The Effect of Chemical Composition of Sintering Atmosphere on the Structure and Mechanical Properties of PM Manganese Steels with Chromium and Molybdenum Additions

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Abstract

The effect of chemical composition of the sintering atmosphere on density, microstructure and mechanical properties of Fe-3%Mn-(Cr)-(Mo)-0.3%C steels is described. Pre-alloyed Astaloy CrM and CrL, ferromanganese and graphite were used as the starting powders. Following pressing in a rigid die, compacts were sintered at 1120 and 1250°C in atmospheres having different H_2/N_2 ratio and furnace cooled to room temperature. It has been found that the atmosphere composition has negligible effect on the as-sintered properties of the investigated materials.

Keywords : PM steels, mechanical properties, chemical composition of sintering atmosphere, furnace cooling

1. Introduction

Mn and Cr are widely used as alloying elements in wrought medium-to-high strength steels. The current trend is to apply these elements on a broader scale in PM steels, where mixtures of Mn and Fe-Cr-0.5%C powders are sintered in excess of 1250°C [1]. The mechanical properties of these steels are affected to a large extent by their microstructure and hardenability. It has been found that the contribution of Mn to the strength of the as-sintered steel depends on the content of Cr, N, C and elements present in the sintering atmosphere [2]. Endogas is not a suitable atmosphere for Astaloy CrL and Astaloy CrM based steels due to its high dew point. These steels require very dry atmospheres as Mn and Cr have high affinity to O_2. Traditionally cracked ammonia has been used as an atmosphere for sintering low-alloy steel components. The latest industrial trend is to use synthetic N_2/H_2 atmospheres with up to 10% H_2 and small CH_4 additions.

Cias et al [3] have shown, that successful exploitation of PM steels containing ~3%Mn is associated with elimination of oxide networks present in such alloys. To ensure MnO reduction, dew points of -55 and -40°C are required at 1120°C and 1200°C, respectively. It is essential that the dew point of the furnace atmosphere is strictly controlled and kept at the possibly lowest level throughout the entire sintering cycle [4]. Only control the "local microclimate", ensured by use of semi-closed container or getter, minimised interactions with the flowing atmosphere. CO generated within a PM component should prove to be a more efficient reducing agent than pure dry H_2 at >900°C. High temperature carbothermic sintering at 1250-1280°C has been found important to produce best combination of strength and ductility [5].

The aim of the present study was to substitute Ni [6] by the use of Mn and producing economically advantageous low-alloy Fe-Mn-Mo-Cr-C structural steels.

2. Experimental Methods, Materials and Procedures

Two steels based on commerical pre-alloyed Astaloy CrL and Astaloy CrM powders were examined. 3% of Mn was used in the form of low-carbon ferromanganese and 0.3% graphite was added to powders mixtures. Mixtures of powders were cold compacted to prepare 55x10x5 mm TRS and ISO 2740 UTS test bars (pressing pressure 820 MPa and 660 MPa respectively). The green density of the compacts did not exceed 7.02 gcm^{-3}. Sintering was carried out in dry atmospheres with different H_2 and N_2 content (A1-$75H_2/25N_2$, A2-$25H_2/75N_2$, A3-$5H_2/95N_2$ and A4-N_2) at T1=1120°C and T2=1250°C for 60 minutes employing slow (1.4 $°Cmin^{-1}$) cooling. To improve the local dew point and to minimise volatilisation of Mn, the specimens were sintered in a semi-closed container. The as-sintered density was in the range of 6.81-7.00 gcm^{-3}. Mechanical properties of the investigated steels are shown in Table 1.

Table 1. Mechanical properties of the investigated steels – mean values for groups of 5 batches.

Sintering temperature and atmosphere		UTS, MPa	$R_{0.2}$, MPa	A, %	TRS, MPa	Impact toughness, J/cm^2	HV_{30} surf.
CrL+3%Mn+0.3%C							
T1	A1	512	428	1.3	907	3.2	190
	A2	438	361	0.9	1042	2.1	207
	A3	400	429	0.8	691	2.2	247
	A4	374	285	0.7	922	2.0	229
CrM+3%Mn+0.3%C							
T1	A1	584	498	1.1	987	3.1	255
	A2	532	451	1.1	1036	3.0	302
	A3	515	386	1.0	915	2.7	341
	A4	495	479	1.0	965	3.0	353
CrL+3%Mn+0.3%C							
T2	A1	602	398	1.6	1027	4.4	260
	A2	510	466	1.1	1214	4.5	249
	A3	456	484	0.8	1148	3.0	235
	A4	466	429	1.2	970	3.0	225
CrM+3%Mn+0.3%C							
T2	A1	816	587	2.5	1454	5.5	326
	A2	672	569	1.5	1153	3.6	345
	A3	572	526	1.1	1041	3.7	351
	A4	670	ND	2.0	1061	2.9	362

