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Dust formation in the environments of hot stars

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1 Introduction

Dust is a ubiquitous component of the interstellar medium (see Chapter 4 and 5) and plays a vital and indispensable role in the overall cycle of cosmic material processing. During stellar evolution, from stellar birth up to the late stages, the solid phase is intimately interwoven with the gas component and the radiation field (see Chapters 11–13). The processes of nucleation and grain growth are well known to occur in the outflows of cool late-type stars.

Surprisingly hot stellar environments have also been identified to be places of efficient grain production. Although their central objects are characterized by stellar temperatures of about 7 000 K (RCB-stars and novae) up to about 25 000 K (Wolf-Rayet and Be-stars), thus supplying a very intensive radiation field interacting with the surrounding material of their shells, nevertheless, dust is still produced. In contrast to cool late-type giants where the physical modelling can rely on the observationally confirmed facts of a steady and nearly spherically symmetric outflow, these assumptions do not hold in the case of hot shells. Unlike the dust driven winds, where the gas temperature and matter density monotonically decreases in a slowly expanding ($v_\infty \approx 30-40$ km/s) envelope, the outflows of hot stars consist of fast winds (up to 2 500 km/s) and non-homogeneous environments.

Thermodynamic conditions favouring the formation of solid structures are generated as a local phenomenon which results from a local density increase and/or temperature decrease. Basically, the situation of primary grain formation can be described in the scenario of a cooling flow, where initially hot matter expands, subsequently cools down, and finally is diluted up to the point where the gas temperature is well below the condensation temperature of the favoured monomer species which can nucleate and form small stable clusters. By further addition of suitable molecules the clusters will grow to homogeneous or heterogeneous specimen (Gail *et al.* 1984; Gail and Sedlmayr 1988).

Many cosmic sources are contributing to the solid phase in the ISM, but primarily dust is created in the vicinity of stars, and the explosive events of novae and supernovae (see Chapter 18). Although these objects significantly differ in their observational appearance as well as in their stellar masses and temperatures, they have one thing in common: solid particles are formed in their environments. Thus the phase transition of gaseous material to the solid state must be accepted as a very general phenomenon independent from a specific object. Its as a physical process taking place under certain conditions of pressure and temperature which can be supplied by a variety of different astrophysical situations. Exemplifying this idea, we concentrate in this review on the description of the dust formation in the hot environments of Wolf-Rayet (WR) and R Coronae Borealis (RCB) stars. In this connection "hot" winds are seen in contrast to the dusty outflows of cool AGB-giants, with stellar temperatures below 3 500 K.

2 Observational status of hot winds

2.1 Wolf-Rayet stars

Wolf-Rayet stars are massive, evolved and hot stellar objects at the end of their nuclear burning phase (see Chapter 11), and they have a formative influence on the interstellar environment by their massive input of mass and momentum (van der Hucht *et al.* 1988; van der Hucht 1995; Cohen 1991). WR stars are the sources of hot and dense stellar winds and the emission lines originating from the outflow provide direct information about their physical properties (for typical WR parameters see Table 1 and 3). Two different emission contributions can be distinguished in their prominent infrared excess: the part emerging from free–free radiation and those photons due to heated circumstellar dust. Analysis is undertaken by combining spectrophotometry between 3 300 Å and 11 100 Å, with infrared photometry between 1.6μ and 11.3μ (Nussbaumer *et al.* 1982; Eenens and Williams 1992; van der Hucht *et al.* 1996). Whereas WN-type stars show pure free-free emission, the IR radiation of some WC stars could be unequivocally attributed to dust particles. There is clear evidence for a correlation between dust formation and the spectral subtype of the WR-star (Cohen *et al.* 1991). In 18 of 21 WC9 stars emission from heated dust has been found, but only 4 of 9 WC8 and 3 of 13 WC7 stars show this feature. Thus single WC stars earlier than WC8 generally do not show any evidence of dust formation. Exceptions only exist for long period binaries with eccentric orbits. Therefore, an IR excess due to solid particles only develops in cool and carbon enhanced WR environments.

Observations of the *persistent* infrared emission by solid particles are found in about 20% of the WCL stars (WC "late" subtypes: WC7 - WC10), which indicates that dust is formed continuously, permanently replacing the older grains, which have been swept further out by the fast wind. Those fossil dust particles outside the inner wind region couple to the outflowing gas on short time scales (ca. 1 day) and are therefore blown away from the star (Williams *et al.* 1987). This material is now part of some type of ring nebulae (Chu 1991) surrounding some of the WR-stars (Lozinskaia *et al.* 1986; Cassinelli *et al.* 1991). This indicates the post mass loss history and is identified by their characteristic 60μ IRAS

