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Applications of Tungsten Pseudo-Alloys in the Energy Sector

Adéla Macháčková [1,*], Otakar Bárta [2] and Silvie Brožová [1]

[1] Faculty of Materials Science and Technology, Vysoká škola báňská – Technical university of Ostrava, 70800 Ostrava-Poruba, Czech Republic
[2] UJP Praha a.s., Nad Kaminkou 1345, 15600 Praha-Zbraslav, Czech Republic
* Correspondence: Corresponcence: adela.machackova@vsb.cz; Tel.: +420596994344

Abstract: New ways of generating energy are currently being discussed, with a transition from traditional primary sources to more environmentally friendly options, particularly renewables. Energy storage is also closely related to this transition. Battery storage currently dominates this area. However, flywheel energy storage system (FESS) technology offers an alternative that uses stored kinetic energy to be transformed into mechanical energy and, using a motor-generator, electrical energy. FESS technology is thus flexible and can be applied in different industrial applications. The management of the technology of recycling W-MMC waste material from other products and the subsequent trial production of high-strength W-MMC material with a density of more than 17 500 kg/m^3 from recycled powders allowed to test the limits of the so-called "heavy" flywheels used in rotor production. Materials with densities ≥ 7 800 kg/m^3, and operating at lower to medium speeds up to 20 000 rpm. The results achieved lead to the conclusion that the developed recycled materials of the W-MMC type with a density ≥ 17 500 kg/m^3, with a yield strength of 1 200 - 1 700 MPa depending on the production method, can be used as a substitute for the structural steels used today, without an enforced reduction of the maximum allowed rotor speed due to exceeding the maximum allowed stress.

Keywords: tungsten pseudoalloys; high temperature alloys; tungsten recycling; energy storage systems

1. Introduction

New methods of energy harvesting are currently being widely discussed. We are gradually moving away from traditional primary energy sources such as coal, natural gas or oil towards the use of other ones. In particular, those that do not burden the environment. Such energy sources include secondary or renewable sources. These are already in common use today, are technologically mastered and utilize energy available from the sun, water or wind. It is the replacement of primary energy sources by these new sources that goes hand in hand with their storage. Energy storage is a topic that is an integral part of the gradual transition to renewable energy sources.

Currently, energy storage is mainly embedded in battery storage. However, there are also other ways of storing energy, or energy that is available, especially at times when renewable energy sources cannot provide sufficient energy to satisfy actual demand to ensure smooth operation in different application areas. Therefore, ways of not only obtaining but also storing energy are constantly being sought. One of the options for energy storage is FESS technology.

The technology of power generation using FESS technology is based on the use of a flywheel. The flywheel is capable of storing kinetic energy. Kinetic energy is generated when the flywheel rotates. By rotating the flywheel around its own shaft, to which the motor-generator is connected, electrical energy is generated. The design arrangements of such systems depend mainly on the shape and type of the flywheel rotor, the bearings used, the method of converting mechanical energy into electrical energy, and other technological components including, for example, the cooling system or vacuum technology [1,2]. The advantage of energy produced in this way is the possibility to regulate its generation according to the need. Electricity produced in this way can be used for systems operating in both the island-mode and the grid-feeding mode.

Flywheels are also a good complement to systems that produce energy and serve as stabilizers of the power grid. This is due to the fact that the energy produced can be fed in or out depending on how much energy is currently needed or to satisfy the peak demand. Therefore, they are used as energy accumulation systems [3]. Other applications in which FESS technology can be applied are railway transport - energy recovery during braking of trains [4], similarly in the automotive industry flywheels are implemented to provide additional energy to propel the vehicle by using the kinetic energy recovery system (KERS) during braking. Another possible application is aircraft carriers, where flywheels help to provide the necessary energy during aircraft take-off [5].

Another interesting solution is charging stations for electric vehicles. Wherever the electricity grid does not have the capacity to supply energy for both fast and slow car charging, charging stations based on FESS technology are a very convenient alternative. In fact, they are local energy storage devices enabling charging electric vehicles with a double power and thus are especially suitable for installation in locations where such fast charging would not be possible [6].

In the context of renewable energy sources, flywheels are part of power systems in which they compensate for power failures of solar or wind power plants, especially in the case of cloudy and windless weather, when they supply the necessary energy. In this way, they replace part of the energy produced by diesel generators, which are able to provide a continuous supply of energy when needed. Diesel generators can then be switched off and turned on only to assure for continuity of supply [7,8].

In general, the findings can be summarized this way: Amount of stored energy and its subsequent release depends on the choice of material from which the flywheel rotor is made. As can be seen from the kinetic energy equation, the moment of inertia of the rotor is directly proportional to the square of the angular velocity. The magnitude of the rotor moment of inertia depends on the mass of the rotor. Another parameter that needs to be monitored is the ultimate strength. This is shown in Table 1 [1,3].

Table 1. Examples of materials for flywheel rotor.

Material	Density (kg/m^{-3})	Strength (MPa)
Steel	7800	500 -1800
Titanium	4500	1200
Carbon-fibre composite (S2)	1920	1470

Currently, and in terms of material availability, steel rotors are the most commonly used, however, there are also other options such as aluminium alloys [9], or carbon fibre [1].

Technology of the steel flywheel rotor and its use in energy storage was the inspiration to see if other materials could also be used for the rotor. The initial idea was further developed and the assumption was made that the flywheel rotor would be made of composite materials. From the wide range of materials that can be used not only for design but also for the function, materials with different properties as compared to steel, were selected. Among these there are tungsten-based materials.

From the wide range of applications of tungsten-based materials, W-MMC composites, namely WNiCo and WNiFe pseudo-alloys, were selected to be used as power unit rotor components. These composite materials are mainly used in the field of medical technology as shielding of radioactive emitters or in military applications as part of armour-piercing ammunitions. Both composite materials have a high density of around 17.5 kg/m^3. This property will be exploited in the manufacture of the flywheel rotor. Tungsten composite material has a higher mass than a traditional steel rotor, which theoretically leads to a higher moment of inertia, while its strength characteristics are better or comparable to steel and therefore there is no need to reduce the allowable rotor speed. However, to meet this assumption, many other aspects in the overall design and especially the functionality of the power unit must be taken into account.

