**Wolf-Rayet Stars**
*W.-R. Hamann, A. Sander, H. Todt, eds.*
*Potsdam: Univ.-Verlag, 2015*
*URL: http://nbn-resolving.de/urn:nbn:de:kobv:517-opus4-84268*

# Dust formation in carbon-rich Wolf-Rayet colliding winds

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Carbon-rich Wolf-Rayet stars are efficient carbon dust makers. Despite the strong evidence for dust formation in these objects provided by infrared thermal emission from dust, the routes to nucleation and condensation and the physical conditions required for dust production are still poorly understood. We discuss here the potential routes to carbon dust and the possible locations conducive to dust formation in the colliding winds of WC binaries.

## 1 Introduction

An infrared (IR) excess radiated by circumstellar dust grains was detected decades ago in the wind of the most evolved, carbon-rich Wolf-Rayet (WC) stars (Allen et al. 1972; Gehrz & Hackwell 1974; Cohen et al. 1975). WC stars are characterised by strong mass loss, emission lines of ionised carbon and relatively low effective temperatures for evolved massive stars. Dust was only detected in the latest sub-types (WC7-WC9) of the WC sequence and the spectral energy distribution (SED) was reproduced by assuming graphite as a potential condensate located in a circumstellar shell (Williams et al. 1987). Photometric data often reveal variability in the IR emission indicative of an episodic dust formation event, like in the case of WR 140 (Williams et al. 1978, 1987) and WR 137 (Williams et al. 1985). These dust production events are periodic and relates to binarity and the nature of the orbit. Both WR 140 and WR 137 are binary systems with eccentric orbits and dust forms at periastron passage where the stellar winds collide and induce shocks and gas density enhancement in the wake of the shocked region. Several successive dust formation events have been observed in WR140 at times corresponding to the system orbiting period of ~ 8 years (Monnier et al. 2002; Williams et al. 2009).

While some WC stars appear as periodic dust makers, others seem to form dust steadily, as the prototype star WR 104, which shows spiral dust plumes. These plumes or pinwheels were first observed by Tuthill et al. (1999, 2008) in the near-IR, and orbit parameters were deduced from the geometry of the pinwheels. The analysis revealed that WR 104 was characterised by a circular orbit (Tuthill et al. 2008). Furthermore, the IR flux dis not show significant variability over long epochs, which suggested the dust formation rate was steady and constant at all orbital phases (Tuthill et al. 2008). Typical dust formation rates for both episodic and constant dust makers are in the range $10^{-9} - 10^{-6}$ $M_\odot$/yr. The percentage of carbon depleted in dust is ~ 1% for most stars (Cohen 1991; Zubko 1998). These rather modest rates argue for a negligible contribution of WC stars to the dust budget in galaxies, although their contribution may increase at high redshift (Dwek & Cherchneff 2011).

Despite the wealth of IR data of dust thermal emission in WC winds, we have yet no clue on the exact nature of the dust and how it so efficiently forms. The WC wind environment is harsh. Intense ultraviolet (UV) stellar radiation fields pervade the steady winds while shocks control the wind-collision region (WCR). The growth of carbon grains was studied by Zubko et al. (1992) and Zubko (1998). These studies considered the growth of small charged grains with supra-thermal velocities in a shell located at a large distance from the star and assumed the growth occurred from carbon ions impinging on the charged grains. However, no clue was provided as to how the initial population of small carbon grains formed in the first place. The final grain size was in the range $90 - 200$ Å. In contrast, the modelling of mid-IR imaging of WC systems indicates the presence of much larger grains. In the case of WR 112, a massive episodic dust maker, Marchenko et al. (2002) derive a grain radius of $\sim 0.5$ $\mu$m, in line with the size value derived from ISO data (Chiar & Tielens 2001).

Another study based on a chemical kinetic approach showed that the formation of carbon dust at large radii in the homogeneous wind was unlikely (Cherchneff et al. 2000). The study considered both neutral and ion chemical processes as well as photo-processes induced by the stellar radiation field. Owing to the low gas densities at large radii, the ionisation fraction of the gas remained high and the chemistry was inefficient at building up molecules and dust clusters. An increase by several orders of magnitude of the gas density led to the formation of chemical species and very small clusters. Therefore, clumps or high density regions in the wind are a prerequisite to the production of dust in WC stars, and these dense regions are naturally found in the shocked environment of the WCR. Interestingly, a recent study of the formation of dust in the gas ejected by core-collapse supernovae leads to a similar conclusion: a clumpy ejecta is required to explain the production of the large amount of dust recently detected in supernova remnants (Sarangi & Cherchneff 2015).

