Optimisation and characterisation of tungsten thick coatings on copper based alloy substrates

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Abstract

Tungsten is a promising armour material for plasma facing components of nuclear fusion reactors because of its low sputter rate and favourable thermo-mechanical properties. Among all the techniques able to realise W armours, plasma spray looks particularly attractive owing to its simplicity and low cost. The present work concerns the optimisation of spraying parameters aimed at 4–5 mm thick W coating on copper–chromium–zirconium (Cu,Cr,Zr) alloy substrates. Characterisation of coatings was performed in order to assess microstructure, impurity content, density, tensile strength, adhesion strength, thermal conductivity and thermal expansion coefficient. The work performed has demonstrated the feasibility of thick W coatings on flat and curved geometries. These coatings appear as a reliable armour for medium heat flux plasma facing component.
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1. Introduction

In magnetic confinement fusion reactors the plasma thermal energy and particle flux are absorbed by dedicated shielding devices and heat exchangers called plasma facing components (PFC). In the ITER reactor [1] the amount of the impinging thermal power ranges from 5 to 20 MW m^{-2} depending on PFC position in the reactor; this power is released continuously or in form of thermal transients events that determine, in addition to overheating, also thermal fatigue. The PFC conceptual design foresees that such a huge amount of power is transferred to a cooling fluid that circulates in a loop made of high thermal conductivity metals (heat sink) like copper alloys. For example, in the ITER reactor [2] the use of precipitation hardened (PH) copper alloy (e.g., copper–chromium–zirconium, Cu,Cr,Zr) or aluminium oxide dispersion strengthened (DS) copper is foreseen. Unfortunately, copper alloys cannot be exposed directly to the particle flux coming from plasma because of their low melting point and

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erosion lifetime. Therefore, the actively cooled component exposed to plasma must be protected by means of high erosion resistance materials (armour materials). Tungsten has a very high physical sputtering threshold energy that provides good erosion lifetime, a very high melting point and a good thermal conductivity, thus it is an excellent candidate for armour material [3]. Conversely, the high elastic modulus, the high thermal expansion mismatch with other metals, and in particular copper alloys ($\alpha_{Cu} \approx 4\alpha_W$), and the high brittleness make the joining of W to heat sink metals really challenging. The thickness of the W armour capable to provide sufficient erosion lifetime ranges from 5 to 10–15 mm depending on the armour position in the reactor [4]. There are different techniques to provide W armour on the heat sink material of PFC. One solution consists in the brazing of sintered tiles or pins on the heat sink, in this way it is possible to use W with the best properties and reach superior erosion resistance and thermo-mechanical performances [5]. Unfortunately, this technique is time consuming, expensive and is difficult to be applied on complex components. Other techniques that can be used to provide good quality W armour are physical vapour deposition (PVD) and chemical vapour deposition (CVD) but both are extremely expensive for coating of large surfaces and are not suitable for high thickness coatings. Plasma spray (PS) technique is attractive for the fabrication of W armour-coatings because of its simplicity, its possibility to cover complex extended surfaces and its relatively low cost, however PS coatings have also some drawbacks such a higher impurity content, intrinsic porosity and lower physical and mechanical properties. Nevertheless, these coatings can be used in some region of the reactor where the heat and particle flux is expected to be lower.

The deposition of thick W–PS coatings is a challenging activity because of the high melting point of W and its intrinsic brittleness. W–PS coatings for fusion application have been successfully manufactured on refractory substrates (molybdenum or graphite) [6,7] by high temperature spraying obtaining coatings with sufficient cohesion and low residual stress.

In our case, the spraying on Cu,Cr,Zr alloys [8] has the further complication that it must be performed keeping the substrate temperature low enough in order to avoid coating detachment from the substrate (due to the thermal mismatch) and the overheating of the substrate that induce a strong degradation of its properties (at a temperature higher than 703 K). However, a low substrate temperature affect the cohesion of deposited layers as well as the porosity amount and thermal–mechanical properties of the coatings.

In a previous work [9] we have demonstrated the feasibility of 5 mm thick W coatings on precipitation hardened Cu,Cr,Zr alloy tubular substrates and their capability to withstand heat fluxes up to 5 MW m^{-2} in cooling condition relevant for ITER reactor (i.e., pressurised water cooling) [4].

The present work was undertaken to improve the W–PS coatings and to investigate morphology, structure and integrity of the coating manufactured and their mechanical properties.