Wherever W-MMC composite material is used, there is always certain amount of waste material generated during production of the final product. The use of waste materials in the form of recycling is a suitable alternative to the use of original expensive raw material sources of individual chemical elements. For this reason, the recycling of the W-MMC pseudo-alloy and its "conversion" into the energy component of the flywheel rotor is not only an actual part of the life cycle of the tungsten material, but is also an important part of the material (resources) savings.

2. Materials and Experimental Works

As mentioned in the introduction, one way to increase the stored energy capacity is to change the flywheel material, either by increasing the strength of the flywheel to allow operation at higher allowable speeds, or by simply increasing the mass while maintaining the original allowable speed.

Tungsten pseudo-alloys are very heavy metal composite materials prepared by powder metallurgy. Some of them have exceptional mechanical properties. The basic component of the composite is tungsten, supplemented by small amounts of alloying elements, which include mainly cobalt, nickel, iron, copper. The appropriate choice of alloys and the composition of the initial powder mixture determines, together with the technological process, the future mechanical properties of the material [10–12].

From the set of W-MMC materials, the high-strength W/Ni/Co or W/Ni/Fe/Co are particularly suitable for the construction of the flywheel rotor. Their chemical composition is shown in Table 2.

Table 2. Chemical composition of W-MMC system materials and their density.

Sample	Chemical composition (wt%)				Density ($g.cm^{-3}$)
	W	Ni	Fe	Co	
TN	91	6.0	-	3.0	17.45
DS	95.8	3.01	1.05	0.14	18.30

The manufacturing process of selected W-MMC composite materials is shown in Figure 1. It breaks down into three logical technological units - the moulding preparation node, the node of high-temperature metallurgical operations (sintering, quenching, annealing) - and in our case - the node of recycling of waste from chip machining.

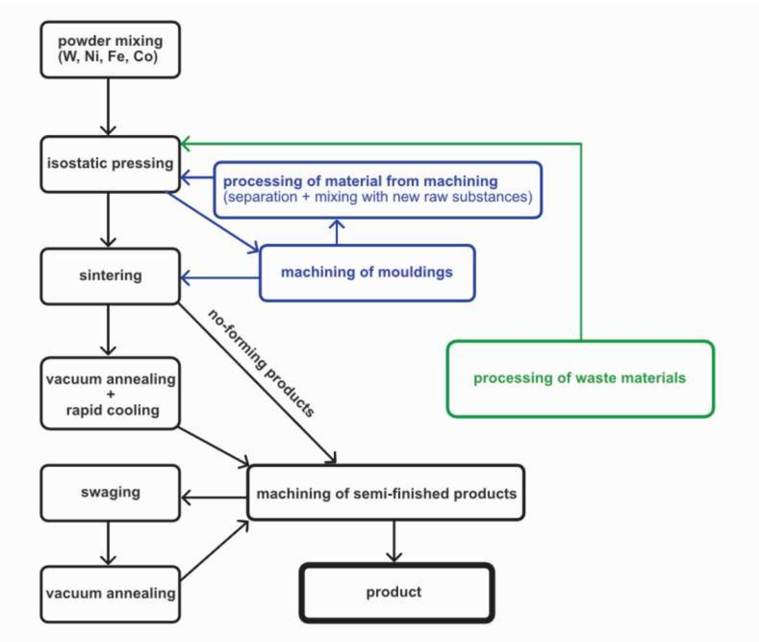

Figure 1. Technological scheme of production of W-MMC composite materials.

The input technological node involves preparation/mixing of the initial powder mixture, either from primary original powders or from powders obtained by recycling, followed by the filling of the initial powder mixture into a suitably shaped vibrationally compacted elastomeric mould. After filling, the mould is placed in the compression chamber of an isostatic press and moulded. After removal of the mould from the isostatic press chamber, the finished product is obtained.

The next technological node includes high temperature and metallurgical processes. At first the product - pressed part - is placed in a suitable sintering furnace [13,14] and after sintering in a vacuum or protective atmosphere, annealed and quenched in water, cold or hot formed, and in the last step aged by vacuum annealing. The sequence of operations and the characteristic temperature curves are shown in Figure 2. Depending on the chemical composition of the composite materials, the heat treatment temperature curves may vary. Some examples of heat treatment are given in [15].

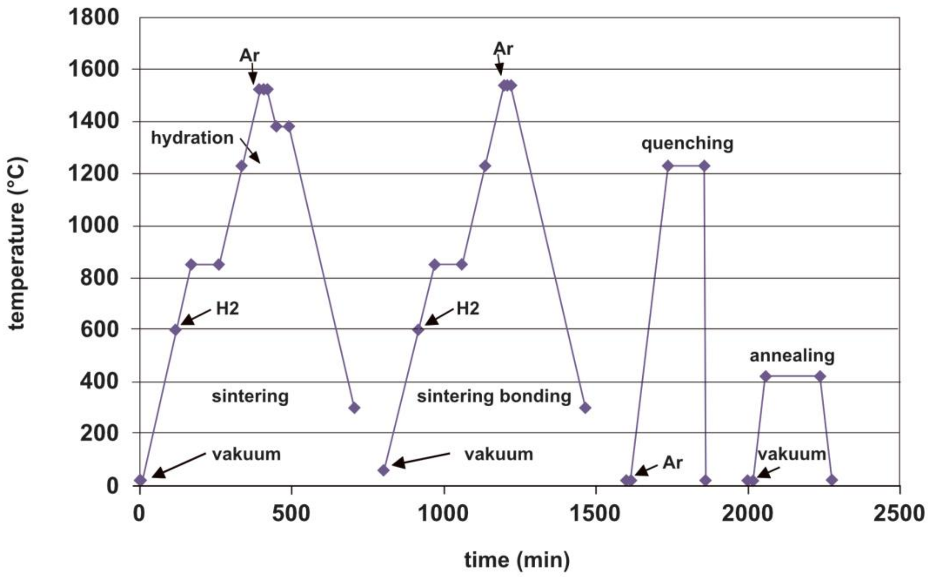

Figure 2. Sequence of high-temperature technological operations during manufacturing of W-MMC composite materials.

