APPLICATIONS OF ATOMIZATION AND SPRAY PROCESSES IN STEEL INDUSTRY

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Abstract

The spray formed Cr12MoV steel microstructure was investigated by OM, TEM, electron probe microanalysis and X-ray diffraction, and was compared to that of the conventionally processed one. The spray formed microstructure is devoid of the blocky eutectic carbides associated with conventional processing. The as-sprayed Cr12MoV steel has the depressed Ms temperature and the reduced hardenability in comparison with the conventionally processed one. The lattice parameter of 0.3619 nm was determined for the supersaturated austenite in the as-sprayed steel, which contains the tetragonal martensite with the axial ratio c/a of 1.03.

Introduction

Spray Forming or Spray Atomization and Deposition is a newly emerging science and technology in the field of materials development and production in recent years. Spray forming technology, as an advanced processing, combined the advantages of rapid solidification, semi-solid processing, and near net shape processing. The metallurgists in Shanghai Iron & steel Research Institute (SISRI) were involved in R&D of spray forming technology more than ten years, and substantial progress has been made recently. The processing and materials characterization of spray formed Cr12MoV steel are reported in this paper.

The manufacture techniques of rolls for metallurgical rolling mill receive a considerable attention because of the yearly output of crude steel over one hundred million tons for years in China. The mill rolls are currently manufactured by ingot casting and forging, and these conventional processing routes impose severe restrictions on the alloy compositions due to pronounced macro-segregation and highly inhomogeneous microstructures comprising coarse interconnected eutectic carbides. Spray forming offers an advanced way for roll manufacture. It allows the production of rapidly solidified performs, which are free of macro-segregation and display a high degree of microstructural refinement. Thus, spray forming is particularly well suited to the production of rolls. The steady progress has been made of clad rolls prepared by spray forming at SISRI. Cr12MoV, which is the designation of cold-work steel in national standard of GB1299 and is similar to D2 (AISI) in USA and BD2 (BS4659) in UK, is one of the typical materials for making rolls by conventional processing. Therefore, Cr12MoV was chosen as the materials for spray forming in this investigation. Since spray forming is a rapid solidification processing, near net shape processing, and semi-solid processing, it is believed that there are many differences of microstructure and properties between the spray formed and conventionally processed Cr12MoV steel. Therefore, a comparative study of spray formed and conventionally processed Cr12MoV steel is needed for the development of a new type of advanced rolls by using spray forming. This paper presents the microstructure and properties of spray formed Cr12MoV steel, as compared with those of conventionally processed one.

Experimental

The spray atomization and deposition equipment utilized in this investigation was designed and constructed by SISRI. The processing parameters employed may be described as follows. The feedstock for spray forming was as-received commercial Cr12MoV steel of hot rolled rods with a diameter of 20mm. The charge weight was 4.5Kg. The superheat was 120℃. The liquid metal flow rate was set at approximately 0.10Kg/s. Nitrogen was used as the atomizing gas with pressure of 1.5 MPa. The distance from the nozzle to the substrate was 360 mm.

The chemical composition of the steel was analyzed with a vacuum emission spectrometer. Density measurements were made by using Archimedes' principle. The continuous cooling transformation (CCT) diagrams of the steel were determined using cylindrical rods, which were subjected to different rates of cooling, and the onset of transformation is detected by dilatometry.

A microstructural investigation was carried by optical metallography, X-ray diffraction analysis, electron probe microanalysis, and transmission electron microscopy (TEM).

