DUST FORMATION IN HOT STELLAR WINDS

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Abstract. WC-type Wolf-Rayet stars show episodic or persistent infrared emission attributed to amorphous carbon grains forming in their winds. The process of dust formation in the hydrogen-poor environments characteristic of WC winds is reviewed and compared to the chemical pathway to soot particle production in AGB stars. Emphasis is put on the formation of the dust precursors, and the physical conditions necessary to nucleate them in WC winds. In particular, it is concluded that dust formation around WC stars occurs in a dense, largely neutral, circumstellar disk.

Key words: stars: Wolf-Rayet – AGB – circumstellar dust – dust chemistry

1. Introduction

Dust is found in a variety of astrophysical environments which differ widely in their physical conditions. The chemical nature of the dust grains is governed by the physical conditions and the chemical composition of the environments they condense in. For example, in the cool envelopes of carbon-rich AGB stars, dust has been identified as amorphous carbon (AC), while in oxygen-rich AGB stellar envelopes, silicate particles are believed to condense in the wind. An amazing fact is that dust not only condenses under the "mild" physical conditions of cool late-type giants, but is also present in harsh environments such as the hot, hydrogen-deficient winds of carbon-rich Wolf-Rayet (WC) stars. Futhermore, infrared photometry has provided evidence the AC nature of the grains condensing in WC stellar outflows (Williams *et al.* 1987), and it appears that the same type of dust can form in winds characterized by very different physical conditions.

Most of the theoretical modelings of dust condensation has been devoted to carbon-rich AGB stars (Keller 1987; Gail & Sedlmayr 1987, 1988; Frenklach & Feigelson 1989; Cherchneff *et al.* 1991, 1993), because dust plays an important role in the mass loss mechanism of these objects. Indeed, these stars are characterized by extensive gaseous and dusty circumstellar envelopes, a consequence of efficient stellar mass loss, which is believed to be driven by the combined action of periodic shocks forming at the stellar phostosphere, and by radiation pressure acting on newly formed dust grains in the inner part of the envelope (Cherchneff & Tielens 1994a). The AGB

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outflows are hydrogen- and carbon-rich, cool and dense enough to allow for the nucleation of polycyclic aromatic hydrocarbon (PAH) molecules as dust precursors in the inner part of the envelope (Cherchneff & Tielens, in preparation).

Goeres & Sedlmayr (1992) were the first to address the problem of dust condensation in C-rich, H-deficient objects, such as the R CrB stars. These stars show regular pronounced minima in their visual light curves, probably due to extinction caused by dust formation. Although Goeres & Sedlmayr did not carry out a full time-dependent treatment of dust precursor nucleation, their study based on equilibrium considerations provided insight on the chemical nature of the dust, as well as the possible chemical pathways to grain condensation in a H-poor environment.

The challenging task of modeling dust condensation in the winds of WC stars has not been considered yet, and the purpose of this review is to shed light on this problem. This review is organized as follows: in Section 2, the chemical nature of the condensate is studied under thermal equilibrium, Section 3 deals with the possible chemical routes to AC dust formation, preliminary results on kinetic calculations are presented in Section 4, and conclusions are drawn in Section 5.

2. What thermal equilibrium tells us

The pioneering studies on dust condensation in stellar outflows (Salpeter 1974, 1977) were based on the assumption that the gas in which grains formed was in thermal equilibrium (TE), *i.e.,* the dust condensed in a slowly cooling gas. The molecular content of the wind at TE therefore depended only on the initial elemental composition of the gas, and on the gas temperature and total pressure. Although this assumption is not valid for most of the astrophysical situations in which dust condenses, TE calculations give an indication of the kind of material expected to condense in a gas. For a C, H-rich mixture, the results are illustrated in Figure 1(a). The dashed line represents the AC stability line, above which carbon is gaseous and locked up in various molecules (depending on the gas total pressure and temperature), and below which carbon is in solid form. The conditions for the photosphere of a C-rich AGB star are superimposed and correspond to the "acetylene regime", *i.e.,* the gaseous carbon available for condensation is in the form of C_2H_2. We see from Figure 1(a) that, in C-rich AGBs, AC particles are expected to form as the dust condensation region is located below the AC stability line. However, TE does not prevail due to the low gas densities and the passage of strong periodic shocks in the deep envelope.

