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Morphologies of coke deposited on surfaces of pure Ni and Fe-Cr-Ni-Mn alloys during pyrolysis of propane

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Morphologies of coke deposited on pure Ni and Fe-Cr-Ni-Mn alloy surfaces during pyrolysis of propane at 750–1000 °C have been investigated in detail. It is found that surface scales developed initially on pure Ni and Fe-Cr-Ni-Mn alloy surfaces have no catalytic effect on deposition of filamentary coke. But metal or alloy substrates under cracked scales strongly catalyze nucleation and growth of filamentary coke along the cracks. Ni is more efficient to catalyze the growth of filamentary coke than Fe-Cr-Ni-Mn alloys. The structure of oxide scales has marked influence on distribution and size of filamentary coke deposited on alloy surfaces. Coking morphology is closely dependent of coking temperature and time. Either increasing coking temperature or prolonging coking time results in coking morphology changes from filamentary to spherical. Both dissolution/precipitation mechanism and direct nucleation and growth mechanism may make a contribution to the development of graphitic film coke. © *2000 Kluwer Academic Publishers*

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1. Introduction

Coke is one of main side products in hydrocarbon cracking in petrochemical plants. The coke deposited on inner wall of cracking tube will give rise to a loss of thermal efficiency, decrease the effective cross section of tube and block cracking reactions, all of which greatly lower cracking output and increase production cost. Moreover, coke can also promote carburization, especially during the period of decoking [1]. Carburization results in volume expansion of cracking tube and makes it more susceptible to creep rupture failure. In fact, it has been proved that the most of failures of expensive cracking tubes are due to the deposition of coke [2].

The formation of coke in cracking system is very complex and is influenced by various factors such as cracking temperature, feeding gases and tube materials. In practical cracking operations, the temperature in hottest section of radiant tube may be up to 1100 °C, while the temperature in boiler heated by residual heat after cracking is about 400 °C, so coke may be developed in an extensive temperature. Most of coking processes are closely associated with gas phase reactions, so the compositions and mixture ratio of feeding gases are the important factors that influence coke formation. Based on the studies of Graff *et al.* [3], alkyne, alkene, and aromatic hydrocarbon are coke precursors. The addition of hydrogen, or hydrogen sulfide, or ammonia in feeding gases is effective to retard the surface coking [4–6]. In addition, the inner wall of cracking tube is the main spot for coke deposition, thus tube materials, especially surface chemical compositions of tube have a marked influence on coke deposition.

Since 1960s, many studies have been done to retard coke deposition on inner wall of cracking tube. The main ways used can be divided into three types. One is to optimize the cracking process parameters such as cracking temperature, pressure, compositions and mixture ratio of feeding gases and retention period, which is the ripest coking-resistant skill applied in petrochemical industry. The second is primarily focused on surface

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alteration of materials, in which the aluminized processing and ceramic coating processing are the typical ways. However, on account of more expensive cost and more complex processing, these ways are only realized in laboratory and are difficult to be applied in industry production. Another way is to adjust the compositions of tube materials and improve their inherent coking resistance. A series of modified heat-resistant tube materials are developed in the past three decades [7–13]. But it is unfortunate that much interest in previous modification has been focused on the improvement of high temperature properties rather than coking resistance of tube materials. Some composition adjustment is even contrary to the demand of improving coking resistance of materials [14].

To develop a new type of tube material that inherently has a good resistance to surface coking and carburization, a series of investigations are carried on to reveal the surface coking and carburizing mechanisms of metal and alloys. As part of above study, this paper primarily describes the coking morphologies on pure Ni and Fe-Cr-Ni-Mn alloy surfaces and discusses the formation mechanisms of coke with different morphologies and their relation to material surfaces.

2. Experimental

The reaction gas chosen to crack is propane (C_3H_8), which is one of main feeding gases in petrochemical plants. The diluent used in present work is nitrogen (N_2) rather than steam, which may partly remove the coke by water gas reaction [15] and alter surface character of metal or alloys [16, 17]. Nitrogen is completely inert in cracking reactions and does not alter the results. The flow rates of propane and nitrogen are measured by the calibrated flow meters and are adjusted by the needle valves. The equipment used in coking experiments is essentially identical to that employed by Shinohara *et al.* [14].

The materials used in present study are pure Ni and two types of Fe-Cr-Ni-Mn alloys. The compositions are listed in Table I. All the specimens are cut into 1 cm × 1.5 cm × 0.4 cm and ground with 200 grit SiC paper. Prior to using, the specimens are ultrasonically washed in ethanol. Then, the specimens are laid on a supporting boat and put into the primary reactive tube that is 52 cm I.D. and 130 cm long. The specimens are heated in flowing nitrogen up to the cracking temperature. A mixture gas of nitrogen and propane then replaces the nitrogen. The experimental parameters are listed in Table II. After coking, the specimens are cooled in the reactor with flowing nitrogen up to room temperature. A JSM-6301F scanning electron microscopy (SEM) with a ISIS 300 Series energy-dispersive X-ray analyzer (EDAX) is used in morphology observation and qualitative chemical analyses.