Based on initial raw materials used, W-MMC composite materials can be divided into two basic groups. The first group consists of materials made from new powders, while the second group consists of materials made partially or completely from recycled powders obtained by processing the materials of the first group.

2.1. Materials Produced from New Raw Materials - TN and DS

From this group of W-MMC materials, two materials are considered for possible substitution of high strength steel in the manufacture of the flywheel rotor. The first one is a material with the type designation TN, which is intended for the manufacture of extremely mechanically stressed components of penetrating ammunition projectiles. The second one is a material with the type designation DS, which is intended for the manufacture of shielding elements of containers for transport and storage of isotopes, and/or collimation systems of radiotherapy irradiators.

The first technological node whose last operation is the removal of the moulded part from the mould is common to all types of W-MMC materials. For this reason, the manufacturing process of the selected materials will be described starting from the sintering step.

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2.1.1. High Strength Material with Lower Tungsten Content - TN

The microstructure of the material is determined by the sintering mode of the initial powder mixture [16–18]. The gradual evolution of the sinter microstructure during the sintering process is shown in Figure 3. At sintering temperatures below the melting point of the impurities forming the future matrix, i.e. iron, nickel and cobalt, a fine-grained structure of slowly growing tungsten grains is formed (Figure 3). A gradual uniform shrinkage of the material occurs, without shape deformation. However, this fine-grained structure does not allow for subsequent metallurgical processing (annealing, quenching and forming) to achieve the desired mechanical properties of the final TN product ($R_{p0.2}$ = R_m > 1600 MPa while maintaining ductility A_5 > 6 %). It is only at sintering temperatures above the melting point of the alloying elements that the growth of spherical tungsten agglomerates (grains) in the liquid matrix consisting of Ni/Co and Ni/Co/Fe melts accelerates (Figure 3b-d). The sinter becomes plastic and, depending on the tungsten content of the material, more or less dimensional deformation of the sinter occurs due to creep. In free sintering without the use of a mould, significant shape deformation of the sinter occurs.

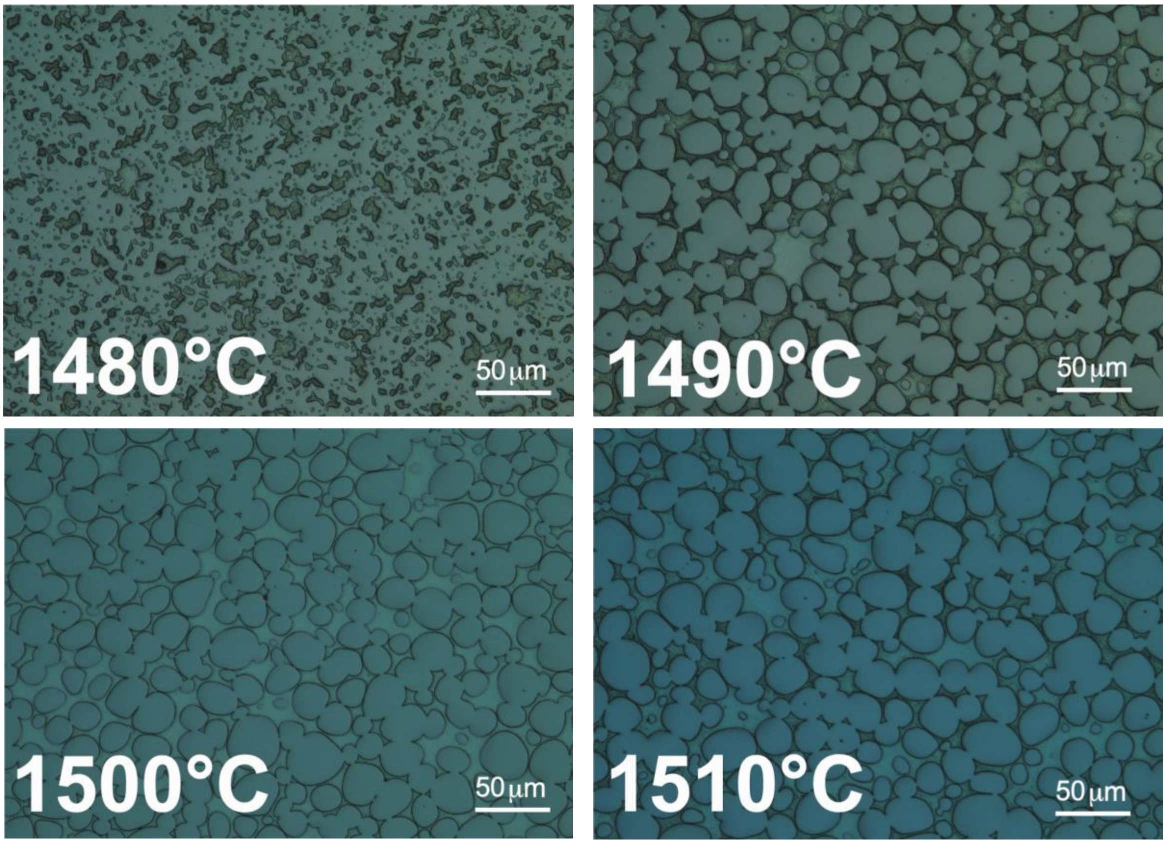

Figure 3. Structures of the TN-type semi-finished product depending on the sintering temperature a) 1480 °C, b) 1490 °C, c) 1500 °C, d) 1510 °C.