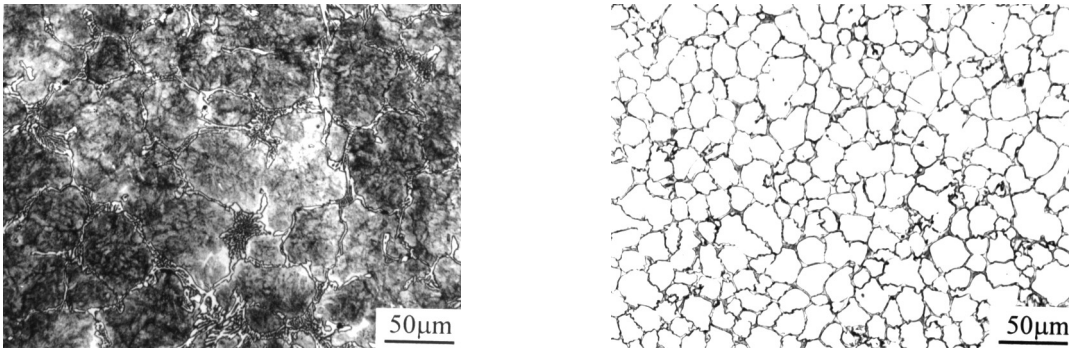
Results and Discussion

Table 1 shows the chemical composition of the as-sprayed Cr12MoV steel and the specification of GB1299 for the designation of Cr12MoV steel.

Table 1 Chemical Composition of the As-sprayed Cr12MoV steel (wt.%)

	C	Si	Mn	P,S	Cr	Mo	V
Analysis	1.49	0.27	0.26		11.65	0.48	0.22
Specification	1.45/1.70	≤0.40	≤0.40	≤0.030	11.00/12.50	0.40/0.60	0.15/0.30

The densities of the as-sprayed steel at different position of the deposit were measured and ranged from 7.66 to 7.82 g/cm^3. The average value of densities is 7.75 g/cm^3. A higher density often results when a smaller value of the gas to metal mass flow ratio is used so that there is enough liquid available to fill the deposit interstices.



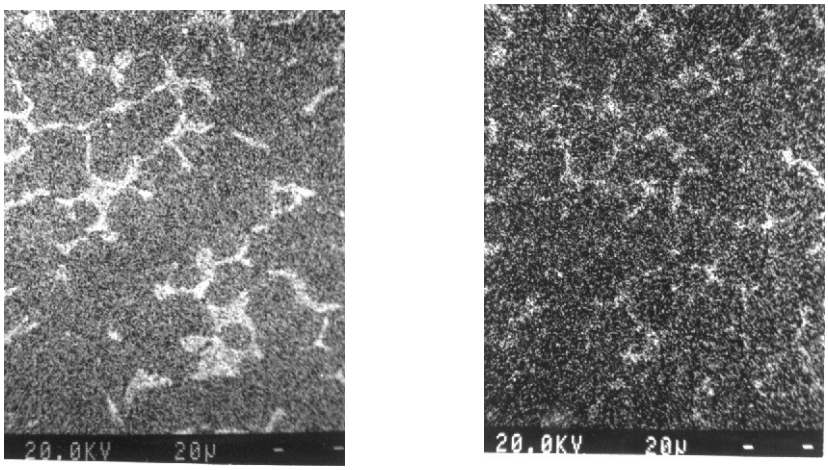
(a) *(b)*

Figure 1. Optical micrographs of (a) the as-received and (b) the as-sprayed Cr12MoV steel

Optical micrographs of the as-received and the as-sprayed microstructure are shown in Figure 1. The most significant effect of spray forming on the microstructure is its influence on the carbide size and distribution. As shown in Figure 1(a), the formation of primary carbide networks during solidification and cooling to ambient temperatures results in a coarse particle dispersion in the as-received microstructure. In contrast to the as-received microstructure, Figure 1(b) indicates the as-sprayed microstructure is a relatively homogeneous and fine one, and has a finer, more uniform carbide dispersion than the as-received one. The further evidence is given in Figure 2. The severe segregation of chromium at grain boundaries is observed in as-received microstructure shown in Figure 2(a). As contrasted with Figure 2(a), Figure 2(b) reveals much less segregation of chromium, showing the advantage of spray forming over conventional processing [1].

As shown in Figure 3(a), the X-ray diffraction analysis reveals the presence of martensites and carbides of M_7C_3 in the as-received steel. In contrast to Figure 3(a), the as-sprayed microstructure consists of martensites, carbides of M_7C_3, and a considerable quantity of metastable austenites, as illustrated in Figure 3(b). This is due to a decrease of the martensite start temperature Ms confirmed by CCT thermograms shown in Figure 4. A comparison of the lattice parameters of austenite in the as-sprayed Cr12MoV steel and in the hardened D2 steel prepared by conventional processing (i.e. 0.3619 nm evaluated from Figure 3(b) and 0.3597nm reported from Bhargava and Tiwari[2], respectively) shows that the former has a much higher solute content than the letter because of the rapid solidification of spray forming processing. Since the Ms temperature is depressed by the

presence in solid solution of the principal alloying elements in this steel, the austenite in the as-sprayed steel has a lower Ms temperature. A similar result [2] has been reported for the D2 steel subjected to rapid solidification by chill block melt spinning(CBMS). The lattice parameters of 0.3624~0.3626nm were obtained in D2 steel prepared by CBMS. A slight difference of lattice parameters between the present study and the Ref. 2 can be explained by the fact that the cooling rate for CBMS is higher than that for spray forming.



