Parent alloys	dSIGN98*	1031	1055	1036	1212	1170	1170
	Aqu. Hard**	1016	1010	1031	1155	1135	1150
	dSIGN91	1090	1175	1094	1267	1305	1269
	Lodestar	1157	1215	1132	1301	1290	1315
	W	1146	1230	1193	1285	1280	1287
	dSIGN59	1152	1230	1174	1284	1310	1291
	Pisces Plus**	1239	1255	1278	*1253*	1330	*1352*
	4ALL	1295	1260	1277	1316	1350	1352
Pre-solder alloys	HGPKF1015Y	970	975	971	1041	1035	1041
	SHFWC	1032	1045	1038	1088	1105	1113
	HFWC	*1045*	1100	1084	1168	1165	1169
	SuperSolder	1073	1085	1082	1178	1135	1194
Post-solder alloys	.650	772	785	789	848	835	863
	.615	640	690	692	779	775	785
	.585	691	655	600	719	785	725
	LFWG	663	670	660	799	730	734

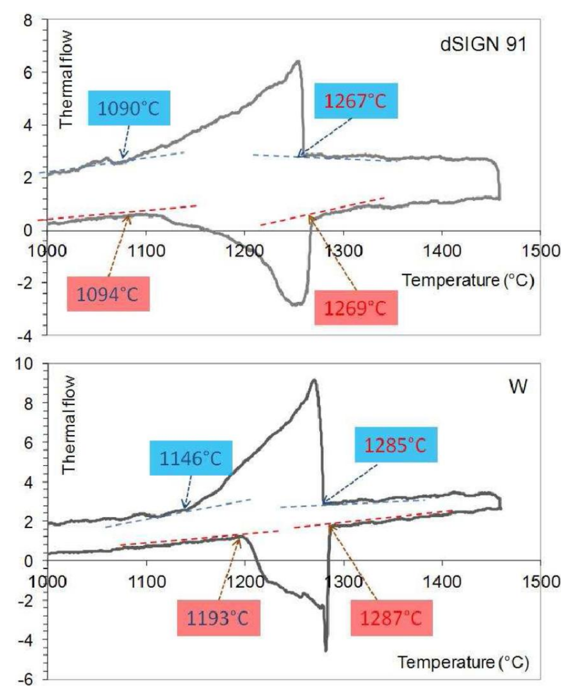

Figure 1 : Two examples of DTA results displaying only one peak at heating and one peak at cooling (case of the two parent alloys dSIGN91 and W); examples of determination of the temperatures of fusion start (e.g. 1193°C for W), fusion end (e.g. 1287°C for W), solidification start (e.g. 1285°C for W) and solidification end (e.g. 1146°C for W).

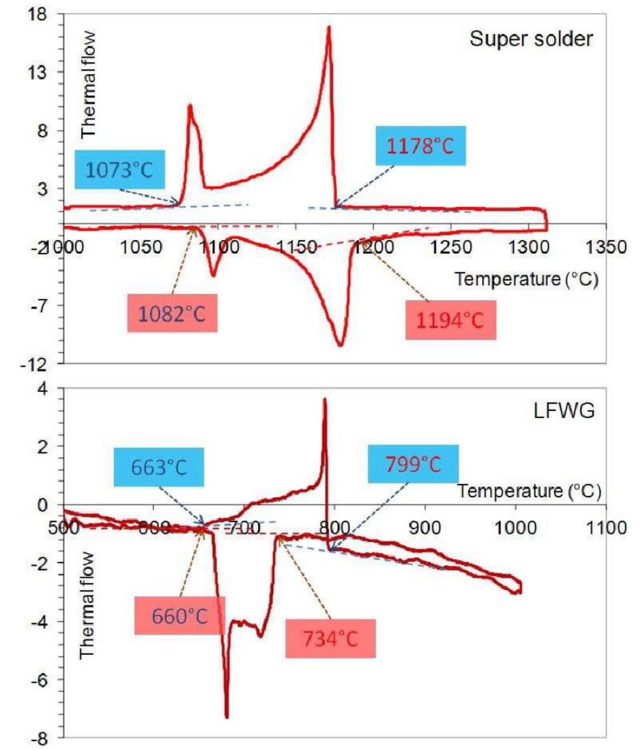

Figure 2 : Two examples of DTA results displaying two peaks at heating and two peaks at cooling (case of the two solder alloys Supersolder (pre-solder) and LFWG (post-solder); examples of determination of the temperatures of fusion start (e.g. 660°C for LFWG), fusion end (e.g. 734°C for LFWG), solidification start (e.g. 799°C for LFWG) and solidification end (e.g. 663°C for LFWG).