The desired final sinter structure (see Figure 3d) is composed of spherical tungsten aggregates with mean diameters in the range of 20-30 µm, which are uniformly dispersed in the "frozen" matrix. After cooling, the sintered TN-type material exhibits a yield stress value Rp0.2 of about 650 MPa, and a strength R_m of about 1025 MPa at a fluctuating tensile value A_5.

In the next step, the sinter is annealed followed by quenching in water. The basic quenching parameters are shown in Figure 2. The typical quenching temperature is 1230 °C with a temperature endurance of one hour. Quenching removes the internal stresses at the grain boundaries between the Ni/Co matrix and the tungsten grains, and stabilizes the high ductility of the A5 material, which exceeds 30% for the quenched sinter (see Figure 4 and Table 3). The strength Rm and yield strength Rp0.2 remain unchanged after quenching.

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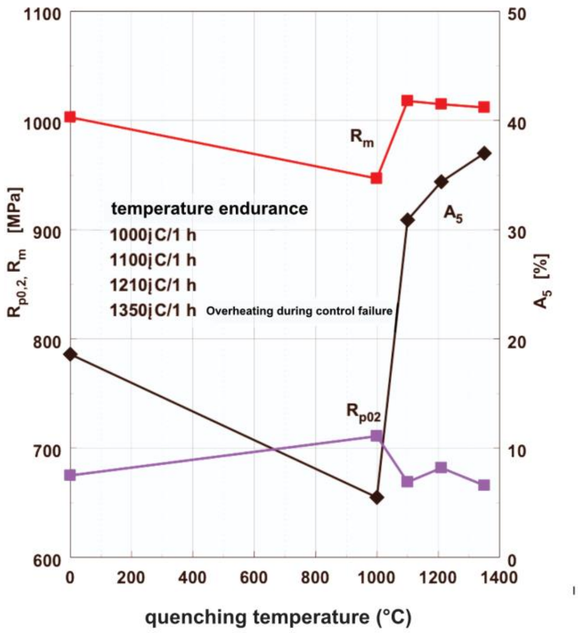

Figure 4. Effect of quenching temperature on the strength, yield strength and ductility of the quenched TN material.

Table 3. Mechanical properties of TN material samples in the hardened (quenched) sinter phase.

Sample	$R_{p0.2}$ (MPa)	R_m (MPa)	A_5 (%)	Impact test (J/cm²)
TN	648 - 665	1015 - 1026	32.1 – 39.5	>248

The quenched sinter is subsequently hardened by forming. The high initial ductility of the quenched TN sinter indicates sufficient reserve of plasticity, which allows for increase in strength $R_m = R_{p0.2} > 1350$ MPa with a cross-sectional reduction > 30%, while maintaining sufficient residual ductility $A_5 > 9$ % (see Figure 5.).

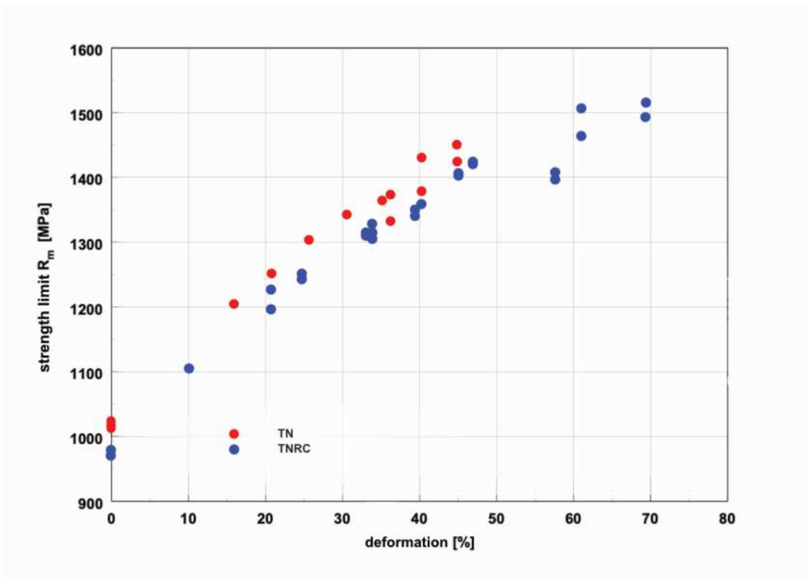

Figure 5. Strengthening of TN material after forming.

The last technological operation is the ageing of the forged product by annealing in vacuum at annealing temperature in the range of 400-500 °C (see Figure 2). Matching the requirements for high strength of the TN material and to maintain sufficiently high ductility requires mutual optimization of the last two technological operations (forming and ageing) so that the resulting strength value is $R_m = R_{p0.2} > 1600$ MPa while maintaining ductility A_5 higher than 6 %, as can be seen in Figure 6. A material with such properties is the final semi-finished product for the production of extremely strength-stressed products such as penetrating cores of arrow-stabilised sub-calibre missiles in the military industry.