2. Coating manufacturing

The spraying campaign was performed on tubular and bar geometry samples made of Cu,Cr,Zr alloy (composition weight percentage: Cr 0.65, Zr 0.05, Cu balance) in order to evaluate the effect induced by different geometries on coating reliability. The deposition process [10] was carried out at Centro Sviluppo Materiali SpA laboratories (Rome) using the low pressure plasma spray technique by means of the controlled atmosphere plasma spray (CAPS) facility. The powders used are composed of two parts with different size: between 15 and 35 μm and <5 μm.

In order to increase the adhesion of the W on copper alloy and to reduce the residual stress, due to the thermal expansion mismatch, a bond-coat and an interlayer, consisting of a mixture of Al–Si, Ni–Al and W, were provided on Cu,Cr,Zr alloy before spraying the pure W. The bond-coat plus interlayer reach a thickness of about 800 μm.

The spraying pressure was chosen in order to increase the deposition efficiency and to optimise the W microstructure (reduce the fraction of unmelted particles and porosity). The optimisation and control of the temperature of the substrate and coating during the deposition was fundamental for the integrity of the coating. Different cooling systems have been tested and finally a cryogenic cooling, based on liquid and gaseous Ar, was selected. After optimisation, coatings were produced successfully keeping the substrate and coating temperature below 453 K.

All the spraying campaigns were carried out in argon atmosphere. Different spraying pressure were investigated, from 300 to 2000 mbar: the tests at 300 mbar showed low deposition efficiency, high
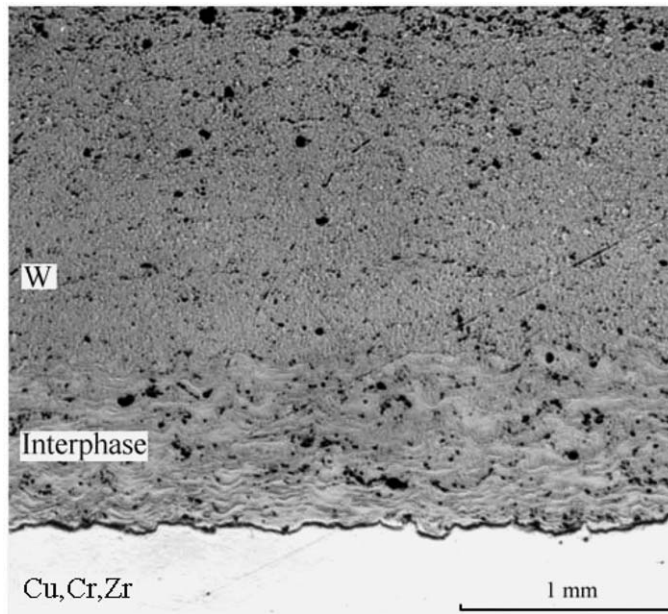
Fig. 1. Coating micrography ((Cu,Cr,Zr) substrate + interphase + W coating).

Table 1
Main deposition parameters

Plasma gas	Argon + hydrogen
Plasma power	45 kW
Torch to substrate distance	180 mm
Torch speed	800 mm s^{-1}
Spraying atmosphere	Argon
Deposition temperature	<453 K

amount of unmelted particles and low cohesion, the high pressure tests (1500 and 2000 mbar) showed a good melting of particles but problems of lack of cohesion between the W layers. The pressure of 600 mbar led to intermediate results and for this reason it was finally chosen (Fig. 1).

The main deposition parameters are summarised in Table 1.

The coating thickness uniformity was also a problem faced during the deposition. Several programs for the torch movement were tested and the selected one represents a good compromise for deposition efficiency and thickness uniformity. The final total thickness of the coatings (interlayer + W) ranges from 4.5 to 5.8 mm.

3. Coating characterisation and testing

The chemical composition of the powders and coatings, measured by means of glow discharge optical emission spectroscopy, is summarised in Table 2. The coatings show a remarkable amount of non-metallic species (O, C, S) that were present also in the used powders. These amounts might be critical for the plasma but they can be strongly reduced by using high purity powders and better controlled devices and processes.

The W coating mean density, measured by a water picnometer, was 17.8 g cm^{-3} corresponding to about 92% of the theoretical bulk density: this value is slightly lower with respect that of W–PS deposited on refractory materials [6,7] but still of interest for fusion reactors. The mean surface roughness was $R_a = 7.3 \, \mu m$ (min 6.4 μm, max 9.1 μm).