images showing a significantly higher colour temperature than the background, which is due to heating of the dust from the central star (Smith 1995). The typical size of a surrounding WR dust cloud has been derived from speckle observations (WR104) at 2.2μ, 3.8μ and 4.8μ (Allen *et al.* 1981; Dyck *et al.* 1984) to a value of 0.04 arcsec ($d = 1.9$ kpc).
By contrast, some candidates of type WC4 - WC7 show an *episodic* dust event. The conditions for grain formation are sustained only for a limited time and then, as it is indicated by the fading of the IR emission, they become dust free for a certain period before showing distinct events of new dust formation. This time-dependent behaviour has been observed in the cases WR137 (Williams *et al.* 1985) and WR140 (Williams *et al.* 1978; Hackwell *et al.* 1979), the most prominent example for episodic dust formation. By analysis of the IR data and its spectroscopic variation this object seems to have a period of 7.94 yr (Annuk *et al.* 1991; van der Hucht 1991) and a brightening of the IR-luminosity by $\Delta L \approx 2.5$ mag. Thus dust formation takes place at a distance of about $2\,300\ R_*$. The re-occurrence of this phenomenon may be caused by the interaction of WR stellar winds in a binary system, undergoing a period of compression during periastron. Time dependent optical depths and phase-dependent orbital modulation due to an eccentric orbit affects the infrared appearance and leads to a substantial variability. Additionally, colliding winds in WR binary systems cause strong shocks emitting X-rays. Weak X-ray emission is a common phenomenon especially for binary WR+OB stars with luminosities of the order of $L_X/L_{bol} \approx 10^{-7}$ (van der Hucht 1992; Rawley 1993; Willis *et al.* 1995).
Further observational indicators of the interaction of winds in WR binaries are the large and variable non-thermal radio emissions (Dougherty *et al.* 1996; White and Becker 1995), tracing particle acceleration in the magnetic field of the shock region, where the fast winds of the WR-star ($v \approx 2500$ km/s) and its accompanying O-star ($v \approx 2\,000$ km/s) collide. Therefore, it may be concluded that episodic dust formation is enabled due to an increased gas density in the wind collision zone resulting in enhanced infrared emission (see Table 1 for data on episodic dust formation). Therefore, it seems to be very likely that all episodic WR dust producers are long-period binaries with large eccentricities. There is also some evidence for the supposition that persistent WR dust sources are part of colliding wind binaries, whose separations, luminosities and wind parameters fall in a specified range (Williams 1995).

The diagnostic of spectrometric and polarimetric data (Brown and Richardson 1995) clearly demonstrates the inhomogeneous structure of the WR winds (Robert *et al.* 1989; Brown *et al.* 1995). Outflowing mass is located in so called "blobs". It is still under investigation whether these blobs arise from non–uniform mass loss or as a result of turbulent instabilities. Poe *et al.* (1989) developed a two–component wind theory with a fast polar and a slow equatorial wind. In this scenario rapid rotation as a result of WR evolution (Cassinelli 1991, 1992) is an indispensable ingredient. Radio observations of White and Becker (1995) point to the fact that the WR wind is strongly enhanced in the

	WR star	type	R_{dust}/R_*	T_{dust} [K]	ρ [g/cm^3]	M_{dust} [$M_\odot$]
persistent	WR 53	WC8	380	1600	$4.7 \cdot 10^{-21}$	$9.2 \cdot 10^{-8}$
	WR117	WC8	580	1390	$1.1 \cdot 10^{-21}$	$2.3 \cdot 10^{-8}$
	WR 76	WC9	310	1320	$4.2 \cdot 10^{-19}$	$1.5 \cdot 10^{-5}$
	WR104	WC9	470	1110	$1.6 \cdot 10^{-19}$	$6.7 \cdot 10^{-5}$
	WR118	WC10	260	1410	$4.9 \cdot 10^{-19}$	$1.1 \cdot 10^{-5}$
episodic	WR 137	WC7	6130	780	$9.0 \cdot 10^{-24}$	$3.8 \cdot 10^{-8}$
	WR 140	WC7	1490	1460	$2.6 \cdot 10^{-22}$	$1.4 \cdot 10^{-8}$
	WR 48a	WC8	1305	1000	$1.8 \cdot 10^{-19}$	$1.4 \cdot 10^{-5}$

Table 1 Typical parameters for persistent and episodic WR dust makers (Williams *et al.* 1987). R_{dust} is the inner radius of the dust shell, ρ is the mass density at the base of the dust shell and M_{dust} is the total mass of the dust shell.

