

The influence of MoS₂ additions on the densification of water-atomized HSS powders

B. Šuštaršič^{a,*}, L. Kosec^b, M. Kosec^c, B. Podgornik^d, S. Dolinšek^d

^a Institute of Metals and Technology, Ljubljana, Slovenia

^b Faculty of Natural Science and Technology, University of Ljubljana, Slovenia

^c Jozef Stefan Institute, Ljubljana, Slovenia

^d Faculty of Mechanical Engineering, University of Ljubljana, Slovenia

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Abstract

Molybdenum disulphide (MoS₂) might be a useful addition in the production of composite self-lubricating high-speed steel parts, which are used in different anti-wear applications. MoS₂ might also have a favourable influence on the synthesis of sintered high-speed steels (HSSs) improving the compressibility of the metal powder mixture during its cold compaction, as well as acting as a sinterability enhancer of powder compacts during their sintering. In view of this, the compressibility and the sinterability of M3/2 and M35 types of HSS powder mixtures with MoS₂ additions were investigated.

In this article, the influence of MoS₂ additions on the densification during cold compaction and vacuum sintering of selected HSSs is presented. It has been established that the MoS₂ promotes a consolidation of HSS powders during automatic die compaction, as well as final densification during sintering. Sintering of HSS-MoS₂ powder mixtures proceeds by the combination of a reactive and supersolidus liquid-phase sintering process. The added MoS₂ reacts with the steel matrix, enhancing densification. Fine dispersion of complex sulfides (Cr, V, Fe)S is formed, which improves the machinability and tribological properties of sintered steel.

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1. Introduction

Concerning the methods of manufacturing, HSSs can be divided into two groups: conventional and PM (manufactured by powder metallurgy routes) HSSs. Conventional HSSs are produced by the conventional high-temperature metallurgical procedures (melting in electro-arc furnaces, continuous or discontinuous casting into billets or ingots, followed by forming with hot rolling and/or forging). Furthermore, PM HSSs can be divided into two groups: HIP-ped and sintered PM HSSs.

High quality HIP-ped PM HSSs are produced by the direct consolidation of clean (nonoxidised), hard, spherical gas-atomized high-alloyed powders. The powder consolidation to a full-density product (ingot) is usually performed in two steps. First step is a consolidation by the cold isostatic pressing (CIP

at 400 MPa), and the second consolidation step is a hot isostatic pressing (HIP at approximately 1150 °C and 100 MPa pressure of Ar or N₂) of evacuated containers filled with a selected powder. In Europe, this method of manufacturing is known as the ASEA-STORA process and the manufactured steels as ASP or recently as Vanadis steels (Böhler-Uddeholm Co.) [1–5]. Then, further forming of HIP-ped ingots to the final product is similar to the conventional HSS production. Simultaneously in the USA, practically the same manufacturing procedure was developed by the Crucible Steel company [1–3]. HIP-ped PM HSSs have a fine grained and chemically very homogenous microstructure. This can be attributed to the rapid solidification (RS) and cooling of melt particles, which are formed during the manufacturing of high-alloyed powders by atomization [1,4,6]. The microstructure of PM HSS contains a uniform distribution (15–30 vol.%) of fine, complex carbides in a tough, tempered martensitic matrix. Complex (mixed) carbides are formed from the main alloying elements (Mo, W, V and Cr) during solidification by a eutectic reaction (primary or blocky carbides), as well as during heat

* Corresponding author. Tel.: +386 1 470 19 20; fax: +386 1 470 19 39.
E-mail address: borivoj.sustarsic@imt.si (B. Šuštaršič).

treatment (pro-eutectoid and fine coherent carbides) [7–9]. The main types of carbides have the following formulae: M_6C , MC and $M_{23}C_7$. Sometimes, undesired metastable M_2C can also be found. In comparison with the conventional manufacturing procedure of HSS, powder preparation with RS technology enables the production of PM HSS with the increased content of carbon and alloying elements, without the risk of forming either chemical segregations, or exaggerated carbide/grain growth and the formation of carbide stringers during hot forming. This gives HIP-ped PM HSSs an improvement in mechanical properties (hardness, fracture toughness and yield strength) resulting in better wear resistance, thermal stability and machinability. As a consequence, these HSSs are well-recognised and established in many applications replacing the usually cheaper, conventional HSSs.