Globally the alloys can be classified in three groups corresponding to their uses: the highest temperatures of {solid ↔ liquid} transformations for the parent alloys, the intermediate ones for the pre-solder alloys and the lowest ones for the post-solder alloys.

In general the fusion's start and solidification's end temperatures on one hand, and the fusion's end and solidification's start temperature on the other hand, seem being in rather good agreement with the corresponding values of the solidus temperature and of the liquidus temperature given by the manufacturer, but there are seemingly several exceptions.

In order to compare more efficiently the different values, measured by DTA and given by the manufacturer, graphs are plotted in Figure 3 for the parent alloys, Figure 4 for the pre-solder alloys and Figure 5 for the post-solder alloys. On these curves it appears that the fusion's end and solidification's start temperatures red on the DTA curves well correspond to the manufacturer's liquidus temperatures (except for Pisces Plus, Supersolder, .585 and maybe LFWG). The mismatch is greater for the lower temperature limits of the melting and solidification ranges for four of the parent alloys (dSIGN91, Lodestar, W and dSIGN59), one of the pre-solder alloys (HFWG) and maybe also for two of the post-solder alloys (.615 and .585).

General commentaries

The results obtained by DTA are thus globally in good accordance with the manufacturer's data. The measured temperatures as well as the manufacturer's temperatures seem evaluating monotonously with the nobility of the alloys and it can be interesting to study their variation versus the cumulated contents in selected elements, for example by considering (TABLE 4) the elements with fusion temperatures lower than the base element's one or in contrast the elements with fusion temperatures higher than the base element's one.

TABLE 4 : Temperatures of fusion (in °C) for the elements present in the parent and solder alloys.

Au	Pt	Pd	Ag	In	Ga	Sn	Zn	Cu
1063	1769	1552	961	156	30	232	420	1083
Ni	**Cr**	**W**	**Mo**	**Ir**	**Ru**	**Ta**	**Al**	**Si**
1453	1875	3410	2610	2454	2500	2996	660	1410

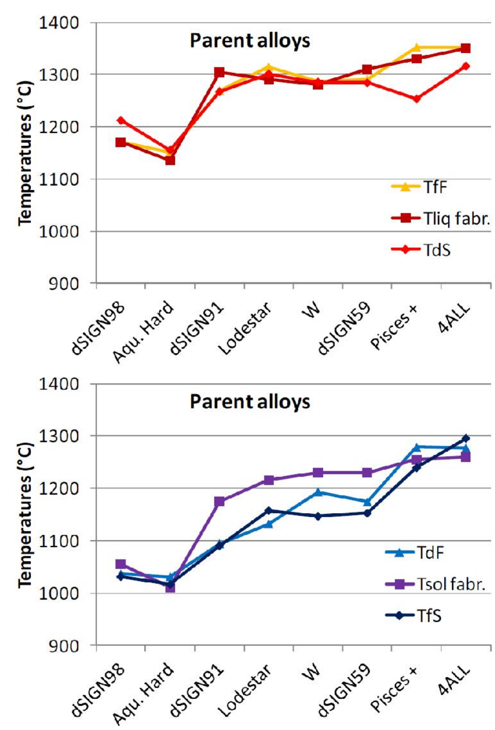

TABLE 3 : Values of the limit temperatures of the fusion ranges and of the solidification ranges for all the studied alloys; comparison with the manufacturer's data.

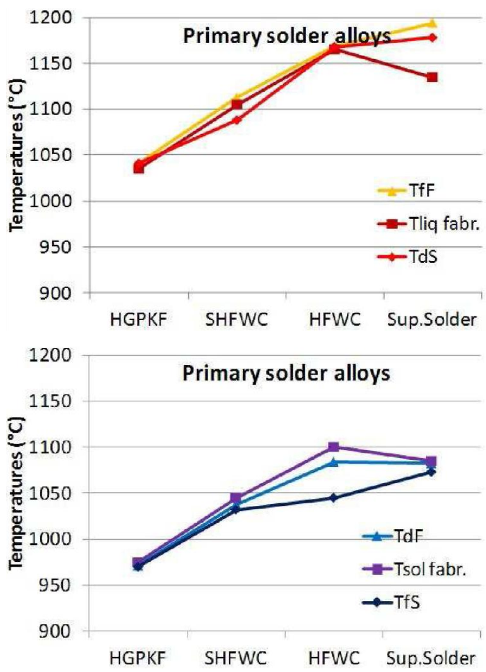

Figure 4 : Pre-solder alloys; top: temperatures of fusion's end ("TfF") and of solidification's start ("TdS"); bottom: fusion's start ("TdF") and of solidification's end ("TfS"); comparison of the previous DTA results with the solidus and liquidus temperatures given by the manufacturer.