equatorial plane. Therefore, most of the mass loss is confined to a plane implying an obvious similarity to the two–component outflow of Be-stars, for which this theoretical approach can also be applied (Cassinelli 1990; Chen *et al.* 1992).
These mass loss rates of WR stars have been reviewed by Prinja *et al.* (1990) and Willis (1991), presenting typical values of $\dot{M} \approx (2-10) \cdot 10^{-5} M_\odot yr^{-1}$. Those mass loss rates are deduced from the electron densities and their values depend on the uncertain state of ionization. To date there exists no apparent difference in the mass loss rate between single and binary WR–stars.
Based on the estimations of Gehrz (1989) and Tielens (1990), Cohen (1991) derived the contribution of WR stars to the galactic dust component, utilizing the galactic model of Wainscoat *et al.* (1992). Despite the fact that approximately 85% of WC9 and about 50% of the WC8 stars show evidence for heated circumstellar dust, the contribution of WC stars to the galactic dust production is only small (ca. 1%). However, massive WR stars provide a substantial part of the heavy element enrichment in the interstellar medium (Cohen 1991) during their lifetime of ca. $5 \cdot 10^5$ yr. This results in a typical mass loss of $M \approx 1 M_\odot$ per star.
Early analysis of IR-data (Gehrz and Hackwell 1974; Dyck *et al.* 1984) first led to the assumption of a graphitic nature of WR dust. The alternative suggestion of Lewis and Ney (1979), that Fe or FeC (cohenite) are possible condensates around WR stars, could not be confirmed by later observations. Further studies of Williams *et al.* (1987) showed that the infrared emission spectra from WR140 can be best fitted with the assumption of a power law for the mass absorption coefficient of amorphous carbon ($\kappa \propto \lambda^{-1}$). It seems to be certain that pure graphite can be ruled out because neither in the persistent dust-maker WR104 nor in the episodic case of WR140 the 11.52μ resonance feature has been observed (Glasse *et al.* 1986; Williams, 1995), which undoubtedly would allow for an unambiguous identification.
The temperature of the heated circumstellar amorphous carbon dust has been deduced to lie between 900 K to 1 250 K (Allen *et al.* 1972; Cohen *et al.* 1975). For WR104 and WR112A a broad emission feature exists (IRAS spectra at

$7.7\mu m$). This emission is attributed to a carbonaceous carrier with small domains of aromatic structure (Cohen *et al.* 1989). However, the common $11.3\mu m$ feature indicating PAHs is absent. The nature of the solid phase is in agreement with the observed enhanced abundances of carbon in WC star shells with $[(C+O)/He] \geq 0.03$ (Smith and Maeder 1991).
The dominant observed carbon ion is CIII (Smith and Hummer 1988). No emission of molecular carbon, suspected of being an important precursor of carbon dust formation, has been detected in WR spectra. Since the amount of neutral seed particles needed to start the nucleation process is only a small part of the subsequently formed amount of dust, the density of nuclei is possibly too low to be detectable.

2.2 R Coronae Borealis stars

Another class of objects showing spectacular behaviour connected with massive solid particle formation are the R Coronae Borealis stars (RCB). About 40 objects have been identified to date (Clayton 1996; Milone 1990). These low-mass but high luminosity stars, mostly with effective temperatures of $T_{\rm eff} \approx 5\,000 - 7\,000$ K, are characterized by non-predictable decline events accompanied by brightness decreases of up to 8 magnitudes (for RCB parameters see Table 3). During an event optically thick dust clouds are produced which re-radiate about 10% to 50% of the stellar energy in the infrared spectral region. Spectroscopic observations (Alexander *et al.* 1972; Cottrell *et al.* 1990; Rao and Lambert 1993a,b; Clayton *et al.* 1995a) have been made for several declines of the three brightest RCBs - RCrB, RY Sag, V854 Cen. During the phase of brightness decrease, typically lasting for some weeks, an emission spectrum appears simultaneously with the dust cloud, showing lines of neutral and single ionized metals. In some cases lines of C_2 and CN bands have also been observed (Whitney *et al.* 1992; Benson *et al.* 1994).
Recent investigations to detect the presence of fullerenes in the atmospheres of RCBs (Clayton *et al.* 1995b; Jeffery 1995b) have not been successful. Already Buss *et al.* (1993) have pointed out that, from the low resolution of the IR spectroscopic data, definite spectral identification of characteristic dust features cannot be obtained. The extinction curve has been analyzed by Hecht (1991) pointing to amorphous carbon as the most likely form of the dust. The grain sizes derived by the extinction spectrum during declines range from 0.005μ to 0.06μ (Hecht *et al.* 1984).
RCB stars normally show elemental abundances differing significantly from the solar mixture. Helium is by far the most abundant element, hydrogen is underabundant by a factor of 10^2 to 10^5, whereas carbon is overabundant by a factor 10 ($[C/He] \approx 0.03$ and $[C/Fe] \approx 1$ (Lambert 1986; Rao and Lambert 1994)).
Comparison of different wavelength bands of infrared photometry (Feast 1990) shows that dust forms only over a small solid angle over the surface of the RCBs, not producing a complete shell, but establishing a massive cloud. This observa-