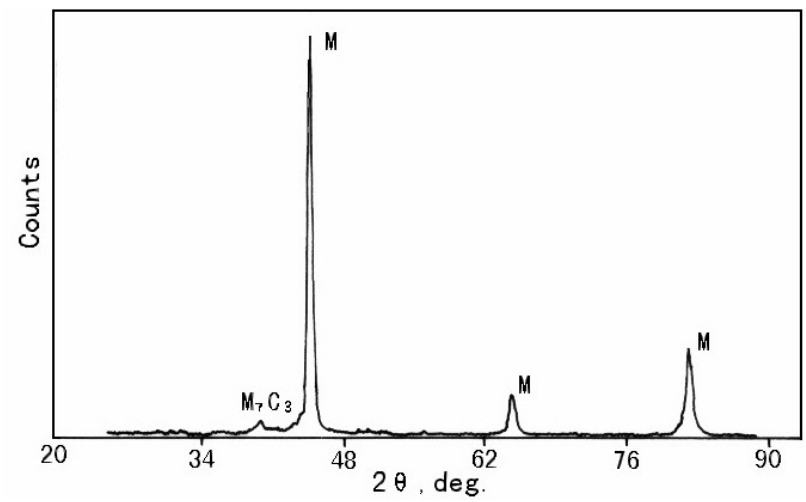
(a) *(b)*

Figure 2. The X-ray area scan of (a) the as-received and (b) the as-sprayed Cr12MoV steel specimens for Cr

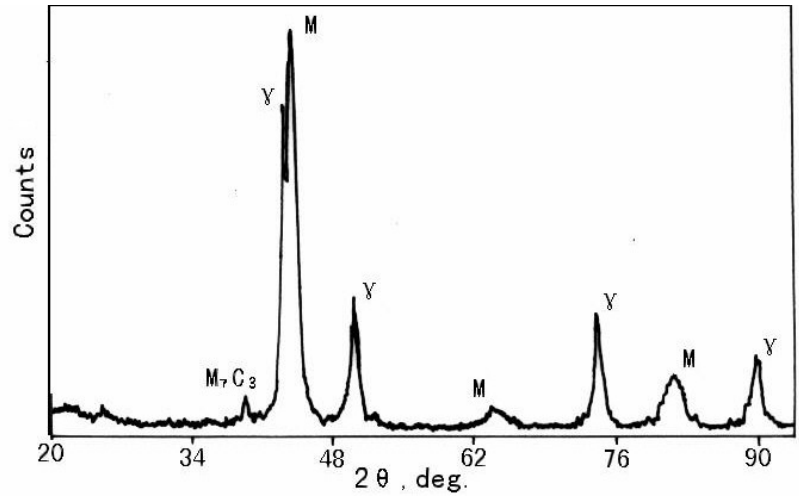
A comparison of Figure 4(a) with 4(b) demonstrates the other characteristic of phase transformation of the steel, which is the increased critical cooling rate corresponding to the beginning of the pearlite reaction in the as-sprayed steel, as compared with that in the as-received steel. The decrease of the hardenability in the as-sprayed steel can be attributed to the nature of rapid solidification of spray forming processing. As shown in Figure 1, the austenite grain size of the steel processed by spray forming is apparently reduced, resulting in the increased grain boundary area, and it means that the sites for the nucleation of ferrite and pearlite are increased, with the result that these transformations speed up, and the hardenability is therefore reduced.

