RECYCLABLE MULTIMETALLIC HIGH TEMPERATURE MATERIALS FOR ENERGY APPLICATIONS

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Abstract

Nowadays, the use of waste materials from various technologies is increasingly discussed, not only in terms of environmental impact, but especially in terms of reducing primary raw materials wherever appropriate. One such use appears to be the reuse of material by recycling and subsequent processing of selected multi-metallic high temperature materials (in this case, for example, tungsten-based alloys/composites). It is this reuse of waste as a substitute for original, relatively expensive raw materials supplied by external suppliers and the application of selected recycling technologies that will serve as a suitable alternative compared to the use of original raw materials. Selected high-temperature composite materials are, for example, part of transport containers (together with steel elements) or radiation shielding elements. These materials have specific material properties (e.g. high material density) that can be clearly exploited in the design and construction of energy components. These material properties, as well as the recycling technology of multi-metallic materials will be discussed in this presentation. Furthermore, the use of such prepared and manufactured components in a defined energy system, which is part of alternative energy sources, will be described.

Keywords: High temperature alloys, composite materials, tungsten pseudo-alloys, material recycling, energy storage system

1. INTRODUCTION

Multimetallic heavy-density compounds are nowadays represented by high-density materials. These materials undoubtedly include tungsten alloys. Tungsten alloys can be very difficult to prepare due to its high melting temperature, so alloys are prepared by powder metallurgy, where several metal powders can be joined together to form a pseudo-alloys of tungsten. The powder metallurgy method allows the formation of composite materials that can be further processed, for example, by rotary forging [1] or machining, into a final product. It is during the machining of the composite material into a final product that waste material is produced and can be further processed.

The waste material can also be used as a substitute for the input pure tungsten powder in cases where high demands are not placed on the resulting purity of the tungsten pseudo-alloy and where accurate material property values may not be achieved. One such use is as a subsequent component for power generation units. The aim of this work is therefore to create components from tungsten pseudo-alloys using unused waste material. Thus, products made of recyclable tungsten pseudo-alloys can take a good place in the field of alternative energy sources, especially in energy storage systems, or in power systems, e.g. as components of charging stations, where the demand for an instant energy source is needed [2].

2. METHODOLOGICAL BASE

Tungsten-based composite multimetallic materials are used in various technical fields. They are high density materials with applications in medical technology (as shielding for radioactive emitters) or in the military industry (waste in the production of armour piercing munitions). Their production generates a sufficient amount of waste material that can be used further. One possible use of waste is in the energy area, for example in the form of various components of an energy system. A properly designed and manufactured component of such an energy system finds its place not only in the life cycle of the tungsten material, but also in the economics of the company in the form of financial and material savings.

The components of power units are electromechanical devices that are used to store the kinetic energy of the rotating rotor. It is in the rotor that energy is stored for future instant use. Rotors are used in a wide range of nominal outputs and time intervals for charging and discharging [3] and find applications to compensate for uneven running of machines, to power hybrid vehicles, to power space satellites and probes, as backup power sources and also as electrical energy storage [4].

The specific technical applications in power units have specific requirements for their design and the design of the rotor used. At present, there are different rotor component shapes based on an axi-symmetric disc shape [3], there are different rotor concepts based on vertical or horizontal rotor arrangement [5,6]. These findings can also be used as a basis for the development of a new component based on tungsten pseudo-alloys.

3. BRIEF OVERVIEW OF TUNGSTEN RECYCLING

Based on recent studies performed by ITIA [7], the global tungsten flow has been mapped for the year 2019. The total input for production of intermediates was 108,500 t (metric tons tungsten content) from which 37,500 t were scrap (new and old scrap), which results in a recycling input rate of 35 %. 98,000 t of tungsten were consumed in end-use products and based on the estimate for old scrap generated (29,000 t) an end-of-life recycling rate of 30 % can be calculated. Thus, tungsten belongs to the group of metals with a recycling input rate above 25 % (ie. 35 %) which, according to a recent UNEP Report [7], is only achieved by one third of the sixty metals investigated. Today, the tungsten processing industry has developed technologies to treat nearly every type of oxidic, metallic or carbide scrap generated in the production and end-use cycle. As these technologies were adapted to the materials made from tungsten and these materials are reflected in the first-use segments, it is worth studying the global breakdown and the recycling efforts in each segment better to understand the current state of recycling and future potential.