tional clue is supported by the fact that there is no obvious correlation between the IR brightness and the frequency of decline events, implying that dust only is produced in the line of sight of the observer in some random cases (Feast 1986). Pulsations are now identified in all RCB stars by photometry over long periods (Lawson *et al.* 1994; Lawson and Kilkenny 1996). Long term spectroscopic and polarimetric measurements of RCrB (Clayton *et al.* 1995a) near maximum light show large C_2 and CN band variations correlated with pulsational phase. Additionally, a coincidence of pulsational phase and the onset of decline (RY Sgr, V854 Cen) strongly indicates a connection between the RCB star atmosphere itself and the process of dust formation (Clayton *et al.* 1995b). These facts imply that pulsation induced shocks could lead to a substantial local density increase of volume elements of gas which, first heated but then effectively cool down, thus intersecting favorable regions for grain formation in the $p - T$ plane (Woitke *et al.* 1996).

2.3 General aspects

WR stars and RCB stars are hot stellar objects surrounded by a rather hostile environment for chemistry and dust formation (see Table 2), compared to late-type stars. However, dust formation associated with these objects seems to be a quite natural phenomenon. In some cases the dust even determines the

object	T$[K]$	log $n_{<\mathrm{H}>}[cm^{-3}]$	log $t_{\mathrm{typ}}[s]$	log $t^C_{\mathrm{cond}}[s]$
R Coronae Borealis stars	7000	$7-9$	$\approx 6-7$	≈ 9
Wolf Rayet stars	< 25000	$6-8$	≈ 8	≈ 9
Classical novae	≈ 10000	$\approx 8-10$	$\approx 6-7$	$\approx 7-8$

Table 2 Different astrophysical situations and their relevant physical parameters and time scales for dust formation: $n_{<\mathrm{H}>}$ total density of hydrogen in the gas, t_{typ} is the hydrodynamical time scale of the system and t_{cond} is a typical condensation time scale of carbon dust. For comparison the values for the hot winds of classical novae have been added (Sedlmayr and Dominik 1995).

structure of the stellar wind (Sedlmayr and Dominik 1995; Gail and Sedlmayr 1987, 1985). For the majority of the RCBs a photospheric temperature of about 7 000 K seems to be appropriate. However, in some peculiar cases like DY Cen, MV Sgr and V348 Sgr, the temperature is substantially higher, up to 20 000 K (Drilling *et al.* 1984; Jeffery and Heber 1993; Jeffery 1995a), comparable with the WCL stars. The elemental abundances for both classes of objects vary, but the large carbon overabundance, in combination with an absence of hydrogen, is a common feature. The elemental composition of the atmospheres is sensitive to the radiative transfer used to model the spectral appearance. Depending on the intrinsic parameters and the quality of the models, large differences in the deduced abundances can occur, as can be seen for RCBs in Table 4. Switching from the model grid of Schönberner (1975) to the Uppsala models (Gustafsson

	WR	RCB	Novae
system	single/double	only single	only double
class.	WCL	F-G supergiant	A – F*
L_* [$L_\odot$]	$10^{4.5} - 10^{5.9}$	$\approx 10^4$	10^5
T_* [K]	< 25.000	5.000 - 7.000	7.000 – 10.000*
R_* [$R_\odot$]	2-5	$\approx$ 60-80	70*
M_* [$M_\odot$]	30-50	≈ 1	≤ 1
$\dot{M}$ [$M_\odot$/yr]	$\approx 10^{-5}$	$(10^{-7})^a$	$10^{-4} - 10^{-5}$
v_{wind} [km/s]	1000-2000	$(50\text{-}200)^b$	500 – 3000

Table 3 Parameters characterizing WR and RCB stars. For comparison the values of Classical Novae have been added. Notes: [a] *mass loss only in connection with dust.* [b] *velocity seen in spectral lines during decline phases.* * *values are approximately valid for maximum light.*

and Asplund 1996), which include updated opacity data, demanded a revised input ratio of [C/He] = 0.1 resulting in a change of the abundances by −1 dex.

Nevertheless, in all those RCB environments with carbon abundances $\epsilon_C$ranging from $log\,\epsilon_C = 7.8$ (MV Sgr) to $log\,\epsilon_C = 10.6$ (V348 Sgr) and hydrogen abundances ϵ_H from $log\,\epsilon_H \leq 4.1$ (XX Cam) to $log\,\epsilon_H \leq 10.8$ (V348 Sgr) (Jurcsik 1996) solid particles are effectively formed. Therefore, one may conclude that a phase transition can take place despite the specific elemental composition of the gas. This conclusion also applies to WR stars, where the abundances also vary widely (Willis 1996). One important difference between WR and RCB stars is

	H	He	C	N	O	Si	Fe
RCB a	$H/He \ll 1$	11.51	9.8	9.7	9.1	8.0	7.5
RCB b	$H/He \ll 1$	11.54	8.91	8.64	8.20	7.15	6.55
sun	12.00	10.77	8.55	7.97	8.87	7.51	7.55
	H/He		C/He	N/He	O/C		
WR	≈ 0		$\approx 0.1 \ldots 0.7$	$\approx 10^{-3}$	≈ 0.2		