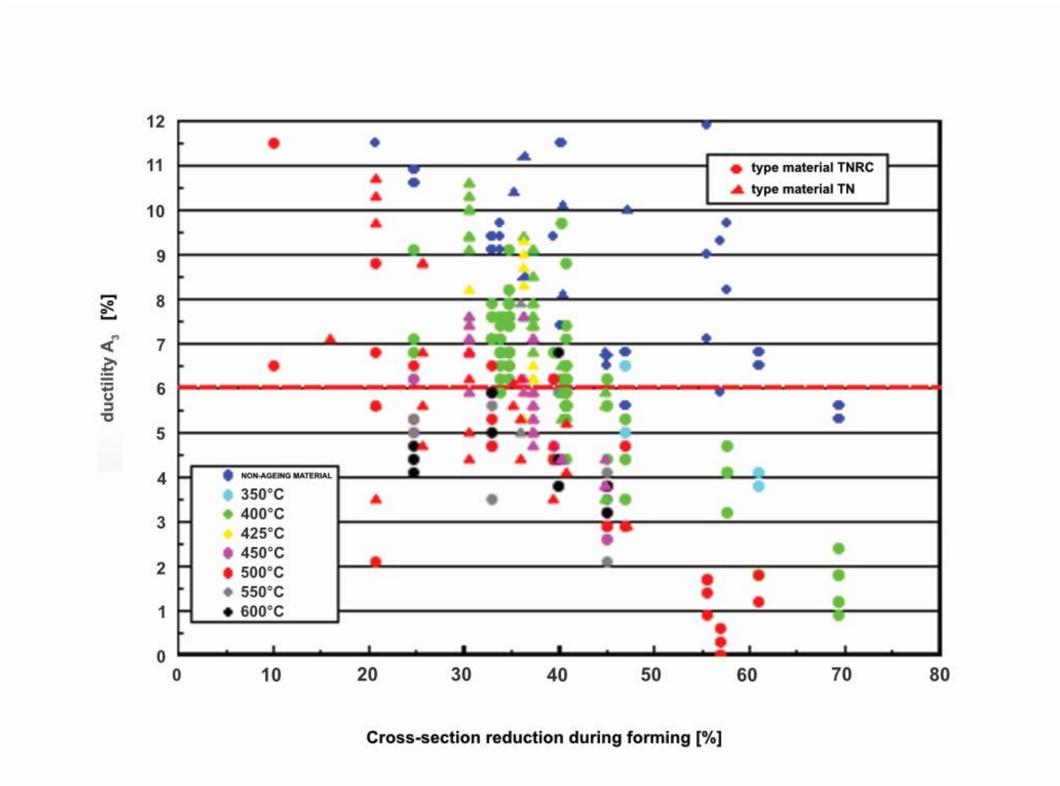

Figure 6. Effect of forming and ageing technology on the final ductility of TN and TNCR material.

Ageing is also manifested by a change in the microhardness value of the TN material (see Table 4). Table 4 shows the measured microhardness values before and after ageing of the TN material.

Table 4. Microhardness values of tungsten aggregates and matrix for TN type material.

Structural component	initial state of reduction 24.8 %	Reduction 24.8 % and ageing 500 °C/2hrs	Relative change
	(HVM 100)		
Tungsten component	746.0 ± 39.5	991.6 ± 19.4	+ 33 %
Matrix	672.2 ± 46.4	791.7 ± 27.6	+ 18 %

2.1.2. Material with Higher Tungsten Content for the Manufacture of Shielding Elements - DS

W-MMC DS type material has a higher tungsten content in contrast to TN material, thus a higher density. It has been developed primarily for the manufacture of medical components using ionising radiation, such as radiotherapy irradiators (irradiation heads and beam collimation systems) or containers for the transport and storage of radioisotopes. Thus, there are not high requirements for mechanical durability, on the other hand, these parts have large dimensions and complicated shapes where the size of the press chamber of the isostatic press can be a limiting element.

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The process as shown in Figure 1 also applies to the DS material. The resulting microstructure of the sinter (Figure 7) shows no difference as compared to the material.

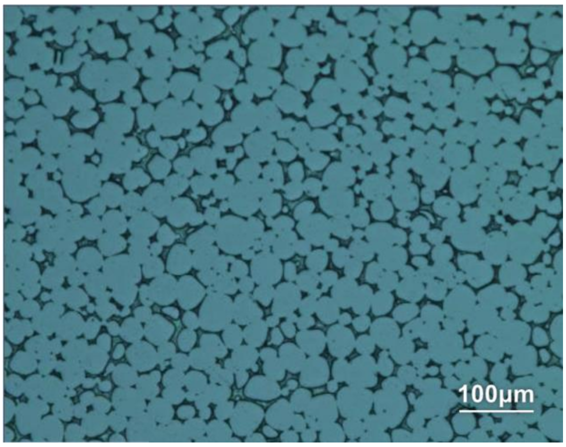


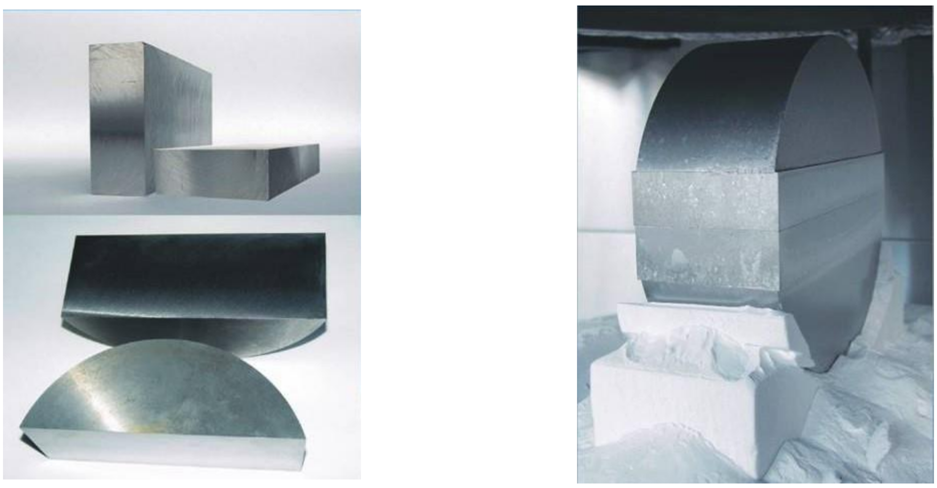
Figure 7. Microstructure of hardened W-MMC DS type sinter.

For most applications, the required mechanical properties are already achieved in the hardened sinter state, so the process of forming is not necessary (see Table 5). However, the high ductility values enable further strengthening of the DS material by forming, if it is required by the way of final use.

Table 5. Mechanical properties of DS material samples in the quenched sinter phase.