TABLE II Parameters of coking experiments

Cooking specimens	Temperature (°C)	Coking time (min)	N_2/C_3H_8 Molar ratio	Flow velocity (ml/min)
Pure Ni	750, 800, 900	30		
	1000	5	10 : 1	1250
	800	300		
Fe-25Cr-35Ni-2Mn	750, 800, 900	30		
	1000	5	10 : 1	1250
	800	300		
Fe-25Cr-35Ni-15Mn	750	30		
	1000	5	10 : 1	1250

3. Experimental results

Fig. 1 shows the morphologies of coke deposited on pure Ni surface at different temperatures. It is clear that coking is aggravated with increase of coking temperature. At 750 °C, the surface of pure Ni is primarily covered by a layer of carbon scale as revealed by EDAX analysis (Fig. 2a). Some floccular coke is locally deposited at cracks in the scale (Fig. 1a). At higher magnification, it is clear that the floccular coke consists of some longer spiral filaments (Fig. 1b). As coking temperature is raised up to 800 °C, an amount of floccular coke is deposited along the grind tracks on pure Ni surface (Fig. 1c). At 900 °C, the floccular coke disappears, instead, a type of coke similar to sesame ball is deposited on Ni surface, causing a rougher surface and hiding the metal matrix completely (Fig. 1d). Fig. 3 reveals the initial morphology of coke deposited on Ni surface at 1000 °C. In this case, a type of coke films with clear boundaries covers the whole surface of pure Ni. EDAX analysis reveals that the films are similar to that formed at 750 °C and basically composed of carbon.

The morphologies of coke deposited on Fe-25Cr-35Ni-2Mn alloy surface are illustrated in Fig. 4. Distinguished from pure Ni, at relatively lower temperature (750 °C and 800 °C), most of alloy surface is covered by an smooth scale composed of coarser oxides. EDAX analysis indicates that the oxides are primarily rich in Cr (Fig. 2b). The short-filamentary coke, which has interwoven into network and spread out, is predominantly deposited at local places where oxide scale has been cracked (Fig. 4a and b). After 30 min coking at 900 °C, the short-filamentary coke disappears, instead, a type of flat-spherical coke appears. The whole surface of alloy has been covered completely by the

TABLE I Compositions of materials used in study (wt.%)

Materials	Cr	Ni	Mn	Si	Fe	Other
Pure Ni	—	Bal.	—	3 ppm	10 ppm	Ag, Al, Cu < 1 ppm
Fe-25Cr-35Ni-2Mn	24.3	34.5	1.9	1.6	Bal.	P, S < 0.03
Fe-25Cr-20Ni-15Mn	25.1	21.6	15.2	1.5	Bal.	P, S < 0.03

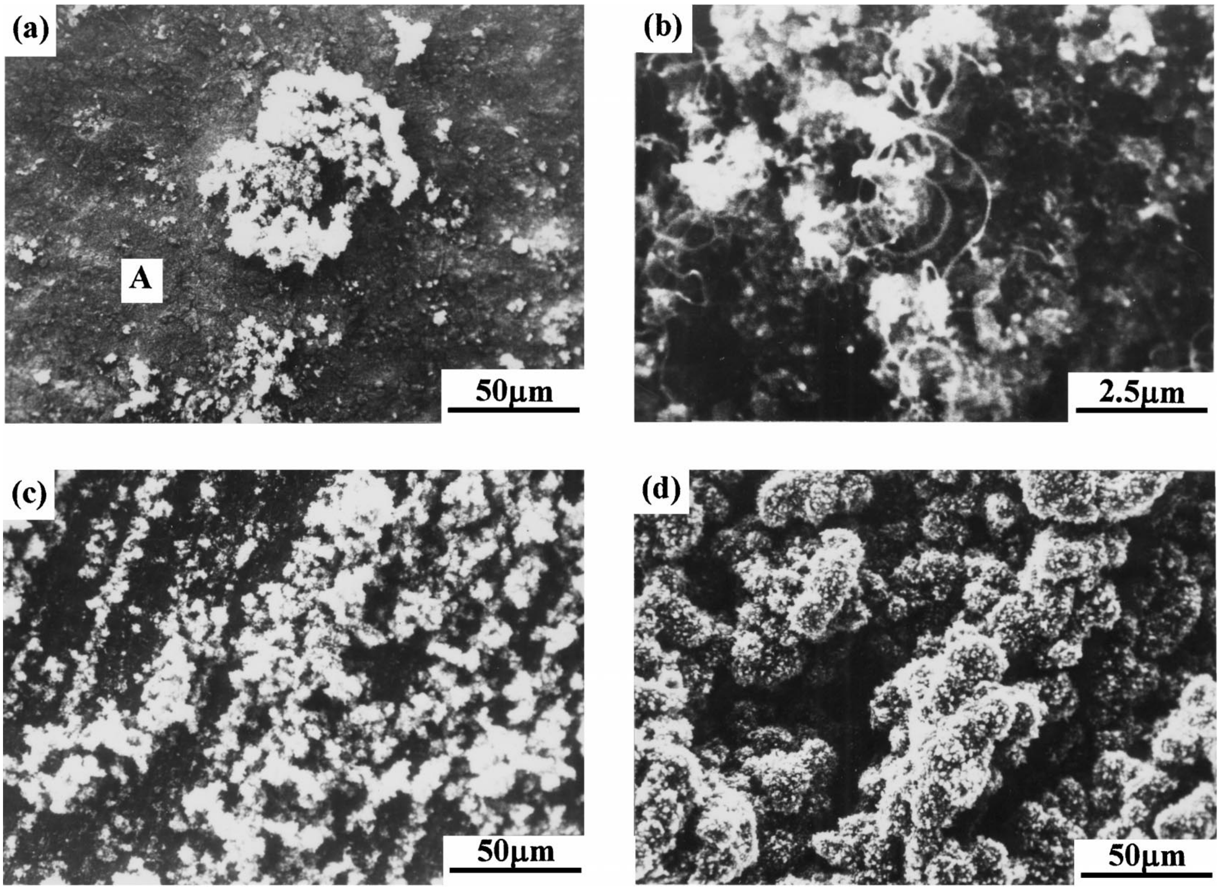

Figure 1 Morphologies of coke deposited on pure Ni surface at different temperature: (a) 750 °C, 30 min, (b) high magnification of (a) showing filamentary coke, (c) 800 °C, 30 min (d) 900 °C, 30 min.

flat-spherical coke (Fig. 4c). At 1000 °C, after a short time (5 min) coking, the alloy surface is covered by a large number of small and roundish coke particles (Fig. 5a). EDAX analysis indicates that these coke particles are deposited on an oxide scale rich in Cr formed initially (Fig. 6a). The particles are piled up each other with massive cavities between the piles. Observed at higher magnification, the connection between coke particles is similar to melting balls (Fig. 5b).