Figure 5 illustrates TEM micrograph of the as-sprayed Cr12MoV steel and selected area diffraction patterns from the austenitic area and martensitic area respectively. Figure 6 demonstrated bright field and dark field TEM micrograhs of the carbide of M_7C_3, and its SADP. It is of interest to note the tetragonality of the martensite shown in Figure 5. It is difficult to determine the tetragonality of martensites from the X-ray diffractogram shown in Figure 3(b) due to the overlapping of the broad lines and the merging of doublets. Therefore carefully measuring the distance on the TEM plate between the transmitted beam (zero order) and a diffraction spot R in SADP was performed for detecting the tetragonality of martensites in this study. For example, the ratio of $\mathbf{R_{200}/R_{011}}$ estimated from [011] zone SADP of the martensite shown in Figure 5(c) is related to an axial ratio c/a of martensite by the formula

$c/a = \sqrt{2}\ \mathbf{R_{011}/R_{200}}$, which is independent of diffraction constant or camera constant. The average value of axial ratio c/a of 1.03 was determined from different SADP of martensites. The low value of c/a means that there is low carbon martensite in the as-sprayed Cr12MoV steel. It is a rather surprising finding because supersaturated austenite contains high carbon content as mentioned above and it is well known that the martensite reaction is a diffusionless transformation. Further work is needed to clarify certain details of the martensite in the as-sprayed Cr12MoV steel.

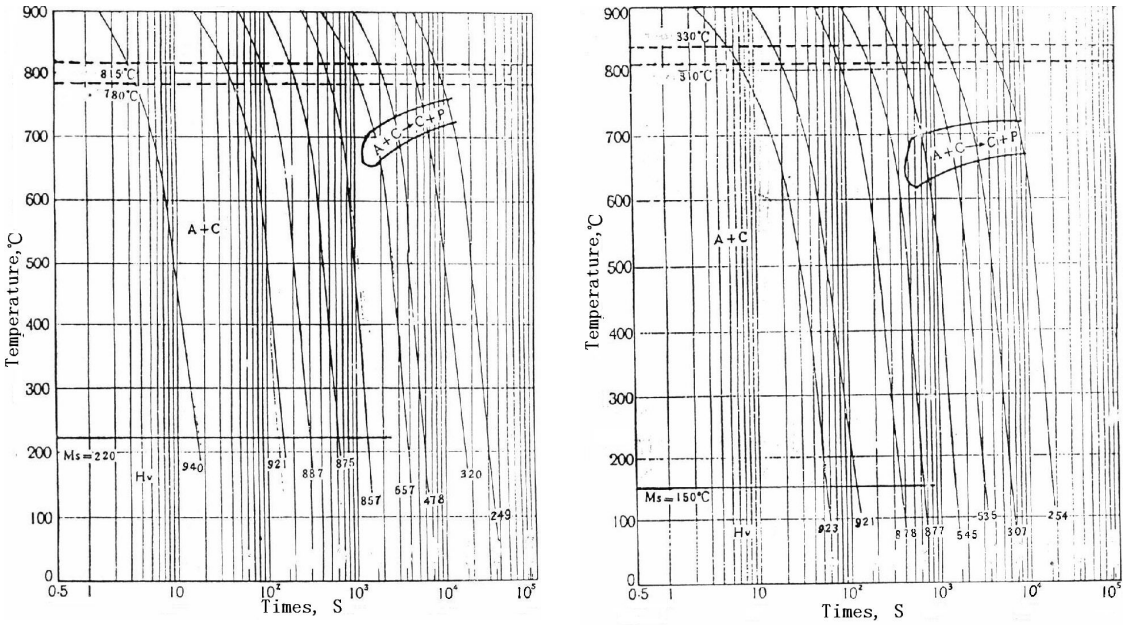


(a)