Sample	$R_{p0.2}$ (MPa)	R_m (MPa)	A_5 (%)	Impact test (J/cm^2)
DS	653 - 663	953 - 957	22.3 – 27.0	>35

In the case of semi-finished products whose dimensions exceed the capabilities of the pressing chamber of the isostatic press, an intermediate step of connecting already sintered parts by repeated sintering is included before hardening. The touching surfaces of the individual sintered parts (Figure 8a) are machined at the points of contact, assembled into their final form in the sintering mould and re-sintered (Figure 8b).



a) b)

Figure 8. Methods of manufacturing large components from several parts. (Courtesy: UJP Praha a.s).

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2.2. Materials Made from Recycled Powders (TNRC, DSRC and TRC)

In the production of W-MMC materials, recyclable waste material is generated either before sintering during the machining of the moulding or during the machining of the sinter at various stages of production. At present, moulding machining technology is not used. Therefore, the developed recycling technology only addresses the issue of processing waste chips from the machining of sintered TN and DS material. The basic technological scheme of oxidation/reduction chip recycling is shown in Figure 9.

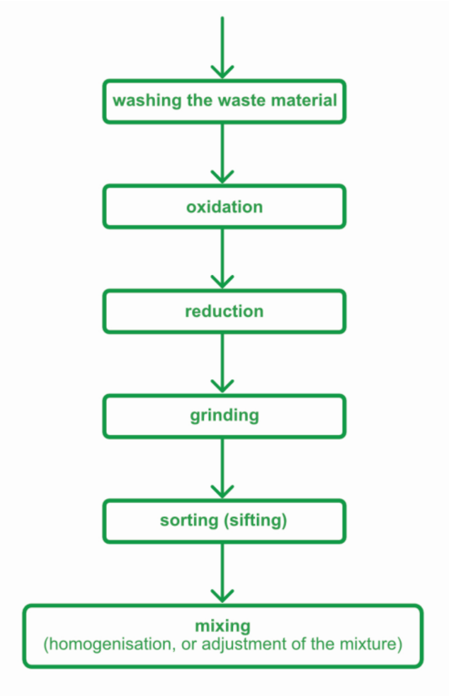


Figure 9. Technological scheme of the recycling node.

Shavings from machining are collected separately according to the type of material being machined, allowing the recycling of material with a well-defined composition. To assess the possibility of using materials made from recycled powders to produce a heavy flywheel rotor, three materials were prepared. The material designated TNRC is made from powder prepared by recycling chips from TN material. Similarly, the DSRC material uses powder obtained by recycling chips from the machining of the DS material. The last material developed and tested was a material called TRC, obtained by recycling chips from the DS material, but differing from the DSRC material in the way it is produced, which includes forming. A detailed description of the developed technology for recycling machining chips is beyond the scope of this paper. We will limit ourselves to an evaluation of the outputs - recycled powders.

Comparison of the morphology of the recycled powder with the morphology of the original powder is made in Figure 10. The images obtained using a line electron microscope did not show any noticeable difference.

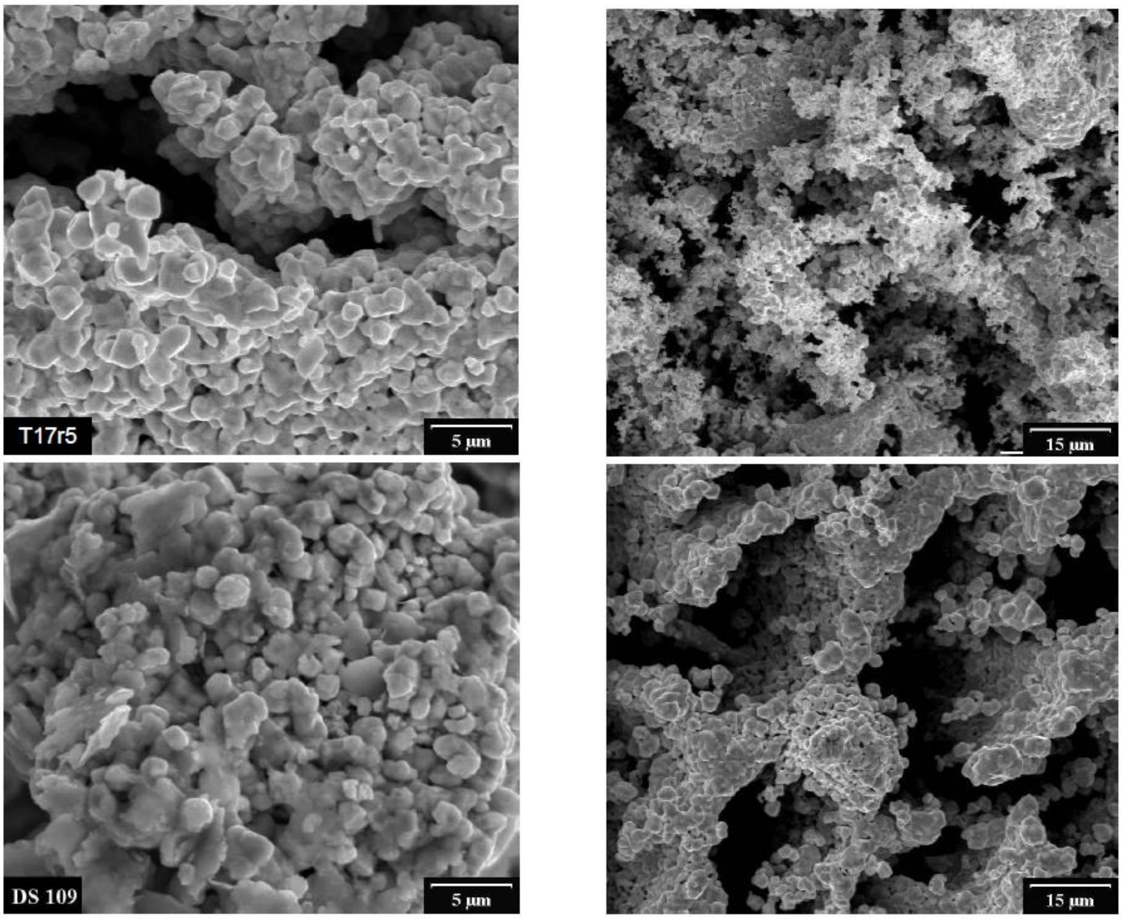
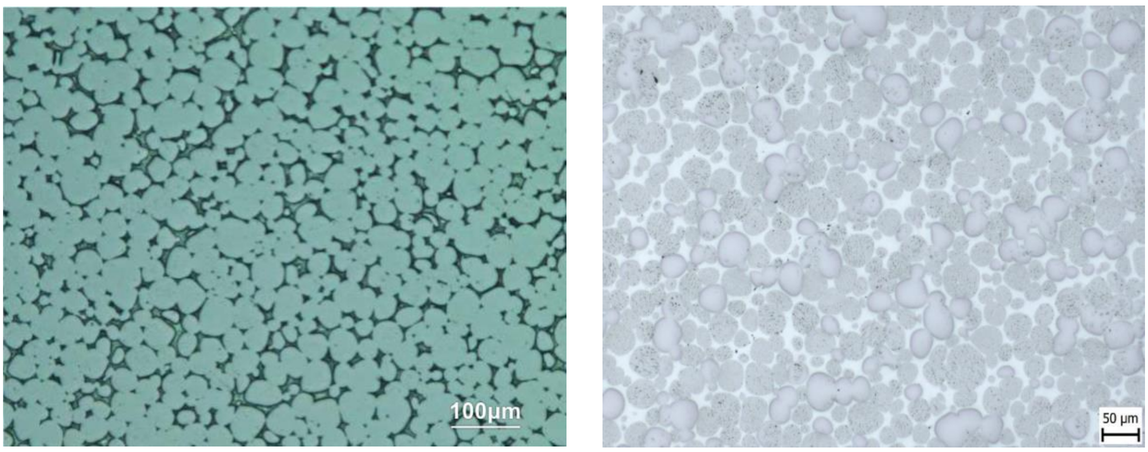