The winds of WC stars are C-rich but H-poor, leading to a different scenario for dust condensation. Furthermore, the wind region in which dust is observed is characterized by low densities and high temperatures for the

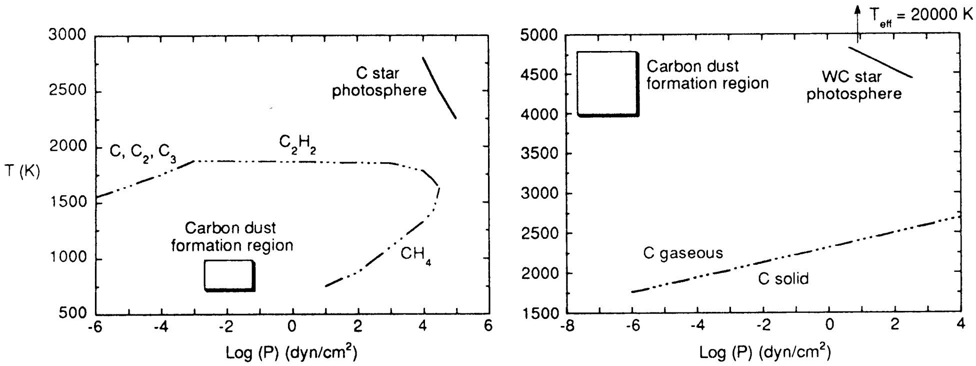

Fig. 1. **(a) TE phase diagram for a C, H-rich gas [adapted from Tielens (1990)]; (b) TE phase diagram for a C-rich, H-poor gas (note that the photospheric temperature is too high to be plotted on the diagram temperature scale).**

gas, as illustrated in Figure 1(b). As in Figure 1(a), the AC stability line (dashed line) divides the region between gaseous carbon, in the form of atomic carbon for a H-poor gas, and solid carbon. The physical conditions of the photosphere are superimposed as well. From TE considerations, it is clear that AC dust **is not** expected to form in WC outflows. However, dust is present and is believed to have a similar nature as that in C-rich AGB stars (Williams *et al.* 1987). This fact leads to two conclusions: 1- TE cannot apply to WC winds, 2- a chemical kinetic model of the nucleation of dust progenitors is necessary to try and explain the presence of AC dust in these winds.

3. A chemical pathway to AC grain formation

Amorphous carbon grains, *i.e.*, soot particles, are commonly produced in terrestrial combustion environments. Small, spherical carbon clusters are the basic units of soot particles (Tielens 1990), and depending on the composition of the gas, the intermediate species to soot formation will differ. For example, in acetylenic flames (*i.e.*, rich in acetylene), the nucleation of soot occurs via the formation of hydrocarbon and PAH molecules. Such a chemistry has been successfully applied to describe the nucleation of AC dust precursors in C-rich AGB winds (Frenklach & Feigelson 1989; Cherchneff *et al.* 1993; Cherchneff & Tielens 1994b), since the chemical composition of AGB inner circumstellar envelopes is very similar to that of acetylenic

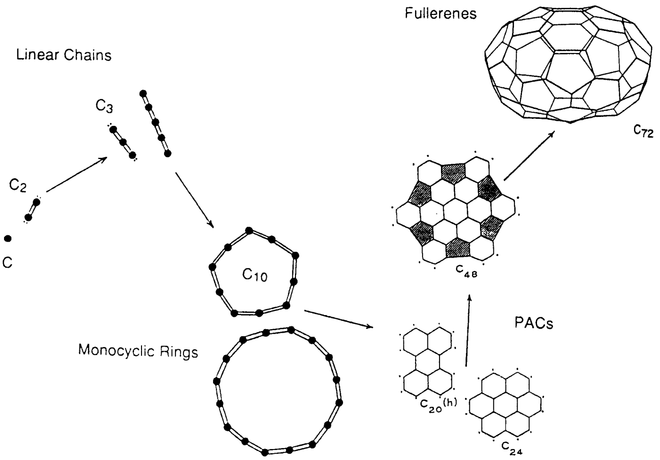

Fig. 2. A chemical model for fullerene formation.