The first materials to be recycled were the processing scraps (so-called new scrap), generated during production of tungsten-bearing goods. They were easy to collect and their value was obvious to those dealing with them in their factories. Technologies to recover tungsten from this new scrap were developed and quickly almost no tungsten was lost any longer from new scrap. Dealing with old scrap, tungsten-containing products at the end of their service life, is more demanding [7-10].

There are technologies to deal with well-defined tungsten scrap and to recycle such scrap in the most direct and efficient way to something which can be used again, while other processes may consume more resources in the form of chemicals and energy, but would be able to deal with a wider variety of tungsten scrap materials. There are recycling processes, which recover tungsten from scrap in a way that the resulting products have virgin quality, opening the door for practically infinite recycling of tungsten without any compromise to end-product quality.

A wide variety of recycling technologies for tungsten exists today. Processes are tailored to deal with different scrap types and to produce well-defined recycling products. For every combination of given input and expected output there is the optimal process (or a combination of such processes). Future developments in recycling technology will focus on

(1) improved process economy and minimisation of environmental impact,
(2) increased flexibility concerning input scrap quality and variety and
(3) improved process stability and ability to deliver the desired quality of the recycled material.

Cost (and resource) efficient direct recycling technologies will increasingly be used where sufficient well-sorted and defined scrap can be collected. Certain end-use applications may perform perfectly well even with a broader property spectrum in the recycled material, leading to either an extended use of tungsten products (ie new applications) or a more cost effective one, via the potential of direct recycling. The higher the global recycling rate becomes, the more important will be the role of the chemical recycling technologies, which are capable of removing impurities effectively and producing recycling products with virgin properties. This is a kind of "reset button" guaranteeing a low impurity level in the top-quality tungsten end products. With this combination of direct and chemical recycling, the tungsten industry is in a position to push recycling activities to the economic limits and to sustain highest quality at the same time. A certain amount of primary tungsten will always be needed to cover global market growth and to replace dissipation and dilution losses [8-10].

4. MULTIMETALLIC HIGH TEMPERATURE ALLOYS FOR COMPONENTS

The tungsten-based pseudo-alloys that are intended and will be used for the chosen energy components are composed of pure tungsten powder and other additives. These impurities are alloying elements such as cobalt, nickel, iron, molybdenum, copper or rhenium. The relative ratios of tungsten and other additives are determined by the purpose of the end use, and at the same time these additives affect the resulting mechanical properties [11,12]. The chemical composition depends on its primary use, however, the tungsten content is in the range of 90-95 % with the remainder being additives. Due to the difference in melting temperatures of these materials, the conventional route of melting together and then casting the material is impossible. For this reason, such materials are prepared by powder metallurgy.

The experimental composite material described here is a WNiCo pseudo-alloy containing 91 % W, 6 % Ni and 3 % Co. The process of producing the final semi-product starts by mixing pure metal powders with the same grain size in the desired stoichiometric ratio. After thorough mixing to guarantee the homogeneity of the prepared mixture, the mixture is compacted using the original vibratory compaction equipment. This equipment enables continuous filling of the moulds and at the same time allows control of the quantity of the metal mixture dosed. The powder is contained in a closed polyurethane cylindrical mould, which is subject to the pressure of the surrounding liquid in all directions. This method of compaction of metal powders utilizes the compression-in-part technology (CIP process).

The compaction only mechanically connects the individual particles of the metal mixture. In the next step, sintering, the particles are connected by a diffusion process. The sintering is already carried out in a rotary tube furnace, in which a homogeneous temperature field is guaranteed along the entire length of the tubes in which the compacted pre-product is enclosed. The sintering is carried out in two steps to ensure that the development of the desired internal structure of the material is completed [13-15]. These steps are applied to selected samples (I to III) and are described in **Table 1**. The sintering process is already followed by technological operations leading to the finalization of the semi-product (sinter) into a final product, for example by tooling. A system for sintering the material in a rotary tube furnace for the subsequent processing of tungsten pseudo-alloy has been patented.