The coating characterisation included the measurement of the thermal diffusivity/conductivity, a property that affect the thermo-mechanical behaviour of the coating under transient and steady state

Table 2
Chemical composition of W powders and coatings (wt–ppm)

Element	Powder	Coating
Al	<1	<1
Fe	5700	6100
Si	410	320
O	369	471
C	18	200
S	10	25
W	Balance	

heat flux. Thermal diffusivity has been measured by means of a laser flash device in the range 373–1273 K. Thermal conductivity has been then calculated by using the coating density and the literature specific heat data of tungsten. Conductivity versus temperature is plotted in Fig. 2. The conductivity obtained is lower than of pure tungsten but is still a value of interest for plasma facing application.

Thermal expansion coefficient has been measured in the interval 473–1773 K by means of a Netzsch 402 dilatometer. The average thermal expansion coefficient between 473 and 1773 K was found to be 5.5×10^{-6} K^{-1}. The thermal expansion coefficient versus temperature is given in Fig. 3 and it is slightly higher respect that of pure W.

In order to provide designers with realistic data for stress analysis, the strength of the coating was assessed by means of different methods.

Ring bending tests have been carried out at RT by using rings made of plasma sprayed W extracted from tubular mock ups. The bending strength
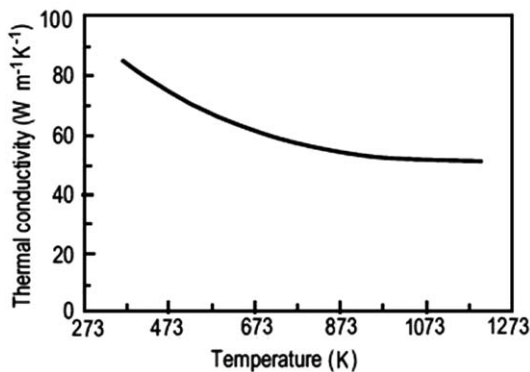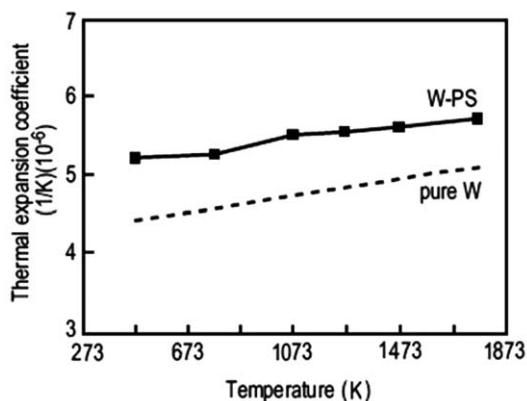
Fig. 2. W coating thermal conductivity.

Fig. 3. W coating thermal expansion.

measured was 185 ± 6 MPa. This test allowed also the determination of Young's modulus; the value was 82 ± 6 GPa and it is much lower than that of pure W (about 400 GPa). The value found cannot be justified by the amount of porosity but is due to the limited cohesion of the coating layers.

Tensile tests have been carried out by using the 'ad hoc' samples extracted from coatings: the specimen were flat and had a thickness of 2.5 mm and a gage length of 24 mm. The tests were performed at RT with a testing velocity of 0.33 mm min^{-1} which corresponds to a strain rate of 2×10^{-4} s^{-1}. The results obtained showed a tensile strength of 170 ± 30 MPa, which is a small fraction of the strength of pure tungsten (about 1000 MPa at RT), a brittle behaviour (elongation <0.4%) and a big scattering.

Flat top cylindrical indentation (FIMEC) has been carried out at different temperatures on W–PS and for comparison on sintered W–1%La$_2$O$_3$. The FIMEC test is an instrumented indentation test based on the penetration, at constant rate, of a flat top cylindrical punch of small size ($\Phi = 1$ mm, $h = 1.5$ mm). From load–penetration curves [11] it is possible to determine the yield stress σ_{cy}. The σ_{cy} values obtained at different temperatures are reported in Table 3 for W–PS and W–1%La$_2$O$_3$. Data from FIMEC tests on W–1%La$_2$O$_3$ are very close to those obtained by means of standard tensile tests [12]. For W–PS the yield stress at RT determined by FIMEC test is higher than the tensile values determined in this work, therefore the material exhibits a different behaviour in tension compared to that in compression. Moreover, the indentation behaviour of W coating changes significantly if the penetration is operated in direction perpendicular to the coating external surface or parallel to this surface when the test is carried out on a

Table 3
Compressive yield stress determined by FIMEC test on W–PS and W–1%La$_2$O$_3$