flames. In WC stars, the winds are He and C-rich, H-poor, and the dust condensation region in these outflows is characterized by quite high gas temperatures (see Figure 1b). This fact led many authors to state that such winds should have chemical and physical conditions close to those encountered in graphite vaporization experiments, where fullerenes (C_{60} family) are observed to form (Kroto *et al.* 1985; Curl & Smalley 1988). Therefore, a dust condensation pathway via fullerene production has been proposed for WC winds (Tielens 1990; Cohen 1991). However, the similarity of the two media resides only in the fact that WC winds and graphite vaporization experiments are both environments free of hydrogen and rich in carbon. There is, however, one major difference between the two environments, *i.e.*, helium acts as a buffer gas in the graphite vaporization experiment and its pressure is very high ($\sim 10^5 - 10^6$ dyn cm^{-2}), while in WC winds, the helium is under ionized form, and is thus very reactive chemically, with a pressure ranging from $\sim 10^{-7}$ to 10^{-6} dyn cm^{-2}. This fact may not alter the nature of the chemical intermediates of the dust condensation process in WC stellar winds, but the attack of helium ions is an important destruction mechanism for dust precursors that needs to be considered in any attempt to model the nucleation of dust progenitors.

Figure 2 illustrates the route to AC dust formation in a H-free medium, based on the thermodynamic and stability properties of the various intermediate species involved. There are three different phases characterizing the growth of fullerenes and soot particles. The first step is the formation of small carbon chains (C_n, with $n<10$). *Ab initio* theory (Raghavachari &

Binkley 1987; Weltner & van Zee 1989) indicates that these early products have low-lying linear electronic states and cumulenic bonding (C-C double bonds) rather than acetylenic bonding (alternating single and triple C-C bonds). The prediction of linearity has been confirmed by high-resolution infrared spectroscopy, with the identification of triplet linear C_4 and singlet linear C_9, which is the largest cluster with a linear ground state (Heath & Saykally 1990, 1991). The second step in the condensation scheme is the formation of monocyclic rings (Raghavachari & Binkley 1987). Unimolecular rearrangement with high activation energy to polycylic aromatic carbon (PAC) rings is made possible due to the high gas temperature (Goeres & Sedlmayr 1992). Futhermore, the plausibility of PAC structures has been confirmed by the detection of the 7.7 μm C-C stretching emission band in the WC9 stars Ve2-45 (WR104) and GL 2104 (WR112) (Cohen *et al.* 1989). Finally, a third phase is the formation of curved molecules leading to the fullerene family. PAC rings have many available valence bonds at their periphery that cannot be satisfied by hydrogen atom chemical bonding. Therefore, the only way to decrease this "surface free energy" is by introducing pentagons in the ring structure, for example via interaction and insertion of C_2 chains. The presence of pentagons will curve the PAC structure, and eventually will lead to the closure of the aromatic structure on itself in which all peripheric valence bonds are satisfied (Tielens 1990), resulting in the formation of fullerene molecules. More generally, the growing curved structures will not perfectly close, and the growing edge may overrun the opposite edge as it curls. A spiral structure will then result, that may play the role of nuclei in the AC cluster formation process (Curl & Smalley 1988).

4. The nucleation of dust precursors

To address the problem of dust condensation in WC winds properly, it is necessary to treat first the nucleation of small carbon chains, as this step is the bottleneck and hence controls the dust formation rate. The following represents preliminary chemical kinetic calculations on the formation of C_2 and C_3 chains in the outflow of a typical WC9 star.

