Influence of Sintering Time on the Structure Formation of Al-ZrW₂O₈ Pseudo Alloys

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Abstract. Al – ZrW₂O₈ pseudo alloys were synthesized by free sintering of Al – ZrW₂O₈ powder mixture. Influence of sintering time on the structure formation of the pseudo alloys obtained was investigated. It has been shown that during sintering process zirconium tungstate decomposes into constituent oxides and re-synthesis of zirconium tungstate proceeds through intermediate stage – formation of WAl₁₂ and ZrAl₃ intermetallic compounds.

1. Introduction
Zirconium tungstate ZrW₂O₈ with isotropic negative thermal expansion (NTE) behavior over a wide temperature range [1] is a perspective material for development of new class of metallic materials with controlled thermal expansion.

It is known that zirconium tungstate decomposes into its constituent oxides WO₃ and ZrO₂ upon heating and recent works [2] showed that decomposition of ZrW₂O₈ may begin already at 400 °C. Therefore the formation of alloy containing ZrW₂O₈ particles will be strongly dependent on sintering time and one can expect some specific behavior of ZrW₂O₈ during interaction with metals. One of the easiest ways to observe these effects is to use aluminum as one of initial components due to low melting point of this metal. In addition aluminum based materials are lightweight, exhibit excellent mechanical properties, thermal and electrical conductivity and therefore are promising candidates for development of multifunctional Al – ZrW₂O₈ pseudo alloy with controlled thermal expansion.

The work presented is aimed at investigating the influence of sintering time on structure and phase composition of Al – ZrW₂O₈ pseudo alloys.

2. Experiment
Commercially pure aluminum powder ASD-6 and zirconium tungstate powder obtained by hydrothermal synthesis [3] were used as initial components. The amount of ZrW₂O₈ addition was 10 wt%. High energy ball milling for 30 seconds, 1 and 5 minutes using AGO-2 planetary ball mill with acceleration of 60g was performed to achieve homogeneous distribution of ZrW₂O₈ in aluminum powder and for mechanical activation of the components. Mechanically activated (MA) Al – ZrW₂O₈ powder mixtures were uniaxially cold pressed into ~ φ20mm×4mm cylinders under 100 MPa and sintered at 600 °C in argon atmosphere for 1h and 5h. Surface of the specimens was etched in hydrofluoric acid. The microstructure of the specimens obtained was observed using TESCAN.
Vega3 scanning electron microscope. Structure and phase composition were investigated using XRD analysis.

3. Results and Discussion

3.1. High energy mechanical activation of Al – ZrW$_2$O$_8$ powder mixtures

Aluminum powder is represented with spherical particles with average size of 3 μm. ZrW$_2$O$_8$ particles are rod-shaped with average length of 5 μm and are agglomerated, figure 1. Morphology and particle sizes of ZrW$_2$O$_8$ are in a good agreement with [3,4].

Figure 1. Morphology of ZrW$_2$O$_8$ powder

Figure 2. Morphology of Al - ZrW$_2$O$_8$ powder mixture after 1 min MA.

Figure 3. Morphology of Al - ZrW$_2$O$_8$ powder mixture after 5 min MA.

Figure 4. XRD pattern of Al – ZrW$_2$O$_8$ powder mixture after 1 minute of MA.

SEM analysis of the powder mixtures after high energy mechanical activation showed that 1 minute of MA time is enough to achieve homogeneous distribution of ZrW$_2$O$_8$ particles in aluminum powder, figure 2. Also during high energy mechanical activation there is a reduction in the length of rod-shaped particles to 1.5 μm, and their transverse size does not change. Increasing of the MA duration up to 5 minutes leads to formation of agglomerates, Figure. 3. However, even after aluminum powder agglomeration ZrW$_2$O$_8$ distribution remains homogeneous. XRD studies of the powder mixture after mechanical activation showed that the phase composition remains the same and there are no reactions between the mixture components during MA, Figure 4.
3.2. Sintered Al – ZrW$_2$O$_8$ samples

In figure 5 the structure of material after 1h of isothermal hold is presented. The structure is not homogeneous, one can observe elongated dense areas, porous matrix and white particles distributed both in the matrix and elongated areas. The content of white particles in matrix and in elongated areas is 3% and 20% correspondingly. The average size of white particles is 0.5 μm. obviously during the sintering process ZrW$_2$O$_8$ is redistributed in the matrix. Since after mechanical activation no irregularities in the initial powder mixture are found, one can assume that the formation of inhomogeneous structure takes place during the sintering process.

EDAX analysis showed that white particles consist of Al, W and Zr atoms. On the XRD pattern peaks corresponding to Al and ZrAl$_3$, WAl$_{12}$ intermetallic compounds are presented, Figure 7. Calculated lattice parameters of intermetallics are in a good agreement with ASTM diffraction data cards: a=7. 5803 Å for WAl$_{12}$ (8-331) and a=4.0130 Å for ZrAl$_3$ (2-1093). The lattice parameter of aluminum a= 4.0527 Å is increased in comparison with data card (4-787). The coherent diffraction domain (CDD) values (D) and lattice microdistortion (ε) for aluminum were calculated by Williamson-Hall analysis[5]: D=50 nm, ε = 2.5·10$^{-3}$.

![Figure 5. Etched surface of Al – ZrW$_2$O$_8$ sintered for 1h](image1)

![Figure 6. Etched surface of Al – ZrW$_2$O$_8$ sintered for 5h](image2)

![Figure 7. XRD patterns of Al – ZrW$_2$O$_8$ specimens](image3)

After 5h of isothermal hold the structure of the material is represented with microfibers with average length of 30 μm homogeneously distributed in porous matrix, figure 6. On the XRD pattern, figure 6, one can observe peaks corresponding to Al and cubic ZrW$_2$O$_8$. Lattice parameter of aluminum increased in comparison with 1h isothermal hold, a= 4.0544 Å. ZrW$_2$O$_8$ lattice parameter a=9.2187 Å is increased in comparison with literature data [6]. CDD value and lattice microdistortions for Al are D=500 nm and ε = 7·10$^{-3}$ correspondingly.

The data obtained using scanning electron microscopy and XRD analysis allow us to suggest that formation of the material proceeds through decomposition of zirconium tungstate into constituent oxides WO$_3$ and ZrO$_2$ and synthesis of WAl$_{12}$ and ZrAl$_3$ intermetallic compounds after 1 hour of isothermal hold. According to [7] WAl$_{12}$ may be produced by exothermic in situ reaction between Al and WO$_3$. The generated heat may cause heating of aluminum higher than the melting point and subsequent cooling of the mixture leads to WAl$_{12}$ crystallization. Formation of ZrAl$_3$ [8] goes on in a similar way. The further increase of isothermal holding time up to 5h leads to subsequent formation of ZrW$_2$O$_8$ microfibers. Lattice parameter and microdistortions of aluminum increase with increasing isothermal holding time, which may indicate the formation of internal stresses in the material.

4. Conclusions

It was shown that during sintering of Al - ZrW$_2$O$_8$ powder mixture zirconium tungstate decomposes into its constituent oxides WO$_3$ and ZrO$_2$ with subsequent formation of WAl$_{12}$ and ZrAl$_3$ intermetallic compounds. Increasing the isothermal holding time up to 5 hours leads to re-synthesis of the
zirconium tungstate represented with elongated particles – microfibers. The formation of internal stresses in the material was shown using XRD and Williamson-Hall analyses.

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