Table 4 Abundances of WR and RCB star. For RCB stars the abundances were taken from Lambert and Rao(1994) (RCB-a) and Rao and Lambert (1996) (RCB-b) which are both valid for the majority of the RCBs (for details see text). However there are substantial deviations from these values for about four stars (V854Cen, VCra, V3795 Sgr, VZ Sgr). The RCB and the solar abundances (Grevesse and Noels 1993) are given as logarithmic numbers. For the WR stars the given abundance ratios are taken from Willis (1996).

the type of mass loss. In WR stars a strong radiation driven wind exists, and mass loss is a dramatic effect which can eject well over half of the initial stellar mass (Moffat and Robert 1994). The determination of a more or less reliable value for $\dot{M}$ depends on the underlying theoretical models (e.g. Hamann 1995), which always include assumptions (e.g. a homogeneous atmosphere) to make the problem tractable. In fact, the outflowing gas is far from homogeneously distributed, but shows strong deviations from spherical symmetry (Moffat *et al.*

1994b; Lepine 1994). Strong shocks induced by the radiative instability of the wind (Antokhin 1995) along with supersonic turbulence (Moffat *et al.* 1994a) is assumed to be a likely cause of the observed clumpy structure of the winds.
Mass loss in RCBs does not arise from a stellar wind driven by some intrinsic mechanism. In these objects mass loss is a phenomenon periodically initiated by the formation of dust in a clump of limited extension. This characteristic event shapes the course of the lightcurve and may be closely connected to the characteristic 40 day stellar pulsation (Lawson *et al.* 1992). WR stars however are varying mostly with an erratic behaviour (Bratschi and Blecha 1996) on a shorter time scale, which might be responsible for the stellar wind acceleration.

3 Ionization structure and chemistry

A basic requirement for the applicability of dust formation models is, that carbon remains predominantly neutral (cf. Chapters 12, 18 and 24). Thus, a decisive factor for the possibility of carbon nucleation is the degree of ionization in the outflowing gas. Accounting for the abundance situation in WC stars and under the assumption of a stationary wind, the extension of the Strömgren sphere can be determined. Considering the local balance of ionization and recombination in a pure carbon mixture, the radius R_{C} of carbon ionization is given by (Sedlmayr and Gass 1991)

$$R_{\mathrm{C}}/R_* = \left[1 - \left\{2\int(\pi F/h\nu)d\nu\right\}/\alpha n^2 R_*\right]^{-1} \tag{3.1}$$

Attempting to have a more realistic estimate of R_{C}, one has to modify the influence of the radiation field by the inclusion of a reasonable optical depth factor $\exp(-\tau)$. Assuming a value of $\tau = 5$, one yields finite values of R_{C} for $T_* < 25\,000$ K and $n < 10^{11}$—cm^{-3} (Sedlmayr and Gass 1991).
A more sophisticated treatment accounting for the non steady nature of the wind must solve the time development of the degree of ionization, as has been done for nova shells (Beck *et al.* 1995, 1990). Hydrodynamic models also involving the non-equilibrium ionization evolution under the influence of dense clumps have been performed by Arthur *et al.* (1996). It is found that the observed correlation between the velocity of ultraviolet absorption features and the ionization potential of the absorbing ion can be qualitatively reproduced by such a model.

Although at first glance all of the considered objects (WR, RCB) seem not to have physical conditions favouring effective molecule formation, the observations of solid particles tells us that complex chemical processes must occur. We shall restrict the analysis of the chemistry to one main case: In RCB stars and dust-forming WR stars of the classes WC8-WC9 in which carbon is overabundant, whereas hydrogen is underabundant (Willis 1996; Rao and Lambert 1996; Nugis 1994). Thus, this situation can be characterized by a pure carbon chemistry.
Although the specific abundance ratios in RCB and WCL stars are varying, with

$[(C+O)/He]$ from $0.03\ldots1$ for WCL $\rightarrow$ WCE (Smith and Maeder 1991) and $[C/He] \approx 0.1\ldots0.5$ (Nugis 1994), $[C/O] \approx 1.0\ldots10$ for RCBs (Goeres 1992), the outcome of the condensation process is well known to be some kind of pure carbon solid.
In this environment the CO molecule will be the first to form, thus inhibiting an oxygen chemistry from developing. N_2 is the next molecule to form by virtue of its high binding energy. Like CO, N_2 will not take part in further nucleation processes. A typical formation sequence of chemical species according to their abundances then would be (Goeres 1996):

He - (C_n, CO) - N_2 - (CN, C_2N_2, C_2N, HCN, CNO, C_2H, CH)
(CS, SiS, SiC_2, Si_2C, SiO)