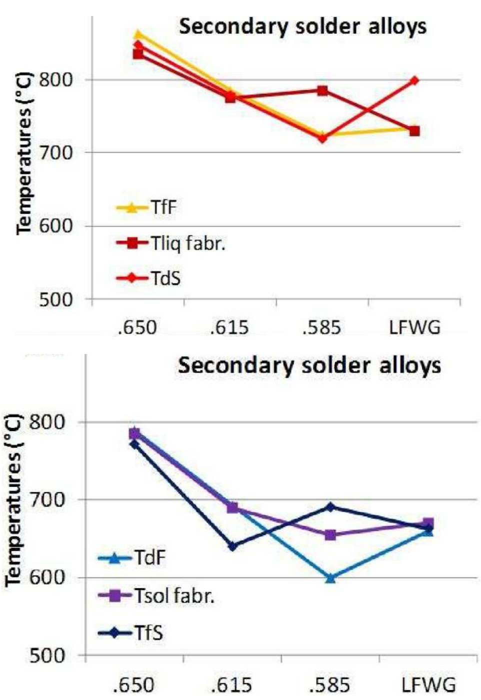

Figure 5 : Post-solder alloys; top: temperatures of fusion's end ("TfF") and of solidification's start ("TdS"); bottom: fusion's start ("TdF") and of solidification's end ("TfS"); comparison of the previous DTA results with the solidus and liquidus temperatures given by the manufacturer.

This can be undertaken for all the alloys based on gold (Tf = 1063°C) in which one finds elements with lower fusion temperatures (Ag, In, Ga, Sn, Zn...) as well as elements with higher fusion's temperatures (Pt, Pd, Ir, Ru, Ta...). The graph presented in Figure 6 shows a general increase of the two temperatures of fusion's start and of fusion's end (manufacturer's data) for all the alloys for which the [wt.%(Pt+Pd+Ir+Ru+Ta) – wt.%(Ag+In+Ga+Sn+Zn)] / wt.%(Au+Cu) ratio is higher than -0.5. The ratios lower than -0.5 are obtained for the pre-solder alloys HGPKF 1015 Y, SHFWC and HFWC, as well as for the post-solder alloy LFWG, which all contain a lot of silver (27.4 to 41.5 wt.%, manufacturer's data).

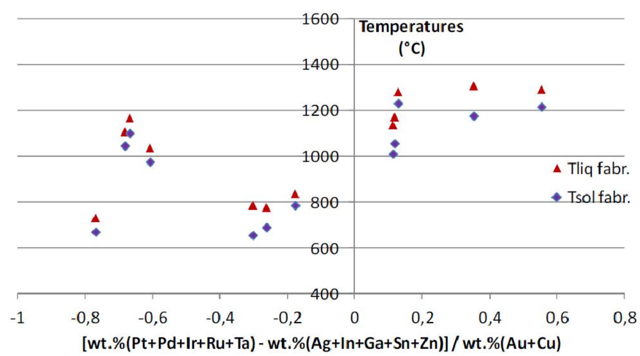

Figure 6 : (Melting ranges provided by the manufacturer) Temperatures of liquidus and of solidus versus the chemical composition ratio (cumulated contents in elements more refractory than gold, subtracted by the cumulated content in elements less refractory than gold, and divided by the cumulated content in gold and copper (which have both almost the same fusion temperature).

The graph presented in Figure 7 shows the same plotted results but with the experimental results:

- temperature of fusion's start and of fusion's end measured by DTA (closer to the real solidus and liquidus temperatures by comparison to the corresponding temperatures measured during the cooling and to the average values between heating and cooling),
- and the Energy Dispersive Spectrometry (EDS) results obtained using a Scanning Electron Microscope (SEM) for the alloys containing less than 20% of silver[14].

It appears that the evolution has become much more monotonous than in Figure 6.

