CRS AMT 2013

The 12th China–Russia Symposium on Advanced Materials and Technologies

Передовые металлы, керамические и композиционные материалы

ADVANCED METALS, CERAMICS AND COMPOSITES

The 12th China–Russia Symposium on Advanced Materials and Technologies

先进金属、陶瓷与复合材料

“第十二届中俄双边新材料新工艺国际会议”论文集

PART I

Edited by
Hailing Tu
Konstantin Solntsev
Rong Zhou

Yunnan Publishing Group Corporation
Yunnan Science and Technology Press

Resorbable Bioceramics in $Ca_3(PO_4)_2$ –$CaMPO_4$ Systems (M = Na, K)

P. Evdokimov[1], V. Putlayev[1], D. Merzlov[2], A. Garshev[2], T. Safronova[1], D. Prosvirnin, E. Klimashina[1]

[1] *Deparment of Materials Science, Lomonosov Moscow State University, Russia*
[2] *Department of Chemistry, Lomonosov Moscow State University, Russia*
[3] *Institute of Metallurgy and Material Science, Russian Academy of Sciences, Russia*
pavel. evdokimov@ gmail. com

I . INTRODUCTION

The goal of bone tissue engineering is to replace lost or injured tissue with bioactive implant. Natural bone consists of organic and inorganic parts. Major component of inorganic part is hydroxyapatite (HA). Due to this fact a lot of materials for bone replacement are based on synthetic analog of bone mineral [1].

Bone scaffolds should obey the following demands:

1) to be bioresorbable that means to be degradable in organism environment, this property roughly correlates with solubility;

2) produce non–toxic degradation products;

3) contain a porous architecture;

4) provide temporary mechanical support to the affected area.

However, using of HA–ceramics is limited, since some properties, like, for instance, bioresorption, doesn' t match the criteria listed above. One of the most popular way to increase resorption of the implants based on HA, is to use more soluble calcium phosphates, like tricalcium phosphate (TCP) [2, 3]. Nevertheless, in some cases solubility of such materials is not enough. Another approach is to replace calcium ion with larger ion having larger radius and/or smaller charge. At last, we can adopt another type of crystal structure with larger molar volume. Increasing of molar volume immediately leads to increasing solubility of corresponding phase.

In this work we have tried to found another calcium phosphates with better bioresorption properties than HA and even than β–TCP has. The main tasks of our work were:

1. Re–visiting the phase diagram of the system $Ca_3(PO_4)_2$–$CaNaPO_4$;

2. Construction of the phase diagram of the system $Ca_3(PO_4)_2$–$CaKPO_4$;

3. Study of $Ca_3(PO_4)_2$, $CaNaPO_4$ and $CaKPO_4$ polymorphic transformations;

4. Study of bending strength and fracture toughness of ceramics based on $Ca_{(3-x)}Na_{2x}(PO_4)_2$ and $Ca_{(3-x)}K_{2x}(PO_4)_2$.

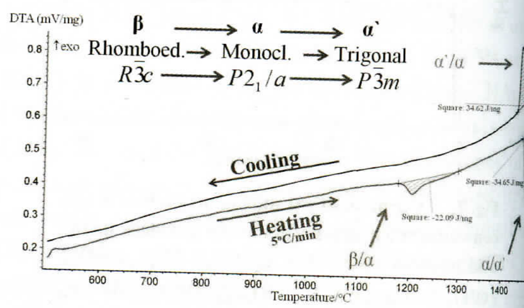

Figure 1. DTA data of $Ca_3(PO_4)_2$ Heating and cooling rate are 5°/min.

II. EXPERIMENTAL RESULTS AND DISCUSSON

The DTA results of $Ca_3(PO_4)_2$ are shown in Fig. 1. In the heating curve there are two different endo–effects, the first one belongs to polymorphic transformation from low–temperature beta–TCP to high–temperature alpha-TCP. It should be noted that this transformation takes a lot of time from the beginning to the end of the effect, so we can report on a low rate of transformation from b-phase to a–TCP.

The second effect is more pronounced and relates to a high rate of transformation; it belongs to thea–/a'-transformation. In the cooling curve one can see only one exo– effect, which belongs to superalpha–/alpha– transformation, it is mirroring alpha–/superalpha– transformations, and this fact clearly indicates that a' –TCP cannot be obtained even by quenching. At the same time, there is no effect belonging to alpha–/beta– transformations and according to XRD – analysis we have found out that our sample was pure alpha–TCP, meaning that a–TCP can be obtained just by natural cooling the furnace.

TTT (Time–Temperature–Transformation) –diagram is shown in Fig. 2. The diagram was constructed using dilatometry measurements, and the critical cooling rate allowing to obtain pure alpha–TCP phase was found to be of about 4.5℃/min.

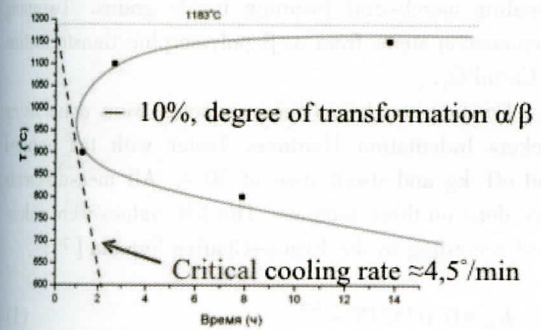

Figure 2. TTT – diagram of a → b transition of $Ca_3(PO_4)_2$.

