The investigation on the microstructure and tribomechanical behavior of hypereutectoid bearing steel AISI 52100 has been carried out during an unconventional thermo-chemical process aiming to improve the wear performance under dry conditions. The effects of NH3 addition rate on microstructure, hardness and wear performance of the carbonitrided specimen were characterized and the results show that two types of nitride (CrN, (Cr,Fe)2N1−x) are formed in the surface layer. The quantity of the nitride and carbide precipitates increase firstly and decrease subsequently with the increasing of NH3 addition rate, whereas the fraction of retained austenite increases monotonically. The wear performance of the carbonitrided specimen is improved during the entire stage of the sliding test with the NH3 addition rate below 0.4l/min, but it decreases sharply at the initial stage of sliding test and then increases gradually when further raising the NH3 addition rate. The possible reasons underlying have been discussed and are attributed to the fraction of retained austenite formed during carbonitriding process and the transformation from retained austenite into martensite during sliding test, respectively.