Fig. 7a and b show the morphologies of coke deposited on Fe-25Cr-20Ni-15Mn alloy surface at 750 °C and at 1000 °C. At lower temperature, most of alloy surface is also covered by oxide scale. But distinguished with the smooth oxide scale formed on Fe-25Cr-35Ni-2Mn alloy surface, the scale is composed of fine grain-like oxides, EDAX analysis indicates the oxides are primarily rich in Mn (Fig. 2c). Similarly, the filamentary coke stems from the cracks in oxide scale and grows around. However, the filaments are finer and more scattered relative to that formed on Fe-25Cr-35Ni-2Mn alloy surface. After 5 min coking at 1000 °C, the surface morphology of coke particles is similar to Fe-25Cr-35Ni-2Mn alloy surface. EDAX analysis shows that the coke particles are deposited on an oxide scale rich in Mn (Fig. 6b). In addition, some local regions are still covered by fine grain-like oxides (Fig. 7c). Moreover, a few irregular protrusions rich in Mn are growing from the fine oxide scale. Observed at higher magnification, these protrusions also consist of grain-like oxides (Fig. 7d).

It should be noted that a change of coke morphology takes place with prolong of coking time either on pure Ni surface or alloy surfaces. After 300 min coking at 800 °C, the surface of pure Ni has been covered completely by sphericizing coke rather than filamentary coke (Fig. 8a). It is interesting that under the scanning of electron beam, a number of dots are induced on initial smooth surface of coke gradually, which consists of little pits in nature at a higher magnification (Fig. 8b). This indicates that there exist some volatile matters in deposited coke. Under the excitation of electron beam, mass heat is accumulated in coke, which gives rise to volatilization of the volatile and many pits resided on coke surface. A similar case is found for Fe-25Cr-35Ni-2Mn alloys (Fig. 8c). Fig. 8d shows the substrate morphology after natural stripping of coke. Clearly, no filamentary coke is kept on the rough substrate. EDAX analysis reveals that the mixtures of oxides and carbides rich in Mn and Cr are formed on the base of alloy (Fig. 9).

4. Discussion

In general, the pyrolysis process of low-chain light hydrocarbon such as propane (C_3H_8) is more complex and dominated by the reactions of free radicals. By way of break reaction, hydrogen shift and decomposition reaction of free radicals, cracking products such as hydrogen (H_2), ethylene (C_2H_4) and ethyne (C_2H_2) and basic free radicals such as methyl radical ($CH_3\bullet$)

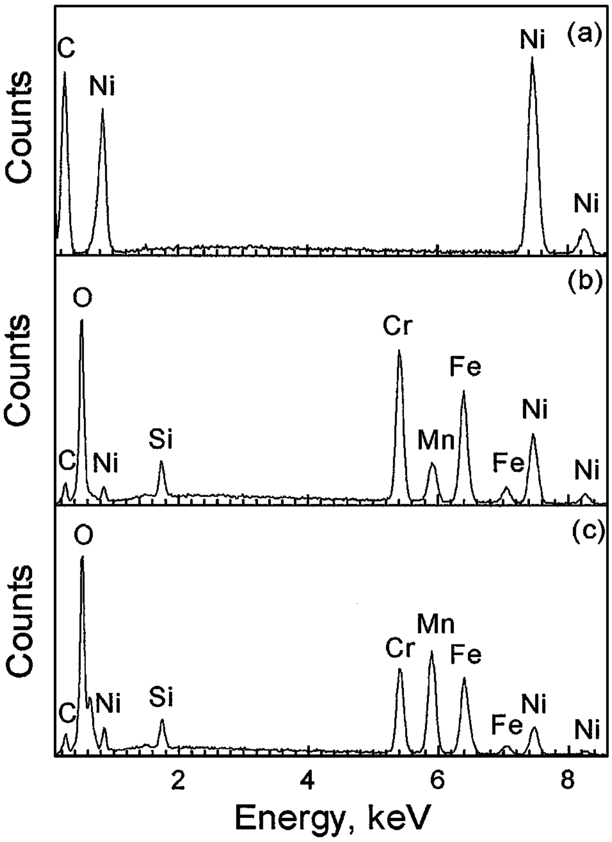

Figure 2 EDAX analyses of pure Ni and Fe-Cr-Ni-Mn alloy surfaces after 30 min coking at 750 °C: (a) zone A in Fig. 1a (pure Ni surface), (b) zone A in Fig. 4a (Fe-25Cr-35Ni-2Mn alloy surface), (c) zone A in Fig. 7a (Fe-25Cr-20Ni-15Mn alloy surface).

and hydrogen radical (H•) are produced. The carbon deposit is built up primarily by decomposition of these basic free radicals (especially by CH_3•) since they are much less stable than corresponding light hydrocarbon [18, 19].