In this review, we discuss the types of carbon clusters that form in WC stars, the possible chemical

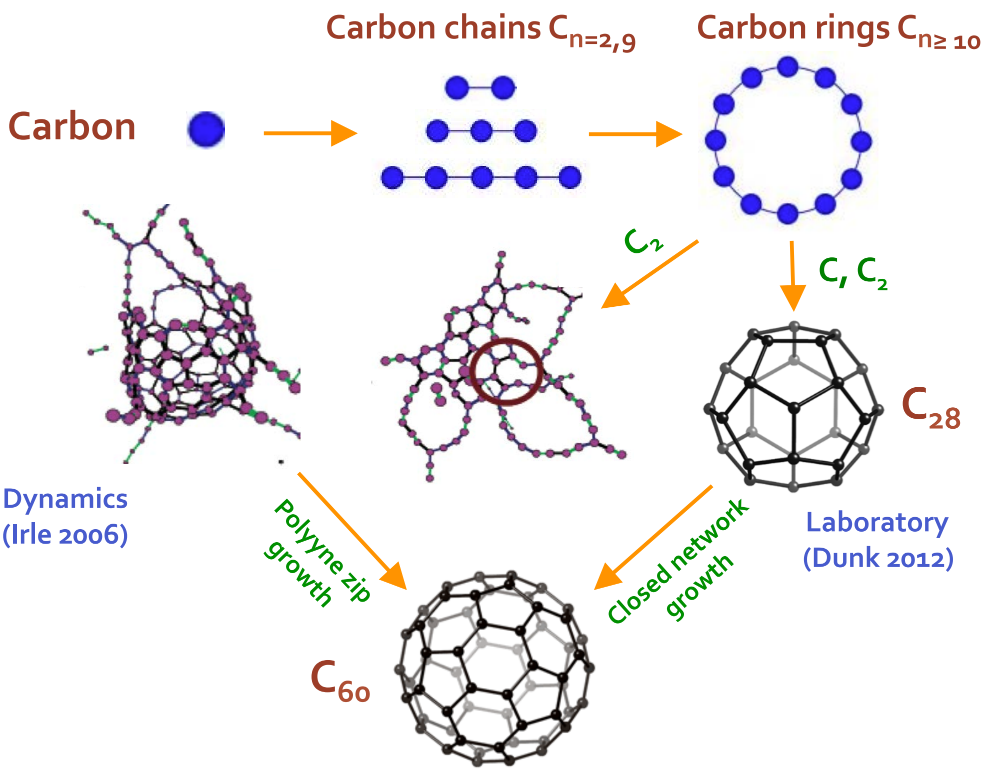

**Fig. 1:** Carbon cluster intermediates and routes involved in the synthesis of fullerene, $C_{60}$, for a hydrogen-poor environment.

routes leading to dust, and the gas conditions required for dust nucleation and condensation in the WCR.

## 2 The routes to carbon dust

Because a WC star has ripped off most of its hydrogen envelope, the WC wind is primarily helium- and carbon-rich. In laboratory experiments and under hydrogen-poor conditions, carbon grains form from a sequence of specific chemical routes that lead to the nucleation of carbon clusters. These routes resemble the formation pathways of the closed-cage carbon clusters of fullerenes that were first identified in a condensing carbon vapour devoid of hydrogen by Kroto et al. (1985). As shown in Figure 1, neutral carbon atoms react through radiative association reactions to form the first carbon chain molecules, which are linear until they reach $C_{10}$. For the latter, a monocyclic ring has the lowest energy and is thus the most stable structure (Jones 1999). These rings continue to grow through reaction and inclusion of atomic carbon and $C_2$ in their structure. A recent study of laser-induced carbon vapour condensation by Dunk et al. (2012a) shows that the smallest fullerene molecule is $C_{28}$, which contains four units of triple-fused pentagons arranged in tetrahedral symmetry. This small stable closed cage continues to growth to larger sizes through the closed network growth mechanism proposed and tested in the laboratory by Dunk et al. (2012b). In this scenario, the inclusion of $C_2$ molecules into the cage with no cage rupture controls the fullerene growth.

Other carbon cluster growth processes have been proposed by dynamic studies (Irle et al. 2006), whereby the steady addition of $C_2$ molecules through irreversible processes under non equilibrium conditions and at high gas temperature (2000 K) leads to the formation of mixed aromatic-cyclic carbon clusters as illustrated in Figure 1. Nucleation of polycyclic structures from entangled polyyne chains first happens, followed by growth supported by ring condensation of carbon chains and ring attachment to the hexagon and pentagon containing nucleus, and finally, the cage closure where polyyne chains reach over the opening and close the structures.