Figure 10. Comparison of the nature of chips after reduction and powder from normal production (DSRC/DS material on the left, TNRC/TN on the right).

The downstream production of W-MMC from recycled TNRC and DSRC powders followed the normal production process – the same as when using new original input raw materials. No difference is evident in the cross-sections of sintered DSRC and TNRC materials prepared from recycled powder and DS and TN materials prepared from new powders (see Figure 11).



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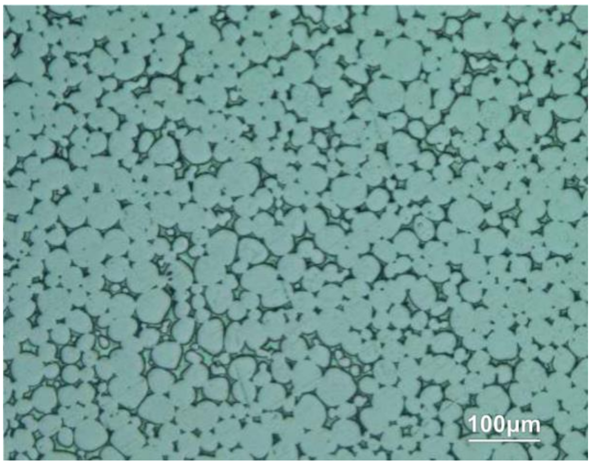

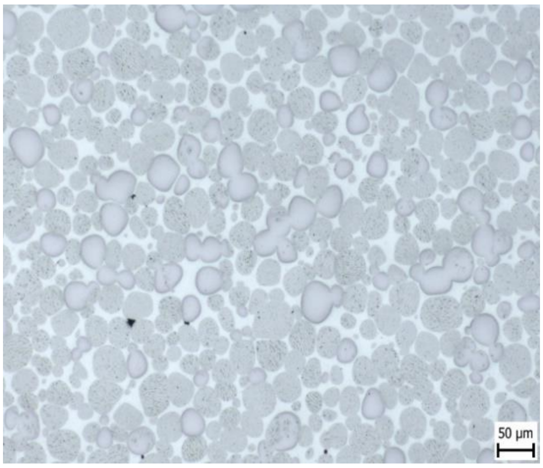

Figure 11. Structure of quenched sinter of recycled material (DS-TN (top)/DSRC-TNRC (bottom)).

Material produced from waste can be expected to have lower and more volatile values than material produced from new feedstock. From this point of view, the mechanical properties of the DS material produced from the new powders seem to be at the lower limit of applicability for the planned use of the material for the production of flywheel rotors. Therefore, in addition to the DSRC material, a forming-strengthened material of the same composition was prepared under the designation TRC.

A relatively small forming deformation is sufficient to significantly strengthen the DSRC material, which after subsequent vacuum annealing, i.e. ageing, gives values of $R_m = R_{p0.2} > 1400$ MPa and ductility < 5 % (see Figure 12).

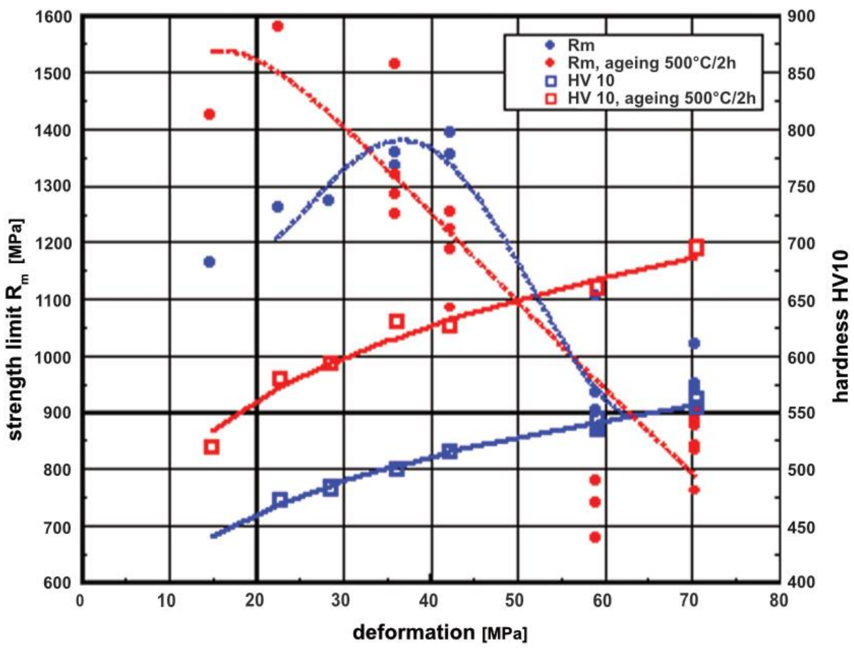

Figure 12. Dependence of ultimate strength and hardness on strain for recycled TRC material.