The pyrolysis reactions of hydrocarbon are significantly influenced by the introduction of catalyzers. In particular, the most efficient catalytic species are transition metal such as Fe, Ni, and Co [20]. One of the most typical characterizations induced by these catalytic species during pyrolysis of hydrocarbon is to form filamentary carbonaceous deposits. In this process, some detached small metallic particles act as catalytic surfaces for the decomposition of hydrocarbon gas to produce

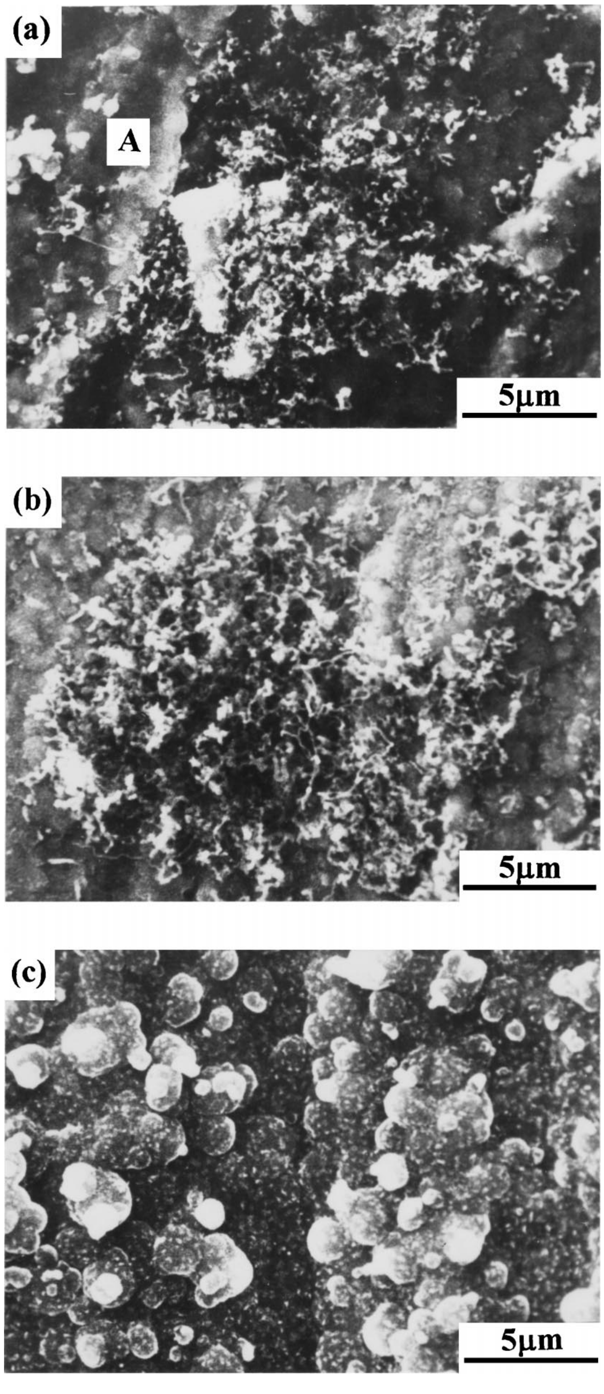

Figure 4 Morphologies of coke deposited on Fe-25Cr-35Ni-2Mn alloy surface at different temperature: (a) 750 °C, 30 min, (b) 800 °C, 30 min (c) 900 °C, 30 min.

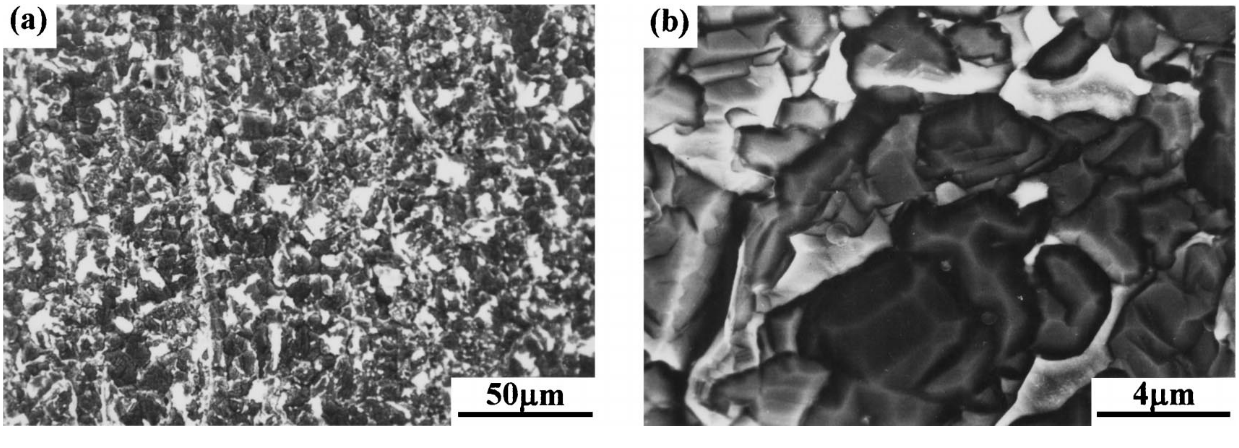

Figure 3 Surface morphology of pure Ni after 5 min coking at 1000 °C: (a) coke films, (b) high magnification of (a).