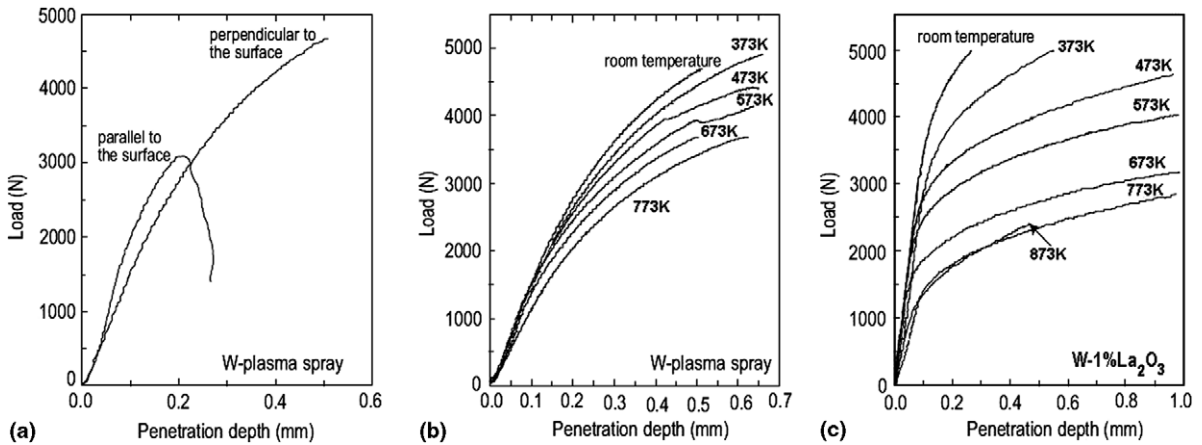| Test temperature (K)	W–PS FIMEC (MPa)	W–1%La$_2$O$_3$ FIMEC (MPa)	W–1%La$_2$O$_3$ tensile test (MPa)
283	794	1010	–
373	615	959	975
473	575	734	750
573	488	637	660
673	425	552	550
773	410	509	520
873	–	425	495

Fig. 4. FIMEC indentation curves: (a) RT indentation on W–PS perpendicular and parallel to the external surface; (b) Indentation on W–PS perpendicular to the external surface at different temperatures; (c) Indentation on W–1%La$_2$O$_3$ at different temperatures.

cross-section. This can be correlated to the limited cohesion of the sprayed layers through the thickness (Figs. 4(a) and 5).

Vickers micro-hardness measurements (load = 300 g, $t = 10$ s) have been carried out on W–PS, interphase and Cu,Cr,Zr (Fig. 6). On W–PS the hardness (mean value 300) shows significant scattering due to the effect of the porosity and the residual stress while the micro-hardness on Cu,Cr,Zr is quite
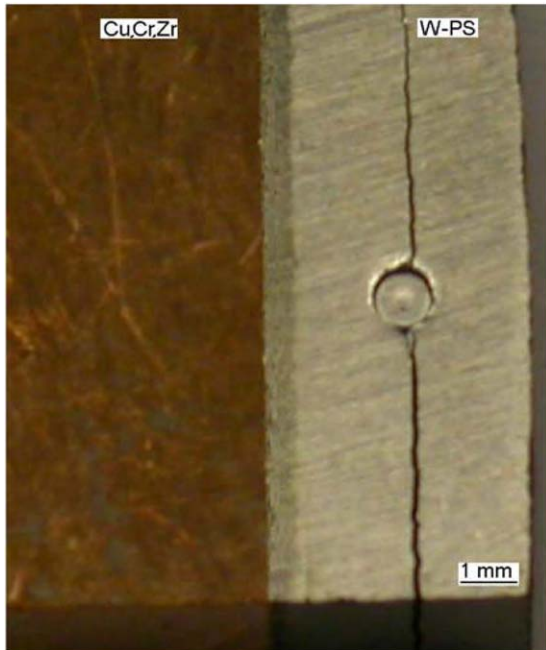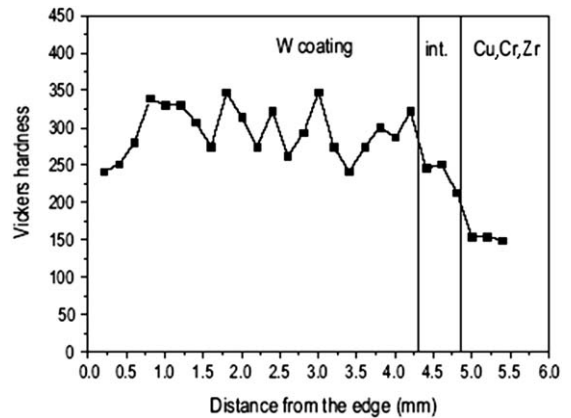

Fig. 6. Vickers micro-hardness measured on a cross-section containing W coating, interphase and (Cu,Cr,Zr) substrate.

constant and in agreement with Vickers hardness data of base material [8].