In Fig. 3 DTA curves for the $CaNaPO_4$ are shown. There are the same types of effects evidencing transformations close to that fora' –/a– in TCP [4]. Thus, b–/a– transformation in sodium rhenanite is a fast transformation and pure alpha – phase cannot be quenched. Therefore, to obtain material containing large enough high–temperature rhenanite phase it was suggested to shift toward lower sodium content use mixtures of TCP and pure sodium rhenanite.

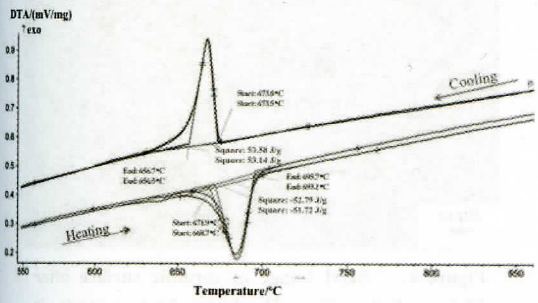

Figure 3. DTA data of $CaNaPO_4$. Heating and cooling rate are 5o/min.

The data of HT (high temperature) –XRD is shown in Fig. 4. Volume increase due to polymorphic transformation of alpha–beta type in sodium rhenanite is clearly visible.

Few variants of $Ca_3(PO_4)_2$–$CaNaPO_4$ phase diagram were found in literature [5, 6], however, there was no consensus on existence of phase "A", so this diagram was revised to understand whether any intermediate phase does present.

According to revised phase diagram (Fig. 5) CaNa-

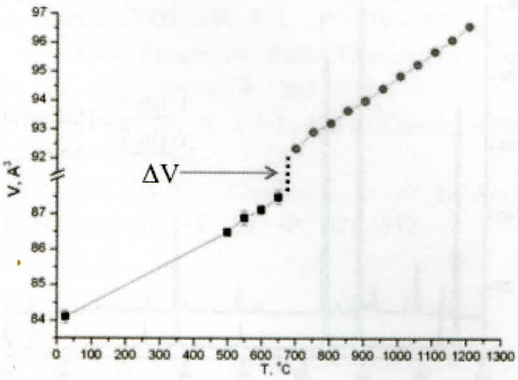

Figure 4. $CaNaPO_4$ cell volume as a function of temperature.

PO_4 forms solid solutions with TCP, therefore, it should have the same crystal structure. TCP has a better resorbable properties compared to TCP, on the other hand, TCP undoubtedly should have better resorption properties than TCP, so TCP should be definitely better than TCP, but it cannot be kept during cooling from high temperature. Similarly, due to essentially the same crystal structure $CaNaPO_4$ should have better resorption properties than beta – TCP. HT – XRD data is shown in Fig. 6. Phase "A" is a superstructure over α–$CaNaPO_4$ with $a_A = 2a_\alpha$, $c_A = 3c_\alpha$.

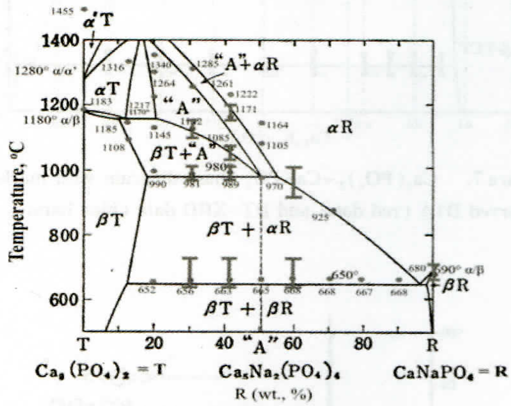

Figure 5. $Ca_3(PO_4)_2$–$CaNaPO_4$ phase diagram [5] with marks of observed DTA (red dots) and HT–XRD data (green bars).

Apart from sodium rhenanite, there is no literature on potassium rhenanite–TCP phase diagram.

To construct such a diagram, first of all, DTA – measurements were done for the mixtures with 0.1 step for x in this formula. Then, using HT–XRD the DTA data was clarified and phase areas were outlined. Finally, the diagram under study looks very similar to $Ca_3(PO_4)_2$–$CaNaPO_4$ diagram (Fig. 8), the phase very similar to phase "A" was found and it was called "B" (solid solution based on $CaKPO_4$ with superlattice a_B =

References

[1] Hench L. L. // J. Am. Ceram. Soc., –1998, –V. 81, –P. 1705–1727.

[2] Doremus R. H. // J. Mat. Sc., –1992, –V. 27, –P. 285–297.

[3] Ito A., LeGeros R. // Z. KeyEng. Mater., –2008, –V. 377, –P. 85–98.

[4] Masatomo Yashima, Atsushi Sakai //Chem. Phys. Lett., –2003, –V. 372, –P. 779–783.

[5] Ando Jumpei // Bull. Chem. Soc. Jap., –1958, –V. 31, –No. 2, –P. 201–205

[6] Bredig, M. A. // J. Phys. Chem., –1942, –V. 46, –P. 747–764

[7] Evans A. G., Charles E. A. // J. Am. Ceram. Soc., –1976, –V. 59, –P. 371–372.