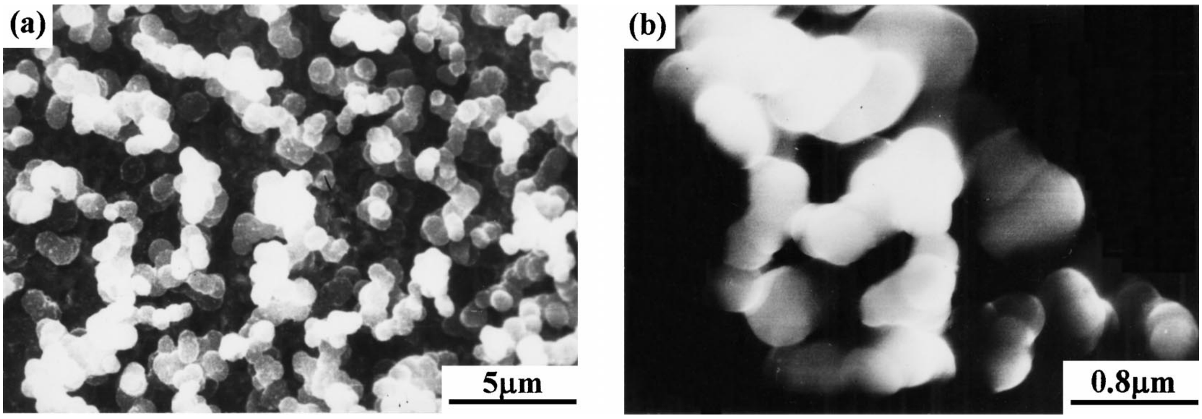

Figure 5 Surface morphology of Fe-25Cr-35Ni-2Mn alloy after 5 min coking at 1000 °C: (a) coke particles, (b) high magnification of (a) showing connection between coke particles.

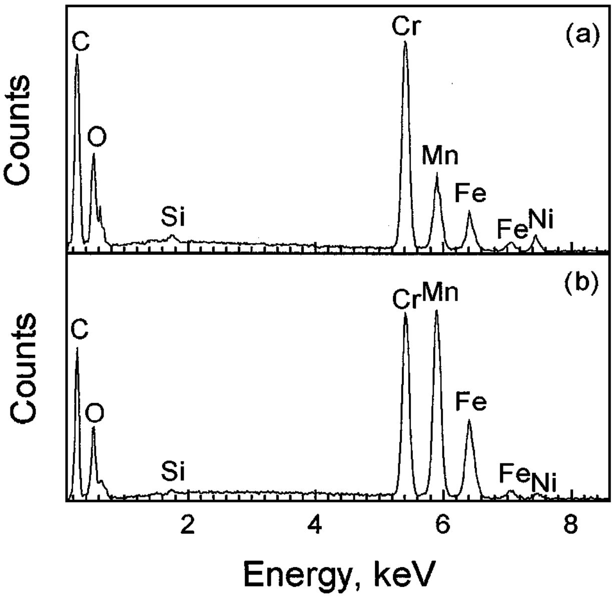

Figure 6 EDAX surface analyses of Fe-Cr-Ni-Mn alloys after 5 min coking at 1000 °C: (a) Fe-25Cr-35Ni-2Mn alloy surface, (b) Fe-25Cr-20Ni-15Mn alloy surface.

carbon that dissolved in and diffuses into the bulk of the metallic particle. Since the solubility of carbon in a metal is temperature dependent, precipitation of excess carbon will occur at the colder zone behind the particle and resulting in the growth of filament coke. Such a process will continue until the leading tip of the catalyst particle is covered completely by coke deposited soon afterwards and filament growth will cease [21]. Moreover, if the metallic catalytic specie is not geometrically symmetrical or has an angular shape, the diffusion distances of carbon dissolved from different surface of metallic particles will be different, thus results in spiral growth of filamentary coke [22].

In present experiments, after short time coking at lower temperature, filamentary coke is observed on both pure Ni and Fe-Cr-Ni-Mn alloy surfaces (Figs 1, 4 and 7). However, based on the results of EDAX analysis, during initial stage of coking, most of surface of pure Ni is covered by a layer of carbon scale, while oxide scales are developed on most of alloy surfaces (Fig. 2). SEM has found that the filamentary coke is only deposited at the pores or cracks of these scales. This indicates that the surface scales developed initially on pure Ni and alloys surfaces have no catalytic effect to the deposition of filamentary coke. But if the scales are cracked, the underlying substrates will be exposed directly to hydrocarbon gases. For pure Ni, since the substrate is active Ni in nature, it strongly catalyzes the decomposition of hydrocarbon gases and also the nucleation and growth of filamentary coke along the cracks. For Fe-Cr-Ni-Mn alloys, the substrates, which are denuded of Cr and rich in Fe and Ni due to the partial consumption of Cr and Mn for the formation of outer oxide scales, also promote the formation and growth of the catalytic filamentary coke along the cracks of the oxide scales. Therefore, the clusters of filamentary coke are only observed where surface scales are cracked. Under same experimental conditions, the filaments formed on pure Ni is longer than that on alloys, which reveals that Ni is more efficient to catalyze the growth of filamentary coke than Fe-Cr-Ni-Mn alloys. In addition, the structure of oxide scale has marked influence on the distribution and size of filamentary coke. The scale formed on Fe-25Cr-20Ni-15Mn alloy surface consists of fine grain-like oxides, the strain induced in scale by thermal or mechanical change is easy to be released by the accommodation deformation between fine oxides at high temperature. So cracks or pores formed along the boundaries of finer oxides are more scattered and smaller in size, in turn filamentary coke deposited subsequently is finer and more scattered. However, the oxide scale formed on Fe-25Cr-35Ni-2Mn alloy surface consists of coarser oxides, the strain induced in this oxide scale is not easy to be released by oxide deformation. So, cracks or pores with larger size are easy to be formed at local regions in oxide scale where stress concentration takes place. Also, coarser filamentary coke is developed from these places.