Another widely used PM manufacturing method of HSSs is powder consolidation by uniaxial cold compaction and sintering of green compacts. In this case, lower-quality but cheaper water-atomized powders are used. Water-atomized powder particles are oxidised on the surface and additional soft de-oxidation annealing is required. However, water-atomized powders have irregularly shaped particles and, because of their mechanical interlocking [10], they are particularly appropriate for uniaxial cold compaction. Water-atomized HSS powders are cold pressed into green compacts of complex shapes with a high-production-rate mechanical or hydraulic presses. Therefore, the improvement of powder mixtures compressibility and other compaction characteristics is one of the main goals. Nowadays, metal powder injection moulding [11,12] is also very popular for forming of small and geometrically very complex products. After cold compaction, sintering of the green compacts is performed. Although de-oxidation annealing of water-atomized powders is performed, high-alloyed HSS powders are coated to some extent on the surface with oxides of alloying elements with a high affinity for oxygen (Cr, V, W, etc.) and sintering must be carried out in vacuum or protecting/reducing ($N_2 + H_2$) atmosphere. The densification of green compacts proceeds by the so-called supersolidus liquid-phase sintering process (SLPS). A significant difference between the sintering of cemented carbides (WC-Co) and HSS exists, in spite of the fact that the final densification occurs in the presence of a liquid in both cases. Recent sintering investigations of cemented carbides [13] show that most of the densification process (50–90%) occurs in the solid state and that the formation of a liquid does not change the densification rate significantly. The sintering process of HSS is different. Densification in the solid state is negligible [14]. Significant sintering starts only after enough liquid is formed at the grain boundaries and when the green compact loses its rigidity. Therefore, sintering of HSSs proceeds at relatively high temperatures (1250–1300 °C). All this gives sintered HSSs a characteristic microstructure [14] with an almost continuous carbide phase, formed at the grain boundaries. The result is usually a lower fracture toughness of sintered HSSs if compared with HSSs produced by the HIP technology. However, the main advantage of this PM procedure is a large scale production of small complex-shaped final products with narrow dimensional tolerances and in many cases almost without any

additional machining costs. Another advantage of this PM procedure is the flexibility to prepare different powder mixtures. Admixing of different hard/soft particulate phases to basic high-alloyed HSS powder is possible. The formed powder mixtures can contain fine carbides, oxides, sulphides or fluorides (NbC, TiC, Al_2O_3 , MnS, CaF_2 , etc.) enabling the synthesis of a special composite or gradient material with target properties for a precisely defined application (e.g.: improved wear resistance, higher thermal or corrosion resistance, better machinability and self-lubricity, etc.) [15–17]. Sintered HSSs are also interesting materials because their surface can be additionally selectively refined by thin multi-layered PVD/CVD coatings of TiN, Ti(C, N), CrN, etc.

The main problem with sintering HSSs is a high sintering temperature and a narrow sintering window [17]. Therefore, investigations are focused on searching for new chemical compositions which could be sintered successfully at lower temperatures (1120–1150 °C), enabling sintering in conventional mesh-belt sintering furnaces [18,19]. The aim of recent research is also investigation and searching for compositions, which would be less sensitive to over-sintering and carbide/grain growth with increased sintering temperature and the amount of liquid, respectively. Investigations are also directed towards the development of new composite materials with an additional part of soft and/or hard phases in order to modify the tribological properties of the surface of the composite material [15,16]. Also of considerable current interest is the improvement of machinability (valve-seat inserts) and self-lubricity (bearings, parts exposed to fretting, etc.) [20,21].

Nowadays, sintered HSSs are no longer used primarily as cutting material. Their name, however, has remained, reminding us of their early development and of the time when these materials were used exclusively for cutting applications and other kinds of machining of metals, wood, polymers, paper and other materials. In many, especially in high-speed cutting applications, they are replaced by new, superior ceramic materials (cemented carbides, PCD, CBN, TiB_2 and Sialons). In spite of this, we are witnessing a renaissance in sintered HSSs and their products. They are well established today in many other applications as structural, anti-wear and bearing materials (valve-seat inserts, slide bearings, tool and other parts exposed to wear, fatigue and/or corrosion) where the excellent compressive strength and wear resistance, as well as suitable fracture toughness and thermal stability are required.

MoS_2 is a well-known and widely used solid lubricant. As such, it might also be a useful addition in the production of composite self-lubricating HSS parts, which are used in different anti-wear applications. MoS_2 might also have a favourable influence on the synthesis of sintered HSS; e.g.: to improve the compressibility of the metal powder mixture during its cold compaction, as well as a sinterability enhancer of powder compacts during their sintering. Therefore, the compressibility, as well as the sinterability of M3/2 and M35 types of HSS powder mixtures with a MoS_2 additions were investigated. In the present paper, the influence of MoS_2 on the consolidation during cold compaction and final densification during vacuum sintering of selected HSSs and the

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