The parent alloys dSIGN59 (rich in palladium: 59%), Pisces Plus (62% Ni alloyed with essentially chromium and tungsten) et 4ALL (61% Ni alloyed with essentially chromium and molybdenum), as well as the pre-solder alloy Supersolder (very rich in palladium and in nickel: respectively 54% and 36%) are not based on gold and cannot be present in figure 6 or figure 7. One can notice only that they are the most refractory in their category here probably because of their higher palladium and/or nickel contents which may lead to fusion's start and fusion's end temperatures particularly high.

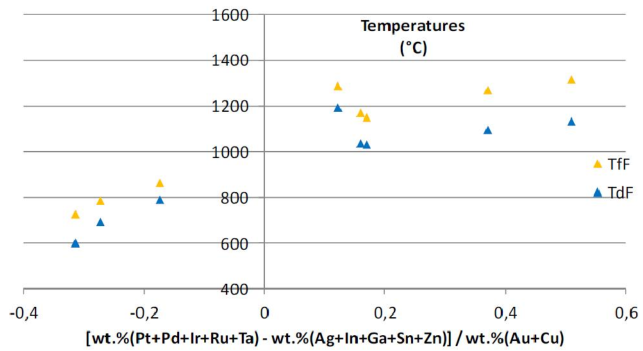

Figure 7 : (Melting ranges measured by DTA) Temperatures of liquidus and of solidus versus the chemical composition ratio (cumulated contents in elements more refractory than gold, subtracted by the cumulated content in elements less refractory than gold, and divided by the cumulated content in gold and copper (which have both almost the same fusion temperature).

CONCLUSION

The values of the temperatures delimiting the fusion ranges or solidification ranges of the eight parent alloys and the eight solder alloys considered here are globally in good agreement with the manufacturer's data, and it appears that the corresponding metallic frameworks are composed of successive alloys of very different refractoriness. The differences observed between the parent alloys in general, the pre-solder alloys and the post-solder alloys (as well as between the three sub-families of parent alloys) can be explained by considering a ratio calculated from the contents in the most refractory elements, the less refractory ones and the content in base element (added with another element with a similar fusion point), which may be considered as a global criterion easy to used and rather efficient despite that thermodynamic modelisation should be much more accurate and scientific.

ACKNOWLEDGEMENTS

The authors would like thank very much the Ivoclar Vivadent company which gave them the alloys for this study, as well as Lionel Aranda who helped them to perform the DTA experiments.

REFERENCES

[1] J.Philibert, A.Vignes, Y.Bréchet, P.Combrade; Métallurgie: Du minerai au matériau, 2nd Edition, Dunod, Paris, **(2002)**.
[2] J.B.Schwartz; Brazing for the engineering technologist, Chapman and Hall, London, **(1995)**.
[3] B.E.Schiffleger, G.J.Ziebert, V.B.Dhuru, W.A.Brantley, K.Sigaroudi; J.Prosthet.Dent., **54**, 770 **(1985)**.
[4] G.J.Ziebert, A.Hurtado, C.Glapa, B.E.Schiffleger; J.Prosthet.Dent., **55**, 312 **(1986)**.
[5] S.Schluger, R.A.Youdelis, R.C.Page, R.H.Johnson; Periodontal deseases, Lea&Febiger, Philadelphia, **(1990)**.
[6] L.Wictorin, H.Fredriksson; Odontol.Revy., **27**, 187 **(1976)**.
[7] R.Kriebel, B.K.Moore, C.J.Goodacre, R.W.Dykema; J.Prosthet.Dent., **51**, 60 **(1984)**.
[8] H.W.Wiskott, J.I.Nicholls, R.Taggart; J.Dent.Res., **70**, 140 **(1991)**.
[9] T.J.Butson, J.I.Nicholls, T.Ma, R.J.Harper; Int.J.Prosthodont., **6**, 468 **(1993)**.
[10] H.W.Wiskott, J.I.Nicholls, U.C.Belser; Dent.Mater., **10**, 215 **(1994)**.
[11] E.B.Hawbolt, M.I.Mac Entee; J.Dent.Res., **62**, 1226 **(1983)**.
[12] H.W.Wiskott, F.Macheret, F.Bussy, U.C.Belser; J.Prosthet.Dent., **77**, 607 **(1997)**.
[13] P.De March, P.Berthod; Materials science, An Indian Journal, **4(4)**, 297 **(2008)**.
[14] P.De March; PhD thesis, University Henri Poincaré Nancy, 1 **(2011)**.