It is not yet clear if these two formation paths exclude one another. The absence of hydrogen fosters the synthesis of carbon chains and rings, with the possible creation of aromatic units. The detection of several sub-peaks along with the clear signature of carbon rings in mass spectra may indicate that clusters including aromatic structures also form in carbon vapour experiments (Dunk et al. 2012a). In any case, these routes will prevail in the hydrogen-poor WC stellar winds.

The companion of WC stars is usually an O-type star. The possibility of some hydrogen being present in the WCR gas may thus not be excluded. Hydrogen would occupy the valence bonds of small carbon chains and lead to the formation of hydrocarbons, including acetylene, $C_2H_2$. The formation processes of soot in acetylenic flames involve the recombination of propargyl radicals ($C_3H_3$) to form phenyl ($C_6H_5$) and benzene ($C_6H_6$), the growth of polycyclic aromatic hydrocarbons (PAHs) through acetylene addition and hydrogen abstraction, and PAH coalescence and coagulation to produce amorphous carbon grains (Cherchneff 2011). Therefore, a dual chemistry may take place in WC colliding winds, which includes the pure carbon routes leading to fullerenes and the aromatic pathways leading to the formation of small amorphous carbon clusters. These clusters will further grow from coalescence, coagulation, and the deposition of atoms, ions, and chemical species on the surface once a critical grain size of several tens of Ångströms is reached.

In the context of WC stars, these chemical routes to carbon remain speculative but are supported by a few observations of the aromatic C-C stretch transitions at ~ 6.2 $\mu$m and ~ 7.7 $\mu$m detected in absorption and emission in WR 104, WR 118, WR 112 and WR 48a (Chiar & Tielens 2001; Chiar et al. 2002).

## 3 The wind-collision region

With stellar temperatures of ~ 20000 K for the latest WC types, the UV radiation field that pervades the wind is strong and most helium and all carbon atoms are ionised at 2 $R_\star$(van Der Hucht et al. 1986). The presence of helium ions in the wind is detrimental to the synthesis of molecules and strongly inhibits the nucleation stage of dust formation in any circumstellar environment (Lepp et al. 1990; Cherchneff et al. 2000; Sarangi & Cherchneff 2013). Therefore, the production of molecules and dust clusters from the gas phase is severely hampered.

The efficient dust production by WC stars points to locations where the gas ionisation fraction remains low, the densities are high and the gas temperatures are sufficiently low. These conditions are found in the wake of the WCR as shown in Figure 2, which illustrates the geometry of the WCR in a plane perpendicular to the orbit of the binary system (Williams 2010). In regions of the compressed wind that are downstream from the stagnation point, the gas is expected to have densities higher than those of the homogeneous WC wind.

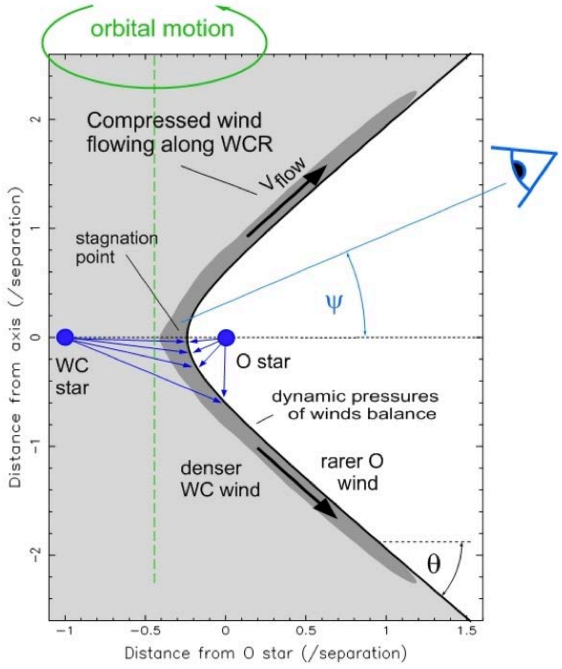

**Fig. 2:** The wind colliding region in the plane perpendicular to the orbit [taken from Williams (2010)]. The dust forms downstream from the compressed wind flow.