3. Results

As is shown in Table 1, for higher Cr and Mo concentration, HTS in N_2 atmosphere has to be employed to improve strength properties. Recorded values for UTS, A and TRS after sintering at 1250°C were higher than that after low temperature process. These values correspond well to the bainitic/martensitic structure of these PM steels - there are no evident percentage differences between sintering in H_2-rich and pure N_2 atmosphere. For lower Cr and Mo concentration, slightly better properties were recorded after sintering in H_2-rich than in N_2 atmosphere, irrespective to the sintering temperature. When we look at plasticity and hardness of Mn-Cr-Mo PM steels, the same tendency as in strength properties can be observed. It can be also pointed out relatively high elongation – up to 2.5%, which really good corresponds to the impact toughness. Microstructure of Mn-Cr-Mo PM steels depends on Cr and Mo concentration and sintering temperature. For lower Cr and Mo content, after sintering in 1120°C, the structure consists of bainitic/martensitic regions. As the effect of increasing Cr and Mo level, mainly martensitic/austenitic structure was observed. After sintering at 1250°C, the structure consists mainly of martensite and bainite regions with small amount of austenite; slightly decarburisation effect near the surface of specimens was also observed.

4. Summary

The work has described the advantages of adding ferromanganese powder to Fe-Cr-Mo-C sintered powder compacts. We are interested in the N_2-sintering route for several reasons. Not the least of which is that the EU has a wish to reduce H_2 level in furnace gases to level less than that which is explosive (<~8%). It was therefore felt necessary to study the influence of type of sintering atmosphere on the utilisation of Mn and Cr additions to obtain better economical results and suitable safety precautions. The work was carried out using N_2/H_2 atmosphere with a dew point of <–60°C (<10 ppm moisture), so that it is not difficult to make a direct comparison with results obtained in industry, and with other published work, where different N_2/H_2 atmospheres had been used. Dew point refers to the dryness of a H_2 only atmosphere; if dilute, the reducing potential is decreased, because the amount of H_2 is reduced. In flowing N_2 atmosphere reduction of MnO oxides by solid carbon below 1425°C is impossible. Only control of CO/CO_2 ratio, ensures optimum conditions for thermocarbic oxide reduction and efficient sintering [2]. Regarding microstructures of the investigated steels, N_2 with a dew point of –60°C proved as successful a furnace atmosphere as equally dry H_2. It is therefore concluded that furnace atmosphere of dry N_2 is as effective in preventing formation of deleterious oxide networks as of dry H_2, or of N_2/H_2 mixtures. Specimens sintered at 1250°C possessed higher mechanical properties, irrespective of the N_2-H_2 ratio in the furnace atmosphere. For the investigated steels the UTS and TRS were approx. directly proportional to the H_2 content in the sintering atmosphere. However, Cr enhances, as compared with previous results [4], the detrimental effects of N_2 on strength of the Mn steels. Nitrogen in solid solution improves hardness and produces little effect upon elongation and impact toughness. Its effect on brittle fracture of these steels should be investigated further, especially regarding to the "clustering" N_2 atoms about substitutional alloy atoms Cr and Mn.

5. References

1. S.C. Mitchell, A.S. Wronski, A. Cias, and M. Stoytchev, PM^{2}TEC'99 Conf. Proc., **2**, Part 7, 129(1999).
2. A. Cias, Habilitation Thesis, AGH-UST, Cracow, 2004.
3. A. Cias, S.C. Mitchell, A. Watts and A.S. Wronski: Powder Metall., **42[3],** 227(1999).
4. A. Cias, S.C. Mitchell, K. Pilch, H. Cias, M. Sulowski and A.S. Wronski, Powder Metall., **46[2]**, 165(2003).
5. S.C. Mitchell and A. Cias, Powder Metall. Progress, **4[3],** 132(2004).
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