A spherically symmetric wind is assumed. Typical properties are listed in Table I, along with some stellar parameters. The parameters are taken from Williams *et al.* (1987). A blackbody radiation field is assumed, corrected by the UV optical depth τ_{UV} due to the carbon edge at the stellar photosphere (van der Hucht *et al.* 1986). The chemical system consists of 13 species and 40 chemical reactions for which rates are measured in the laboratory, or estimated from quantum chemistry calculations. Two sets of reactions are particulary important, *i.e.*, the formation mechanisms and the destruction processes for the carbon chains. The principal formation mecha-

TABLE I

Wind and stellar parameters for a typical WC9 star

$T_{\rm eff}$ =19 000 K	$M = 5 \times 10^{-5} {\rm M_{\odot} yr^{-1}}$	$V_{\rm term.} = 1\,000~{\rm km\,s^{-1}}$
$T_{\rm c}$(gas) = 4000 K	$R_{\star} = 12~{\rm R_{\odot}}$	$R_{\rm c} = 760~{\rm R_{\odot}}$
C/He = 0.2	[CII]:[CIII] = 0.5:0.5	[CI]/[CII] $=10^{-6}$
$n_{\rm c}$(gas) = $7 \times 10^{5}~{\rm cm^{-3}}$	$\tau_{\rm UV} = 5$	

nisms for C_2 (C_3) are radiative association reactions between a C atom and C^+ (C_2^+), and between two neutral C atoms (C and C_2). The rates for these reactions are estimated based on theory (Bates & Herbst 1988). The major destruction processes are: (1) the photo-dissociation processes, for which rates are calculated from the measured photo-crosssections of C_2 and C_3; 2 - the dissociative recombination of C_2^+, which has a very high measured rate (Mitchell 1990); and (2) the attack by He^+ and O^+. Charge exchange reactions, neutral-neutral processes, and other ion-molecule reactions are also included in the chemical scheme (Cherchneff, Williams, & Tielens, in preparation).

Chemical kinetic calculations are carried out for the wind described by Table I (≡ standard case) and for a denser outflow, which is characterized by a gas density in the condensation region four orders of magnitude larger than that listed in Table I (*i.e.*, $7 \times 10^{9}~{\rm cm^{-3}}$). For the standard case, it is found that the carbon chains present in the condensation region are in ionic form rather than neutral, and that the concentrations of C_2^+ and C_3^+ are very low compared to the total gas concentration. This is due to the high net rates for dissociative recombination reactions which represent the major destruction channels for both C_2^+ and C_3^+, while the net rate for their formation via radiative association reactions is much less. An interesting fact is that the calculated C I concentration is higher than that observed by a factor 100. If we define the chain formation yield Y as the ratio of the number of carbon atoms in chains to the number of carbon atoms initially in the gas in the form of C I C II and C III we find that $Y \approx 5 \times 10^{-15}$. This value is much too low to explain the carbon dust content derived by Williams *et al.* (1987), which corresponds to Y values spanning from 10^{-4} to 10^{-3}.

Chain concentrations as functions of stellar radius for the high density case are shown in Figure 3. A striking feature is the change from a "ionic" to a "neutral" carbon chemistry, a trend already announced in the standard case by the quite high C I concentration. For high gas densities, C II and C III quickly recombine to C I leading to an atomic carbon gas. The major formation channels for the chains are therefore radiative association reactions

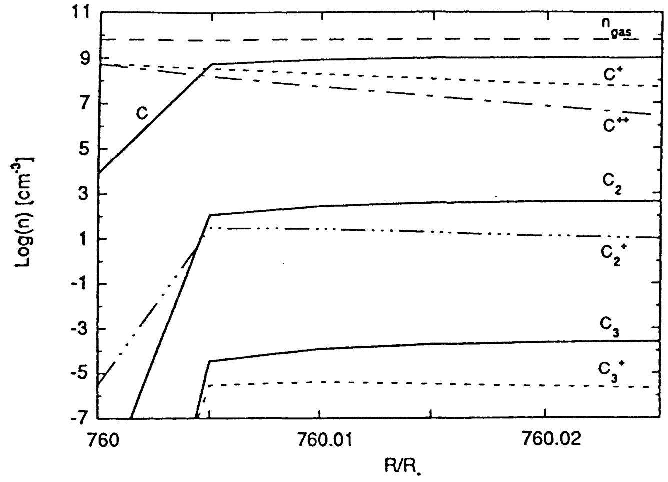

Fig. 3. **Carbon chain concentrations in the condensation zone for the high gas density case.**

between C I atoms and C I and C_2 species, resulting in much higher chain concentrations than for the standard case. The chain destruction routes are He^+ and O^+ attacks, and to a lesser extent, the photodissociation processes. Y is now equal to $\sim 10^{-6}$, which is still lower than the observed value. However, in view of the uncertainty on certain reaction rates, in particular for radiative associations, we consider this result quite satisfactory. Indeed, a better match between the observational and theoretical Y values can be easily obtained by increasing the rate for radiative association reactions by a factor 100 (which leads to a rate value still acceptable for these kind of processes).

