Structure and Properties of Al – ZrW₂O₈ Pseudo Alloys

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Abstract. Al – ZrW₂O₈ powder mixture was sintered to obtain alloys were Al – ZrW₂O₈ pseudo alloys. The structure formation process of the pseudo alloys obtained was investigated. During sintering process zirconium tungstate was found to decompose into constituent oxides with consequent formation of WAl₁₂ and ZrAl₃ intermetallic compounds. Increasing the sintering 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. The value of internal compression stresses was estimated to be 90 MPa. Vickers hardness of the pseudo alloys obtained increases by two times with increasing sintering time from 1h to 5h.

1. Introduction
The development of modern technology, science and industry is impossible without the creation of novel materials with improved physical-mechanical properties. Zirconium tungstate ZrW₂O₈ possessing isotropic negative thermal expansion coefficient (NTE) in a wide temperature interval [1] is a perspective material for development of new class of metallic materials with controlled thermal expansion.

Low-temperature decomposition process of zirconium tungstate into consistuent oxides WO₃ and ZrO₂ upon heating was shown in recent works [2]. Therefore taking this effect into account one can expect some specific behavior of ZrW₂O₈ during sintering near the melting point of metal. 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. Low melting temperature of aluminum will make it possible to observe this effect most simply.

The work presented is aimed at investigating the structure and mechanical properties 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 1 minute using AGO-2 planetary ball mill with acceleration 60g
was performed to achieve homogeneous distribution of $\text{ZrW}_2\text{O}_8$ in aluminum powder and for mechanical activation of the components. Mechanically activated (MA) Al – $\text{ZrW}_2\text{O}_8$ powder mixtures were uniaxially cold pressed into $\varnothing 20\text{mm} \times 4\text{mm}$ samples under 100 MPa and sintered at 600 °C in argon atmosphere for 1h and 5h. Surface of the specimens was etched in HF acid. The microstructure of the specimens obtained was observed using TESCAN Vega3 scanning electron microscope. Structure and phase composition were investigated using XRD analysis with Cu Kα irradiation. After sintering of the specimens the Vickers hardness test was performed, using PMT-3 equipment.

3. Results and Discussion

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

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

![Figure 1. Morphology of $\text{ZrW}_2\text{O}_8$ powder](image1.png)

![Figure 2. Morphology of Al - $\text{ZrW}_2\text{O}_8$ powder mixture after 1 min MA.](image2.png)

![Figure 3. XRD pattern of Al – $\text{ZrW}_2\text{O}_8$ powder mixture after 1 minute of MA.](image3.png)

SEM images of the powder mixtures after high energy mechanical activation is shown in Figure 2. One can observe homogeneous distribution of $\text{ZrW}_2\text{O}_8$ particles in aluminum powder. Also the length of rod-shaped particles reduced during high energy mechanical activation to 1.5 μm, and their transverse size did not change.

XRD studies of the powder mixture after mechanical activation showed that there are no reactions between the mixture components during MA. In the Figure 3 one can observe only peaks corresponding to aluminum and cubic modification of $\text{ZrW}_2\text{O}_8$. 

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3.2. Al – ZrW₂O₈ specimens after sintering
In Figure 4 SEM image of the etched surface of material after 1h of sintering is presented. The structure is not homogeneous, one can observe elongated dense areas (2), porous matrix (1) and white particles distributed both in the matrix and elongated dense areas. The average size of white particles is 0.5 µm. Obviously during the sintering process ZrW₂O₈ is redistributed in the matrix. And 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 one can observe peaks corresponding to Al and ZrAl₃, WA₁₂ intermetallic compounds, Figure 6. Calculated lattice parameters of intermetallics are in a good agreement with ASTM diffraction data cards: a=7.5803 Å for WA₁₂ (8-331) and a=4.0130 Å for ZrAl₃ (2-1093). The lattice parameter of aluminum a= 4.0517 Å is slightly increased in comparison with 4-787 ASTM data card. The coherent diffraction domain (CDD) value and lattice micro distortion for aluminum were calculated by Williamson-Hall analysis D=50 nm, ε = 2.5·10⁻³.

![Figure 4. Etched surface of Al – ZrW₂O₈ sintered for 1h.](image1)

![Figure 5. Etched surface of Al – ZrW₂O₈ sintered for 5h.](image2)

![Figure 6. XRD patterns of Al – ZrW₂O₈ specimen](image3)

After 5h of sintering the structure of the material is represented with microfibers with average length of 30 µm homogeneously distributed in aluminum matrix, Figure 5. On the XRD pattern, Figure 6, one can observe peaks corresponding to Al and cubic ZrW₂O₈. Lattice parameter of aluminum increased in comparison with 1h isothermal hold, a = 4.0544 Å. ZrW₂O₈ lattice parameter a = 9.2187 Å is increased in comparison with literature data [5]. CDD value and lattice micro-distortions for Al D=500 nm and ε = 7·10⁻³ correspondingly are increased in comparison with ASTM data and results for specimens sintered for 1 hour.
Vickers hardness tests were performed to evaluate mechanical properties of the pseudo alloys obtained after 1h and 5h sintering. A sample obtained with an isothermal hold for 1 h has the microhardness of the dense areas (2) containing Zr and W atoms of 455 MPa, which is higher than the microhardness of the aluminum matrix (1) equal to 195 MPa (Figure 4). Microhardness of the material increases with increasing sintering time. After 5h isothermal sintering microhardness value of the pseudo alloy obtained increased up to 530 MPa [6].

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 consistuent oxides WO$_3$ and ZrO$_2$ and synthesis of WAl$_{12}$ and ZrAl$_3$ intermetallic compounds after 1 hour of isothermal hold [7, 8]. 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. After 1h of sintering when the decomposition of zirconium tungstate occurred the lattice parameter increased slightly but after 5 hours of isothermal holding a significant increase of the lattice parameter occurred. This effect may indicate the formation of internal compressive stresses in the material after synthesizing of zirconium tungstate. Their value is estimated to be 50 MPa after 1 hour of isothermal hold and 90 MPa, and after 5 hours of isothermal hold.

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 sintering 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. The value of internal compression stresses was estimated to be 90 MPa. Vickers hardness of the pseudo alloys obtained increases by two times with increasing sintering time from 1h to 5h.

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