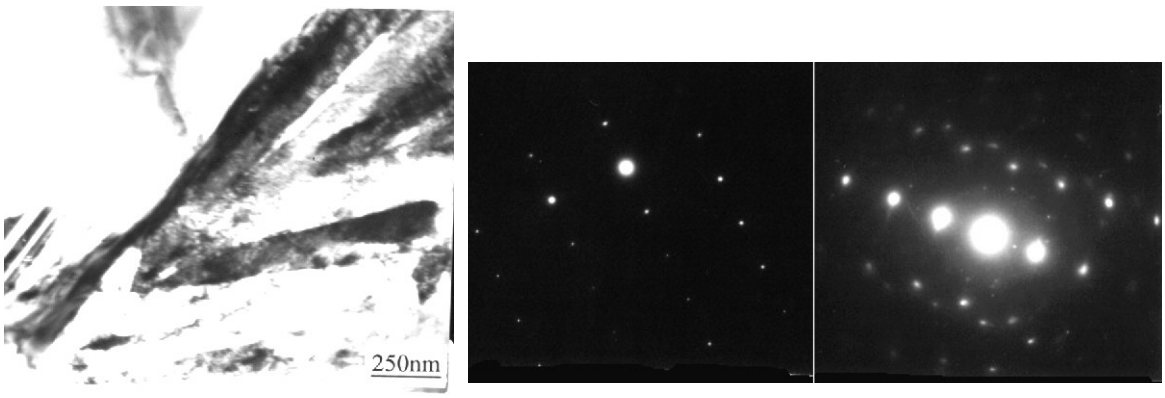
(b)

Figure 3. X-ray diffractograms of (a) the as-received and (b) the as-sprayed Cr12MoV steel



(a) *(b)*

Figure 4. CCT diagrams of (a) the as-received and (b) the as-sprayed Cr12MoV Steel

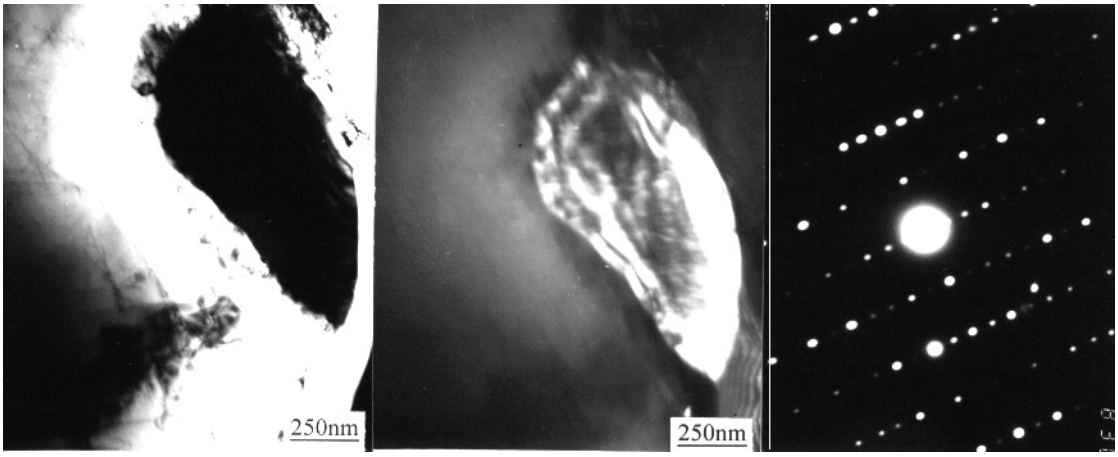


(a) *(b)* *(c)*

Figure 5. (a) Bright field TEM micrograph of the as-sprayed Cr12MoV steel. (b) [112] zone SADP from austenite. (c) [011] zone SADP from martensite.

Conclusion

1. The as-sprayed microstructure of Cr12MoV steel shows a relatively homogeneous and fine one, which has a finer, more uniform carbide dispersion, and less segregation of Cr than the conventionally processed one.
2. The lattice parameter of 0.3619nm was determined for the supersaturated austenite in the as-sprayed Cr12MoV steel.
3. The average value of densities measured from the different position of the Cr12MoV deposit is 7.75g/cm^3.
4. The as-sprayed Cr12MoV steel has the depressed martensite start temperature Ms of 150℃, as compared with the Ms temperature of 220℃ in the conventionally processed Cr12MoV steel.
5. The hardenability of the as-sprayed Cr12MoV steel is reduced in comparison with the conventionally processed one.
6. Primary TEM work revealed the axial ratio c/a of 1.03 for the tetragonal martensite in the as-sprayed Cr12MoV steel.



(a) (b) (c)

Figure 6. (a) Bright field and (b) Dark field TEM micrographs of the carbide of M_7C_3. (c) [010] zone SADP obtained from the carbide shown in (a).

Acknowledgements

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References

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