Adhesion strength is another property that influences directly the thermal–mechanical performances of the coating under high heat flux. Tensile adhesion tests have been performed at RT according with ASTM C 633 standard. The samples consisted in 25 mm diameter copper cylinders provided of a coating composed of 350 μm bond-coat plus interlayer and 400 μm W sprayed with the same procedure of the final coatings. The tensile adhesion strength measured was about 30 MPa. Shear adhesion tests have been also performed at RT according with a modified ASTM D908 standard [13]. The samples consisted in a $10 \times 10 \times 10$ mm^3 and include copper substrate, interphase and W coating. The measured shear strength was 67 ± 7 MPa.

Fig. 5. FIMEC indentation parallel to the external surface with delamination occurrence.

Finally, residual stress measurements were carried out by means of hole drilling method on a segment of coated bar with 4 mm thick W according to ASTM E 837 standard. The measurements have been performed on a flat coating and have involved about 1.6 mm of the coating thickness. Assuming a Young modulus of 82 GPa estimated by the above mentioned ring bending test, 49 MPa transversal stress and 44 MPa axial stresses have been estimated. Both are tension stresses but are well below the strength limit determined in this work.

4. Discussion

The microstructure of the coatings, as shown in Fig. 1, indicates the absence of macroscopic defects such as cracks or unmelted particles and the presence in the W layer of a limited amount of porosity which is not uniformly distributed and increases towards the external surface. This phenomenon has been observed systematically in all the coatings manufactured and it seems independent on the thickness of W layer, i.e., it occurs always towards the external surface of the coatings. An explanation has not yet been provided but one can think to a compacting effect during the coating deposition due to the powder/droplet splashing. Fracture surfaces of W coating at the middle of its thickness evidence that the W layer is composed of lamellae which are the results of the droplet spreading [14]. The contact surface between lamellae is not planar and no elongated porosity appears. The thickness of the W lamellae ranges between 5 and 10 μm. The cohesion of the lamellae depends strongly on the distribution of non-metallic impurities in the coating but this item was not investigated in this work.

The characterisation of the W–PS coatings has shown that the coatings have some good properties (thermal conductivity, adhesion strength) but also a low cohesion dependent properties like Young's modulus and mechanical strength and a not favourable residual stress (tensile). A stress relaxation and an improvement of the microstructure and cohesion can be obtained by means of a high temperature (1273 K) thermal treatment but this procedure is not suitable in our case because of the above mentioned degradation in strength of the Cu,Cr,Zr substrate and the occurrence of possible cracking of the coating induced by the strong thermal stress induced by the isothermal treatment (i.e., in absence of substrate cooling). This not with standing, as already mentioned, actively cooled mock ups of Cu,Cr,Zr tubes coated with 5 mm thick W–PS coatings exhibited encouraging thermal fatigue performances in conditions relevant for the ITER reactor: i.e., up to 1000 cycles under a heat flux of 5 MW m^{-2} acting for 10 s with 413 K pressurized water cooling. These performances were possible because of relatively high thermal diffusivity/conductivity that limits the thermal gradients as well as a very low Young's modulus that contribute to limit the thermal stresses. The experimental results themselves demonstrate that the residual plus working stress do not exceed the coating strength under a medium heat flux. Moreover the good adhesion strength (whose values are comparable with those obtainable with an ordinary brazing) prevent the coating detachment during testing. Therefore, one can conclude that the coating studied showed a favourable combination of properties that make its use suitable for medium flux plasma facing components.

5. Conclusions

An R&D campaign aimed for deposition of W plasma spray coatings can be summarised as follows. High thickness coatings on Cu,Cr,Zr substrates of different geometries can be manufactured without macroscopic defect and with a density of W coating higher than 90% of the bulk material. The coatings exhibited a good microstructure and satisfactory thermal properties but the mechanical properties appear rather poor in comparison with the bulk material ones. The thermal properties can be considered satisfactory for plasma facing component applications. A neutron irradiation campaign is ongoing aimed at investigating the coating performance degradation.

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