Thus, in RCB stars the chemical situation is characterized by a gaseous mixture dominated by pure carbon with some contributions of CO and N_2 and only minor traces of other molecules, in an inert helium buffer gas.
In WR stars the overall picture differs due to the fact that the radiation field is of substantially higher intensity in the UV, therefore helium is ionized from the outer atmosphere (Koesterke and Hamann 1995) up to the wind zone (Eenens *et al.* 1991; Niedzielski 1994). However, if helium is ionized, undoubtedly carbon will be too. The presence of carbon ions in the condensation zone of the wind would significantly influence dust formation which is commonly assumed to occur through neutral species (cf. Chapter 12). Up to now the nucleation of carbon clusters on the basis of ionized precursors has not been investigated. From the observations of emission lines in WR star envelopes (Moffat *et al.* 1994b) it is evident that the outflows of hot stars are dynamically unstable due to the inherent turbulence. This effect, also applying to the winds of Be-stars and novae, is assumed to be most pronounced in WR stars. A direct consequence will be the formation of local high density material distributions, which may be observed as clumps (Moffat and Robert 1994b; Chen *et al.* 1995). Although the degree of density increase in such clumps is still uncertain (Brown and Richardson 1995; Moffat 1995), such non-homogeneous material clouds may offer the opportunity for shielding effects and more favorable conditions for nucleation and growth of grains which, once formed, will amplify the formation processes.

4 Dust formation

As discussed in Section 2.1, dust formation in Wolf-Rayet stars is a strong function of spectral subtype, e.g. of the stellar temperature, as the UV-flux differs by approximately one order of magnitude between 17 000 K and 30 000 K. The ability for clusters to survive is a sensiive function of the UV photon flux. The ability of grains to form is in principle determined by the temperature and the density of the ambient gas, although a significant degree of ionization would complicate the process.
The density differences between dust forming and non-dust forming cases appear to be relatively small and therefore only a small increase in the local density, cou-

pled to a decrease in the local temperature, thus amplifying this effect, must be sufficient to overcome the apparently small barriers between dust forming and non-dust forming situations. For dust particles to be observable, the particle density in the wind has to be in excess of $3 \cdot 10^5$ cm^{-3} (Williams *et al.* 1987), which corresponds to $\rho > 8 \cdot 10^{-18}$ g cm^{-3}. For dust particles to form a minimum density of 10^8 cm^{-3} is necessary.

4.1 Chemical models

Assuming radiative equilibrium of a dust grain, one can determine a minimum distance where dust grains can survive without sublimation. For a typical WC star this distance is a few 10^{17} cm ($\approx 10^4 R_*$), where the particle density under the assumption of spherical symmetry and a uniform wind has dropped to 10^6 cm^{-3}.

This low density seems to be not sufficient for the formation of dust particles.

For carbon rich situations the problem of dust condensation has been investigated by Keller (1987), Gail and Sedlmayr (1987, 1988), Frenklach and Feigelson (1989), Cherchneff *et al.* (1993, 1991) and Gores (1993). However, these chemical models cannot be easily applied to WC environments, as they do not consider the consequences of the specific abundance distribution in hot winds to the chemical pathways to dust. A situation where the gas is carbon rich and hydrogen deficient has been intensively investigated in the laboratory since fullerene synthesis has been detected (Krätschmer *et al.* 1990). Although the scaling of the chemical results from the laboratory to the astrophysical conditions of WR and RCB stars incorporates some uncertainties, it is possible to describe a plausible dust formation process. The nucleation chemistry of the carbon species may proceed along the following steps (Goeres 1996):

A. Linear chains (unbranched) $\rightarrow$ B. Monocyclic rings $\rightarrow$ C. Polycyclic aromatic carbon clusters (PACs).

A. At high temperatures short chains completely dominate the chemical processes. These small carbon molecules are linear chains of polyyne type (alternating single and triple C-C bonds) for even numbers and cumulene type (C-C double bond) for odd numbers of carbon atoms. For longer chains ($n \geq 7$) the cumulene becomes more favorable (Raghavachari and Binkley 1987). The largest cluster with a linear ground state is C_9 (Heath and Sakally 1990, 1991), but there is experimental evidence for linear chains up to $n \approx 20$ (Broyer *et al.* 1992).

B. If the temperature in the gas decreases, the chains successively grow and with increasing chain length the energy of the first vibrational mode rapidly decreases. Also the energy gain of saturating the radical sites by ring closure exceeds the energy loss by bending the chain to a ring. Therefore, the chains close up to monocyclic ring structures, which are less reactive than chains as it requires the opening of a π-bond, which are the more preferred the more the temperature decreases.

