Claims:

1. A process for surface hardening a workpiece made from an iron, nickel and/or chromium based alloy by gas carburization in which an unsaturated hydrocarbon is contacted with the workpiece inside a carburization reactor under a soft vacuum and at an elevated carburization temperature to cause carbon to diffuse into the workpiece surfaces thereby forming a hardened primary surface layer essentially free of carbide precipitates, the process further comprising feeding a carbon-free, halogen-containing activating compound to the carburization reactor simultaneously with feeding the unsaturated hydrocarbon to the carburization reactor.

2. The process of claim 1, wherein the carbon-free, halogen-containing activating compound is HF, HCl, NF_3, F_2, Cl_2.or a mixture thereof.

3. The process of claims 1 or 2, wherein the unsaturated hydrocarbon and the carbon-free, halogen-containing activating compound are combined before being fed to the carburization reactor.

4. The process of claim 3, wherein the unsaturated hydrocarbon and the carbon-free, halogen-containing activating compound are combined with a companion gas before being fed to the carburization reactor, the companion gas being a gas which is not an unsaturated hydrocarbon and further which is capable of reacting with oxygen under the reaction conditions encountered during the carburization reaction.

5. The process of claim 4, wherein the companion gas is hydrogen.

6. The process of claims 1 or 2, wherein the unsaturated hydrocarbon and the carbon-free, halogen-containing activating compound are separately fed to the carburization reactor.

7. The process of claim 6, wherein the unsaturated hydrocarbon and the carbon-free, halogen-containing activating compound are each independently combined with a companion gas before being fed to the carburization reactor, the companion gas being a gas which is not an unsaturated hydrocarbon and further which is capable of reacting with oxygen under the reaction conditions encountered during the carburization reaction.

8. The process of claim 7, wherein the companion gas combined with the unsaturated hydrocarbon is hydrogen, and further wherein the companion gas combined with the carbon-free, halogen-containing activating compound is hydrogen.

9. The process of claims 1 or 2, wherein the amount of the carbon-free, halogen-containing activating compound fed to the carburization reactor is kept low enough and the length of time the carbon-free, halogen-containing activating compound is fed to the carburization reactor is kept short enough so that formation of byproduct soot or thermal oxide or both is essentially avoided.

10. The process of claim 9, wherein the amount of unsaturated hydrocarbon fed to the carburization reactor is selected so that the concentration of this unsaturated hydrocarbon in the gas mixture inside the carburization reactor is about 8 to 35 vol. %, and further wherein the amount of carbon-free, halogen-containing activating compound fed to the carburization reactor is selected so that the concentration of this carbon-free, halogen-containing activating compound in the gas mixture inside the carburization reactor is about 0.5 vol.% to 3 vol.%.

11. The process of claim 10, wherein the duration of time the carbon-free, halogen-containing activating compound is fed to the carburization reactor is ~2 minutes to ~40 minutes, after which feeding of the carbon-free, halogen-containing activating compound to the carburization reactor is terminated.

12. The process of claim 11, wherein the gas mixture inside the carburization reactor consists essentially of the unsaturated hydrocarbon, the carbon-free, halogen-containing activating compound and a companion gas, the companion gas being a gas which is not an unsaturated hydrocarbon and further which is capable of reacting with oxygen under the reaction conditions encountered during the carburization reaction.

13. The process of claim 12, wherein the companion gas is hydrogen.

14. The process of claim 13, wherein the workpiece is made from an AISI 300 or 400 series stainless steel and the carbon-free, halogen-containing activating compound is HCl.

15. The process of claim 14, wherein the flow of carbon-free, halogen-containing activating compound being fed to the carburization reactor during carburization is pulsed.

16. The process of claims 1 or 2, wherein the workpiece is made from an AISI 300 or 400 series stainless steel and the carbon-free, halogen-containing activating compound is HCl.

17. The process of claims 1 or 2, wherein the flow of carbon-free, halogen-containing activating compound being fed to the carburization reactor during carburization is pulsed.

18. The process of claim 16, wherein the carburization potential of the gas mixture inside the carburization reactor is changed over the course of the carburization reaction by at least one of (1) lowering the carburization temperature, (2) lowering the concentration of unsaturated hydrocarbon in the carburizing gas, (3) interrupting the carburization process by terminating the flow of unsaturated hydrocarbon to the carburization reactor while maintaining the workpiece at elevated temperature, and (4) interrupting the carburization process by terminating the flow of unsaturated hydrocarbon to the carburization reactor while maintaining the workpiece at elevated temperature and, during this interruption, reactivating the workpiece by contact with a carbon-free, halogen containing gas.

19. The process of claims 1 or 2, wherein the carburization potential of the gas mixture inside the carburization reactor is changed over the course of the carburization reaction by at least one of (1) lowering the carburization temperature, (2) lowering the concentration of unsaturated hydrocarbon in the carburizing gas, (3) interrupting the carburization process by terminating the flow of unsaturated hydrocarbon to the carburization reactor while maintaining the workpiece at elevated temperature, and (4) interrupting the carburization process by terminating the flow of unsaturated hydrocarbon to the carburization reactor while maintaining the workpiece at elevated temperature and, during this interruption, reactivating the workpiece by contact with a carbon-free, halogen containing gas.

20. ~~A~~ The process ~~for producing~~ of claim 1, wherein a surface-hardened, corrosion-resistant stainless steel workpiece exhibiting a shiny metallic appearance is produced without requiring removal of byproduct soot or thermal oxide from the workpiece surfaces, ~~this process comprising contacting~~ wherein the workpiece is contacted with an unsaturated hydrocarbon inside a carburization reactor under a soft vacuum under conditions of time and temperature which are sufficient to cause carbon to diffuse into the workpiece surfaces thereby forming a hardened primary surface layer essentially free of carbide precipitates but insufficient to cause byproduct soot or thermal oxide to form to any significant degree, wherein the process further comprises feeding a carbon-free, halogen-containing activating compound to the carburization reactor simultaneously with feeding the unsaturated hydrocarbon to the carburization reactor, wherein the amount of carbon-free, halogen-containing activating compound fed to the carburization reactor is kept low enough and the length of time the carbon-free, halogen-containing activating compound is fed to the carburization reactor is kept short enough so that formation of byproduct soot or thermal oxide or both is essentially avoided.

21. ~~A~~ The process ~~for surface hardening~~ of claim 1, wherein a workpiece made from an iron, nickel and/or chromium based alloy is surfaced hardened by gas carburization ~~in which an unsaturated hydrocarbon is~~ by ~~contacted~~ contacting ~~with~~ the workpiece with an unsaturated hydrocarbon inside a carburization reactor under a soft vacuum and at an elevated carburization temperature to cause carbon to diffuse into the workpiece surfaces thereby forming a hardened primary surface layer essentially free of carbide precipitates, wherein the unsaturated hydrocarbon and a carbon-free, halogen-containing activating compound are fed to the carburization reactor simultaneously.