5. MECHANICAL PROPERTIES OF TUNGSTEN PSEUDO-ALLOYS

Samples of the previously mentioned pseudo-alloy were analysed for their material properties because of the design of the production of the component itself for energy systems. For these multimetallic high temperature alloy TN 831 after different modes of sintering and subsequent processing described in **Table 1** was carried out using a tensile test according to ČSN EN ISO 6895-1 and a Vickers hardness test according to ČSN EN

ISO 6507-1. For the tensile test, samples with a diameter of d_0 = 6 mm and L_0 = 30 mm were used. The loading rate was$v$ = 2 mm/min. The hardness was measured under a load of 294 N, i.e., HV30. The yield strength $R_{p0.2}$ for all evaluated samples fluctuated between 645 and 683 MPa, regardless of material processing. The hardness did not differ significantly within the individual samples and was measured at 328 ± 2 HV30. The tensile strength R_m = 1015 ± 2 MPa and ductility A_5 = 30.2 ± 0.3 % also did not change significantly depending on the processing method. It can be stated that the method of preparation of the evaluated samples and the subsequent hardening did not have a significant effect on the mechanical properties in this case.

Table 1 Labelling of selected samples and examples of technological processing

Sample	Sintering conditions
I	without compaction, hold at a temperature of 1475 °C for 30 minutes
II	sintering in a tube of ∅ 15 with corundum powder, compaction in a rotary furnace, sintering without rotation, holding at a temperature of 1545 °C for 15 minutes
III	rotary furnace sintering as II, hold at 1230°C for 90 minutes, followed by quenching in water in an Ar atmosphere

The microstructure of all samples can be seen in **Figure 1**. It can be observed that it does not show changes depending on the sintering process of the samples. Tungsten aggregates are seen here, with Ni-Co matrix around them. In this case, the structure of the sintered material (composite) is formed by these phases.

The presence of other phases in the WNiCo pseudo-alloy was also discussed in [16]. Neutron diffraction was used for the analysis, which showed the presence of two phases. The first phase is a fine-grained spherical α-W structure (B2 structure). The second is the coarse-grained structure of the NiCo2W matrix. The phase consists of nickel and cobalt in the same ratio as the initial composition with the addition of 2%W. Knowledge of these phases was important for the correct choice of the technological procedure for the subsequent mechanical processing, in this case swaging.

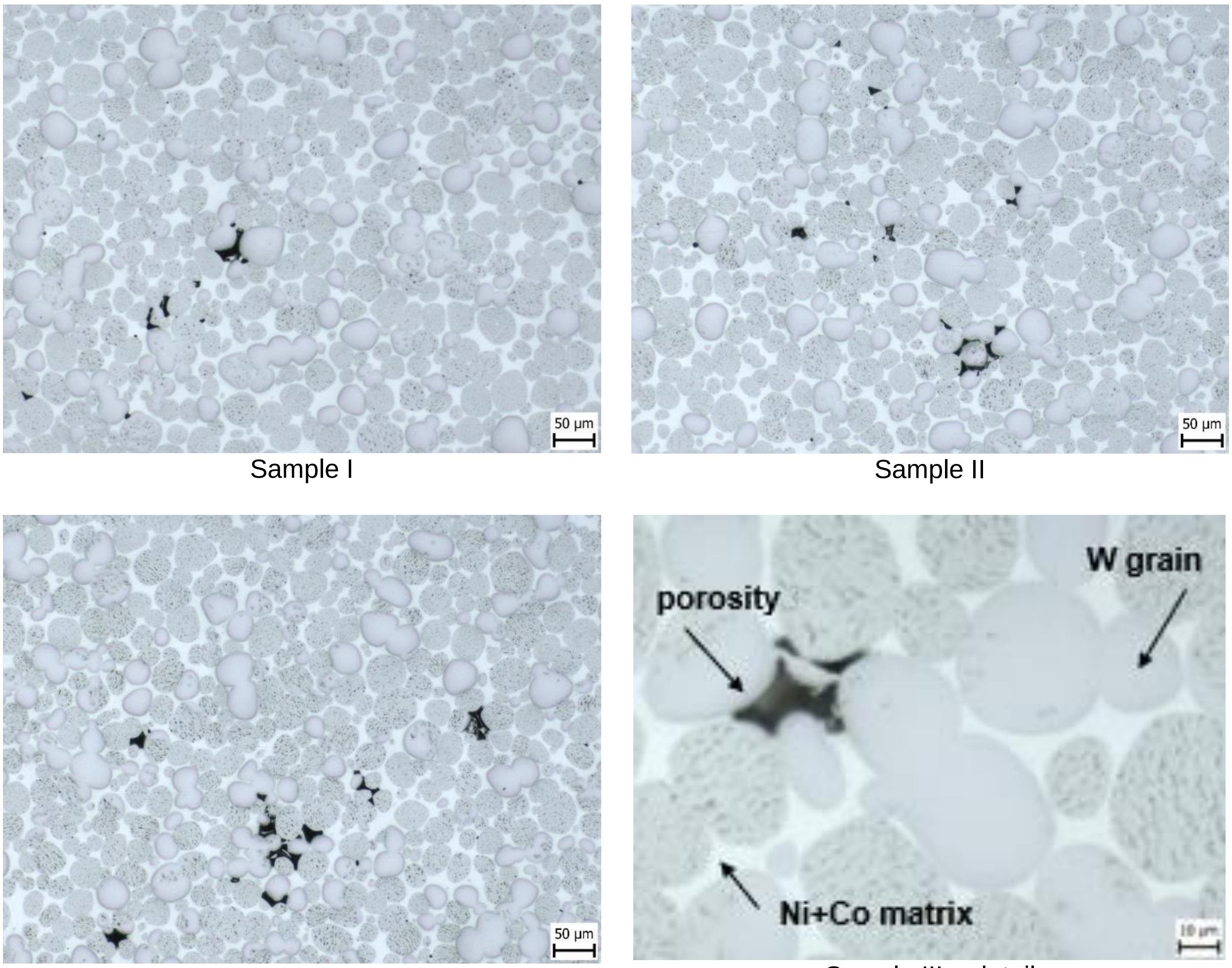
The other phases of the WNiCo pseudo-alloy would be seen if we apply, for example, temperature ageing to the material. As reported in [17] the temperature aging was carried out between 800 and 1050 °C for a duration of 3 h, and the intermetallic phase (Co_2W) appeared. Another heat treatment, annealing at a higher temperature between 1100 and 1200 °C for 1.5 h, generated precipitates. The microstructure of the WNiCo composite and the subsequent mechanical properties can be influenced by the heat treatment technology.