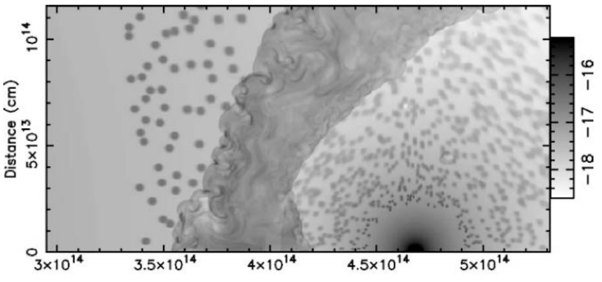

**Fig. 3:** Gas density in the wind-collision region of WR 140 [taken from Pittard (2007)]. Both stellar winds are clumpy.

Figure 3 represents the WCR of the WR 140 binary from the hydrodynamical study by Pittard (2007). Both stellar winds are assumed to be clumpy and the study follows the evolution of the inhomogeneities in the WCR. The turbulent regions of the compressed wind are shown in dark grey, and are characterised by gas densities in the range $\sim 10^6 - 10^8\,\mathrm{cm}^{-3}$. These values are sufficient to drive the recombination of helium ions and the nucleation of carbon dust by radiative association processes, which are usually temperature independent (Cherchneff et al. 2000). Therefore, when the downstream post-shock gas temperature drops to values in the range $1000 - 2000\,\mathrm{K}$ for which vaporisation of carbon dust can be excluded, carbon grains will likely nucleate and grow by coalescence, coagulation and surface deposition of carbon atoms and ions.

An interesting point resulting from the study by Pittard (2007) relates to mixing in the WCR. According to the model, the inhomogeneities initially present in the clumpy wind of WR140 (shown on the left-hand side of Figure 3) are disrupted by the WCR, which tends to smooth out the clumps initially present in both winds. If so, hydrogen-poor gas will mix with hydrogen-rich gas in the WCR. Such a mixing will drive the dual chemistry controlling carbon dust formation as described in §2. Depending on the location in the WCR, some regions will be richer in hydrogen than others, and will trigger the formation of acetylene, hydrocarbons and aromatic species, as in the shocked wind of carbon-rich AGB stars (Cherchneff 2012). Another important component acting on the WCR is the stellar radiation field of the companion star, which penetrates the WCR and generates photo-processes that play an active role in the local carbon chemistry. These photo-processes will generate a chemistry controlled by ions and radicals, which will have an uncertain impact on the nucleation of carbon dust. Warm, dense media sheltered from harsh radiation field are usually cradles of dust production, so the regions penetrated by intense UV radiation may not be conducive to dust formation, whatever their hydrogen content.

Hydrogen will not only affect the chemistry of carbon dust but the entire gas chemistry in the WCR. The occurrence of hydrogen in the WCR will trigger a chemistry that resembles that of the carbon-rich zone of supernova ejecta. There, Raleigh-Taylor instabilities induced by the explosion have mixed some hydrogen from the supergiant wind with the heavy elements, including carbon, that are present in the outermost ejecta zone. Species such as CO, CS and $\mathrm{HCO}^+$ have recently been detected with ALMA in the young supernova remnant SN1987A (Matsuura, private communication). The molecules CO and CS were predicted to form in physico-chemical models of the outermost, hydrogen-free ejecta zone of supernova explosions (Sarangi & Cherchneff 2013), and similarly, these two molecules have been predicted to be present in the dense WC winds (Cherchneff et al. 2000). The chemistry responsible for the build up of molecules, carbon clusters and dust in the WCR should then be complex and include neutral-neutral and ion-molecule processes in hydrogen-poor or -rich gas.

## 4 Outlook

If the WCR in WC binaries is efficient at producing carbon dust, the evolution and fate of these grains are still unclear. Marchenko et al. (2002) derived that ∼ 20 % of the grains formed in the innermost region of WR 112 survived to the outermost arcs. Destruction of grains may be the result of the strong UV radiation field combined with sputtering due to the high drift velocities of charged grains (Zubko 1998). Despite the lack of study of dust formation and destruction in the WCR of WC stars, results from supernova studies show that carbon is resilient to sputtering in shocks (Nozawa et al. 2010; Silvia et al. 2010; Biscaro & Cherchneff 2015). Therefore, WCR-produced carbon grains that are larger than several hundreds of Ångströms will likely be incorporated to the local interstellar gas.

The synthesis of molecules such as CO and CS is predicted to go hand in hand with that of dust in the post-shocked gas of WCRs. By-products of dust condensation (fullerenes, aromatics) might also be present in the gas phase. Yet no detection of molecular species has been reported for dust-forming WC stars. Observational attempts to characterise the molecular content of the wind-collision region of WC binaries are therefore highly desirable.

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