With increase of coking temperature, the filamentary coke stops growing. Instead, a type of spherical coke is deposited randomly on pure Ni and alloy surfaces. This indicates that coking mechanism change with coking temperature. In fact, increasing coking temperature aggravates the reactions between gas phases. Except for the aggravation of break reaction, hydrogen shift and decomposition reaction of free radicals mentioned

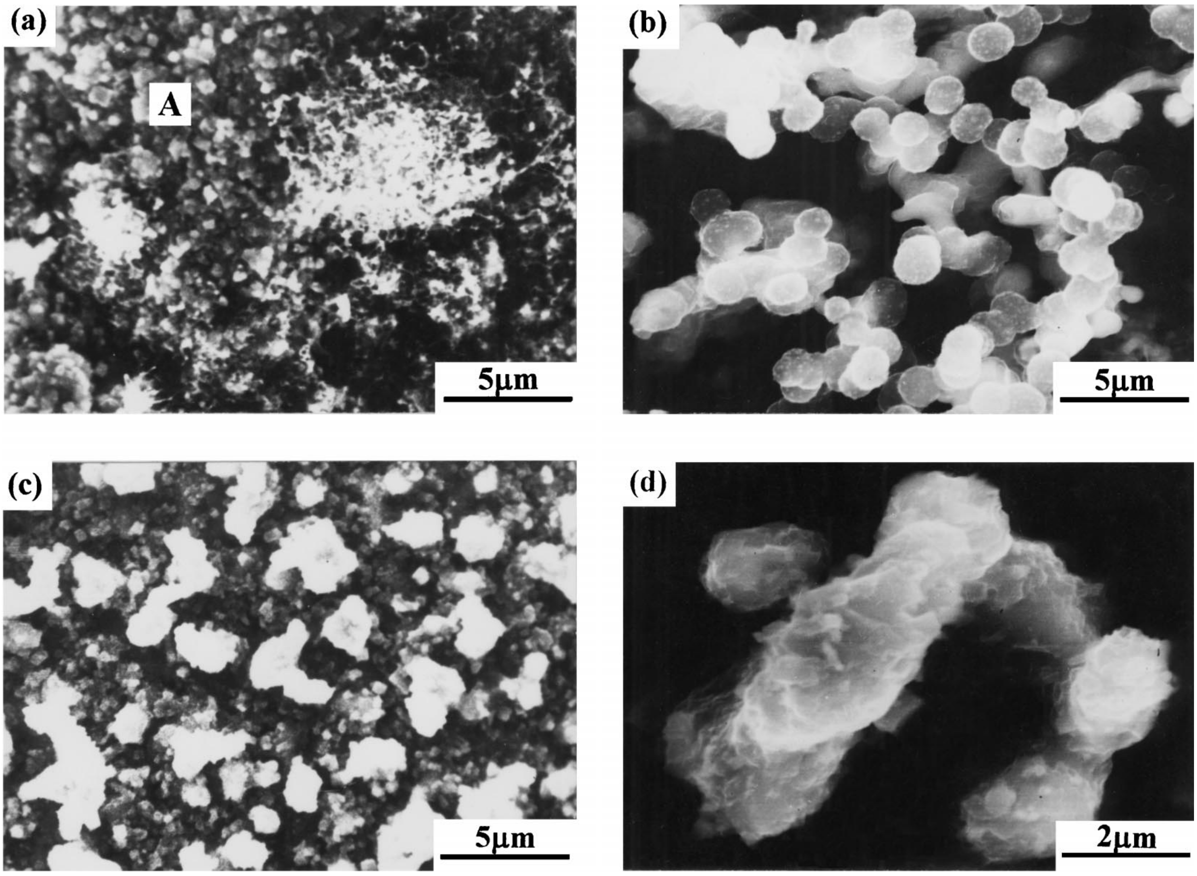

Figure 7 Surface morphologies of Fe-25Cr-20Ni-15Mn alloy after coking: (a) 750 °C, 30 min, filamentary coke, (b) 1000 °C, 5 min, spherical coke, (c) 1000 °C, 5 min, fine grain-like oxides and protrusions above grain-like oxides, (d) magnification of the protrusion in (c).

previously, corresponding reversal reactions such as coupling and addition reactions are also intensified, by which some monomoleculars of larger unsaturated free radicals may be produced. The polymerization and cyclization of these monomoleculars may result in the formation of superpolymer aromatic hydrocarbon that is the primary component of tar (one of side product of cracking reactions) [2, 23]. Some tars condense forming droplets that may be either suspended in the gas phase or absorbed by solid surface (metal or coke surface), which will be transferred into coke by dehydrogenation soon afterwards. When coking at relatively lower temperature (900 °C), the dehydrogenation is slower and the tar droplets either suspended in gas phase or deposited on solid surface have enough time to agglomerate each other. So, the coke is deposited in flat-spherical morphology with a larger size (Fig. 4c). However, at higher temperature (1000 °C), the tar droplets have no time to agglomerate on account of rapid dehydrogenation. Thus, the coke deposited keeps spherical morphology with a smaller size similar to the tar droplets (Fig. 5). Since the spherical coke is produced by a sequence of reactions starting in gas phase, it bears no relation to the surface compositions of metal or alloy naturally. Moreover, the spherical coke can prevent the catalytic metal or alloy particles from contacting with hydrocarbon and retard the continuous growth of filamentary coke deposited initially. In addition, some tars that still resided in spherical coke will volatilize under the excitation of scanning electron beam, which gives rise to many pits resided on the coke surface (Fig. 8b). At temperature suited for the formation of filamentary coke (800 °C), prolonging coking time also results in similarly change of coking mechanism. Moreover, the filamentary coke formed previously also dissolves into or reacts with substrate and consequently is turned into carbides (Figs 8d and 9).