5. Conclusions

The results of Section 4 confirm what was already stated in Section 2 from equilibrium considerations, *i.e.*, it seems impossible to form dust grains in WC winds under the physical conditions derived from observations, and considering a spherical symmetric, homogeneous flow. Futhermore, if we assume that the chemistry in Section 4 is "right", *i.e.*, the overall chemical processes are well known and the corresponding reaction rates have rather conservative values, it implies that high gas densities are required to drive the neutral chemistry necessary to form dust precursors. The increase in the gas density (by a factor $10^3 - 10^4$) is larger than that suggested by Moffat (these proceedings) for his clump model (average density jump by a factor 3). However, the condition on the gas density could be satisfied by the following possible scenario: a two-component WC wind, including a high density, neutral favored plane (≡ equatorial disk) and a spherical, low-density, ionized outflow.

If high densities are conceivable for WC outflows, further improvements of our simple wind model should be made and consist of: (1) the inclusion of three-body reactions which may be efficient in forming carbon chains and thus will boost the chain formation yield; (2) a better estimate of some crucial reaction rates, such as the radiative association processes; and (3) the extention of our chemical scheme to the closure of rings and the formation of PAC molecules and fullerenes.

Acknowledgements

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DISCUSSION:

Cohen: I'd like to suggest an analogy with GL2688, probably an RCrB-type star in a reflection nebula. There one sees scattered starlight with an interstellar $A_v \sim 3$ mag but the C_2- Swan band emission in the nebular lobes shows $A_v \sim 5\text{-}10$ mag. This surely suggests hot-centred gas clumps with CI, C_2, C_3 inside and an outer crust of C_4, C_5.... carbon chains and PACs that create the extra extinction. In this scheme you don't see the neutral carbon or the precursor molecules to the grains.

Magalhaes: Would you like to comment on the resulting grain size distributions? Would they be a power law on some peaked distribution such as a Gaussian?

Cherchneff: It's too early to address such a question. A grain size distribution is obtained when the dust condensation problem is solved. I have not reached this stage yet because I have studied so far the nucleation stages and the formation of dust precursors.

Brown: I would like to emphasise that although clumpy wind models may only have mean densities of 2-3 compared to a smooth wind, Moffat's turbulence models for example involve a hierarchy of local densities. The smallest 'blobs' have huge densities compared to the spatial mean. What consequences would this have for the chemistry?

Cherchneff: This would need to be worked out in detail but we are certainly keen on finding high density situations.

Cassinelli: An advantage of disks, other than their increased density, is that the disk structure leads to a stronger decrease in the radiation field, J_v, than is the case for a spherical wind. Radiation tends to be scattered or reradiated out of the disk and is not replenished by light from the polar zones. Since J_v is reduced, the temperature of gas in the disk is reduced; the ionization can reach to lower stages closer to the star. All of these effects tend to increase the probability for molecule and grain formation.

Hillier: From Williams' talk earlier it appears that 80% of the WC stars are binaries, and that the dust formation appears to be related to wind-wind collisions. It is reasonable that all dusty WCs are binaries. The resulting wind-wind compression may supply the higher density needed for dust formation. Therefore there is no need to resort to an intrinsically clumped wind.

Conti: Colliding winds, in addition to increasing time densities, also bring in the O star wind with hydrogen or oxygen. Could this affect the chemistry?

Cherchneff: You may end up with a mixed chemistry: a pure carbon chemistry leading to formation of carbon chains and PACs, and a carbon-hydrogen chemistry forming PAHs and aromatic planes, both cases resulting in dust condensation. Whether one or the other type of chemistry takes place will depend on the structures of the colliding winds.