C. The third step in the formation sequence is quite controversial. The more favourite possibility is based on the idea that the reaction enthalpy of a ring-ring addition enables the cluster to overcome the activation energy barrier towards the PACs (Goeres and Sedlmayr 1991, 1993). An alternative path invokes the subsequent growth of monocyclic rings by C_2 addition to sizes beyond $n = 60$, a large curved framework containing hexagons as well as pentagons and which has the tendency to close to form a fullerene stabilized by thermal C_2 dissociation (McElvaney 1993). Goeres (1996) has pointed out that there is a profound difference between these two model pathways. The effectiveness of fullerene production would be significantly higher in the second case, whereas the first path only allows for the production of larger fullerenes ($n > 70$). However, the observations of the Wolf-Rayet stars WR104 and WR112 (Cohen *et al.* 1989) detecting the $7.7\mu\,m$ C-C stretching feature supports the PAC hypothesis, whereas no fullerenes have been observed at all in WC or RCB winds.

A comparable dust formation route is described by Cherchneff and Tielens (1995). Their model, based on the theoretical arguments of Tielens (1990), Frenklach and Feigelson (1989) and Cherchneff *et al.* (1993), is also favouring a chemical picture where small, spherical carbon clusters are the basic units of soot particles, and involving monocyclic ring condensation in an intermediate phase, they also end in PAC production. Furthermore they argue, that it is unlikely that the growing curved PACs will perfectly close but they will form a spiral structure, which can serve as condensation nuclei in the formation process of amorphous carbon clusters. The classical approach involving a pathway $C_1 \longrightarrow C_2 \longrightarrow C_3 \longrightarrow C_4 \ldots \longrightarrow C_n$ and essentially based on the addition of neutral carbon monomers seems to be in question or maybe not applicable. As inferred from the strength of the CII and CIII lines, the abundance of neutral carbon, suspected to be an essential precursor molecule of carbon dust formation, is very low (10^{-6}, CI lines have not been found (Torres and Conti 1984)). This is in contrast to normal C stars as well as RCB stars and it might be due to the fact that the life time of the precursor molecules is too short to build up a reasonable optical depth.

If one assumes the existence of grains, further growth by heterogeneous nucleation of ions may be possible (Czyzak *et al.* 1982). It requires the presence of negatively charged grains, where the actual grain charge is determined by a competition between the processes of grain–electron collisions and the photoelectric effect (Feuerbacher *et al.* 1973; Spitzer 1978). Critical parameters therefore are the UV-field and the local electron density. A small increase in the density of the electrons may push the grain charge to become negative and as a result would create favourite conditions for the growth of particles by the accretion of ions.

However, a serious problem remains for the nucleation phase, where no negative charge for small clusters can be expected.

4.2 Condensation in clumpy media

A first approach to clarify the chemical situation in WR winds has been undertaken by Cherchneff and Tielens (1995). In their chemical kinetic model consist-

ing of 13 carbon species and 40 reactions using standard WC9 star parameters, they assumed a steady spherically symmetric outflow, a blackbody radiation field and a simple adiabatic cooling of the gas starting from $T_{\rm gas} = 4\,000$ K. From their modelling some important results come to light: a) the carbon chains were predominantly present in ionic form, but b) the concentrations even of C_2^+ and C_3^+ are quite low due to high net rates of dissociative recombination, even though the CI concentration is a factor 100 higher than observed. These disadvantageous chemical conditions lead to a very small formation yield, e.g. the number of carbon atoms bound in chains compared to the number of initially available carbon atoms is $\approx 10^{-15}$ for carbon dust precursors. The bottleneck reactions are the formation reactions of C_2 and C_3, which do not proceed effectively. This result has to be compared with the formation yield derived by Williams (1987) of $10^{-3} - 10^{-4}$, which is necessary to comply with the observations.
However, the gas outflow in WR and also in RCBs is far from being spherically symmetric. An artificial increase of the gas density by a factor of 10^4 to simulate the existence of clumps and to stimulate the dust formation therein results in a higher concentration of neutral carbon. Generally the clump model shows a dominance of neutral carbon species, which were mainly formed via radiative associations. Destruction routes of the carbon chains are mainly via He^+ and O attacks and with lower efficiency by photodissociation. The largely enhanced formation yield now is 10^{-6}. We conclude that while dust formation in WC stars is impossible under the assumptions of a spherically symmetric and homogeneous outflow, a large density increase may promote carbon dust formation.