It should be noted that the surface compositions have significant influence on the surface properties of metal or alloys such as roughness, wettability and integrity and adhesion of oxide scales, which in turn influence the nucleation and absorption of tar droplets and also the deposition of spherical coke. In this meaning, the improvement of Mn content in alloy is not beneficial to resist the deposition of non-catalyzed spherical coke since it promotes a rougher oxide scale developed on alloy surface that is easier for the nucleation and collection of tar droplets.

For pure Ni, a layer of films with clear boundaries are formed on metal substrate after 5 min coking at 1000 °C (Fig. 3). EDAX analysis reveals that the films are basically composed of carbon. Many researchers have observed this type of pyrolysis graphitic films. However, the mechanism of formation and growth of these films is not clear so far. Evans *et al.* [19] have suggested that the graphitic films or platelets result from decomposition of basic free radicals and/or the other light hydrocarbons and an epitaxial process at the surface of alloy or metal. It was suggested by Tammi *et al.* [24] that formation and later decomposition of unstable carbides is the primary reason that graphitic film is developed. Iring and Walker [25] supports this viewpoint.

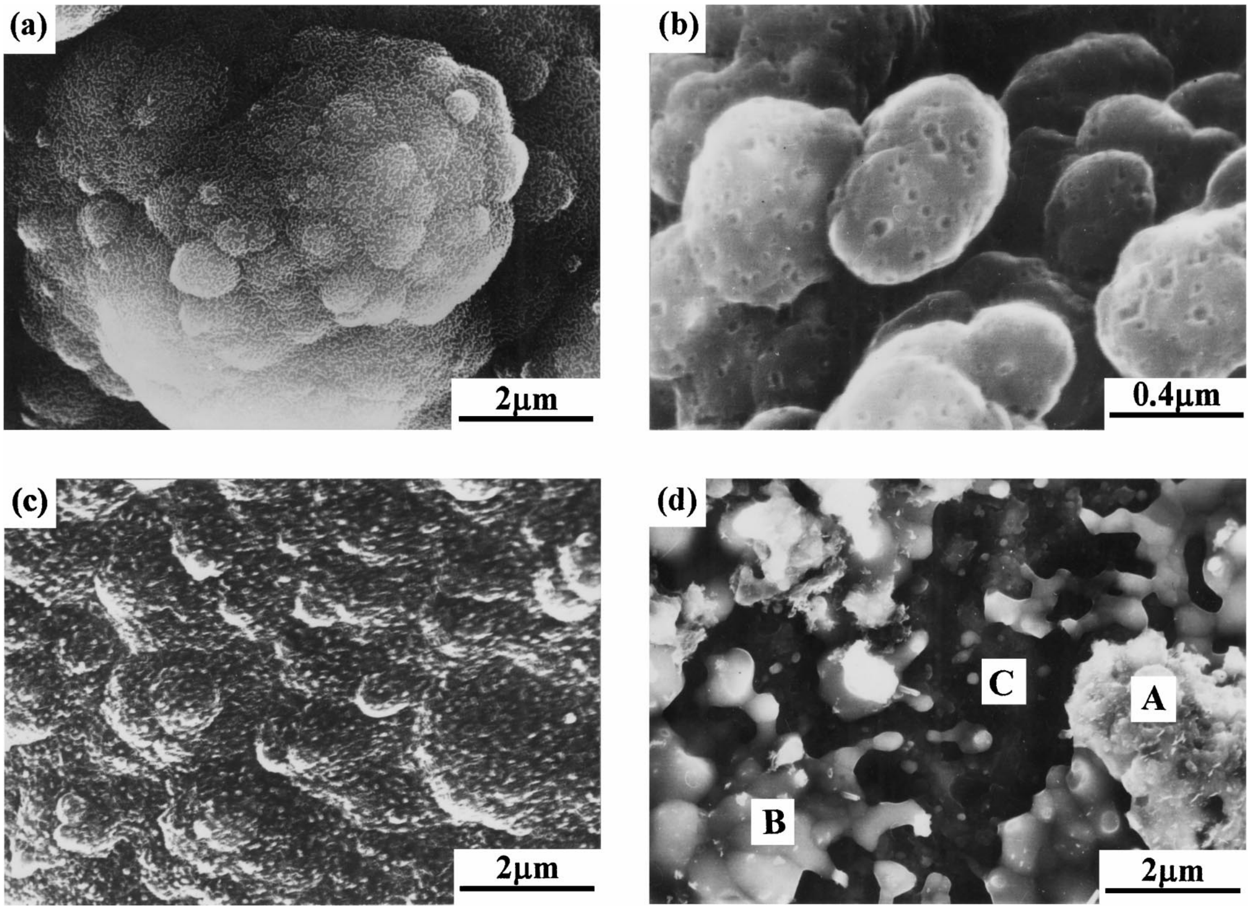

Figure 8 Surface morphologies of pure Ni and Fe-25Cr-35Ni-2Mn alloy after 300 min coking at 800 °C: (a) pure Ni surface, (b) high magnification of (a) showing the pits resided on coke surface, (c) Fe-25Cr-35Ni-2Mn alloy surface, (d) substrate morphology after natural stripping of coke for Fe-25Cr-35Ni-2Mn alloy.