Figure 1 (I to III) shows also two types of defects that have occurred through the sintering of the materialand may cause damage to the material (fracture). The first is the contact between two tungsten agglomerates. The contact of W agglomerates is not desirable but is common due to the high W content by mass of the material. The second is the presence of pores in the matrix or in the tungsten grains (porosity). Porosity can be a significant factor affecting the mechanical properties of individual and precision shaped samples. Both the presence of different phases in the pseudo-alloy and the resulting defects in the microstructure do not significantly affect the use of the WNiCo composite material as a component for energy units.

6. EXPERIMENTAL PART AND DISCUSSION

Connecting two topics, or rather two technical areas, namely the recycling of tungsten-based pseudo-alloy materials and their subsequent use in the energy field is an interesting and useful topic.

In this paper, the recycling of tungsten-based waste material that is generated after technological processing into a final product for defined application areas is lightly outlined and discussed. Both the original and the waste material can be and is expected to be further used specifically in the energy sector, as a rotating component of the upcoming energy unit. For this reason, the idea was to perform simple but indicative mechanical tests on the material prepared in this way, with the hypothesis of whether the strength of the future energy component is sufficient. Hardness and tensile tests were performed for different prepared materials and then compared. The results show that for the two mechanical tests performed, they are not significantly different. It is hypothesised that the recycled material of the pseudo-alloy from which the component will be manufactured will not be significantly affected by the original processing in the future. This hypothesis will of course be the subject of further investigation. Experimental technical and technological designs and parallel numerical calculations are currently underway for the original component so that it can be suitably used as a rotor in a power unit.



Sample I
Sample II
Sample III
Sample III – detail

Figure 1 Microstructure of selected samples (LM)

7. CONCLUSION

The utilization of waste materials, in particular the use of multimetallic composite recyclate, is being increasingly implemented. The example given here shows how the original multimetallic composite materials used in exposed industries are further processed and reused. Today, it is very important that recyclate, i.e. waste raw material, does not end up in landfill and burden the environment, but is further used and processed. Such a process is also applied to the above-mentioned tungsten pseudo-alloys. These, due to their specific properties (in particular their density), can be further used as components of power generation units. The design and implementation of such a component from tungsten recyclate is currently the subject of experimental research and development, especially in the areas of metallurgy, subsequent construction and design.

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