4.3 Shock induced condensation

Dust formation in WR stars not only takes place in the vicinity of single stars, but is also closely connected with the occurrence of strong shocks in colliding winds of binary WR+O systems. In the wind collision zone a gas element is first heated, compressed and afterwards re-expands resulting in very effective cooling (Usov 1991, 1995). This mechanism generally shows similarities with those assumed to be applicable for RCB stars. Woitke *et al.* (1996) have developed a detailed model for shock induced condensation. Chemistry, nucleation and the thermal balance were studied for fixed fluid elements, which are periodically hit by shock waves caused by stellar pulsation. Non-LTE radiative heating and cooling processes in the shocked gas have been accurately modeled including free-free, bound-free and atomic line transitions, as well as rotational and vib-rotational contributions of molecules.
The gas, heated and compressed by a shock, radiates away its excess internal energy, afterwards re-expanding. The phase of re-expansion is dominated by adiabatic cooling, which may cause gas temperatures substantially lower than in radiative equilibrium, if the particle density of the gas is tuned to a specific, but not too narrow range of $10^{7.5} - 10^{10}\rm cm^{-3}$. Favorable preconditions for carbon nucleation may occur, if a mechanism is present, which pushes the gas volume

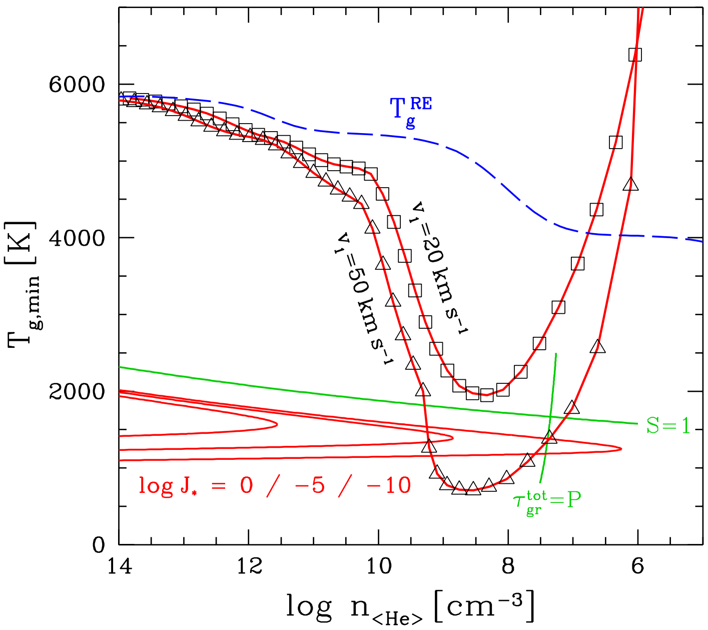

FIG. 1. Dust formation in shocked gas (Woitke *et al.* 1996). The figure shows the minimum gas temperature $T_{g,min}$ (full lines and points) occurring in a periodically shocked gas element for two different shock velocities as indicated, and the radiative equilibrium gas temperature T_g^{RE}. The condensation regime is depicted by contour lines of the logarithm of the classical nucleation rate J_* [$cm^{-3}\,s^{-1}$]. As the growth is limited by the pulsation period the maximum growth time is indicated by τ_{gr}^{tot}.

out of its equilibrium state. Temporarily a fluid element with an appropriate density can cool down below the condensation temperature of dust resulting in high supersaturation ratios. A large nucleation rate J_* (see Fig. ??), e.g. a high number of newly formed seed particles (per volume and per second), will evolve, leading to a sufficient number of small clusters, which can subsequently grow to macroscopic particle sizes. The specific range of favourable conditions of a shocked gas element in a RCB atmosphere is indicated by the intersection of the condensation regime (below $S = 1$ line) and the slope of the minimum gas temperature available during one pulsational period.
Generally this mechanism only causes the gas element to depart from its equilibrium state. Thus it can be expected that it is not restricted to pulsational shocks, but whenever a strong shock hits an atmospheric element with the appropriate density shock induced, condensation may take place.
The inherent instability of radiation driven winds in WR stars also can lead to shock waves which permeate the WR wind, and the density enhanced shock regions might be identified with the inhomogeneities (blobs) (Moffat and Robert 1994a; Antokhin 1995). Recent observations of WR 104 (Crowther 1997), the

brightest WR star in the IR due to its huge circumstellar dust shell and of the occasional eclipses of the dusty WC9 star WR121 (Veen *et al.* 1997) can both be interpreted in terms of the temporary condensation of an optically thick dust shell in the line of sight, which is subsequently dispersed by the radiation pressure. All this points to the fact that there is a close similarity between the physical processes related to dust formation in RCBs as well as in WR stars.

5 Summary

Although the amount of dust formed in the vicinity of hot stellar objects is considerably less than in the expanding shells of obviously more favorable systems like cool late-type stars, the detection of solid particles shows that even in these apparently hostile environments a rich chemistry may arise. Present modelling of thermodynamics, chemistry and dust formation are satisfactory for cool, homogeneous winds but are not applicable to the conditions prevailing in the shells of WR and RCB stars. The observational evidence points to three types of phenomena, which are of key importance for the dust formation process: these are density inhomogeneities, shocks and temperature fluctuations. All of these phenomena lead to one fundamental consequence: they generate favorable conditions for the onset of dust nucleation and growth.
The full understanding of the physical processes involved is a challenge for at least the next generation of model calculations.

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