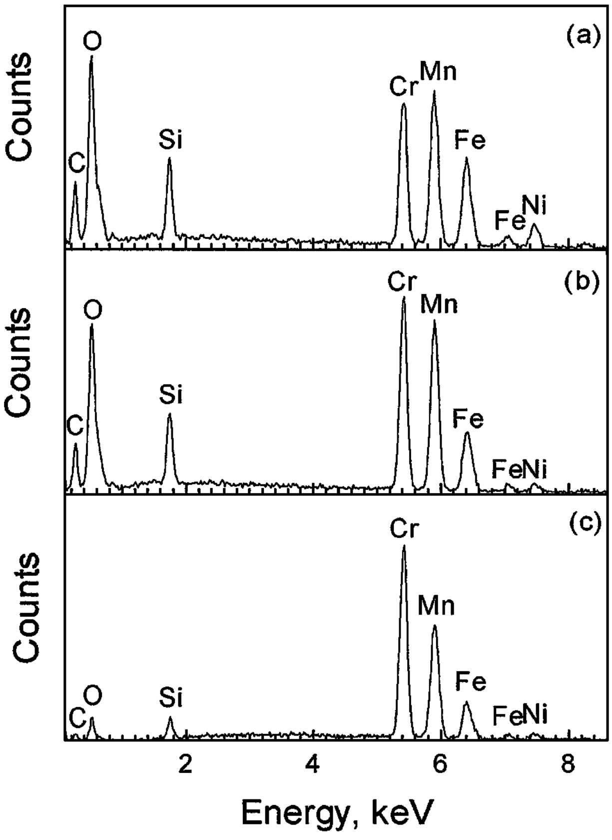

Figure 9 EDAX analyses of zone A (a), zone B (b), zone C (c) in Fig. 8d.

They extended it and suggested that the graphitic films can also be produced by dissolution of carbon in metal at a higher temperature followed by precipitation at a lower temperature. The experimental results obtained by Debyshire *et al.* [26] were consistent with above dissolution/precipitation mechanism. Another explain proposed by Baker *et al.* [27] is also based on dissolution/precipitation mechanism, but they mentioned that graphitic films are developed with the consumption of filamentary or amorphous spherical coke. However, it was shown by Ando *et al.* [28] that graphitic films deposited on pure Fe is developed at a constant temperature, which seems to be in contradiction to the dissolution/precipitation mechanism. Based on their suggestion, the formation of graphitic films is due to that supersaturating austenite has no ability to accommodate more decomposed carbon. Excess carbon coalesces at surface-active places such as grain boundaries and dislocations by surface diffusion and results in direct nucleation and growth of graphitic films. In view of solubility of carbon in Ni (0.23 wt-% at 1000 °C), it is possible for deposited carbon to dissolve into Ni substrate. Since the solubility is dependent of temperature, and specimens are cooled with reactor, the precipitation of graphitic films from Ni substrate during cooling is also possible. However, both dissolution and precipitation are involved in diffusion process of carbon atoms in metal or alloy matrix, which is slower relative to the deposition process of carbon from gas phases. Thus, the undissolved carbon deposited at metal or alloy surfaces may also coalesce at surface-active places and results in direct nucleation and growth of graphitic films. It is interesting that the graphitic film does not appear on surface of Fe-Cr-Ni-Mn alloy after 5 min coking at 1000 °C. This difference may be resulted from the different solubility and diffusivity of carbon in pure Ni and Fe-Cr-Ni-Mn alloys which in turn influence the dissolution/precipitation process of carbon. In addition, in cracking atmosphere (reduction atmosphere), the oxide scales formed on Fe-Cr-Ni-Mn alloys are more stable than that on pure Ni in terms of free energy of formation, which can retard either dissolution/precipitation or surface diffusion of deposited carbon, so the sphere coke instead of graphitic films is predominantly developed on oxide scales of Fe-Cr-Ni-Mn alloys after 5 min coking at 1000 °C, which also can be indicated by the analysis results of EDAX (Fig. 6).

5. Conclusions

1. Surface scales developed initially on pure Ni and Fe-Cr-Ni-Mn alloy surfaces have no catalytic effect on deposition of filamentary coke. But if these scales are cracked, the substrates (active Ni or Fe-Ni alloy in nature) strongly catalyze decomposition of hydrocarbon gases and also nucleation and growth of filamentary coke along the cracks. Ni is more efficient to catalyze the growth of filamentary coke than Fe-Cr-Ni-Mn alloys. Moreover, the structure of oxide scales has marked influence on the distribution and size of filamentary coke deposited on alloy surfaces.

2. Coking morphology is closely dependent of coking temperature and coking time. With increase of coking temperature, the filamentary coke stops growing, and a type of spherical coke is instead deposited randomly on pure Ni and alloy surfaces. Prolonging coking time also results in similar change of coking morphology even at a temperature suited for deposition of filamentary coke.

3. The spherical coke bears no relation to the surface compositions of metal or alloy naturally since it is produced by a sequence of reactions starting in gas phase. Surface properties such as roughness, wettability and integrity and adhesion of oxide scales, which are dependent of surface compositions of metal or alloys, have an influence on nucleation and growth of the spherical coke.

4. Both dissolution/precipitation mechanism and direct nucleation and growth mechanism may make a contribution to the development of graphitic film coke. The solubility and diffusivity of carbon in metal or alloy matrix, and the stability of oxide scales developed on metal or alloy surfaces may influence the formation of graphitic films.

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