The mechanical properties of materials prepared from recycled powders at different stages of production are summarised in Table 6.

Table 6. Overview of the achieved mechanical properties of materials made from recycled powders.

Material	$R_{p0.2}$ (MPa)	R_m (MPa)	A_5 (%) after quenching (min/avg/max)	density (g/cm³)
TNRC				17.48-17.49
quenching	651/660/671	1023	21.1/26.6/28.0	
Forging, ageing		1600/1610/1619	5.7/7.6/8.2	
DSRC				18.25-18.30
quenching	652/660/671	948/956/967	17.4/18.7/19.1	
Forging, ageing				
TRC				18.26-18.29
quenching	658/665/677	948/965/1001	17.1/18.1/19.3	
Forging, ageing		1281/1484/1501	1.1/2.6/4.9	

The sensitivity of mechanical properties of the W-MMC prepared in this way to slight contamination by iron of the powders obtained by recycling the chips released from the retort of the oxidation-reduction furnace during recycling was also investigated. The measurements did not show any change in the mechanical properties of the product obtained. No change in strength or ductility values was observed (see Table 7).

Table 7. Effect of chemical composition of TNRC on mechanical properties.

Material		TN	TNRC 0.15	TNRC 0.09
Chemical composition (wt.%)	W	91.00	91.35	91.38
	Ni	6.00	5.70	5.75
	Co	3.00	2.80	2.78
	Fe	0.00	0.15	0.09
Mechanical properties*	$R_{p0.2}$ (MPa)	648;659;649;652;658	649;649;652;653	656
	R_m (MPa)	1023;1026;1020;1023;1022	1018;1016;1018; 1015	1017
	A_5 (%)	39.5;37.1;35.7;36.8; 37.0	36.1;33.6;36.0;32.7	28.0
	Impact test (J/cm²)	248;>300;170 >300;>300	277;164; >300;184	186
Mechanical properties**	R_m (MPa)	1605;1622;1610; 1604;1608;1622; 1615	1603;1600;1602; 1608;1602;1619; 1616	1601;1499;1589
	A_5 (%)	7.3;9.5;7.2;9.6;9.8;7.3;9.8	6.8;8.2;7.6;8.0;6.5;7.1;5.7	0.4;0.0;0.2

* material was sintered and quenched only. ** after swaging (reduction 36 %) and ageing (423 °C/2hrs).

3. Conclusions

The maximum amount of kinetic energy stored in the rotating flywheel is limited by the properties of the material used. Increasing the density of the material used places increased demands on its strength under otherwise identical conditions, thus limiting the maximum allowable rotor speed. From this point of view, flywheels can be divided into two groups: 'heavy' flywheels operating

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at low to medium speeds up to 20 000 rpm, using materials with a density of steel or higher, and 'light' flywheels using high-strength, lower-density materials capable of operating at speeds above 20 000 rpm. However, this leads to increased demands on other components of the FESS (bearing systems, control system, etc.). The decisive criteria for the selection of a FESS are the reliability of the system, as the FESS is expected to operate for approximately 20 years without maintenance, and the cost.

In generally, "heavy" flywheels are conceptually simpler and therefore more reliable, while high-speed "light" flywheels usually have higher specific storage capacities, tend to be more expensive and generally less reliable.

For the experiment, three W-MMC materials, made from powders obtained by oxidation-reduction recycling of machining waste chips, were prepared with strength characteristics suitable for the expected use. However, only two of them have sufficient properties to be considered as full replacements for steel flywheels. These materials are TNRC with strength $R_m = R_{p0.2} > 1600$ MPa, and TRC with $R_m = R_{p0.2} > 1250$ MPa .

The substitution of steel for other metallic construction materials only makes sense if it leads to an increase in the storage capacity of the flywheel under the same conditions. A low-alloy steel flywheel in the shape of a disc made from a commercially available material with the specification DIN/EN 2CrMo4 (AISI 4142) was chosen as a basis for comparison. This steel is characterised by its toughness, good torsional strength and good fatigue strength. It is typically used for statically and dynamically stressed vehicle components, engines and machinery, as well as for larger cross-section parts, crankshafts, gears. The yield strength of this steel depends on the dimensions of the semi-finished product, with larger diameters reaching 500 MPa [19].

In this case, the substitution of the flywheel material by replacing a conventional structural steel with yield strength $R_{p0.2} = 500$ MPa with TNRC material with $R_{p0.2} >1600$ MPa, will increase the amount of stored energy per unit mass by 36%. However, the situation is turned around when using steel with a yield strength of $R_{p0.2} \geq 665$ MPa.

The reason for using W-MMC material made from recycled powders for the purpose under consideration can therefore only lie in economic and environmental terms. However, this requires that the material made from recycled powder be comparable in price to high-strength steel and at the same time allow the production of dimensionally and shape demanding prefabricated parts, thus minimising work. Trying to make a realistic estimate of unit production costs at any given time is beyond the authors' capabilities. They do, however, note that W-MMC materials made from recyclates can be seen as a relatively stable and well-liquid capital investment. With their purity requirements, composition (W, Ni, Co), corrosion resistance and stability in the air, they represent a good way of storing strategic raw materials whose price is almost certain not to decline and for which there will be a sustained demand.

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